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Topics:
PCB
Chemical analysis
Fires
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Pollution control
Insulating oils

EPRI CS/EL-4104
Project 2028
Proceedings
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Workshop Proceedings: PCB By-product Formation

Prepared by
Electric Power Research Institute
Palo Alto, California

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REPORT SUMMARY

SUBJECTS: Transmission: Substations / Distribution: Substations / Hazardous/toxic substances

TOPICS: PCB; Chemical analysis; Fires; Transformers; Pollution control; Insulating oils

AUDIENCE: Environmental scientists and managers

Workshop Proceedings: PCB By-product Formation

Fires involving PCB-filled transformers occur infrequently, but concern exists about the release of potentially toxic combustion by-products. Responding to proposed EPA regulations on PCB-filled building transformers, experts gathered to review current information on the partial-oxidation products of PCB.

BACKGROUND

In March 1984, EPA announced its intention of drawing up regulations to cover polychlorinated biphenyl (PCB) fires in electric transformers. A preliminary version of the proposed EPA rules was prepared, and public hearings were scheduled for January 1985. Before final regulations were determined, EPRI sponsored a workshop to make available the most current knowledge on PCB fires and research.

OBJECTIVES

To compile the latest information and review the current research on the effects of fires in PCB-filled transformers—including PCDF formation, chemical analyses, risk assessment, and cleanup techniques.

APPROACH

Twenty-seven papers dealing with PCB conversion were presented at the EPRI workshop in December 1984. The agenda called for three background presentations and four half-day sessions focusing on (1) analysis of polychlorinated dibenzofurans (PCDFs) and polychlorinated dibenzo-p-dioxins (PCDDs); (2) pyrolysis and combustion; (3) fires, spills, and cleanup; and (4) risk assessment. More than 70 representatives of EPA, EPRI, the chemical industry, major equipment manufacturers, utilities, research organizations, and universities participated in the meeting.

RESULTS

The presentations covered a wide range of PCB conversion subjects, including improved approaches to sample preparation and PCDF analysis; advances in decontamination techniques and preventive measures that would decrease accident response time and costs; and the implementation of risk assessment and risk minimization techniques. There was agreement that an improved understanding of PCB pyrolysis and combustion under varying conditions would provide insight into designing installations for minimum risk. Participants also agreed that better methods of assessing risk would lead to the establishment of more realistic risk levels. As a result, substantial cost reductions could be achieved.

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EPRI PERSPECTIVE

This workshop provided a useful opportunity for experts in PCDF analysis, PCDD analysis, and PCB combustion problems to exchange current, reliable information that should be of significant value to those charged with the responsibility of establishing PCB regulations. The discussions indicated that there is a need for more accurate chemical analyses, more realistic risk assessments, and more timely and efficient decontamination and cleanup following spills and fires.

A new report on a related EPRI project is now available: CS-4094, *Design Manual for Reducing Airborne PCB Contamination.*

PROJECT

RP2028
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For further information on EPRI research programs, call EPRI Technical Information Specialists (415) 855-2411.

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Workshop Proceedings: PCB By-product Formation

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Research Project 2028

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ABSTRACT

The EPRI PCDF workshop was held to assemble current data on PCB fires, a subject of vital interest to the Electric Utility Industry. It was timed to precede the public hearings on the EPA's proposed regulation on PCB fires. It is hoped that some of the ideas expressed were useful input to those active at the hearing.

Four half-day sessions covered Analysis, Pyrolysis and Combustion, Documentation of Fires, Spills and Clean-up, and Risk Assessment.

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We would like to acknowledge the help of our session chairmen, Jacques Guertin, Marcus Cooke, Brian West and Vic Niemeyer. Ellen Lanum provided excellant meeting arrangements. Other EPRI personnel who helped were:

Gary Cobbley
Barbara Cole
Eleanor Keith
Kay Kidd

Thanks to all.

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PART 1:

BACKGROUND

EPRI'S PCB INTERDIVISIONAL TASK FORCE

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EPRI

Paper not available at time of publication.

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REGULATION DEVELOPMENT PROCESS AS IT APPLIES TO PCB

DENISE KEEHNER

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Paper not available at time of publication.

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COST-EFFECTIVENESS ANALYSIS OF THE PROPOSED RULE FOR INDOOR PCB TRANSFORMERS

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EPA's Office of Toxic Substances prepared a cost-effectiveness analysis for the proposed rule regulating the use of indoor PCB transformers. The analysis estimated the cost-effectiveness of a number of regulatory alternatives to reduce the risks associated with indoor PCB transformers.

The following alternatives were analyzed:

- 15 year, 10 year, and 5 year phase-out of indoor PCB askarel transformers
- Retrofill of indoor PCB askarel transformers within one year to less than 500 ppm PCBs
- Physical isolation of each indoor PCB askarel transformer by 1987 and by 1989 (Isolation is defined as the physical enclosure of a transformer in a sealed vault or smoke-proof barrier)
- Inspection of indoor PCB askarel transformers for incipient failure on a quarterly basis
- Installation of increased electrical protection on each indoor PCB askarel transformer
- Installation of external electrical switches at each indoor PCB askarel transformer location
- Labeling each indoor PCB askarel transformer location for indentification by fire or emergency response personnel
- Registration of each indoor PCB askarel transformer with the local fire department.

The estimated costs include direct labor and capital costs as well as changes in transformer operating costs. Benefits include: 1) a reduction in the number of catastrophic events resulting from PCB transformer fires or failures, 2) clean-up costs associated with PCB transformer fires or failures, and 3) a reduction in PCBs released to the environment. The only benefits measure which we attached a dollar value to was avoided clean-up costs. Costs and benefits were estimated on an incremental basis using a base case of an indefinite use authorization of PCB transformers with quarterly inspections.

The cost-effectiveness measure used to summarize cost and benefits calculations was:

$$\text{Cost-effectiveness} = \frac{\text{Net Cost}}{\text{Avoided Catastrophic Events}}$$

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where: Net Cost = Cost of Regulation - Clean-up Costs Avoided

In addition, the reduction in PCBs released to the environment was calculated for each alternative where sufficient data was available.

There were many data gaps and uncertainties in the data used to estimate the effectiveness of risk reduction alternatives. We did not attempt to estimate the effectiveness of the following regulatory alternatives because of a lack of data: 1) a requirement to install increased electrical protection, 2) a requirement to install external cut-off switches, and 3) labeling and registration of indoor PCB transformers.

Following is a summary of the results of the cost-effectiveness analysis: (See attached table)

- Total regulatory costs range from $5.2 million for registration of indoor PCB transformers with local fire departments to $1.5 billion for retrofill of all indoor PCB transformers.

- When avoided clean-up costs are considered, net regulatory costs are reduced from 4 percent (for the inspection alternative) to 56 percent (for the 3 year isolation program).

- For all indoor PCB transformers the cost-effectiveness of regulation ranges from $5.48 million per avoided catastrophic event for an isolation program implemented in 5 years to $166 million per avoided event for quarterly inspection.

- The estimated cost of the proposed alternative is $612 million. The proposed alternative includes the following provisions:

  - immediate registration of all (indoor and outdoor) PCB askarel transformers with fire departments,

  - marking of all (indoor and outdoor) PCB askarel transformers with labels on the exterior with labels on the exterior of the vault, grate, door, etc.,

  - immediate registration of PCB askarel transformers in or near buildings with building owners,

  - installation of additional protective devices on PCB askarel transformers with higher secondary voltages, and

  - isolation of all PCB askarel transformers in or near buildings over a three-year period, including preparation and retention.

Following are the major assumptions used to make these estimates:

- The total annual failure rate (including catastrophic and noncatastrophic failures) is .2 percent per year. The catastrophic failure rate is .003 percent per year.

- 47.7 percent of noncatastrophic failures result in a spill of PCB fluid.

- 25 percent of contained volume is lost in a spill.

- The clean-up cost for a catastrophic failure is $20,000,000.

- The total number of indoor PCB transformers at the end of 1984 is 104,284.

- 50 percent of the indoor PCB askarel transformers operate at a higher secondary voltage (480/227 volts).

- Preparation and retention of a plan for isolating each transformer was estimated to cost $280 per isolation.

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Table 8-1

COST-EFFECTIVENESS ANALYSIS OF
ALTERNATIVE REGULATIONS FOR REMOVAL AGAINST TRANSFORMERS

TOTAL FOR ALL TRANSFORMERS

Alternative	Cost Measure	Benefit Measures			Cost-Effectiveness	
	Total Real Resource Cost (Millions of Dollars)	Total Clean-Up Cost Avoided (Millions of Dollars)	Total Catastrophic Events Avoided (Number of Events)	Total PCB Release Avoided (Pounds)	Net Cost (Millions of Dollars)	Net Cost per Catastrophic Event Avoided (Millions of Dollars/Event)
Phase-Out by 1999	288.66	65.81	15.81	214,992	201.82	12.77
Phase-Out by 1994	610.58	110.59	26.41	359,534	502.39	19.81
Phase-Out by 1989	1,372.47	250.58	39.86	542,152	1,111.96	27.95
Immediate Retrofill to Nonlocosity	1,693.94	365.69	67.68	647,286	1,128.26	21.66
Isolate by 1989	427.16	236.31	34.80	10,196	190.84	5.48
Isolate by 1987	480.79	270.55	37.29	14,255	210.25	5.64
Quarterly Inspection for Incipient Failure	829.03	36.75	4.77	0	792.20	166.18
Increased Electrical Protection	288.57	NA	NA	NA	NA	NA
External Cut-Off Switch	72.24	NA	NA	NA	NA	NA
Labeling 5.69	NA	NA	NA	NA	NA	
Registration	5.21	NA	NA	NA	NA	NA

Reference Case: Indefinite use authorization with quarterly inspection; retrofilling precluded.

Parameters: Catastrophic Failure Rate = 0.605 percent of in-service transformers per year.
Clean-Up Cost of Catastrophic Failure = $20,000,000 per event.
Total Number of Transformers = 184,284, end of year 1984.

NA: Not Available.

SOURCE: Putnam, Hayes & Bartlett, Inc., July 1984. All dollar measures reflect 1981 present value calculated using a 10 percent real discount rate.

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PART 2:

ANALYSIS

JACQUES GUERTIN - MODERATOR

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FACTORS AFFECTING THE RELIABILITY OF QUANTITATIVE ANALYSES FOR CHLORINATED DIBENZODIOXINS AND DIBENZOFURANS IN PCB-CONTAINING TRANSFORMER FLUIDS AND THEIR PRODUCTS OF COMBUSTION

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The sequence of analytical operations which is usually applied in characterizing and quantitating polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) in PCB-containing samples is as described in the following.

SPIKING OF SAMPLES

Reliable quantitetive analyses to determine trace levels of PCDDs and PCDFs in any sample require the utilization of internal standards which are added to the samples prior to analysis in known quantities. Ideally, isotopically-labelled PCDDs and PCDFs are used for this purpose, since they are expected to closely mimic the native PCDDs/PCDFs already present in the sample in terms of their chemical behavior and the efficiency with which they are extracted from the samples and ultimately recovered through the various clean-up procedures applied to the samples. At the same time, these labelled PCDDs/PCDFs give mass spectral responses at different ion masses than those monitored as indicators of the corresponding native compounds. By using the observed signal responses for the native compounds relative to those observed for the labelled compounds as the basis for quantitation, much more accurate quantitative results are thus obtained. While ideally, it would be desirable to utilize a labelled PCDD and PCDF internal standard for each chlorinated class to be determined, this is not practically possible at present because of the limited availability of such standards. A set of labelled standards which is presently recommended for use includes $^{13}C_{12}$-2,3,7,8-TCDD, $^{13}C_{12}$-2,3,7,8-TCDF, $^{13}C_{12}$-1,2,3,4,7,8-HxCDD, $^{13}C_{12}$-1,2,3,4,7,8-HxCDF, $^{13}C_{12}$-OCDD and $^{13}C_{12}$-OCDF. With this approach, the labelled TCDD and TCDF are used as the representative standards for mono-, di-,

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tri- and tetra-CDDs and CDFs, the labelled HxCDD and HxCDF are used as the representative standards for penta- and hexa-CDDs and CDFs, and the labelled DCDD and OCDF are used as the representative standards for hepta- and octa-CDDs and CDFS. In general, the fewer the number of internal standards utilized, the less reliable are the quantitative results obtained in such analyses.

EXTRACTION OF PCDDs AND PCDFs FROM THE SAMPLE MATRIX

Solid samples (soils, combustion particulates, surface wipes) are generally extracted in a Soxhlet apparatus with toluene (or benzene). Tests of the efficiency of extraction of spiked samples have shown that the most efficient extraction is achieved with this solvent and an extraction period of 12-16 hours.

PRELIMINARY FRACTIONATION OF THE SAMPLE EXTRACT AND ELIMINATION OF PRELIMINARY MATRIX CONSTITUENTS AND OTHER CHLORINATED RESIDUES

Table 1 shows a series of fractionation and liquid chromatographic column procedures which are efficacious for the concentration of PCDDs/PCDFs in the sample extract, while concurrently removing other major constituents of the matrix (oil, PCBs and other chlorinated compounds). In order to demonstrate that such procedures yield good recoveries for PCDDs and PCDFs, and that quantitative analyses using these methods are accurate, it is necessary to process typical sample extracts which have been spiked with a representative set of these compounds through these procedures. Data obtained in such experiments is also shown in Table 1, and indicates that with proper selections, good recovery of PCDDs/PCDFs representative of the entire chlorinated spectrum can be achieved.

GC-MS ANALYSIS OF SAMPLE EXTRACTS

GC-MS analyses of sample extracts to measure quantitatively the levels of PCDDs/PCDFs are based on the premise that complete gas chromatographic separation of each chlorinated class of these compounds can be achieved, so that a unique set of mass spectral indicator ions can be monitored for each of the appropriate GC retention time windows. If the objective of the analysis is to obtain data on the concentrations of PCDDs/PCDFs by total chlorinated class (that is, total tetra-, penta- and so on), then complete separation of the individual isomers of each class is not required. For such analyses, a 60-meter fused silica DB-5 capillary column has been shown to be a particularly good choice as the GC column, because when properly temperature-programmed, this column yields resolution of each of

the chlorinated groups of PCDDs/PCDFs from the other chlorinated groups and permits analyses of the entire tetra- through octa- groups from a single extract injection in about 75 minutes. The sequences of GC and MS operating parameters required for such analyses are shown in Table 2.

CALIBRATION STANDARDS

Rigorous quantitative analyses of PCDDs/PCDFs requires that GC-MS response factors be determined for an appropriate set of PCDD and PCDF isomers using pure standards of known concentration. An appropriate set of such standards should include representative isomers from each chlorinated group of PCDDs/PCDFs which is to be determined in the analysis. Use of an appropriate group of isomers for this purpose permits one to also simultaneously define the GC retention time windows for each chlorinated class of PCDDs/PCDFs.

CRITERIA APPLIED TO GC-MS DATA TO ENSURE RELIABILITY

In order to identify specific PCDD/PCDF in samples analyzed, the GC-MS data obtained must satisfy the following criteria:

a. Mass spectral responses must be observed at both the molecular and fragment ion masses corresponding to the ions indicative of each chlorinated class of PCDD/PCDF identified (see Table 2) and intensities of these ions must maximize essentially simultaneously (within ± 1 second). In addition, the chrometographic retention times observed for each PCDD/PCDF signal must be correct relative to the appropriate stable-isotopically labelled internal standard and must be consistent with the retention time windows established for the chlorinated group to which the particular PCDD/PCDF is assigned.

b. The ratio of the intensity of the molecular ion $(M)^+$ signal to that of the $(M+2)^+$ signal must be within ± 20% of the theoretically expected ratio (for example, 0.77 in the case of TCDD; therefore the acceptable range for this ratio is 0.62 to 0.92).

c. The intensities of the ion signals are considered to be detectable if each exceeds the baseline noise by a factor of at least 3:1. The ion intensities are considered to be quantitatively measurable if each ion intensity exceeds the baseline noise by a factor of at least 5:1.

d. For reliable detection and quantitation of PCDF it is also desirable to monitor signals arising from chlorinated diphenyl ethers which, if present could give rise to fragment ions yielding ion masses identical to those monitored as indicators of the PCDF. Accordingly, in Table 2, appropriate chlorinated diphenyl ether masses are specified which must be monitored simultaneously with

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the PCDF ion-masses. Only when the response for the diphenyl ether ion mass is not detected at the same time as the PCDF ion mass can the signal obtained for an apparent PCDF be considered unique.

e. Measurements of the concentration of the congeners in a chlorinated class using the methods described herein is based on the assumption that all of the congeners are identical to the calibration standards employed in terms of their respective chemical and separation properties and in terms of their respective gas chrometographic and mass spectrometric responses. Using these assumptions, for example, the $^{13}C_{12}$-2,3,7,8-TCDD internal standard is utilized as the internal calibration standard for all of the 22 TCDD isomers or congeners. Furthermore, the concentration of the total TCDD present in a sample extract is determined by calculating, on the basis of the standard procedure outlined above, the concentration of each TCDD isomer peak (or peaks for multiple TCDD isomers, where these coelute) and these individual concentrations are subsequently summed to obtain the concentration of "total" TCDD.

f. Frequently, during the analysis of actual sample extracts, extraneous compounds which are present in the extract (those organic compounds not completely removed during the clean-up phase of the analysis) can cause changes in the liquid and gas chromatographic elution characteristics of the PCDD/PCDF (typically retention times for the PCDD/PCDF are prolonged). Such extraneous organic compounds, when introduced into the mass spectrometer source may also result in a decrease in the sensitivity of the MS because of suppression of ionization, and other effects such as charge transfer phenomena. The shifts in chrometographic retention times are usually general shifts, that is, the relative retention times for the PCDD/PCDF are not changed, although the entire elution time scale is prolonged. The analyst's intervention in the GC-MS operating sequence can correct for the lengthened GC retention times which are sometimes observed due to the presence of extraneous organics in the sample extract. For example, using the program outlined in Table 2, if the retention time observed for 2,3,7,8-TCDD (which normally is 19.5 minutes) is lengthened by 30 seconds or more, appropriate adjustments in the programming sequence outlined in Table 2 can be made, that is, each selected ion-monitoring program is delayed by a length of time proportionate to the lengthening of the retention time for the 2,3,7,8-TCDD isomer. In the case of ionization suppression, this phenomenon is inherently counteracted by the internal standard approach. However, if loss of sensitivity due to ionization suppression is severe, additional clean-up of the sample extract may be required in order to achieve the desired detection limits.

QUALITY ASSURANCE/QUALITY CONTROL PROCEDURES

Quality assurance and quality control in these analyses are ensured by the following provisions:

a. Each sample analyzed is spiked with stable isotopically labelled internal standards, prior to extraction and analysis. Recoveries obtained for each of these standards should typically be in the

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range from 60-90%. Since these compounds are used as true internal standards however, lower recoveries do not necessarily invalidate the analytical results for native PCDD/PCDF, but may result in higher detection limits than are desired.

b. Processing and analysis of at least one method blank sample is accomplished for each set of samples (a set being defined as 20 samples or less).

c. It is desirable to analyze at least one sample spiked with representative native PCDD/PCDF for each set of 20 or fewer samples. The result of this analysis provides an indication of the efficacy of the entire analytical procedure. The results of this analysis will be considered acceptable if the detected concentration of each of the native PCDD/PCDF is within ± 50% of the known added concentration.

d. At least one of the samples analyzed out of each set (of 20 samples or less) is analyzed in duplicate and the results of the duplicate analysis are included in the report of data.

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Table 1

RECOVERY OF PCDD/PCDF SPIKES FROM CONTAMINATED SOIL MATRIX CONTAINING PCNs, PCBs, CHLORINATED PARAFFINS, AND HYDROCARBON OILS FOLLOWING APPLICATION OF VARIOUS CLEAN-UP PROCEDURES TO SAMPLE EXTRACT

PCDD/PCDF SPIKED	% OF SPIKED RECOVERED				
	Base and Acid Prewashes[a]	Acid, Base, Neutral Silica Column[b]	Alumina Column[c]	PX-21 Carbon Column[d]	Carbopack C Carbon Column[e]
2,4-DiCDF	67	108	83	83	0
2,7-DiCDD	46	101	85	80	0
1,2,4-TriCDD	84	99	96	90	0
2,3,7,8-TetraCDF	95	98	99	98	70
2,3,6,8-TetraCDF	98	99	101	96	32
1,2,4,8-TetraCDF	92	97	93	92	39
1,2,3,4-TetraCDD	92	94	99	99	62
2,3,6,8-TetraCDD	95	100	94	95	86
1,2,4,7,8-PentaCDF	99	101	96	98	97
1,2,3,7,8-PentaCDD	99	100	96	103	98
1,2,4,6,7,9-HexaCDF	96	98	91	97	98
1,2,3,4,7,8-HexaCDD	99	101	93	100	85
1,2,3,4,6,8,9-HeptaCDF	96	98	88	94	66
OCDF	98	98	91	89	0
OCDD	98	109	94	83	0

a. Hexane extract in contact with 40% KOH for 1 hour, followed by contact with concentrated H_2SO_4 for 1 hour.

b. Column containing 1g Bio-Sil-A (100/200 mesh) 2g Bio-Sil-A containing 30% (W/W) H_2SO_4, 2g Bio-Sil-A containing 40% (W/W) KOH, and 1g Bio-Sil-A eluted with total of 90 mL of hexane; Bio-Sil-A is activated at 180°C after series of solvent rinses.

c. Bio-Rad AG-4 Acid Alumina, Activated at 190°C, eluted with 65 mL hexane, 20 mL 20% methylene chloride-in-hexane, and 15 mL methylene chloride, collecting only last fraction.

d. 18% Amoco Px-21 activated carbon on (elite 545, eluted with 1 mL hexane, 1 mL methylene chloride: Cyclohexane (1:1), and 2 mL, 20% benzene in ethylacetate, then reverse eluted with 4 mL toluene.

e. Carbopack C mixed with Celite 545, activated at 130°C, eluted with 2 mL hexane, 1 mL cyclohexane, methylene chloride (1:1), 1 mL of methylene chloride: methanol: benzene (75:20:5) and 2 mL toluene, collecting last fraction.

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Table 2

SEQUENCE OF OPERATIONS IN GC-MS-DS QUANTITATION OF CDDs/CDFs IN EXTRACTS OF ENVIRONMENTAL SAMPLES

Elapsed Time (min)	Event	GC Column Temperature (°C)	Temperature Program Rate (°C/min)	Ions Monitored by Mass Spectrometer (m/z)	Identity of Fragment Ion	Compounds Monitored	Approximate Theoretical Ratio of $[M]^+:[M+2]^+$
0.00	Injection, splitless	190					
1.00	Turn on split valve	190					
1.00	Begin temp. program to 220°C	190	5				
6.00	Open column flow to mass spectrometer	215	5				
7.00	Column temperature hold	220					
14.00	Start Tetra Program; sweep = 350 ppm; time/mass = 0.00 sec.			240.938	$[M-COCl]^+$	TCDF	
				258.938	$[M-COCl]^+$	TCDD	
				303.902	$[M]^+$	TCDF	0.77
				305.899	$[M+2]^+$	TCDF	
				315.942	$[M]^+$	$^{13}C_{12}$-TCDF	
				319.897	$[M]^+$	TCDD	0.77
				321.894	$[M+2]^+$	TCDD	
				327.885	$[M]^+$	$^{37}Cl_4$-TCDD	
				331.937	$[M]^+$	$^{13}C_{12}$-TCDD	
				373.840	$[M]^+$	$HxDPE^a$	
22.00	Stop Tetra Program	220					
22.50	Start Penta Program; sweep = 350 ppm; time/mass = 0.12 sec.			274.899	$[M-COCl]^+$	PeCDF	
				290.894	$[M-COCl]^+$	PeCDD	
				337.863	$[M]^+$	PeCDF	0.61
23.00	Begin temp. program to 235°	220	5	339.860	$[M+2]^+$	PeCDF	
26.00	Column temperature hold	235		353.858	$[M]^+$	PeCDD	0.61
				355.855	$[M+2]^+$	PeCDD	
				407.801	$[M]^+$	$HpDPE^a$	
32.00	Stop Penta Program						
32.50	Start Hexa Program; sweep = 350 ppm; time/mass = 0.20 sec.	235		310.857	$[M-COCl]^+$	HxCDF	
				326.852	$[M-COCl]^+$	HxCDD	
				373.821	$[M]^+$	HxCDF	1.23
				375.821	$[M+2]^+$	HxCDF	
				385.861	$[M]^+$	$^{13}C_{12}$-HxCDF	
				389.816	$[M]^+$	HxCDD	1.23
				391.813	$[M+2]^+$	HxCDD	
				411.856	$[M]^+$	$^{13}C_{12}$-HxCDD	
				443.759	$[M]^+$	$ODPE^a$	

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Table 2 (Continued)

SEQUENCE OF OPERATIONS IN GC-MS-DS QUANTITATION OF CDDs/CDFs IN EXTRACTS OF ENVIRONMENTAL SAMPLES

Elapsed Time (min)	Event	GC Column Temperature (°C)	Temperature Program Rate (°C/min)	Ions Monitored by Mass Spectrometer (m/z)	Identity of Fragment Ion	Compounds Monitored	Approximate Theoretical Ratio of $[M]^+:[M+2]^+$
33.00	Begin temp. program to 250°C	235	5				
36.00	Column temperature hold	250					
42.50	Stop Hexa Program						
43.00	Start Hepta Program; sweep = 350 ppm; time/mass = 0.30 sec.	250		344.810	$[M-COCl]^+$	HpCDF	
				360.813	$[M-COCl]^+$	HpCDD	
				407.782	$[M]^+$	HpCDF	1.03
				409.779	$[M+2]^+$	HpCDF	
				423.777	$[M]^+$	HpCDD	1.03
				425.774	$[M+2]^+$	HpCDD	
				477.720	$[M^+]$	HBDPE[a]	
53.00	Stop Hepta Program	250					
53.50	Start Octa Program; sweep = 350 ppm; time/mass = 0.30 sec.	250		370.768	$[M-COCl]^+$	OCDF	
				394.774	$[M-COCl]^+$	OCDD	
				441.732	$[M]^+$	OCDF	0.88
54.00	Begin temp. program to 270°	250	5	443.740	$[M+2]^+$	OCDF	
58.00	Column temperature hold	270		453.772	$[M]^+$	$^{13}C_{12}$-OCDF	
				457.738	$[M]^+$	OCDD	0.88
				459.735	$[M+2]^+$	OCDD	
				469.779	$[M]^+$	$^{13}C_{12}$-OCDD	
				471.776	$[M+2]^+$	$^{13}C_{12}$-OCDD	
				511.681	$[M]^+$	NDPE[a]	
66.00	Stop Octa Program						
66.00	Begin temp. program to 300°	270	5				
71.00	Column temperature hold	300					
75.00	Cool Column to 190°						

[a]HxBFE, HpBPE, OBPE, NBPE, DBPE are abbreviations which designate (respectively) hexachloro-, heptachloro-, octabromo-, nonachloro-, and decachlorodiphenyl ethers.

[b]The parameters given here are applicable for a 60-meter fused silica capillary GC column coated with DB-5.

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MATHEMATICAL MODELING OF THE PHYSICAL PROPERTIES USED IN ANALYSIS OF PCDFs

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INTRODUCTION

The analysis of polychlorinated dibenzofurans (PCDFs) has always been difficult due to the many possible arrangements of chlorines about the two aromatic rings which can yield 135 possible congeners. This analytical difficulty arises from the need to identify a particular congener which may be present in a given matrix. The physical property most widely used to identify a given PCDF congener is its gas chromatographic retention behavior. A variety of parameters have been used to characterize this behavior. These include relative retention to 2,3,7,8-tetrachlorodibenzofuran (1,2), relative retention to lindane (3) and relative retention to various esters of 1,3,5-benzene tricarboxylic acid (4). When analyzing for series of compounds with a wide elution range, such as the PCDFs, the use of a single reference compound is not as desirable as using a series of indexing compounds which elute quite closely to the PCDF being indexed. The Kovats retention index system (5,6) is based on a series of straight chain hydrocarbons and can be adapted to temperature-programmed conditions (7) which were used in this work to assign retention indices to all the PCDFs that had been prepared.

Once indices were assigned to the PCDFs, a mathematical model was devised based on molecular structure to explain their elution behavior. Regression techniques were used to derive quantitative relationships between these structural parameters and the retention indices. The model could then be used to look for PCDFs that were outliers, or did not agree with the predicted retention index derived from other PCDFs. Furthermore, the model could also be used to predict the retention indices for PCDFs that had not been synthesized.

EXPERIMENTAL

The PCDFs were prepared by the carefully controlled oxidative degration of individual polychlorinated biphenyl (PCB) congeners (8). In certain instances a selected PCDF was isolated using normal and/or reverse phase HPLC. The isolated PCDF could then be either chlorinated using antimony pentachloride or dechlorinated using UV photolysis (9) to form additional PCDF congeners.

Retention indices were determined on a 30 meter J&W DB-5 capillary column. A Hewlett Packard 5985B GC/MS system was used to detect both the eluting PCDFs and normal hydrocarbons. The column was programmed in a feshion such that the hydrocarbons were eluting linearly in the range of monochloro through octachlorodibenzofuran.

MODEL OEVELOPMENT

The development of a mathematical model began by dividing tha PCDF through biphenyl and ether linkage to form two symmetrical halves. The retention index would then be a sum of the derived index for each half. A similar approach has been used for modeling PCBs (10). To assist in this model develop-

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ment, the PCDFs were renumbered replacing the conventional 6, 7, 8 and 9 with 4', 3', 2' and 1', respectively (11). This scheme emphasizes the symmetry of the molecule and greatly simplified the model development.

Through repeated data analyses, a series of variables were established representative of various structural properties of the PCDFs. These variables included the number and position of the chlorines about the aromatic rings and the relationship of these chlorines to each other (i.e., ortho, meta and para). In the final model development it was necessary to include two variables involving the 1 and 1' as well as the 4 and 4' positions to describe the interaction of the two rings with each other. This type of interaction was not accounted for in the simple model of two independent halves being combined to form a whole.

These variables were then assigned values dependent on the number of times that varieble occurred in a given PCDF. The regression of these variables against the retention indices was carried out and the derived regression coefficients serve as a quantitative measure of the retentive effect of the molecular structural component represented by that variable.

RESULTS

Using the described variables and regression techniques an R^2 value of 0.9995 and a standard deviation of 6.78 was obtained for the observed versus predicted retention index for 110 PCDFs which have been synthesized to date. This standard deviation is quite acceptable in view of the fact that the error in the measurement of the retention index of a PCDF is ±4 index units. The model has proven useful in detecting errors in the structural assignment given to PCDFs (12). Furthermore, it has allowed retention indices to be assigned to PCDFs which we have not yet synthesized.

At the present time the minimum number of PCDFs that would be necessary to accurately determine the regression coefficients is being established. This is important in that, as the analytical conditions are changed (e.g., different chromatography columns or different analytical systems such as HPLC), it would only be necessary to run the subset of PCDFs to allow the retention characteristics for all other PCDFs to be determined.

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FORMATION OF PCDD AND PCDF IN ASKAREL AND CONTAMINATED MINERAL OIL EQUIPMENT

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ABSTRACT

The Electric Power Research Institute (EPRI) is conducting a program to determine if polychlorinated dibenzofurans (PCDF) and/or polychlorinated dibenzo-p-dioxins (PCDD) are present, or if they can be formed, in dielectric fluids used by the electric utility industry. The program includes the following tasks.

- Literature Review
- Round Robin Analytical Method Evaluation Study
- Survey of In-Service Dielectric Fluids
- Arcing/Corona Tests
- Pyrolysis/Combustion Tests
- Development of a Rapid MS/MS Analytical Technique

DISCUSSION

The Literature Review, prepared by SCS Engineers of Long Beach, California, summarizes much of the background litarature on PCDD/PCDF. It describes accidents that generated PCDD/PCDF, degradation of PCDD/PCDF, toxicology, and future research needs. This review is available from EPRI as publication number EPRI CS-3308.

The Round Robin Analytical Method Evaluation Study was designed to validate current methodologies and to determine the accuracy with which specific PCDD/PCDF isomers can be quantified. Four sample preparation methodologies and three mass spectrometry techniques are currently being compared. The study includes the synthesis of native and isotopically labelled standards and the analyses of spiked sample matrices. Radian Corporation synthesized the standards, and prepared the spiked

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matrix samples, which will be analyzed by Battelle, the Illinois Institute of Technology Research Institute (IITRI), Radian, and the University of Umea (Sweden). The isotopically labelled standards will be used to show true recoveries and to provide accurate quantification within congener classes. Presently 1,2,3,7,8-pentachlorodibenzofuran-$^{13}C_{12}$ has been prepared and purified. A labelled hexachlorodibenzofuran is also being synthesized. The native standards were used for spiking and to generate standard curves and response factors. The native isomers that were synthesized include 1,2,3,7,8-pentachlorodibenzofuran, 1,2,3,4,7,8-hexachlorodibenzofuran, and 1,2,3,4,6,7,8-heptachlorodibenzofuran.

The Round Robin Analytical Method Evaluation Study is presently in progress and a comparison of data from the various laboratories will soon be completed to show reliability, accuracy, and ruggedness of the various analytical methods.

The In-Service Dielectric Fluid Survey consists of developing a selection criteria document, obtaining samples of dielectric fluids, and determining the levels of PCDD/PCDF in selected fluids. General Electric (GE) completed the selection criteria document, while Battelle, IITRI, Radian, and the University of Umea are presently carrying out the analyses. This study will show the absence or presence of PCDD/PCDF in currently used dielectric liquids. Hopefully the study will evaluate a broad range of liquids and operating conditions that mirror the dielectric liquid usage of various utilities throughout the United States.

The Arcing/Corona Tests were designed to determine if arcing and corona discharges could produce PCDD/PCDF isomers in dielectric fluids. The tests, which were carried out by GE, consisted of loading various mixtures into a test vessel and producing a short duration arc with an energy of between 5-10 kjoules. Aroclor 1254 at concentrations of 50-10000 ppm (w/w) in mineral oil, and a trichlorobenzene reference liquid containing 50% (w/w) of Aroclor 1254 were arced. The unarced mineral oil, as well as the trichlorobenzene/Aroclor 1254 mixture, were also analyzed as positive controls. The preliminary results from these analyses, summarized in Tables 1 and 2, show little difference in PCDD/PCDF levels between the arced and unarced fluids. This indicates that arcing appears to have minimal effect on either the PCDD or the PCDF levels in dielectric liquids. These data show the type of information that can be gained from this study.

The Pyrolysis/Combustion Tests were designed to characterize the production of PCDD/PCDF isomers during pyrolysis. These tests are being carried out by the New York State Department of Health, and are presently in progress.

The goal of the Rapid MS/MS Technique Study is to develop an analytical method that minimizes the need for extensive sample workup prior to analysis. The advantages of this approach would be a rapid and lower cost analysis as compared to conventional gas chromatography/mass spectrometry (GC/MS). Ideally this technique will provide the same sensitivity and selectivity as conventional GC/MS.

SUMMARY

This research program is designed to evaluate the potential presence of PCDF and PCDD in utility dielectric liquids currently in use in the United States. The study is based on development of well characterized methods to detect PCDF/PCDD in order to generate high quality data for the diverse class of compounds that are expected only at trace concentrations. The in-service fluid characterization will show the relative magnitude of PCDF/PCDD background levels in fluids from various utility operations. The arcing and pyrolysis experiments are designed

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to show potential for production of PCDF/PCDD in unusual situations or upset situations.

The overall program is a comprehensive attempt to characterize the potential presence of PCDF/PCDD in operating utility dielectric fluids and to investigate the potential for their production in unusual situations such as catastrophic failure, or overheating.

Table 1

PCOD DATA FOR ARC STUDY SAMPLES
(limit of detection), ppb (w/w)

Samples	Tetra-CDD	Penta-CDD	Hexa-CDD	Hepta-CDD	Octa-CDD
Arced Aroclor 1254	(0.06)	(0.36)	(0.38)	(1.4)	(1.7)
Arced Aroclor 1254	0.20	(0.14)	(0.09)	(1.6)	(2.6)
Arced Aroclor 1254	(0.06)	(0.13)	(0.12)	(1.8)	(1.4)
Arced 50/50 TCB/1254	23.9	12.1	1.7	(1.0)	(1.4)
Unarced Oil	(0.09)	0.11	0.05	1.04	1.00
Unarced 50/50 TCB/1254	21.2	(0.78)	(0.21)	(5.9)	(6.8)
Method Blank	(0.10)	(0.09)	(0.07)	(0.65)	(0.52)

Table 2

PCDF DATA FOR ARC STUDY SAMPLES
(limit of detection), ppb (w/w)

Samples	Tetra-CDF	Penta-CDF	Hexa-CDF	Hepta-CDF	Octa-CDF
Arced Aroclor 1254	0.69	4.2	1.6	(1.7)	(1.6)
Arced Aroclor 1254	(0.07)	(0.19)	(0.10)	(2.2)	(1.7)
Arced Aroclor 1254	(0.07)	(0.12)	(0.08)	(2.6)	(1.2)
Arced 50/50 TCB/1254	173	1740	1180	1360	171
Unarced Oil	(0.06)	(0.03)	(0.01)	(0.6)	(0.71)
Unarced 50/50 TCB/1254	367	1850	1790	2960	217
Method Blank	(0.08)	(0.08)	(0.04)	(0.35)	(0.48)

MONS 215588

Chlorodibenzofuran Analysis Using Two-Dimensional

Gas Chromatography-Mass Spectrometry

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We have developed a two-stage gas chromatography system for sample cleanup prior to mass spectrometry. Schematics of this system in its three modes of operation are shown in Figs. 1,2,3.

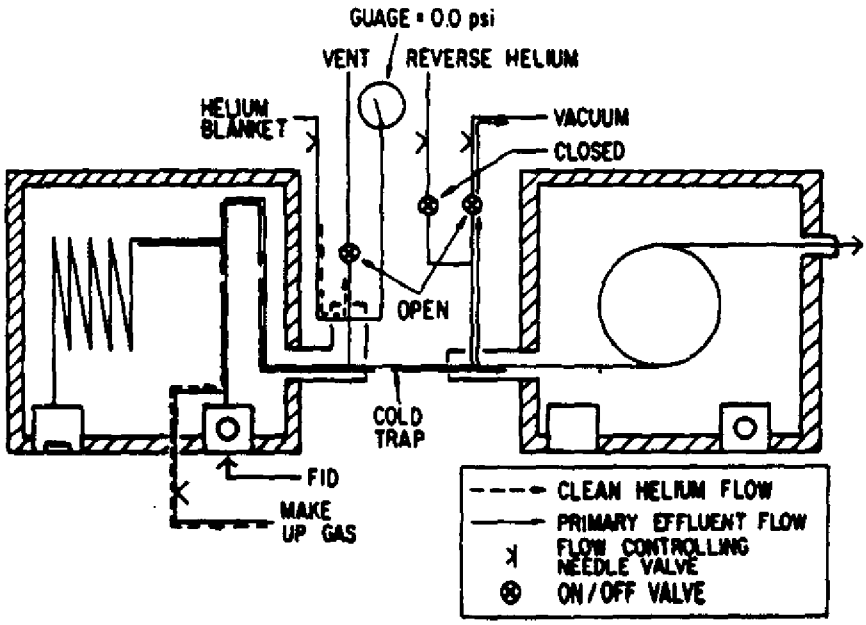


Figure 1. Schematic of the GC-GC system in the "SAVE" mode of operation.

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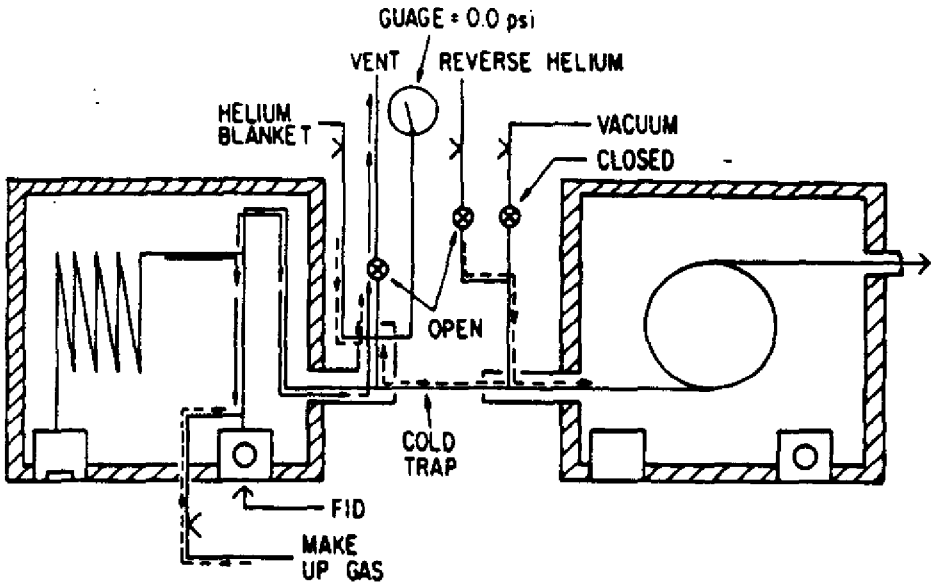


Figure 2. Schematic of the GC-GC system in the "DIVERT" mode of operation.

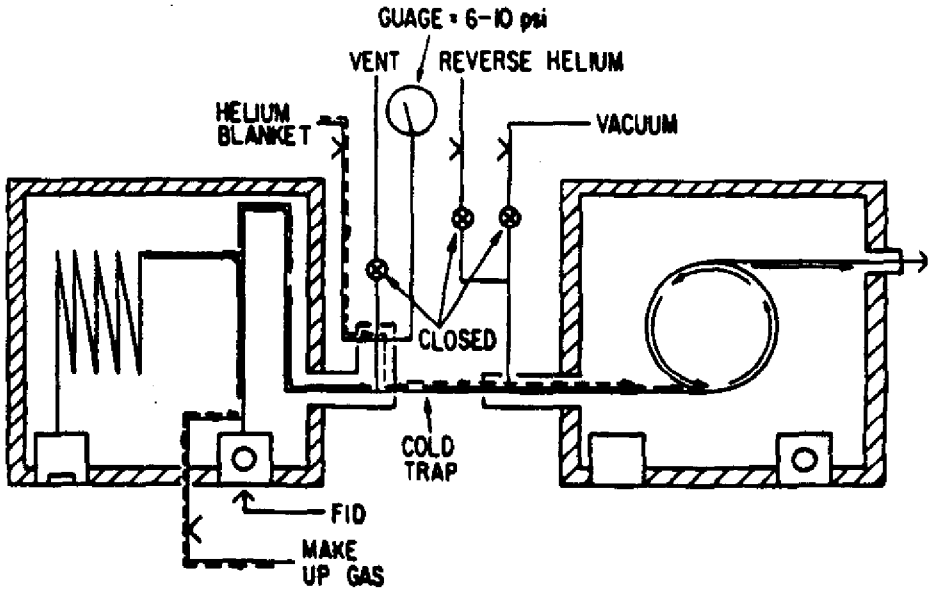


Figure 3. Schematic of the GC-GC system in the "SECONARY SEPARATION" mode of operation.

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The system consists of two coupled gas chromatographs. The first chromatograph uses a high capacity low resolution packed GC column (10 ft x 2 mm , 3% Silar 10C). This column provides a preliminary separation. In the case of the chlordibenzofurans, it serves to limit the number of isomers which must be resolved in the secondary separation and it prevents the great majority of the matrix comoonents from reaching the high resolution secondary column. This column is essentially expendible and serves to collect involatile residues before they reach the secondary column. The condition of the primary column should be monitored regularly because both absolute and relative retention times can change as residues are deposited.

When the system is operated in the "save" mode selected portions of the primary chromatogram are stored in a cold trap. See Fig. 1. When the system is operated in the "divert" mode unwanted components eluting from the primary chromatograph are vented from the instrument. See Figure 2. Changes in operating mode are accomplished by opening and closing valves--none of which is in a heated region.

After the primary separation is complete the system is switched to the "secondary separation" mode and the cold trap is heated to transfer its contents into the secondary chromatograph. See Fig. 3. The secondary chromatograph can contain any high resolution capillary which is comoatible with mass spectrometer operation. For the case of 2,3,7,8-TCDF analysis, this chromatograph is fitted with a capillary system which has been described previously. (J. Chromatogr., 294 (1984) 87). This capillary combination was arrived at using the method of Krupcik et al (J. Chromatogr., 213 (1981) 189. The computer model of the separation is shown in Fig. 4. This capillary combination provides baseline resolution of 2,3,7,8-TCDF from all isomers which co-elute from the secondary column. Using this system full baseline separation of 23478 and 123789 from their isomers has also been obtained using various secondary capillaries.

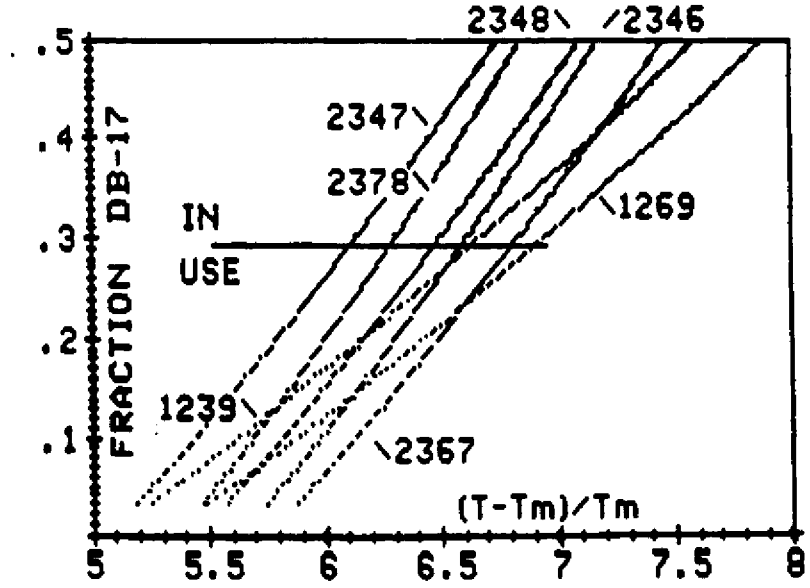


Figure 4. Predicted separations for 7 TCDF isomers using the (DB-17)-(SP2330) capillary system as determined by computer modeling employing the Krupcik equations.

A typical quantitative analysis for a chlorodibenzofuran starts with addition of a labeled internal standard to the sample. At GE standards have been prepared which are 99 atom-% ^{13}C (R. A Bell and A. Gara). Full mass spectra of the standards have been recorded in order to compare them with analogous spectra of the un-labeled materials. It was found that the %-total ionization for the molecular ion and its isotopomers was the same for the labeled and unlabeled materials. Therefore no correction is applied for enrichment errors or isotopic effects on fragmentation.

After addition of appropriate standards, samples are either analyzed by direct injection into the primary chromatograph or are subjected to a modified Stalling clean-up procedure. Arochlors up to 1242 can be analyzed directly by injection of about 2 mg of Arochlor. Flyash extracts and 10C oil have also been analyzed successfully in this way. Larger Arochlors, fish, sediment, etc. require the Stalling procedure.

The sample is co-injected with a retention index marker which elutes from the primary chromatograph just ahead of the component of interest. Collection of the component of interest is accomplished relative to this marker. After the primary chromatogram is complete the system is switched to the secondary separation mode and the cold trap is heated. The components eluting from the secondary chromatograph are carried directly into the electron beam of the mass spectrometer ion source using a section of fused silica capillary.

The mass spectrometer operating conditions are as follows:

Mass Spectrometer:	Vg Zab
Ionization:	Electron Impact
Resolution (10% Valley):	3000

Acquisition by Selected Ion Monitoring:
e.g. for 2,3,7,8-TCDF ions at 304,306,308,316,318, 320 and 328 are monitored using voltage switching. Mass 328 is generated as a lock mass signal using 4,4'diaminooctafluorobiphenyl added at a very low level from a heated inlet. The lock mass signal is monitored in full profile mode.
Great care is taken to ensure that ion source focusing does not change with voltage switching. Very minor source contamination can cause this effect in the Vg Zab.
Great care is taken to ensure that interfering materials do not co-elute with the lock mass thereby shifting its centroid and causing systematic errors in mass selection.
No data is accepted which does not show the theoretical distribution of intensities for the isotopomers of the respective molecular ions.

MONS 215592

PCDF ISOMERS AND ISOMER LEVELS FOUND IN PCBs

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EXPERIMENTAL

We have developed a new clean-up technique for the determination of PCDFs in PCBs.

1. Dissolve PCB in CH_2Cl_2/c-hexane.
2. Add surrogate.
3. Column Carbon PX 21 on fibers.
4. Reverse elution by toluene.
5. Evaporate toluene, 35°C, 20 mm Hg.
6. Dissolve in n-hexane.
7. Fluorosil column.
8. Reverse elution CH_2Cl_2.
9. Evaporate, add known amount final solvent.
10. Inject 1-2 µl in HRGC/MS using a 60 m fused silica SP 2330 column. The temperature program allows isomer specific analyses. The MS instrument is operating with EI or NCI (methane), SIM.
11. Quantification of 2,3,7,8-substituted isomers as well as total levels of PCDFs.
12. Calculation of recovery of surrogates.

RESULTS

We have analyzed a series of commercial PCB products and the results are given in Table I.

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DISCUSSION

We have found contamination by PCDFs in all PCB products analyzed. The total level of PCDFs varied from a few ug/g up to 40 ug/g. The chlorination pattern of the PCDFs was found to vary with the chlorination level of the PCBs.

Discussing individual isomers, the toxic 2,3,7,8-substituted Cl_4-, Cl_5- and Cl_6 PCDFs were always middle or major constituents within each group of congeners.

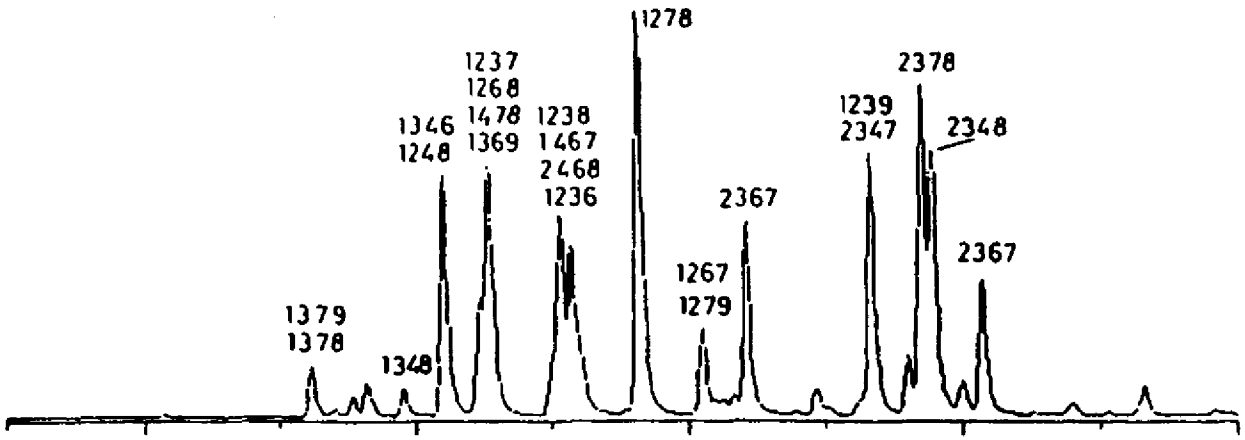
The 2,3,7,8- and 2,3,4,8-tetra-CDFs are eluting very close together. The toxic effect of these two isomers is very different. The ratio of these two isomers was found to vary from 10:1 to 1:10. For a risk evaluation it is essential to have an analytical method where it is possible to separate between these two isomers (see Figure 1).

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Table 1. PCDFs in commercial PCBs.

PCB-typ	TRI- Tot	TRI- 2378	TETRA- Tot	TETRA- 12348 12378	PENTA- 23478	PENTA- Tot	HEXA- 123479 123478	HEXA- 123678	HEXA- 123789	HEXA- 234678	HEXA- Tot	HEPTA- Tot	Rec 2378 TCDD-%
Pyralene	700	53	630	10	T	35	ND	ND	ND	ND	ND	ND	79
A1254	63	19	1400	690	490	4000	2500	2100	190	130	10000	960	78
A1260	10	13	110	48	56	260	500	120	190	27	1500	1300	88
A30	500	35	573	14	28	160	50	59	ND	ND	220	T	79
A40	1300	180	2600	96	8	1700	79	68	ND	T	310	ND	79
A50	7400	3300	20000	760	1100	8000	700	360	18	98	3100	75	95
A60	770	840	6900	1100	990	8100	1600	330	170	330	6800	2000	95
T64	47	23	360	97	122	840	520	390	58	41	2600	220	72
Clophen C	710	54	1200	34	30	270	ND	T	ND	ND	T	ND	79
Blank	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	90
Blank	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	87

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PART 3:

PYROLYSIS AND COMBUSTION

MARCUS COOKE - MODERATOR

MONS 215597

FORMATION OF POLYCHLORINATED DIBENZO-p-DIOXINS AND DIBENZOFURANS FROM BURNING OF SILICONE DIELECTRIC FLUID SPIKED WITH POLYCHLORINATED BIPHENYLS

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INTRODUCTION

Since 1982 Dow Corning Corporation has had a program of retrofilling PCB containing transformers, using its silicone fluid RetroSil™ process. The concerns over the combustion of PCB's has lead to the desire to better understand the by-products formed during the burning of silicone fluids containing small amounts of PCB's which may remain after the RetroSil™ process. Thus a contract to study this matter was initiated with the Brehm Laboratory of Wright State University under the direction of Dr. Thomas D. Tiernan.

The study had 2 objectives. One was to determine amounts and species of polychlorinated dibenzodioxins (PCDD's) and polychlorinated dibenzofurans (PCDF's) formed, when a silicone fluid spiked with various levels of PCB was pyrolyzed. In addition, the effect of pyrolysis temperature on this same system was to be evaluated. This paper discusses the results of these studies.

METHODOLOGY

All spiked samples were prepared at Dow Corning. Burning studies were conducted at the Brehm Laboratory, at Wright State University under the direction of Dr. Thomas Tiernan. Samples of 50 centistoke polydimethylsiloxane (DOW CORNING® 561 Fluid) were spiked with 5, 50, 500 and 11,300 ppm of PCB from Arochlor 1260. The 11,300 ppm sample was initially studied at 4 different temperatures to determine which temperature produced the maximum amount of PCDD's and PCDF's. This was determined to be 600°C. Then the samples spiked with various amounts of PCB were burned in air at this temperature and the by-products analyzed.

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The burning apparatus is shown in Figure I. It consisted of a high temperature tube furnace containing a quartz tube reactor, a cooled sample injection system and a series of three traps to collect the volatile combustion products. Five ml. of sample were used for each test with an average residence time in the burning zone of two seconds. Table I summarizes the weights of the combustion products based upon the 5 ml (4.7 g.) sample injected. The combustion products include any water produced in the burning reaction. Thus the total weight of the combustion products could, and indeed did, at times exceed the amount of sample injected.

Preparation of the pyrolysis products for analysis consisted of soxhlet extraction in toluene for 16 hours and a series of washing steps using KOH, H_2SO_4 and anhydrous sodium sulfate, concluding with a hexane elution through a column packed with silica, and then concentrated by evaporation of the hexane. This was then transferred to a laboratory prepared liquid chromatography column packed with Woelm basic alumina which was previously activated at 600°C. After conducting a series of methylene chloride/hexane elutions, the samples were evaporated to dryness and stored in a freezer until analysis. These samples were then reconstituted by adding tridecane before injection of the appropriate aliqnot into the analytical test instrument.

Analyses of the extract were done using a Perkin Elmer Sigma III Gas Chromatograph coupled through a custom fabricated interface including a single-stage glass jet separator to a Kratos MS-25 Mass Spectrometer equipped with a DS-505M Data System.

RESULTS OF ANALYSES

The results of the analyses of the combustion products from the burning tests for chlorinated dibenzo-o-dioxins (CDDs) and dibenzofurans (CDFs) are summarized in Tables II and III. Also shown are the results of analyses of a method blank, of a sample of polydimethylsiloxane containing 11,300 ppm of PCBs (which was not pyrolyzed), and a sample of the polydimethylsiloxane containing 130 ppm PCB which had been previously subjected to electrical arcing.

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As can be seen from the data presented in Table II, the initial series of tests, in which samples of polydimethylsiloxane fluid containing 11,300 ppm of PCBs were burned at temperatures of 400°C, 600°C, 800°C and 1000°C respectively, revealed that chlorinated dibenzofuran was formed in the 400° and 600° tests. In particular, the tetra-, penta- and hexa-CDFs were produced at these temperatures. All data is presented in the concentration of total CDD & CDFs in nanograms/gram of total combustion products or Parts Per Billion. Minimum Detectable Concentrations are given in parenthases. While the presence of several isomers of each of these chlorinated classes can be discerned from the mass chromatograms obtained in the analyses, it is noteworthy that the tetra-CDFs appear to include 2, 3, 7, 8-TCDF (or at least a TCDF isomer which coelutes with the 2, 3, 7, 8-TCDF). No CDDs other than OCDD were detected in the combustion products from any of these initial tests. There were essentially no detectable CDFs in the products from the 800°C and 1000°C burning tests.

It was clear from the initial series of tests that the quantities of CDFs produced from burning of the PCB-contaminated silicone fluid were greater when the temperature was 600°C. After these results had been reported to Dow Corning and reviewed, the Brahm Laboratory was requested to conduct several additional tests in which each of three samples of the silicone fluid containing 500 ppm, 50 ppm and 5 ppm, respectively, of PCBs, were to be burned at a temperature of 600°C. The results of analyzing the combustion products from these tests for CDDs/CDFs are shown in Table III. As these data indicate, tetra-, penta- and hexa-CDFs were detected in all of these combustion products, although the quantities of these CDFs were clearly directly related to the concentration of PCBs in the fluid pyrolyzed. That is, the greater the concentration of PCBs in the field, the greater the concentrations of CDFs in the pyrolysis products. This trend is, of course, as expected if the PCBs are the precursors of the CDFs which are formed in the combustion process. Table III also shows that the second series of tests found no CDDs (except some OCDD, which may be questionable) when the silicone fluids containing 500, 50 and 5 ppm of PCBs were pyrolyzed.

The analytical results obtained for the polydimethylsiloxane fluid containing 11,300 ppm PCBs which was not pyrolyzed, as well as for the fluid sample containing PCBs which had been previously subjected to electrical arcing, indicate

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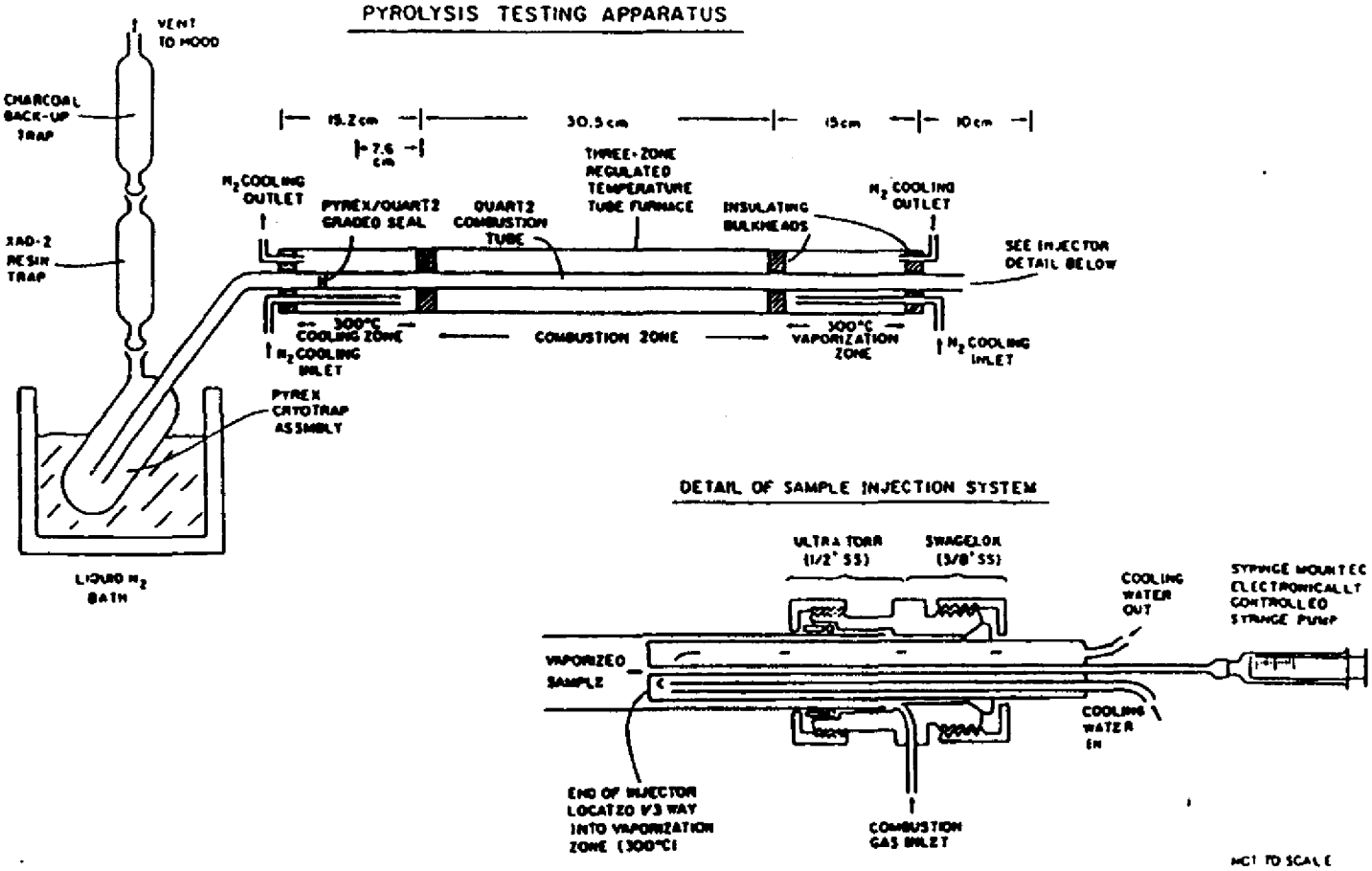
that these samples contain essentially no detectable CDDs/CDFs. It will be noted that the detection limits reported for these samples are for the fluid samples themselves (and not for combustion products), since these samples were not pyrolyzed.

CONCLUSION

Burning studies of polydimethylsiloxane spiked with various levels of PCB show that no polychlorinated dibenzo-p-dioxins are detected but that tetra, penta and hexa species of chlorinated dibenzofurans are detected.

A sample of PCB spiked polydimethylsiloxane fluid which had been subject to electrical arcing showed no detectable PCDD's or PCDF's formed.

Maximum formation of PCDF's appeared to occur at 600°C.



APPARATUS FOR TESTING PYROLYSES OF SELECTED CHEMICALS FOR PRODUCTION OF CDDs/CDFs

Figure 1.

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TABLE I

WEIGHTS OF COMBUSTION PRODUCTS FORMED FROM PYROLYSIS OF POLY DIMETHYLSILOXANE FLUIDS CONTAINING POLYCHLORINATED BIPHENYLS[a]

PCB Level (ppm)	Burning Temperature	Total Weight of Combustion Products (grams)
11,300	400°C	4.6
11,300	600°C	5.3
11,300	800°C	4.6
11,300	1000°C	5.1
500	600°C	4.6
50	600°C	4.6
5	600°C	4.5

a. In each experiment, 5.0 mL of the silicone fluid were burned. Since the density of the fluid is 0.9428 g/mL, 4.7 g. of fluid were pyrolyzed in each case. The combustion products include any water produced in the pyrolysis reaction, as well as incompletely pyrolyzed fluid in cases where combustion was not complete (lower temperatures).

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TABLE II

THE EFFECT OF TEMPERATURE ON THE PYROLYSIS PRODUCTS OF PDMS SPIKED WITH 11,300 ppm PCB
(Data in parts per billion)

Burning Internal Temp.	TCDFs	TCDDs	Recovery of $^{37}Cl_4$-2,3,7,8-TCDD Internal Standard	PCDFs	PCDDs	HxCDFs	HxCDDs	HpCDFs	HpCDDs	Recovery of $^{37}Cl_4$-1,2,3,4,6,7,8- HpCDD Internal Standard	OCDF	OCDD	Recovery $^{13}C_{12}$-OCDD Standard
Method Blank	N.D. (0.18)	N.D. (0.05)	56%	N.D. (0.20)	N.D. (0.20)	N.D. (0.40)	N.D. (0.30)	N.D. (0.20)	N.D. (0.20)	41%	N.D. (0.40)	N.D. (0.10)	56%
Not Pyrolyzed	N.D. (0.10)	N.D. (0.45)	61%	N.D. (2.0)	N.D. (2.0)	N.D. (2.5)	N.D. (2.5)	N.D. (2.5)	N.D. (2.5)	62%	N.D. (2.5)	N.D. (14)	40%
400°C	3,670	N.D. (2.5)	78%	1,260	N.D. (17)	1,600	N.D. (10)	N.D. (7.5)	N.D. (7.5)	51%	N.D. (44)	10	41%
600°C	46,235	N.D. (24)	68%	11,500	N.D. (20)	3,600	N.D. (10)	N.D. (10)	N.D. (10)	82%	N.D. (30)	8.0	31%
800°C	N.D. (4.0)	N.D. (4.0)	50%	N.D. (5.0)	N.D. (10)	N.D. (25)	N.D. (15)	N.D. (5.0)	N.D. (5.0)	88%	N.D. (42)	N.D. (10)	81%
1000°C	N.D. (2.0)	N.D. (2.0)	73%	N.D. (10)	N.D. (10)	N.D. (20)	N.D. (20)	N.D. (10)	N.D. (5.0)	59%	N.D. (44)	12	45%

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TABLE III

PYROLYSIS PRODUCTS OF PDMS SPIKED WITH VARIOUS CONCENTRATIONS OF PCB
(Data in parts per billion)

PCB Level (ppm)	Burning Temp.	TCDFs	TCDDs	Recovery of $^{37}Cl_4$-2,3,7,8-TCDD Internal Standard	PCDFs	PCDDs	HxCDFs	HxCDDs	HpCDFs	HpCDDs	Recovery of $^{37}Cl_4$-1,2,3,4,6,7,8- HpCDD Internal Standard
11,300	600°C	46,235	N.D. (24)	68%	11,500	N.D. (20)	3600	N.D. (10)	N.D. (10)	N.D. (10)	82%
500	600°C	2,778	N.D. (7.0)	60%	450	N.D. (15)	142	N.D. (15)	N.D. (10)	N.D. (10)	100%
50	600°C	138	N.D. (4.0)	59%	12	N.D. (4.0)	N.D. (38)	N.D. (30)	N.D. (10)	N.D. (10)	86%
5	600°C	12	N.D. (5.0)	63%	2.0	N.D. (4.0)	N.D. (10)	N.D. (10)	N.D. (10)	N.D. (10)	71%
Arced	Not Pyrolyzed	N.D. (12)	N.D. (20)	53%	N.D. (4.0)	N.D. (10)	N.D. (25)	N.D. (25)	N.D. (12)	N.D. (12)	17%

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SIMULATED BUILDING FIRE STUDY USING RETROFILLED TRANSFORMER DIELECTRIC COOLANT

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ABSTRACT

In this program a model combustion system was built in the Battelle pilot plant facility. The unit was a 40,000 Btu per hour vertically fired tube furnace with a combustion zone 4.3 ft (131 cm) in length with a 5.5 in. internal diameter (14 cm). A schematic diagram of the combustion system used in this study is shown in Figure 1. The combustion experiments were designed to produce conditions favorable for production of polychlorinated dibenzofuran (PCDF) and polychlorinated dibenzo-p-dioxin (PCDD).

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PROJECT SUMMARY

The tests were conducted using kerosine with 1% (w/w) silicone coolant added to generate condensation nuclei for catalytic production of PCDF/PCDD. The kerosine-silicone mix was injected through the primary injection port. The test dielectric liquids were atomized and sprayed into the near flame region of the combustor where contact temperatures of 700-900 C were obtained at the point of injection. The dielectric fluid was injected through the secondary injection port, resulting in an opposed flame condition. The primary-secondary injection ratio was approximately 2 to 1 for all tests. Test conditions were maintained to produce a combustion gas oxygen concentration of 3 to 5 volume percent.

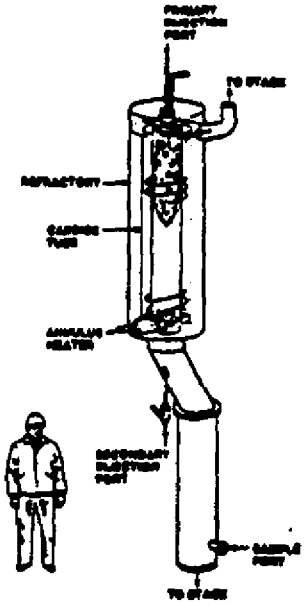


FIGURE 1

SCHEMATIC DRAWING OF THE COMBUSTION TEST APPARATUS

Prior to injecting the dielectric fluid, the combustion gas oxygen concentration was approximately 8 to 9 percent. Hence the dielectric fluid was injected into a high temperature, oxygen deficient environment similar to that expected in an uncontrolled fire. Samples were collected by EPA Modified Method 5 train sampling (MM5).

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The test liquids were simulated retrofill dielectric fluids with 50 ppm (w/w) Aroclor, and residual tri/tetrachlorobenzene (TCB/TTCB) diluents, in a liquid silicone solution. Three Aroclors 1260, Aroclor 1254, Aroclor 1242, TCB/TTCB blend, and a blank with silicone only were combusted.

Samples were extracted by Battelle (BCL), and submitted to three participating laboratories: the University of Umea (Umea), Oneida Research Services (ORS), and BCL, for blind analysis of PCDF/PCDD. Each laboratory used their standard preparation and analysis procedures. Battelle and Oneida used high resolution mass spectrometry(HRMS), while the University of Umea used a quadrupole mass spectrometer (QMS), for analyte detection. All three laboratories used high resolution capillary gas chromatography(HRGCC). The three laboratories split the same samples while preforming blind analyses. This independently verified results and showed the variability in reported data. An illustrative chromatogram of a total ion mass spectrum (TIMS) from the Aroclor 1254 burn is given in Figure 2.

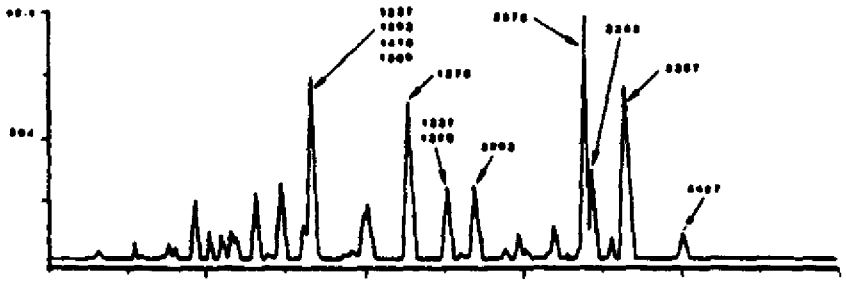


FIGURE 2

AROCLOR 1254 PRODUCT TIMS CHROMATOGRAM (COURTESY OF C. RAPPE)

Umea and ORS analyzed all furan and dioxin congener classes for four to eight chlorine substitution (tetra through octa isomers), and both laboratories reported the 2,3,7,8-tetrachlorodibenzo isomer concentrations for both the furan (2,3,7,8-TCDF) and dioxin (2,3,7,8-TCDD) classes. BCL analyzed and reported the tetra furan/dioxin congener concentrations, 2,3,7,8-TCDF, and 2,3,7,8-TCDD concentrations in the MM5 combustion samples. In addition Umea analyzed and reported the individual isomer concentrations of all tetra and penta isomers, of both furans and dioxins found in these samples.

The three laboratories showed good agreement in overall results and found no detectable dioxin isomers in any congener class for the four tests reported; a system blank, the Aroclor 1260 test, the Aroclor 1254 test, the Aroclor 1242 test. The averages for the three laboratories reporting the four test burns are given below (PnCDF represents pentachlorodibenzoburans):

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[ppb (w/w) dielectric consumed basis]

TEST	DOPANT	TCDF	2,3,7,8-TCDF	PnCDF
Blank	None	0.003	<0.002	ND
1	1260	0.43	<0.15	0.31
2	1254	0.38	<0.08	0.14
3	1242	0.08	<0.01	0.04

From these data the polychlorinated biphenyl (PCB) conversion rates were calculated. Conversion of Aroclor 1260 to TCDF ranged from 0.9 to 17 parts per million (ppm) on a weight basis. Conversions of Aroclor 1254 [4 - 11 ppm (w/w)] and Aroclor 1242 [2.4-2.6 ppm (w/w)] to TCDF gave similar values, and were consistent with pyrolysis conversion rates reported in the literature (1). Tri and tetrachlorobenzenes at concentrations up to 1.5% (w/w) in the silicone burned, were found to produce no measureable PCDD or PCDF.

In this study the measured furan concentrations produced by combustion of retrofill dielectric liquids tended to decrease as the degree of chlorination of the spiked PCB decreased. Aroclor 1260 spiked into silicone resulted in higher levels of PCDF than found in the experiment with Aroclor 1242. In all cases, the PCDF levels were extremely low (ppb) on a dielectric fluid consumed basis.

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FORMATION OF PCDFs UNDER "OPTIMIZED" COMBUSTION CONDITIONS FROM LOW-LEVEL PCB DIELECTRIC FLUIDS

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The Environmental Protection Agency (EPA) issued a final rule on August 25, 1982, authorizing indefinite use of certain electrical transformers containing polychlorinated biphenyls (PCBs). This rule is known as the PCB Electrical Use Rule. At that time, information available to the EPA indicated that fires involving electrical transformers were rare, isolated incidents. However, several recent transformer fires in buildings have brought into question EPA's earlier assumption. The Agency has therefore issued an Advance Notice of Proposed Rulemaking (ANPR) (USEPA 1984a) and proposed rule (USEPA 1984b) to gather data on the specific risks posed by fires involving electricel transformers that contain PCBs and also on mechanisms for mitigating or eliminating these risks. Depending upon the results of EPA's enalysis of these dete, the Agency may proposa further control measures on the use of this equipment.

This abstrect describes the methods and results of a study, conducted in support of EPA's deta gathering activities under the ANPR, of the potantiel for formetion of polychlorinated dibenzofurens (PCDFs) and polychlorinated dibenzo-p-dioxins (PCDDs) from uncontrolled fires involving PCB-containing dielectric fluids.

At high temperatures, such as those in transformer fires, polychlorinated biphenyls (PCBs) raact to form polychlorineted dibenzofurans (PCDFs) and other toxic by-products. The purpose of this study was to optimize conditions for PCDF formation in order to examine the potential for formetion of PCDFs and polychlorinated dibenzodioxins (PCDDs) from combustion of selected PCB-containing dielectric fluids.

The study was conducted in three phases. In Phase 1, a bench-scale thermal destruction system, developed by MRI, was refitted with specific components installed to accommodate this study as shown in Figure 1. Then, a few test runs

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were made under preliminary temperature and oxygen conditions to ensure an acceptable system blank. The concentrations of CO, CO_2, and O_2 in the effluent were monitored continuously. The entire effluent from the thermal destruction system was passed through an XAD-2 trap to collect PCDFs and other semivolatile organics. The XAD-2 trap and a rinse of connective tubing were Soxhlet-extracted and cleaned using column chromatography to isolate the PCDFs and PCDDs. All samples were analyzed for PCDFs (and PCDDs in Phase 3), using high resolution (capillary) gas chromatography/electron impact mass spectrometry (HRGC/EIMS) in the selected ion monitoring (SIM) mode. No PCBs or PCDFs were detected in the Phase 1 samples.

The Phase 2 experiments were conducted to determine the optimum temperature, oxygen, and residence time conditions for PCDF formation. The feed into the system was mineral oil spiked with three individual PCB congeners which form PCDFs by the four known reaction mechanisms. A statistical analysis of the results for 33 runs indicates that both temperature and oxygen have significant effects on the PCDF yield and that the interaction between temperature and oxygen is synergistic. The results indicate that the optimum values are a temperature of 675°C and an excess oxygen concentration of 8%. The residence time did not significantly affect the yield in the range of 0.3 to 1.5 s, although lower times appeared to yield less PCDFs. Since residence time does not appear to significantly affect the PCDF formation, 0.8 s was chosen as convenient for the Phase 3 runs.

In Phase 3, duplicate test runs were conducted with mineral oil and silicone oil dielectric fluids conteining PCBs (Aroclor 1254) at concentrations of 0, 5, 50 and 500 ppm. A PCB askarel containing 70% Aroclor 1260 and a non-PCB askarel, containing mostly trichlorobenzene with some tetrachlorobenzene, were also tested in duplicate. PCDFs were found in all samples, except blanks, as shown in Figure 2. PCDDs were found in the samples from the trichlorobenzene runs and occasionally at low levels in some of the other samples. Up to 5,700 ng total PCDFs/mL of spiked feed oil or 4% conversion efficiency (PCBs to PCDFs) was observed for the mineral oil and silicone oil runs. The PCB destruction efficiencies calculated for the 5, 50, and 500 ppm runs ranged from 79 to > 99%. Up to 19,000,000 ng total PCDFs/mL feed oil (19 mg/mL) or 3% conversion efficiency was observed for the askarel fluid. Statistical analysis showed a linear relationship for PCDFs formed versus the amount of PCBs (Figure 3). Although not statistically different, about twice the quantity of PCDFs was formed from PCBs in silicone oil than from the corresponding mineral oil samples. All eight PCDF homologs were detected in the askarel runs with a maximum at the penteCDF (Figure 4). With a few exceptions, only tri- through hexaCDFs were observed in the lower level runs, with a maximum generally at the triCDF homolog.

PCDFs and, to a lesser extent, PCDDs are formed from the trichlorobenzene dielectric fluid under the optimum PCB-to-PCDF conversion conditions. Up to > 110,000 ng total PCDFs/mL feed oil (> 0.004% yield) and 1,900 ng total PCDD/mL feed oil (0.0001% yield) were observed for the trichlorobenzene runs. The homolog distribution of PCDFs is similar to that found from feeding PCBs. The amount of PCDFs formed is one to two orders of magnitude lower than for the askarel, but substantially higher than that for dielectric fluid containing 500 ppm or less PCBs.

The results of this work indicate that the optimum conditions for PCDF formation from PCBs are near 675°C for 0.8 s or longer, with 8% excess oxygen. Under these

conditions, PCDFs are formed from mineral oil or silicone oil contaminated with PCBs at 5 ppm or greater. PCDFs are also formed from a trichlorobenzene dielectric fluid which contained no detecteble PCBs.

Further work is focusing on identification and quantitation of other products from combustion of these samples, and on running samples of other dielectric fluids, including paraffinic hydrocarbons, ester hydrocarbons, end tetrachloroethylene.

The work was supported by the U.S. Environmental Protection Agency under Contract No. 68-02-3938. A more detailed report was published as EPA Report No. 560/5-84-009.

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THERMAL COMBUSTION SYSTEM TO MODEL PCB FIRE CONDITIONS

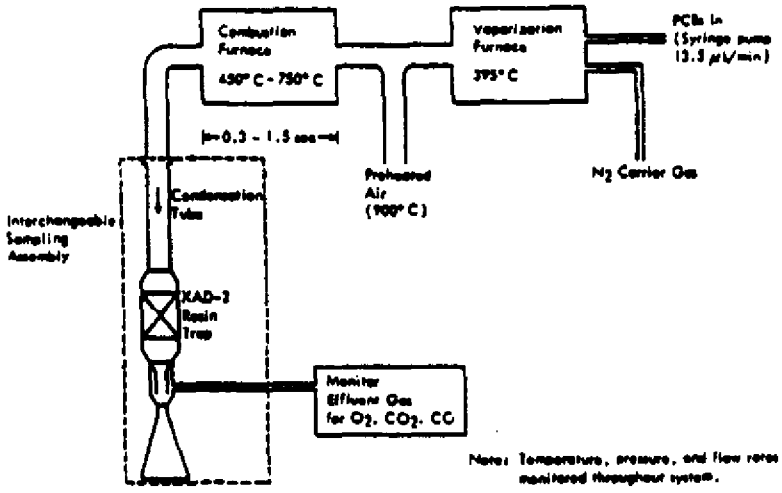


Figure 1

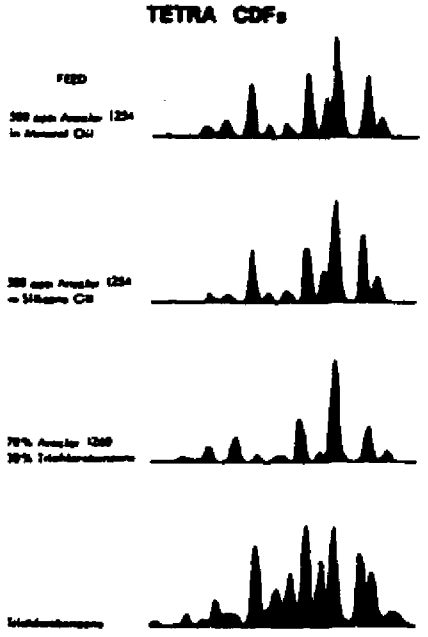


Figure 2. Tetrachlorodibenzofurans formed from various matrices. Note similar isomer distribution for the TCDFs formed from PCBs. Consistent patterns were noted for the other homologs.

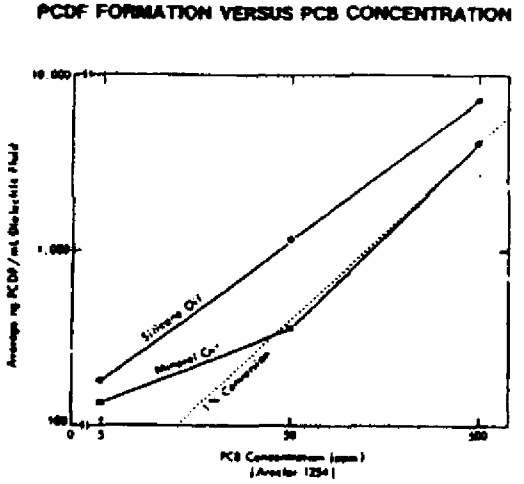


Figure 3

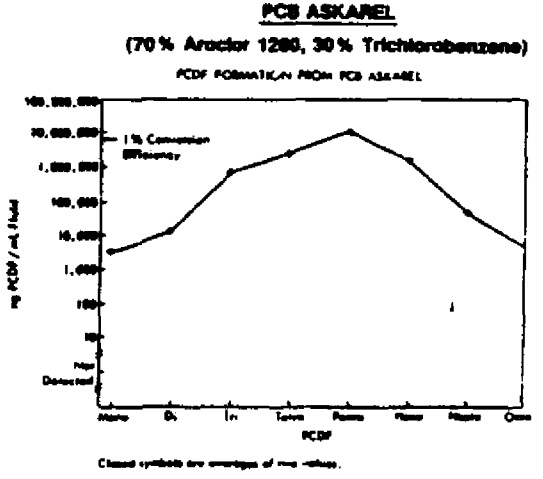


Figure 4

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LABORATORY INVESTIGATION OF THE HIGH TEMPERATURE FORMATION AND DESTRUCTION OF PCDFs

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The formation of polychlorinated dibenzofurans (PCDFs) as a result of the thermal degradation of polychlorinated biphenyls (PCBs) has become an area of intense interest due to the reported toxicity of these partial oxidation products. Reports of their formation as a result of fires in PCB containing transformers, has caused the United States Environmental Protection Agency (US-EPA) to consider expanded regulations to reduce the risk of accidental combustion of PCB containing material.

Most previous studies of the formation of PCDFs have been concerned with the optimization of conditions for their formation from PCBs. In this study, we have investigated the effect of temperature and oxygen concentration on the rate of formation and destruction of PCDFs as well as the thermal stability of the parent PCB. Additional objectives were to identify other degradation products and provide some information to elucidate the mechanism of PCB destruction and PCDF formation in a flow reactor system.

The thermal degradation of a single PCB isomer was conducted under four reaction atmospheres at a constant gas phase residence time of 2.0 seconds. The isomer selected for study was 2,3',4,4',5-pentachlorobiphenyl (2,3',4,4',5-PCB). The oxygen availability in the reaction atmosphere is described using the equivalence ratio, phi. Phi is defined as the ratio of fuel to oxygen actually in the reactor divided by the ratio of fuel to oxygen required for complete combustion. The values of phi used in this study were 3.0, 1.0, 0.2, and 0.05 which range from oxygen starved to very oxygen rich conditions as the values of phi become progressively smaller. A phi of 1.0 means there is exactly enough oxygen available for complete combustion; thus, the percent excess air is zero. Thermal degradation experiments were conducted at various temperatures ranging from 500-1000C.

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The thermal decomposition profiles and reaction products were determined using the Thermal Decomposition Unit-Gas Chromatographic (TDU-GC) system and the Thermal Decomposition Analytical System (TDAS). Both pieces of laboratory instrumentation are closed continuous systems that contain a narrow-bore quartz tubular reactor which is capable of subjecting gaseous species to controlled thermal exposures with precise control of residence time and other reaction variables. Mixtures of oxygen and nitrogen were used to obtain the various reaction atmospheres tested in this study. A 40ug sample of 2,3',4,4',5-PCB was used in all experiments.

Following thermal exposure, the remaining parent material and the various thermal reaction products were cryogenically trapped. The numerous trapped samples were subjected to in-line chromatographic analysis using a capillary column, 15 m length by 0.25 mm ID and possessing a 0.25 micron DB-5 film thickness. On the TDU-GC, a hydrogen flame ionization detector was used for detection of the various solutes, and the data were processed and displayed using a Varian CDS 401 chromatographic terminal. The identities of the thermal reaction products from the decomposition of the PCB were tentatively determined from their electron impact ionization mass spectra obtained on the TDAS which incorporates an LKB 2091 GC/MS. The reaction products examined were generated from the degradation of the PCB at 800C and phi = 0.2. Sample handling and chromatographic conditions were the same as those used for the TDU-GC testing.

Table 1 lists the major thermal reaction products tentatively identified for the thermal degradation of 2,3',4,4',5-PCB. A variety of pyrolysis and partial oxidation products have been formed, with PCDF congeners representing the majority of the oxidative products. Significant quantities of partially dechlorinated biphenyl congeners are formed along with dichlorobenzenes and trichlorobenzenes. Tetrachlorobiphenylene isomers were also observed. These are of particular interest due to their suspected toxicity. The formation of tetrachloronapthalene is important because of its apparent thermal stability. At 1000C for phi = 1.0, the reaction product tentatively identified as tetrachloronapthalene exceeded the concentration of the parent PCB. As one might expect, the yield of pyrolysis products decreased with increasing oxygen levels. However, the increase in PCDF concentration with increase in oxygen concentration was far more striking.

Table 2 presents the yields of observed PCDFs at various equivalence ratios. As the oxygen concentration increased by a factor of 60, the yield of total PCDFs increased by a factor of 10. The percentage of total PCDFs identified as tetra isomers ranged from 62-72%. Thermal formation/destruction profiles for observed PCDFs for phi=1.0 are depicted in Figure 1.

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TABLE 1

MAJOR THERMAL REACTION PRODUCTS TENTATIVELY IDENTIFIED
FROM THE THERMAL DEGRADATION OF 2,3',4,4',5-PENTACHLOROBIPHENYL

Product Class	Number of Major Peaks
Tetrachlorodibenzofurans	2
Trichlorodibenzofurans	2
Pentachlorodibenzofurans	1
Tetrachlorobiphenyls	5
Trichlorobiphenyl	1
Trichlorobenzene	1
Dichlorobenzene	1
Trichloronaphthalene	1
Tetrachloronaphthalene	1
Trichlorophenylethyne	2
Dichlorophenylethyne	1
Tetrachlorobiphenylenes	2
C_9H_8OCl	1
$C_{10}H_3Cl_3$	1

TABLE 2

MAXIMUM WEIGHT % YIELD OF PCDFs AS A FUNCTION OF REACTION ATMOSPHERE

ϕ	TEMPERATURE OF MAXIMUM YIELD (C)	WEIGHT % YIELD			
		TRI-CDFS	TETRA-CDFS	PENTA-CDFS	TOTAL-PCDFS
0.05	750	0.66	4.3	2.0	6.9
0.2	800	0.34	1.7	0.56	2.6
1.0	900	0.13	1.3	0.25	1.7
3.0	850	0.068	0.71	0.21	0.99

The relative yields predicted for PCDF isomer production may be estimated by examination of the reaction enthalpies for the global reactions. Calculations reveal that an overall reaction involving elimination of a hydrogen atom and a chlorine atom from ortho positions to form either 2,3,7,8-TCDF or 2,3,6,7-TCDF and HCl, has a reaction enthalpy of -29.7 kcal/mole. Elimination of ortho hydrogens to form either 1,3,4,6,7-PCDF or 1,3,4,7,8-PCDF and H_2 has a reaction enthalpy of -14.2 kcal/mole. Using these values as a "zeroth" order approach to the reaction kinetics of PCDF formation, one would predict that the two tetra isomers would be the predominant reaction products. Two major TCDF peaks were, in fact, observed that accounted for 60-70% of the total PCDF formation. Further isomer specific identification work is strongly indicated.

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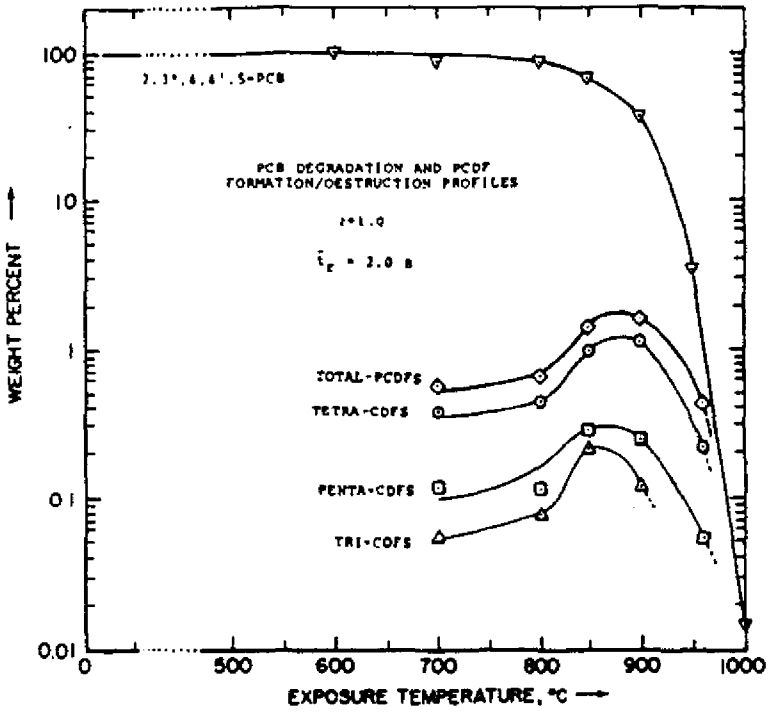


Figure 1. PCDF Formation/Destruction Profiles

In summary, the results of this study show that the yields of PCDFs formed from the thermal degradation of 2,3',4,4',5-PCB are on the order of a few percent; and these yields increase as the oxygen concentration increases (ϕ=3.0→ϕ=0.05). The predominant mechanism for their formation is HCl elimination. For equivalent combustion conditions, it appears that PCDFs can be destroyed at temperatures that are sufficient to destroy the parent PCB. However, there is evidence for formation of pyrolysis products such as tetrachlorobiphenylenes and chlorinated polynuclear aromatics that are major reaction products at very high temperatures.

This work was performed under partial sponsorship by the US-EPA under Cooperative Agreement CR-810783 and has not been subjected to the Agency's peer review process.

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RP-2028-11

PRODUCTS OF INCOMPLETE COMBUSTION OF DIELECTRIC FLUIDS

BY

DR. C. CLAIR CLAIBORNE

INTRODUCTION

Increasing publicity concerning transformer related fires and the resulting public concern over the hazards associated with these fires has prompted governmental action. The Environmental Protection Agency (EPA) consequently issued a request for information as a first step in promulgating a rule concerning transformer fires (1).

Although this rule is primarily directed at transformers which may contain some PCB's, there have been instances such as the BART tunnel fire in San Francisco and the underground fire in New York City in which partial combustion products of mineral oil were suspected of harmful interactions. The growing public concern over combustion products from plastic seat cushions, plumbing materials and other commonly encountered items will likely expand to include electrical insulating materials.

In the advance notice of proposed rulemaking mentioned above, the EPA requested information on the partial and complete combustion products of several transformer insulating materials. The fluids identified were chlorinated hydrocarbons, fluorocarbons, high temperature hydrocarbons, non-PCB askarels, mineral oil, and silicones. Although some information is available on the products of complete combustion, i.e., with an excess of oxygen present, data is lacking on the products of partial combustion. In many fires, partial or incomplete combustion may be the predominant mode of combustion.

When fires occur in confined areas such as a building, tunnel, or vault, the flow of air may be limited or restricted while the rate of burning may be so rapid that the oxygen is consumed faster than it can be replaced. This may result in the formation of many toxic substances such as carbon monoxide, hydrogen cyanide, hydrogen chloride, halogens, or carcinogenic organic compounds.

The objective of the project described in this report was to examine the products formed from either complete or partial combustion of fluids commonly used as dielectric materials, particularly in transformer applications.

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EXPERIMENTAL

Five liquids were selected for evaluation in this program: Tetrachloroethylene (C_2Cl_4), trifluorotrichloroethane ($C_2Cl_3F_3$), polydimethylsiloxane, a mineral oil, and a high temperature hydrocarbon. The particular tradenames of these materials are, respectively: WECOSOL*, Freon 113, Dow Corning 561 Silicone Transformer Liquid, Wemco C, and RTEmp.

In order to characterize the reacting materials in the mixed compounds, mineral oil and the high temperature hydrocarbon, high performance liquid chromatography was carried out on a Dupont 850 liquid chromatograph. The best separations were achieved for Wemco C utilizing gradient elution with methanol and water; for RTEmp, with tetrahydrofuran (THF) and methanol in the gradient elution mode.

To establish boundary levels of likely products of partial combustion to be found in analytical investigations, thermodynamic equilibrium concentrations were calculated from 300 to 1500 K (27° to 1227°C) at 100° intervals for each of the fluids mixed with 20% and 80% air by volume. For C_2Cl_4, calculations with 1% H_2O were also made to approximate atmospheric conditions and evaluate the potential for formation of HCl. These calculations were performed on a main frame computer and the major species of interest were displayed in semilog plots.

Two experimental arrangements were selected to evaluate the combustion process and the resulting products. In the Materials and Manufacturing Technology facilities, the combustion was carried out in Dupont thermogravimetric analysis (TGA) equipment. The material to be investigated was placed in a platinum boat and dry air was admitted to the combustion chamber at a controlled rate in order to achieve the desired levels of 30% and 70% of the air that would be required for theoretical total combustion. The instrument was then programmed to heat the combustion chamber from room temperature to 1000°C at 30°/min. A trap containing ice water was located at the exit of the chamber, in order to contain the reacting material in the combustion chamber. The combustion products were collected in cold traps placed in two separate Dewar flasks, containing a mixture of dry-ice and isopropanol (-90°C), on the one hend, and methyl butane and liquid nitrogen (-160°C), on the other hand. The materials collected in each of these traps were analyzed by gas chromatography.

The other experimental arrangement was located at the Research and Development

Laboratories of Westinghouse. This apparatus consisted of a stainless steel tube which was heated to 1000°C. The reactant was then admitted to the tube. The amount of material injected into the preheated tube was varied in order to achieve the desired levels of 30% and 70% of the air required for theoretical total combustion. The combustion products were then withdrawn with a microliter syringe and injected into a Hewelett Packard 5935 GC-MS (gas chromatography-mass spectrometry) system for analysis. (* Westinghouse trademark)

RESULTS:

The decomposition of C_2Cl_4 at 1000°C in varying levels of air generated substantial quantities of Cl_2 and CO_2. Phosgene was not detectable either by gas chromatography or mass spectrometry. These results are consistent with the thermodynamic predictions. In the Materials and Manufacturing Technology Department apparatus, a small amount of HCl was found. The HCl was likely produced from sorbed water on the interior surfaces of the combustion apparatus, because this system is heated from ambient temperatures.

The silicone fluid generated copious amounts of SiO_2 which tended to plug the tubing leading to the traps, thereby influencing the capture of the product gases. Aside from CO_2, the products of the decomposition were methane, carbon monoxide, and water, on the order of 1% by volume, with amounts of ethylene, acetylene, and ethane between 0.01 and 0.1% by volume.

Tentative results from partial combustion of $C_2Cl_3F_3$, indicated six compounds separable by gas chromatography, besides CO_2. The thermodynamic calculations indicated that likely products of the decomposition of $C_2Cl_3F_3$ would be CF_4, Cl_2, COF_2, CO, $CClF_3$, and phosgene. However, the identification of these compounds will necessitate confirmation by mass spectromatry, as some of these materials are not readily available as standards.

The determination of the combustion products of the mineral oils is currently underway, and will be reportad at a later date.

REFERENCES:

1. Federal Register, March 23, 1984, Page 11070.

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PYROLYSIS AND COMBUSTION OF MINERAL OIL, TETRACHLOROETHYLENE AND SILICONE OIL MIXTURES CONTAINING AROCLOR 1254

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This laboratory has initiated, with Electric Power Research Institute support, a major study of the tendency of various fluids, either neat or contaminated with Aroclor 1254, to form polychlorinated dibenzofurans (PCDFs) and polychlorinated dibenzodioxins (PCDDs) when subjected to high temperatures. Although a broad range of fluids of potential or current use as dielectrics will eventually be studied, this report presents preliminary data obtained from studies of mineral oil, tetrachloroethylene, and silicone oil during pyrolysis and combustion.

For purposes of this work, two distinct heating regimens were studied. Samples were either pyrolyzed (heated in the absence of a flame) or combusted (either injected into a flame or heated under conditions resulting in self-ignition). Pyrolyses were conducted using a simple thermostatically controlled apparatus, capable of accommodating glass or quartz tubes of diameters up to 6 cm within its 9 cm-long heated region. In order to minimize hazards and disposal problems, yet permit sufficient product formation to facilitate detection of PCDDs and PCDFs, pyrolyses were performed on 100 ul samples. In an attempt to differentiate this work from other earlier and ongoing investigations, as well as to simulate more accurately certain catastrophic incidents, pyrolyses were conducted at atmospheric pressure. The necessity of containing the starting materials and non-gaseous pyrolysis products in an open system led to the use of 8 mm ID x 0.5 M glass tubes, sealed at one end, and mounted vertically. The material to be pyrolyzed was deposited at the sealed end, then inserted into a tight-fitting preheated metal block in the heating apparatus. Typically, the liquid refluxed up the inner walls of the tube; the length of the tube and its comparatively large unheated volume kept the reflux level well below the open end in all experiments. To assure containment, the topmost 5 cm of the tube were chilled in dry ice and the end of the tube was connected to a charcoal trap. No visible material was trapped in the chilled region and excellent mass balances were generally observed.

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The design of the combustion apparatus was constrained by the necessity of assuring that all discharged gases pass through a trapping system capable of efficient removal of PCBs and any potentially toxic products. The combustion chamber consists of a 1 M quartz tube with a 22 mm i.d. One end of the chamber accommodates a modified blast burner and inlet tube through which the end of a 1/16" x 24" syringe needle is introduced via airtight connections. The inlet tube and needle are mounted to allow sample introduction into the flame of the blast burner. Sample addition is accomplished using a 10 ml syringe mounted in a worm syringe drive. The combustion chamber is mounted in a pyrolysis furnace capable of maintaining temperatures of 100 - 1100°C in three independently controlled zones. The effluent of the combustion chamber is passed through a water filled impinger, then an XAD-2 packed adsorbent tube which in turn is attached through an orifice to a vacuum line. XAD-2 has been shown here and elsewhere to be an efficient trapping agent for dibenzofurans and dibenzodioxins.

Preliminary experiments to refine experimental apparatus, to develop necessary techniques and to optimize reaction conditions were conducted using single biphenyl congeners. This approach minimized exposure of laboratory personnel to potentially dangerous materials and simplified analytical procedures. It was anticipated that capillary GC/FID or GC/EC would permit quantitation of the one or a few PCDF congeners produced in such reactions. This expectation was realized with one exception; pyrolysis of mineral oil, even in the absence of biphenyls, produces a very complex mixture. Despite elaborate sample cleanup, reliable data could not be produced without resort to GC/MS techniques.

Before discussing results and interpretations it should be emphasized that these studies are on-going and substantial data remains to be gathered. Further, data interpretation is complicated by the nature of the atmospheric pressure pyrolysis experiment. Thus, actual temperatures inside the pyrolysis apparatus in the heated zone are not well defined, since the reflux process may provide an efficient heat-transfer mechanism. Further, the fraction of a particular biphenyl congener in the heated zone versus the fraction in the cooler reflux region will be a complex function of that congener's physical properties, and those of the other constituents of the bulk liquid.

Aroclor 1254 has been pyrolyzed neat, and as 5,000 and 50 ppm mineral oil solutions at 500°, 550°, and 600°C, and the extracts analyzed for tetra and penta CDFs using high resolution GC/MS. Pyrolysis of the 50 ppm mixture gave concentrations

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of 2,3,7,8-TCDF, total TCDF and total penta-CDF below detection limits (0.4, 1 and 1 ng/g, respectively) at all three temperatures. Concentrations of PCDFs produced on pyrolysis of neat Aroclor and 5,000 ppm solutions were moderately sensitive to nominal pyrolysis temperature, with maximum formation at 550°C. All data are consistent with the proposition that tetra and penta CDF yields are roughly proportional to PCB concentrations in the starting mixture. However, the detection limit for the 50 ppm mixtures was about an order of magnitude higher than the concentrations expected based on this assumption. Lower detection limits will be sought for these samples.

An interesting feature of the mineral oil-Aroclor 1254 data is the clear and reproducible differences between the patterns of tetra-CDFs and penta-CDFs formed by pyrolysis of neat Aroclor 1254 versus those formed by pyrolysis of the 5000 ppm mixture. For example, 2,3,7,8-TCDF and co-eluters comprise 16-21% of the tetra CDF mixture formed from neat Aroclor, but 45-55% of the mixture from mineral oil/Aroclor. Other differences are apparent when chromatographic traces are compared.

Preliminary experiments to assess the tendency to form PCDFs from the pyrolysis of biphenyl-containing tetrachloroethylene (TCE) have been completed. Thus, 5,000 ppm solutions of biphenyl, 2-chlorobiphenyl, and decachlorobiphenyl were pyrolyzed at various temperatures. No evidence for the formation of the expected dibenzofuran products was obtained with detection limits corresponding to 0.1% conversion for dibenzofuran itself and 0.001% for octachloro dibenzofuran. However, literature data suggests that pyrolysis of TCE generates free Cl_2 as well as chlorine radicals. Thus, the possibility that biphenyl and 2-chlorobiphenyl were instead forming a complex mixture of chlorinated dibenzofurans not readily identified by simple gas chromatography required investigation. Scanning GC/MS showed that if any PCDFs were formed, their concentrations were below detection limit. It confirmed that chlorination of biphenyl did occur, but yields were low (ca. 1%). Instead, three much larger peaks with empirical formula $C_{14}H_9Cl_3$ were observed. A reasonable structure for this compound postulate ortho, meta and para substitution of a C_2Cl_3 group on the biphenyl structure. Efforts are underway to confirm the identity of this compound. However, if this reaction represents a facile reaction pathway for biphenyl destruction, PCDF formation may be minimal in this matrix. Pyrolysis of TCE (neat) and TCE containing 5,000 ppm Aroclor 1254 were conducted in duplicate at 500°, 550°, and 600° and submitted for high resolution GC/MS analysis.

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Pyrolysis of 2-chlorobiphenyl and 2,3,4,5,6-pentachlorobiphenyl as 5000 ppm solutions in silicone oil suggested that the optimal temperature for PCDF formation was ca. 550°C. Scanning GC/MS experiments demonstrated the formation of significant concentrations of fluorene from 2-chlorobiphenyl (corresponding to CH_2 insertion and Cl loss) and various congeners of methylated/chlorinated fluoranes from pentachlorobiphenyl. Duplicate samples of Aroclor 1254 (5000 and 50 ppm) in silicone oil have been pyrolyzed at 500°, 550°, and 600° and submitted to GC/MS for analysis.

Some interesting general observations have been made on the combustion process. For example, combustion of biphenyl in TCE produced decreasing net dibenzofuran as the residence time was varied from 18 sec to 6 sec and the wall temperature maintained at 450°C. In contrast, at 550°C, there is a net increase in dibenzofuran yield as residence time decreases; this suggests that at the higher temperature, significant dibenzofuran destruction is occurring. There are also large effects on dibenzofuran yield in the presence of different solvents: typically yields obtained on combustion in TCE are much higher than those obtained in silicone or mineral oil. Some sharp differences on the effects of particular variable parameters on dibenzofuran yields have also been noted.

FORMATION OF PCDFs FROM PCBs

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In 1978 it was found in our group that PCBs can be converted to PCDFs under pyrolytic conditions. The pyrolysis of PCBs in sealed quartz ampoules in the presence of air yielded about 30 major and more than 30 minor PCDFs. The optimal yield of PCDFs was about 10% calculated on the amount of PCB decomposed. Later we studied the pyrolysis of 15 individual synthetic PCB isomers. This study showed that the formation of PCDFs can follow several competing reactions. The reactions involve the loss of ortho-Cl_2 and ortho-HCl with and without a 2,3-chlorine shift or loss of ortho-H_2. In the present report we are discussing identification and quantification of PCDFs in the following samples:

a. used PCBs
b. PCBs after sparking experiments
c. samples from thermal PCB degradation
d. samples from PCB fires

The analytical method used is described earlier.

Results

Used capacitors

We have opened some used and swollen capacitors, collected and analyzed the drained PCB. The levels of PCDFs was approximately 2 ppm, mainly tetra-CDFs, which is similar to the levels we found for the new and unused PCB.

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Examination of the paper layer reveaked dark points, probably caused by electrical arcing. The PCB around these dark spots was extracted and analyzed. The levels were similar to the levels found in the drained PCB or new PCB.

Sparking experiments in PCB

No increase in PCDFs (approx. 2 ppm) could be found after up to 7 sparks (18 kV, 2 µF) in pure PCB. In another experiment 1% of 1-epoxyethyl-3,4--epoxycyclohexane (Union Carbide ERL 42 06) was added before the sparking (4 sparks, 15 kV, 2.5 µF). In this experiment the PCDF levels increased, see isomers the increase was 30 times, for others no increase was found.

Thermal degradation of PCB

We have analyzed samples taken from the thermal degradation of PCB in special incinerators including rotary cement kiln. The critical parameters are minimum temperature
minimum residence time
excess of oxygen

A test-burn was performed in a Swedish rotary cement-kiln (>1500°C, >5 sec) obviously with oxygen deficiency. A series of PCDFs were found in the emissions, Figure 2 illustrates the hexa-CDFs found in these samples, 15 of the 16 isomers could be found.

PCB fires

During the period 1981-1984 a series of accidents have been reported in Scandinavia and the United States that can illustrate this risk. These accidents can be subdivided into three different categories.

a) PCB fires with mineral oil as the external energy source
b) PCB fires with electrical energy as the external energy source
c) Explosions in PCB filled capacitors

These accidents all resulted in the formation of PCDFs, in some cases also polychlorinated dioxins (PCDDs), biphenylenes (PCBPs) and pyrenes (PCPYs).

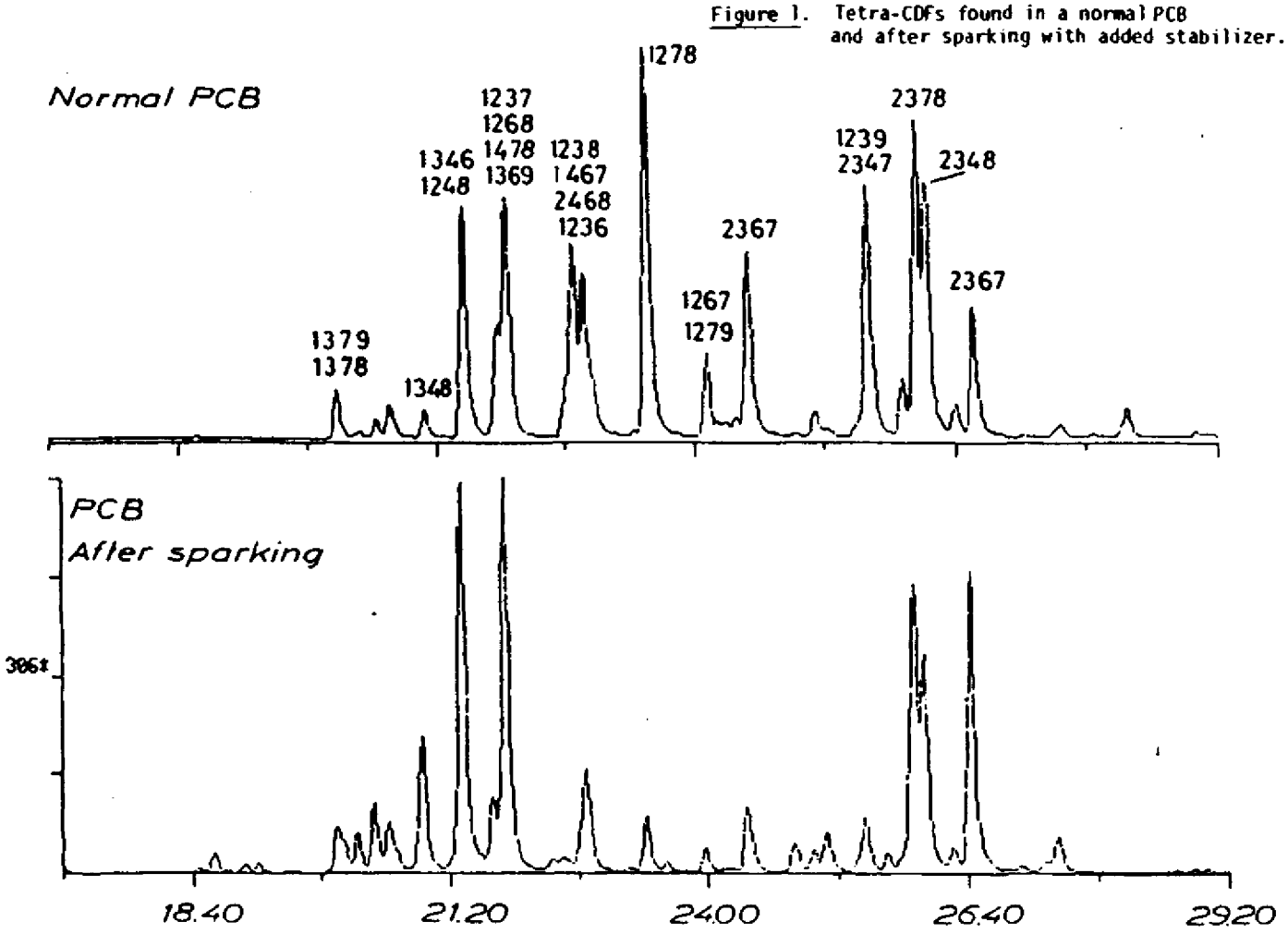
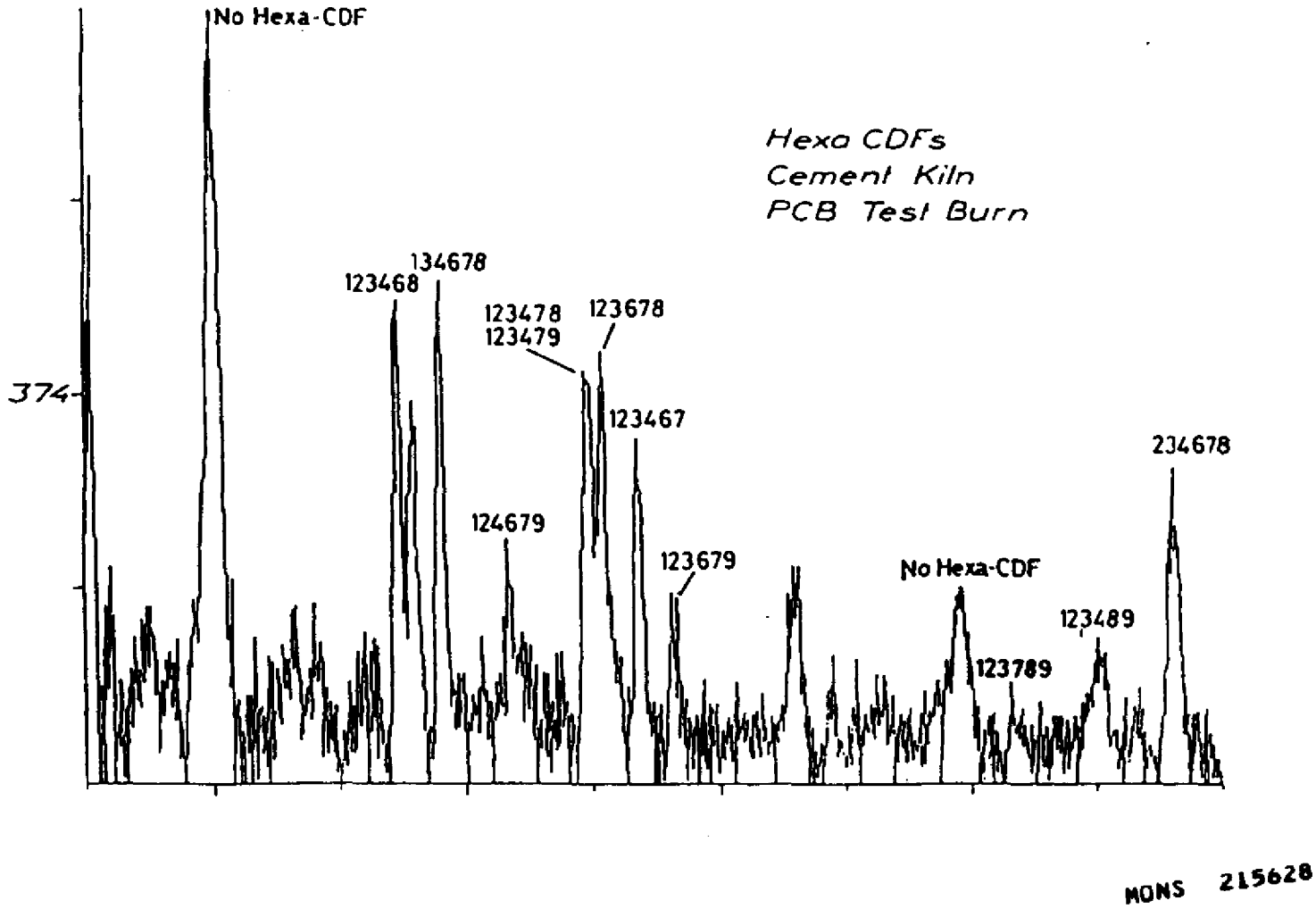


Figure 1. Tetra-CDFs found in a normal PCB and after sparking with added stabilizer.

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Figure 2. Hexa-CDFs from a PCB test burn.



PART 4:

DOCUMENTATION OF FIRES, SPILLS AND CLEAN-UP

BRIAN WEST - MODERATOR

DECONTAMINATION OF FIRE FIGHTERS' PROTECTIVE CLOTHING WITH TRICHLOROTRIFLUOROETHANE

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ABSTRACT

A limited laboratory study was conducted to evaluate the efficiency of a 1,I,2-trichloro-1,2,2-trifluoroethane-based system to decontaminate Nomex® protective clothing worn by fire fighters during a fire at an electrical transformer oil reclamation facility. Both garments contaminated at the site of the fire and garments that were conteminated in the laboratory with a known concentration of polychlorinated biphenyls (PCBs) were laundered using the 1.1,2-trichloro-1,2,2-trifluoroethane-based system. The removal efficiency of the systam was determined by the ratio of the after to before PCB concentrations in terms of micrograms of PCB per gram of fabric. Overall, the PCB removal efficiencies ranged from 66 to 99%. Until permissible fabric concentration levels for PCBs are established, it can not be determined whether this system is adequate to allow the safe reuse of the clothing. Research is urgently needed to define decontamination end-points for reusable protective clothing, i.e., "how clean is clean".

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INTRODUCTION

Uncontrolled fires involving polychlorinated biphenyl (PCB) containing fluids produce a complex and potentially highly toxic mixture of chlorinated products in the soot, including polychlorinated dibenzofurans and polychlorinated dibenzo-p-dioxins (1-6). In some of the incidents, there also has been the formation of polychlorinated derivatives of biphenylene, chrysene, and pyrene (4,5,7). These incidents have resulted in the contamination of fire fighters' protective clothing and equipment with PCBs (8-10) and most probably the polychlorinated pyrolysis products.

In early 1984, a fire occurred at an electrical transformer oil reclamation facility in Jacksonville, Florida (11). The fire destroyed the building and several storage tanks containing PCB-transformer fluids and various organic solvents. A sample of the soot contained 1460 micrograms PCB (as Aroclor 1260) per gram (ug/g), and samples of liquid that hed pooled on the site contained 67 to 5330 ug/g Aroclor 1260 (11). Neither the soot nor the liquid samples contained detecteble concentrations of polychlorinated dibenzofurans, or dibenzo-p-dioxins (tetra-through octa-chloro horologs), or the respective 2,3,7,8-tetra isomers (11).

The protective clothing worn by the approximately 40 fire fighters, Nomex® turnout coats in combination with bunker pants, was assumed to be contaminated with PCBs. An attempt by the on-site cleanup contractor to deconteminate the garments with a common method (i.e., detergent-water wash with a water rinse) showed a mean residual PCB

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concentration of 239 ug/g (S.D. ± 411, range 15 to 1060, n=5). These levels of contamination remaining in the protective clothing after the detergent wash prompted a limited laboratory study to evaluate the efficiency of a 1,1,2-trichloro-1,2,2-trifluoroethane based system to remove PCBs from the Nomex® fabric protective clothing. This paper describes the results of the laboratory evaluation.

METHODS AND MATERIALS

Decontamination Process Description

A RAOKLEEN® Model 1550 Clothing Decontamination System* was used to remove the PCB contamination from the protective clothing (12). The RAOKLEEN® System is a 1,1,2-trichloro-1,2,2-trifluoroethane (Freon® 113)-based dry cleaning machine (Figure 1). The contaminated clothing is placed in the cleaning chamber which consists of a sealed, rotating drum that will cause the garments to tumble through the solvent. Solvent is pumped from the solvent reservoir through the filter adsorber set and then flows through the cleaning chamber. The contaminated solvent then returns to the solvent reservoir. Freon® 113 vapor and vapor pressure buildup within the sealed system are controlled by vapor recirculation across a condenser coil, with condensate returning to the solvent

*Mention of company names or products does not constitute endorsement by the National Institute for Occupational Safety and Health.

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reservoir. Periodically, the solvent is regenerated and purified by a built-in distillation process. Contaminants are removed from the system as still bottoms and materials trapped on replaceable filter-adsorber cartridges.

Fabric Sampling Protocol

The test protocol consisted of decontaminating both site-contaminated and laboratory-contaminated garments. The site-contaminated garments are those that were presumably contaminated during the fire. The laboratory-contaminated garments are those that were site-contaminated, but also were contaminated in the laboratory with a known concentration of PCB as Aroclor 1242. The PCB test concentrations of 2.4, 9.0, 33% (volume-to-volume in dielectric grade mineral oil) and 100% were applied via a brush to selected areas on the garments to the point of saturation. The volume of PCB applied was approximately 20 milliliters.

The fabric sampling technique consisted of marking an area five inches square (12.7 cm) and within that area marking off five one-inch squares (2.54 cm). Four of these five one-inch squares were located at the four corners of the larger square, with the fifth located at the center. To determine the pre-decontamination concentration, each of the five one-inch squares were cut from the larger square to form a composite sample. To determine the post-decontamination concentration within the same area, the remaining fabric within the marked off section was removed. This checkerboard technique was used to average out or minimize

concentration variations within the sample area. To eliminate variations based on cutting errors and unequal areas being removed, all results were normalized by reporting the contaminant concentration in terms of micrograms of PCB per gram of fabric (ug/g). The authors assumed that bulk density variations in the fabric and substrate were minor. For comparison consistancy, fabric sections were removed from the same approximate location nn each turnout coat and bunker pant sampled.

The removal efficiency of the system was determined by the ratio of the after to before PCB concentrations in terms of ug PCB/g fabric. The pre-and post-decontamination changes in PCB concentration were compared using a paired t-test.

The Nomex® fabric samples were extracted with toluene and analyzed by gas chromatography with electron capture detection. The presence of Aroclors 1242 and 1260 was determined by comparison with standard samples of same obtained from U.S. Environmental Protaction Agency. Quantitation was performed by summing the heights of the five major peaks of the standards, and comparing that to the sum of the same peaks in the sample. The instrumental limit of detection was 0.5 ug/g for both Aroclors. Since no recovery studies were performed on the Nomex® fabric, the results are considered to be the minimum amount of Aroclor present.

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RESULTS AND DISCUSSION

Table 1 presents the pre-and post-decontamination concentrations of PCBs and percent removal for the site-contaminated garments. The PCB concentrations prior to laundering ranged from 5.3 to 480 ug/g (mean 85, S.D. $\pm$ 130). By comparison, the post-decontamination concentrations ranged from 1.1 to 25 ug/g (mean 7.8, S.D. $\pm$ 6.4). The percent of PCBs removed ranged from 66 to 99%, with a mean of 88% and a 95% lower confidence limit of 82% removed.

Table 2 presents the pre-and post-decontamination concentrations of PCBs and percent removal for the laboratory-contaminated garments. Although the PCB concentrations applied to the garments ranged from 2.4×10^4 to 1.0×10^6 ug/g (2.4 to 100%, volume-to-volume), the actual concentration in the fabrics ranged from 1.6×10^4 to 9.9×10^5 ug/g (1.6 to 99%, weight-to-weight). The post-laundered concentrations ranged from 5.4 to 230 ug/g (mean 63.5, S.D. $\pm$ 64.2). The reduction in PCB concentration exceeded 99% for all of the garments tested.

Post-laundering inspection of the garments revealed that the tumble-wash action of the machine did not appear to cause any physical damage to the garments such as cuts, abrasions, or alteration of the retro-reflective trim. Tests are currently being conducted by an independent laboratory to determine if solvent-washed garments still meet key performance criteria specified in the National Fire Protection Association (NFPA) 1971 Standard on Protective Clothing for Structural Fire Fighting (13).

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CONCLUSIONS

This limited study indicates that a relatively high percentage of fire-borne and liquid PCB contamination can be removed from fire fighters' protective clothing using a trichlorotrifluoroethane-based system. The toxicological significance of the PCB contamination levels remaining in the garments is uncertain. However, until permissible fabric concentration levels of PCBs are established, it cannot be determined whether this technique is adequate. The discarding and replacement of fire fighters' protective clothing and equipment can be very costly (10,11). The incident described in this paper resulted in the replacement of approximately 40 sets of bunker gear (including turnout coats, pants, and boots) with a replacement cost of approximately $20,000. Research is urgently needed to define decontamination end-points for reusable protective clothing, i.e., "how clean is clean".

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Table 1

PCBs Removed from Site-Contaminated Garments

ug PCB/g fabric		
Pre-Decon	Post-Decon	% Removal
480	25	95
240	13.3	95
200	1.8	99
68	1.3	98
60	5.4	91
56	3.5	94
37	5.1	86
35	4.2	88
35	2.4	93
15	1.1	93
14	2.9	79
10	1.2	88
7.8	1.3	83
6.7	2.2	67
5.3	1.8	66

$p<0.05$, $t=2.49$

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Table 2

PCBs Removed from Lab-Contaminated Garments

ug PCB/g fabric		
Pre-Decon	Post-Decon	% Removal
9.9×10^5	24	99
9.4×10^5	100	99
6.3×10^5	60	99
6.3×10^5	53	99
5.4×10^5	230	99
2.5×10^5	110	99
1.8×10^5	97	99
1.8×10^5	62	99
7.2×10^4	13	99
6.1×10^4	8.2	99
5.8×10^4	63.1	99
5.7×10^4	63.5	99
2.0×10^4	10.4	99
1.8×10^4	5.4	99
1.7×10^4	18	99
1.6×10^4	11.9	99

$p<0.05$, $t=3.34$

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