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EPRI EL/EA-4858
Volume 2
Projects 2026-5, -8, -9
Final Report
December 1986

Polychlorinated Dibenzofurans (PCDF) and Polychlorinated Dibenzo-p-Dioxins (PCDD) in Utility Transformers and Capacitors

Volume 2

Prepared by
IIT Research Institute
Chicago, Illinois

REPORT SUMMARY

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

TOPICS: PCB; Capacitors; Chemical analysis; PCDF-PCDD; Transformers; Insulating oil

AUDIENCE: Environmental managers / Distribution engineers

Polychlorinated Dibenzofurans (PCDF) and Polychlorinated Dibenzo-p-Dioxins (PCDD) in Utility Transformers and Capacitors

Volumes 1–3

Many health effects originally attributed to PCBs appear to result from their pyrolysis and combustion by-products, PCDF and PCDD. This study developed improved techniques for characterizing these products and showed that PCDF and PCDD do not form during catastrophic arcing failure in transformers and capacitors.

BACKGROUND

Partial oxidation of askarels—mixtures of polychlorinated biphenyls (PCB) and tri- and tetrachlorobenzenes—produces polychlorinated dibenzofurans (PCDF) and polychlorinated dibenzo-p-dioxins (PCDD). However, analytic techniques for separating the active components in these mixtures are not yet mature. Information is also sparse on the quantity and types of PCDF and PCDD in as-manufactured PCB and on their formation during normal operation or arcing failure in utility equipment. Because of these uncertainties, utilities and regulators assume the worst-case PCDF–PCDD formation when there is a PCB-related accident and thereby overstate potential toxicity

OBJECTIVE

To improve techniques for measuring PCDF–PCDD in the presence of PCB and in utility transformers and capacitors.

APPROACH

Researchers developed a rationale for selecting transformers and capacitors to be sampled for PCDF–PCDD content. They also simulated catastrophic transformer failure through arcing in askarel and contaminated mineral oil to investigate PCDF–PCDD formation. Several laboratories then performed round-robin gas chromatography–mass spectrometry analyses of PCDF–PCDD samples using specially prepared carbon-13 (^{13}C) PCDF spiking compounds. After the first set of analyses, each laboratory modified its techniques and analyzed a larger group of samples from utility equipment. Another organization statistically analyzed all laboratory results.

RESULTS

These three volumes are the first release in a six-volume report of PCDF–PCDD analytic findings. Results from all participating laboratories correlated remarkably well. Some of those results follow.

• Making use of the ^{13}C compounds, researchers successfully separated the components in several closely eluting pairs of physiologically active PCDF and less-active components.

• The researchers found no PCDF or PCDD in the arcing of PCB, tri- and tetrachlorobenzene, or contaminated mineral oil.

• Analyses of samples from utility equipment suggested that the PCDF–PCDD present did not result from high-load, high-temperature operation.

Volume 1 presents researchers' sampling recommendations for investigating PCDF–PCDD in utility equipment. It also describes arcing simulations and results. Volumes 2 and 3 describe several analytic techniques, with volume 3 including a report on the synthesis of new PCDF spiking compounds. Later volumes will complete the descriptions of laboratory techniques, present comprehensive statistical analyses, and provide an executive summary.

EPRI PERSPECTIVE

This project appears to be a landmark in PCDF–PCDD analysis. One important result is the synthesis of new PCDFs for use as spiking compounds in gas chromatography–mass spectrometry analysis. The ability to separate many of the active PCDF compounds from more-innocuous materials is also of great value. The fact that laboratory results correlated so well indicates that researchers can have great flexibility in selecting techniques and developing facilities.

Utilities benefit from this work in several ways. The study provides data showing that little or no PCDF–PCDD forms in electrical equipment either during normal operation or during arcing failure. Moreover, improved analytic techniques make it clear that past predictions of toxicity have been unnecessarily high.

PROJECTS

RP2028-5, RP2028-8, RP2028-9
EPRI Project Managers: Gil Addis; Jacques Guertin
Electrical Systems Division; Energy Analysis and Environment Division
Contractors: Radian Corporation; General Electric Company; IIT Research Institute

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EL/EA-4358, Volume 2
Research Projects 2028-5, -8, -9

Final Report, December 1986

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Prepared by
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Chicago, Illinois

ABSTRACT

The objective of this study was to analyze dielectric fluids contaminated with polychlorinated biphenyls (PCBs), including in-service transformer fluids, for specific polychlorinated dibenzofurans (PCDFs) and dibenzo-p-dioxins (PCDDs) using ^{13}C-labeled internal standards together with the best extraction and analytical gas chromatography/mass spectrometry (GC/MS) techniques available in-house. On completion of the first phase of the investigation, the methodology was assessed and several improvements were incorporated into the procedure before continuing with a round-robin analytical study.

Samples were spiked with ^{13}C-labeled PCDF and PCDD internal standards before extraction and cleanup using basic and acidic alumina columns. The concentrated extracts were analyzed by high-resolution GC/low-resolution MS in the selected-ion-monitoring mode.

The methodology was applied to eight spiked baseline samples (Aroclors, tri-/tetrachlorobenzenes, and aged mineral oils) and 11 in-service dielectric fluids. For the baseline samples, good agreement was obtained between measured and expected values for the mineral oil and chlorobenzene mixtures. Two of the three Aroclors gave substantially higher concentrations for hexa- through octa-CDFs than expected. In the case of the in-service samples, PCDF levels ranged from "not detectable" to about 30 ppm (w/w).

ACKNOWLEDGMENTS

The valuable assistance of Mr. E. L. Daniels, in preparing the samples for analysis, is gratefully acknowledged. The authors also extend their sincere appreciation to Dr. G. Addis and Dr. J. Guertin of EPRI for their constant encouragement and constructive suggestions.

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SUMMARY

There is increasing interest in the potential formation of polychlorinated dibenzofurans (PCDFs) and polychlorinated dibenzo-p-dioxins (PCDDs) from uncontrolled fires involving polychlorinated biphenyls (PCBs) and chlorobenzanes (PCBzs) in dielectric fluids. At the temperatures that prevail in transformer fires, PCBs may react to form PCDF contaminants and other toxic oxidation products.

Very little published information is available on the occurrence and distribution of PCDFs and PCDDs in the PCB-containing dielectric fluids (generally known as askarels) that are used by the electric utility industry. Even less is known about the effect of service life on the contaminant concentration in PCB-filled electrical equipment. The possibility also arises that abnormal operation (arcing, overheating) may create conditions that lead to the formation of PCDFs and PCDDs in the equipment. Tests using laboratory animals suggest that these compounds at an equivalent concentration are much more toxic than the more abundant PCBs. Moreover, the toxicities of PCDFs and PCDDs vary over a range of five orders of magnitude depending on the specific compound (i.e., degree of chlorination and location of chlorine atoms).

In order to measure isomer-specific PCDFs/PCDDs in PCB-contaminated dielectric fluids, the Electric Power Research Institute initiated the present study, with the following major objectives:

(1) Perform a round-robin analytical methods evaluation, using the best available in-house extraction and analytical techniques

(2) Analyze in-service dielectric fluids for PCDFs and PCDDs of interest.

The round-robin method evaluation was designed to validate the analytical methodology and to determine the accuracy with which specific isomers could be quantified. It included the synthesis of native and isotopically labeled standards, and the analysis of spiked baseline samples. Five laboratories were

involved in this effort: Battelle Columbus Laboratories, IIT Research Institute, New York State Department of Health, Radian Corporation, and the Chemistry Department of the University of Umea, Sweden.

The in-service dielectric-fluid study consisted of developing appropriate selection criteria, obtaining representative samples, and analyzing the selected samples. General Electric Company developed the selection criteria, Battelle Columbus Laboratories collected the samples, and the analyses were performed by the same group of five laboratories mentioned above.

The study was conducted in two phases. In Phase I, five spiked baseline samples (Aroclor 1016, Aroclor 1242, Aroclor 1260, a tri- and tetrachlorobenzene mixture, and aged mineral oil) and four in-service dielectric fluids were analyzed using the best techniques available in-house. Response factors for the components of interest were generated at a single concentration using a standard calibration solution. Phase II was undertaken after the results from Phase I were assessed and improvements to the methodology were implemented. In the second phase, calibration curves were generated over the linear response range of the analytical system at five concentrations using calibration solutions containing eight native compounds and five labeled compounds. The resulting response factors were used to characterize three spiked baseline samples (Aroclor 1016, Aroclor 1260, and aged mineral oil) and seven in-service dielectric fluids. The results were evaluated to determine precision and accuracy.

This report summarizes IIT Research Institute's participation in the program, outlines the analytical methodology used, and discusses results obtained from the analysis of the baseline and in-service samples.

ANALYTICAL APPROACH

Combined capillary column gas chromatography/mass spectrometry (GC/MS) is the method of choice for the isomer-specific analysis of trace concentrations of PCDFs and PCDDs in PCB-containing dielectric fluids. The selectivity of high resolution GC together with the sensitivity and specificity of MS yields detection limits in the low ng/g (parts-per-billion) range for these compounds.

Since capillary GC columns cannot handle these complex sample matrices directly, the samples are extracted first using a basic alumina column to separate the analytes of interest (i.e., PCBs, PCDFs, PCDDs) from them. This is followed by an enrichment step (acidic alumina column) to remove co-extracted interferences and

to concentrate the PCDFs and PCDDs in the sample extract. Finally, GC/MS analysis of the extracts, in the selected-ion-monitoring mode, allows the PCDFs and PCDDs of interest to be identified and quantified. This is based on the premise that each chlorinated compound class can be separated by GC so that a unique set of mass spectral indicator ions can be monitored for each of several appropriate GC retention time windows. The samples are spiked with ^{13}C-labeled PCDF and PCDD internal standards before extraction and cleanup to determine the recovery efficiency and improve quantitation accuracy.

METHOD EVALUATION

The round-robin method evaluation was designed to validate the analytical procedures and determine the reliability with which specific compounds could be identified and quantified. The methodology was applied to eight baseline samples spiked with known amounts of native and isotopically labeled PCDF/PCDD isomers.

Very good agreement was obtained between measured and expected values for the mineral oil and chlorobenzene mixtures. The baseline Aroclor samples showed a strong increase in PCDF content as the weight percent of chlorine was increased. Thus, Aroclor 1016 gave no measurable levels of PCDF, other than those which had been spiked into the samples, whereas Aroclor 1260 showed significantly higher concentrations, especially for the higher congener classes.

ANALYSIS OF IN-SERVICE SAMPLES

The analysis of the 11 in-service samples gave results that ranged from "not detectable" levels of PCDFs to about 30 ug/g. It was difficult, however, to establish clear correlations between PCDF concentrations and dielectric fluid composition as the composition of several of the in-service fluids was not known. Nevertheless, in some cases, it appeared that the concentrations of PCDFs in the in-service fluids could be explained in terms of the amounts present in the original Aroclor 1260 fluid.

CONCLUSIONS

The procedures developed for the sensitive and compound-specific characterization of PCDFs and PCDDs in PCB-contaminated dielectric fluids proved to be reliable when applied to a variety of matrices and over a wide range of concentrations. The study succeeded in characterizing the PCDF/PCDD content of the samples, and permitted the assessment of the precision and accuracy of the procedure under carefully controlled experimental conditions.

Since the occurrence and distribution of PCDFs in in-service fluids may be due in large part to the amounts present in the original Aroclor 1260 fluid, the askarels that have been in use in electrical equipment may not contain higher levels of PCDFs than unused fluids. Although the data obtained in this study provide some indications that this may be the case, there is insufficient information available to draw firm conclusions, and further work is clearly needed.

Section 1

INTRODUCTION

For many years, polychlorinated biphenyls (PCBs) and chlorobenzenes (PCBzs) have been widely used as dielectric fluids in transformers and capacitors. Many of the oil-filled transformers in service also contain trace quantities of PCBs as a result of manufacturing and transformer-servicing practices [1]. When scientific evidence began to accumulate in the late 1960s about their adverse toxic properties, the sale of PCBs was halted in 1971 for all uses except in closed electrical systems. The U.S. Congress promulgated the Toxic Substances Control Act in 1976 and included special provisions for the regulation of PCBs. By 1979 the production of PCBs was banned. However, roughly 130,000 transformers and 2.8 million capacitors that contain PCBs or mixtures of PCBs and tri- or tetrachlorobenzenes, also known as askarels, remain in service. Another 2 million mineral oil transformers contain fluid contaminated with PCBs in concentrations of 50 parts per million (ppm w/w) or greater [2].

Since 1979, the formation of the highly toxic polychlorinated dibenzofurans (PCDFs) and polychlorinated dibenzo-p-dioxins (PCDDs) has been linked to uncontrolled fires involving PCB-containing dielectric fluids. At the temperatures that prevail in such fires, PCBs may react to form PCDFs and other toxic oxidation products. Laboratory studies [3] have shown that pyrolysis of PCBs at temperatures of 200° to 600°C in air could result in the formation of significant amounts of PCDFs (Figure 1-1). Similarly, PCDFs and PCDDs may form when PCBzs are heated in the presence of air [4]. In fact, several transformer fires have been reported in which the resultant soot and ash contained relatively large amounts of PCDFs and PCDDs [5,6]. Although the ambient concentrations of PCDFs and PCDDs are normally very low, tests using laboratory animals suggest that these compounds at an equivalent concentration are much more toxic than the more abundant PCBs.

Information is relatively sparse on the occurrence and distribution of PCDFs and PCDDs in the original PCB fluids [7,8]. Even less is known about how these levels are affected by normal operation of PCB-filled electrical equipment or by abnormal

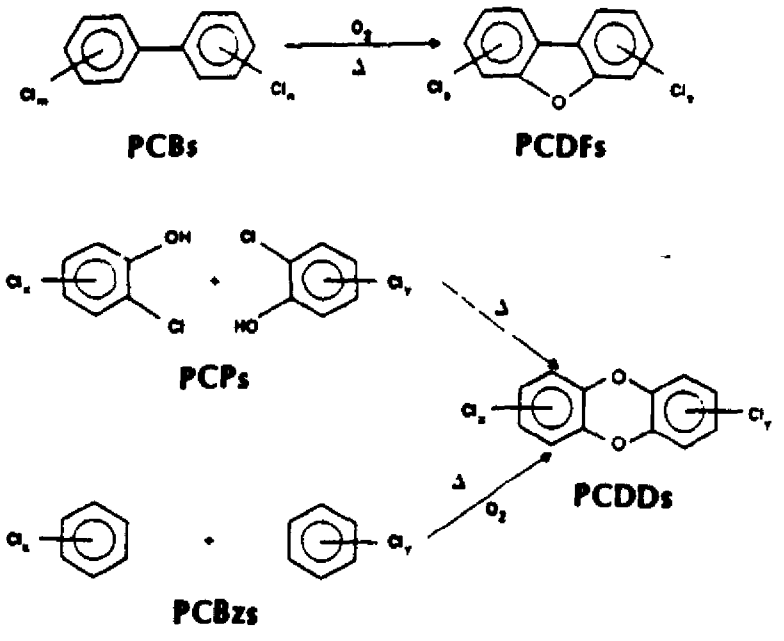

Figure 1-1. Pyrolytic Formation of PCDFs and PCDDs

operation, such as arcing or overheating. One study has suggested that PCDF levels in contaminated transformer askarels increase with the time the transformer is in service [9]. This study, however, was performed using analytical techniques that are generally regarded now as outdated. A more recent study [10] has shown that askarels that have been in use in electrical equipment do not contain higher levels of PCDFs than the unused fluids.

There are 135 PCDF and 75 PCDD isomers (Table 1-1). The toxicities of these compounds vary over about five orders of magnitude, depending on the degree of chlorination and the location of the chlorine atoms [11]. Generally, the most toxic isomers are the 2,3,7,8-substituted congeners, shown in Figure 1-2. A highly sensitive and isomer-specific analytical method is needed to measure specific compounds.

To address these issues, the Electric Power Research Institute (EPRI) initiated a program with the following major elements:

Table 1-1

CHLORINATED ISOMERS OF PCDFs, PCDDs, PCBs, CPs, AND CBzs

Chlorine Substitution	PCDFs	PCDDs	PCBs	CPs	CBzs
Mono-	4	2	3	3	1
Di-	16	10	12	6	3
Tri-	28	14	24	6	3
Tetra-	38	22	42	3	3
Penta-	28	14	46	1	1
Hexa-	16	10	42	--	1
Hepta-	4	2	24	--	--
Octa-	1	1	12	--	--
Nona-	--	--	3	--	--
Deca-	--	--	1	--	--
	135	75	209	19	12

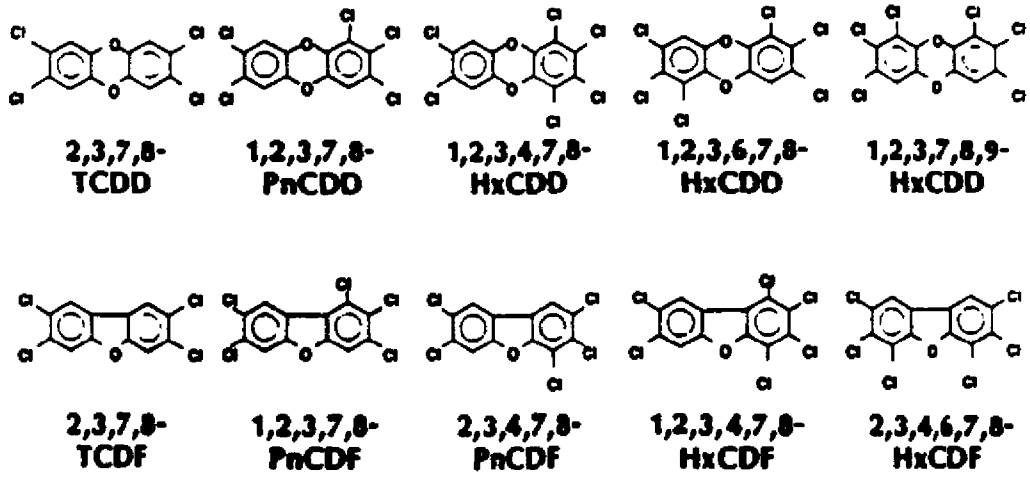

Figure 1-2. The Most Toxic PCDD and PCDF Isomers

- Round-robin method evaluation using the best available in-house extraction and analytical techniques
- Analysis of in-service dielectric fluids for PCDFs and PCDDs of interest.

The round-robin method evaluation was designed to validate the analytical methodology and to determine the accuracy with which specific isomers could be quantified. It included the synthesis of native and isotopically labeled standards, and the analysis of spiked sample matrices (baseline samples). The standards ware synthesized by Radian Corporation, who also prepared the spiked matrix samples. The samples were analyzed "blind" by Battelle Columbus Laboratories, IIT Research Institute, New York State Department of Health, Radian Corporation, and the University of Umea, Sweden.

The in-service dielectric study consisted of developing appropriate selection criteria, obtaining representative samples, and analyzing the selected samples. General Electric Company prepared the selection critaria document, Battelle Columbus Laboratories collected the samples, and the same group of five laboratories listed above performed the analyses.

The study was conducted in two phases. In Phase I, five spiked baseline samples (Aroclor 1016, Aroclor 1242, Aroclor 1260, a tri- and tetrachlorobenzene mixture, and aged mineral oil) and four in-service dielectric fluids were analyzed using the best available in-house extraction and analysis techniques. Response factors for tha components of interest were generated at a single concentration using a standard calibration solution. Phase II was initiated after Phase I results were assessed and several improvements to the methodology were implemented. In this phase, calibration curves were generated over the linear response range of the GC/MS system at five concentrations using calibration solutions containing eight native compounds and five labeled compounds. The resulting response factors were used to characterize three spiked baseline samples (Aroclor 1016, Aroclor 1260, and aged mineral oil) and seven in-service dielectric fluids. The results were evaluated to determine precision and accuracy.

This report documents IITRI's participation in the program, and includes a summary of the analytical methodology used, the results obtained from the baseline fluid study, and the results obtained from the in-service fluid study.

Section 2

ANALYTICAL METHODOLOGY

BACKGROUND

The isomer-specific analysis of trace concentrations of PCDFs and PCDDs in PCB-containing fluids is a challenging problem. The analytical difficulty is compounded by the presence of interfering substances such as PCBs or polychlorinated diphenyl ethers (PCDEs). Combined capillary gas chromatography/mass spectrometry (GC/MS) is the method of choice for such measurements. The selectivity of high resolution GC, together with the sensitivity and specificity of mass spectrometry, yields detection limits in the low ng/g range for these compounds.

Since capillary GC columns cannot handle PCB-contaminated fluids directly, the samples must first be extracted with a suitable solvent to separate the analytes of interest (PCBs, PCDFs, PCDDs) from the matrix. An enrichment step then removes co-extracted interferences and concentrates the PCDFs and PCDDs in the sample extract. Finally, GC/MS analysis identifies the sample extract and provides a quantitative measure of the PCDFs and PCDDs, based on the premise that GC separation of each chlorinated compound class 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.

To improve identification and quantification, appropriate ^{13}C-labeled isotopic analogs of the polychlorinated dibenzo-p-dioxins and dibenzofurans are added to the samples prior to extraction and analysis. ^{13}C-containing compounds are not present in significant quantities in naturally occurring materials and are clearly distinguishable from native compounds (^{12}C) by mass spectrometry. Spiking the samples with labeled compounds thus provides unique internal standards for accurate analysis and determination of the recovery efficiency of the method. An overview of the general analytical protocol is shown in Figure 2-1.

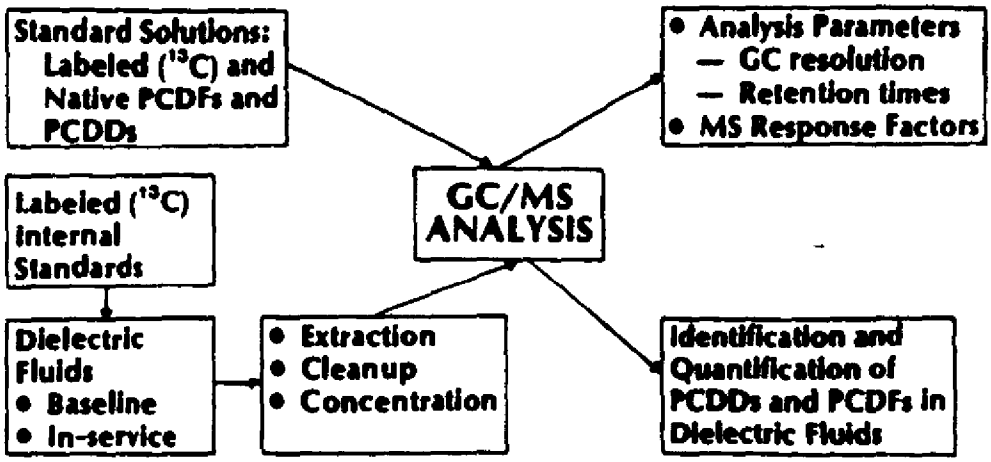

Figure 2-1 Overview of Analytical Protocol

PREPARATION OF CALIBRATION STANDARDS AND SAMPLES

Phase I

Calibration Standards. A set of calibration standards was prepared and distributed by Radian Corporation. The uniformly labeled ^{13}C-standards, in individual ampoules, were mixed with the "Radian PCDF/TCDD Cocktail" to give a calibration solution containing the following compounds at a concentration of 100 ng/ml each in n-nonane:

2,3,7,8-TCDD	^{13}C-2,3,7,8-TCDD
2,3,7,8-TCDF	^{13}C-2,3,7,8-TCDF
1,2,3,7,8-PnCDF	^{13}C-1,2,3,7,8-PnCDF
1,2,3,4,7,8-HxCDF	^{13}C-OCDD.
1,2,3,4,6,7,8-HpCDF	

Baseline Samples. The five baseline samples were prepared at Radian Corporation as solutions in n-hexane at a concentration of 0.25 g/mL. Each sample was spiked with four ^{13}C-labeled internal standards--^{13}C-2,3,7,8-TCDF, ^{13}C-2,3,7,8-TCDD, ^{13}C-1,2,3,7,8-PnCDF, and ^{13}C-OCDD--at concentrations of 100 ng/g each. In addition, the three Aroclors and the tri-/tetrachlorobenzene mixture were fortified with the native isomers 1,2,3,4,7,8-HxCDF and 1,2,3,4,6,7,8-HpCDF at concentrations of 100 ng/g each.

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The aged mineral oil sample contained a number of native PCDF/PCDD isomers, at levels ranging from 0 to 150 ng/g, as well as 510 µg/g Aroclor 1260 and 530 µg/g tri-/tetrachlorobenzene mixture, to simulate the composition of a "real-world" transformer filled with mineral oil (see Figure 3-2 for details).

The tri-/tetrachlorobenzene mixture was prepared by Radian Corporation to approximate a "typical" commercial dielectric mixture. It had the following composition:

1,2,4-trichlorobenzene	51.2%
1,2,3-trichlorobenzene	13.4%
1,2,4,5-tetrachlorobenzene	2.6%
1,2,3,4-tetrachlorobenzene	28.4%
pentachlorobenzene	4.4%

The baseline samples were identified by Radian as follows:

Compound	Radian I.D. Code
Aroclor 1016	E729-09-01
Aroclor 1242	E729-10-01
Aroclor 1260	E729-11-01
Tri-/tetrachlorobenzene mixture	E729-12-01
Aged mineral oil	E729-08-01

In-Service Samples. The preliminary round-robin study was conducted by three of the participating laboratories (including IITRI), using four dielectric fluids taken from in-service transformers and capacitors. The samples were selected by Battelle Columbus Laboratories from a repository of 29 in-service samples obtained by following selection criteria laid down by General Electric Company. The fluids consisted of a mineral oil and three askarels. One of the askarels was taken from a transformer after 20 years of service, while a second was taken from a transformer (of a different manufacturer) after 31 years of service. The third askarel was removed from a capacitor that had bulged, but not ruptured, while in service. The mineral oil sample contained PCBs and was taken from a transformer that had failed in service by arcing.

Upon receipt at IITRI, 0.1-g samples of the four in-service fluids were spiked with 20 ng of each of the internal standards, ^{13}C-2,3,7,8-TCDD, ^{13}C-2,3,7,8-TCDF, and ^{13}C-1,2,3,7,8-PnCDF, and 28 ng of the internal standard ^{13}C-OCDD.

The in-service samples were identified by Battelle as follows:

Compound	Battelle I.D. Code
Transformer mineral oil	ISL-4-D
Capacitor askarel	ISL-1-A
Transformer askarel (20 years' service)	ISL-2-A
Transformer askarel (31 years' service)	ISL-3-A

Phase II

Calibration Standards. Radian Corporation prepared a set of calibration standards containing eight unlabeled components:

2,3,7,8-TCDD	1,2,3,4,7,8-HxCDF
2,3,7,8-TCDF	2,3,4,6,7,8-HxCDF
1,2,3,7,8-PnCDF	1,2,3,4,6,7,8-HpCDF
2,3,4,7,8-PnCDF	OCDF

and five uniformly labeled ^{13}C standards:

^{13}C-2,3,7,8-TCDD
^{13}C-2,3,7,8-TCDF
^{13}C-1,2,3,7,8-PnCDF
^{13}C-1,2,3,4,7,8-HxCDF
^{13}C-OCDD.

The standards were prepared at seven concentrations of each of the native ^{12}C-components: 2.5 ng/mL, 10 ng/mL, 40 ng/mL, 150 ng/mL, 500 ng/mL, 2,500 ng/mL, and 7,500 ng/mL. In each standard, the concentration of the ^{13}C-components was held constant at 500 ng/mL each.

Baseline Samples. Three baseline samples were prepared at Radian Corporation as solutions in n-hexane at a concentration of about 0.2 g/mL. Each sample was spiked with 100 ng/g of each of the five ^{13}C-compounds listed above. Each sample was also spiked with "blind" amounts of the following unlabeled compounds:

2,3,7,8-TCDD	1,2,3,4,7,8-HxCDF
2,3,7,8-TCDF	1,2,3,6,7,8-HxCDF
2,3,4,8-TCDF	2,3,4,6,7,8-HxCDF
1,2,3,7,8-PnCDF	1,2,3,4,6,7,8-HpCDF
2,3,4,7,8-PnCDF	OCDF.

In addition, the mineral oil sample was spiked with 625 µg/g Aroclor 1260 and 1250 µg/g tri-/tetrachlorobenzenes.

The baseline samples were identified by Radian as follows:

Compound	Radian I.D. Code
Mineral oil	E729-53-01
Aroclor 1016	E729-53-02
Aroclor 1260	E729-53-03

In-Service Samples. Seven in-service samples were selected by Battelle Columbus Laboratories for characterization by the participating laboratories. The fluids consisted of five askarels and two mineral oils, all of which were prepared at a concentration of approximately 200 mg/mL in n-hexane. Each sample was spiked at Battelle with the five isotopically labeled internal standards at concentrations of 100 ng per gram of oil.

The in-service samples were identified by Battelle as follows:

Compound	Sample No.	Battelle I.D. No.
Transformer askarel	41159-11-11	ISL-03-A
Transformer askarel	41159-11-12	ISL-08-A
Capacitor Aroclor	41159-11-13	ISL-27-A
Precipitator transformer Aroclor	41159-11-14	ISL-17-A
Transformer mineral oil	41159-11-15	ISL-23-0
Transformer mineral oil	41159-11-16	ISL-04-0
Transformer askarel	41159-11-17	ISL-02-A

SAMPLE EXTRACTION AND CLEANUP

The extraction and cleanup procedure was based on the general method described by Albro and coworkers [12,13] for the fractionation and class determination of complex mixtures of chlorinated aromatic compounds. Briefly, the procedure consists of the following major steps:

1. To the sample (~0.1 g), spiked with a mixture of ^{13}C-labeled PCDF and/or PCDD internal standards, about 30 ng of 2,3,7-tri-CDD is added to serve as a "carrier" compound.

2. The sample is chromatographed on a gel permeation column (20 g Sephadex LH-20), eluting with 50% methylene chloride-in-methanol and collecting the 60-150 mL fraction, to separate halogenated aromatic compounds from any aliphatics present.

3. About 10 µL of propylene glycol are added as a "keeper" compound, to prevent sample loss during evaporation.

4. After reducing the volume of the halogenated aromatic fraction by roto-evaporation, the fraction is chromatographed on an A-540 basic alumina column (20 g topped with a layer of anhydrous sodium sulfate), eluting the PCB fraction with 180 mL of 2% methylene chloride-in-hexane.

5. The PCDFS, PCDDs, polychlorinated quadphenyls, and less chlorinated PCBs are recovered by eluting with 20% methylene chloride-in-hexane (200-220 mL).

6. About 10 uL of propylene glycol are added, then the fraction is concentrated to near dryness and loaded onto a 10 g EM-1078 acidic alumina column, eluting with 80 mL of 1% methylene chloride-in-hexane, to purify the PCDF/PCDD fraction. The eluate is discarded.

7. The purified PCDF/PCDD fraction is eluted with 20% methylene chloride-in-hexane (120 mL).

8. The extract is concentrated to 25 uL immediately before analysis after carrying out a solvent exchange into toluene.

9. If necessary, the extract is purified further by loading it in hexane onto a small (1 cm) column of Carbopack C mixed with Celite 545, eluting with 2 mL hexane, 1 mL of 50% methylene chloride-in-cyclohexane, and 1 mL of methylene chloride:methanol:benzene (75:20:5). The column flow is reversed and the PCDF/PCDD fraction is eluted with 8 mL of toluene.

GC/MS ANALYSIS

Samples and standards were analyzed using combined capillary column gas chromatography/low-resolution mass spectrometry (HRGC/LRMS or GC/MS). The major elements of our analysis protocol were as follows:

- HRGC/LRMS
  --Unit mass resolution -1,000
  --SP-2330, OV-17 columns

- Selected Ion Monitoring
  --Two ion masses monitored per PCDF/PCDD congener class

- Identification Criteria
  --Coincident GC retention times
  --Correct intensity ratios for monitored ions

- Quantification
  --Direct comparison with added internal standards
  --MS response factors from standards.

The gas chromatograph, a Varian 3700, was equipped with a 60 m x 0.25 mm ID fused-silica SP-2330 (Supelco) column. Samples were injected in the splitless mode, with the column programmed from 85°C to 250°C at a rate of 15°C/min, and held at the upper limit for 60 min. The SP-2330 column has been shown to separate the 2,3,7,8-TCDD from all other tetra-isomers, and to partially separate the 2,3,7,8-TCDF from the 2,3,4,8-TCDF [14,15]. However, it is unable to resolve 1,2,3,7,8-PnCDF from 1,2,3,4,8-PnCDF and 1,2,3,4,7,8-HxCDF from 1,2,3,4,7,9-HxCDF. These isomers can be separated to some extent on less polar columns, such as OV-17 or DB-5 [14,15].

An example of the chromatographic resolution obtained using the SP-2330 column is shown in Figure 2-2 for 2,3,7,8-TCDD and several closely eluting tetradioxin isomers. The plot clearly shows that this column is isomer-specific for 2,3,7,8-TCDD. Figure 2-3 shows the separation obtained between the 2,3,7,8- and 2,3,4,8-TCDF isomers. Here the resolution is not as good as in the previous case, but it is nonetheless sufficient to permit quantification of the two isomers in most cases.

All data were acquired by software-controlled multiple ion detection using two ion masses from the molecular ion cluster for each of the PCDF and PCDD levels of chlorination. Two ions were also monitored for each internal standard. This permitted the calculation and comparison of the isotope ratios with their theoretical values to verify their identity. Several additional ion masses were monitored to indicate possible interferences from chlorinated diphenyl ethers [16,17]. The presence of these compounds could give rise to fragment ions with the same masses as those monitored for the PCDFs. Therefore, the absence of a co-response for the diphenyl ether ion mass when a PCDF compound shows a positive response was taken to indicate that the signal for the PCDF was "real."

The masses that were monitored, along with the theoretical isotope ratios, are listed in Table 2-1. In order to obtain maximum sensitivity and selectivity during an experiment, the run was divided into four adjoining time windows. Each window contained up to 16 ion masses (for specific native and labeled PCDFs and PCDDs, and chlorinated diphenyl ethers); the sample dwell times and interchannel delay times were chosen to give the most sensitive and rapid cycle time. Since the GC column used in this work did not yield complete separation of each chlorination level of PCDFs/PCDDs from the other groups in a given time window,

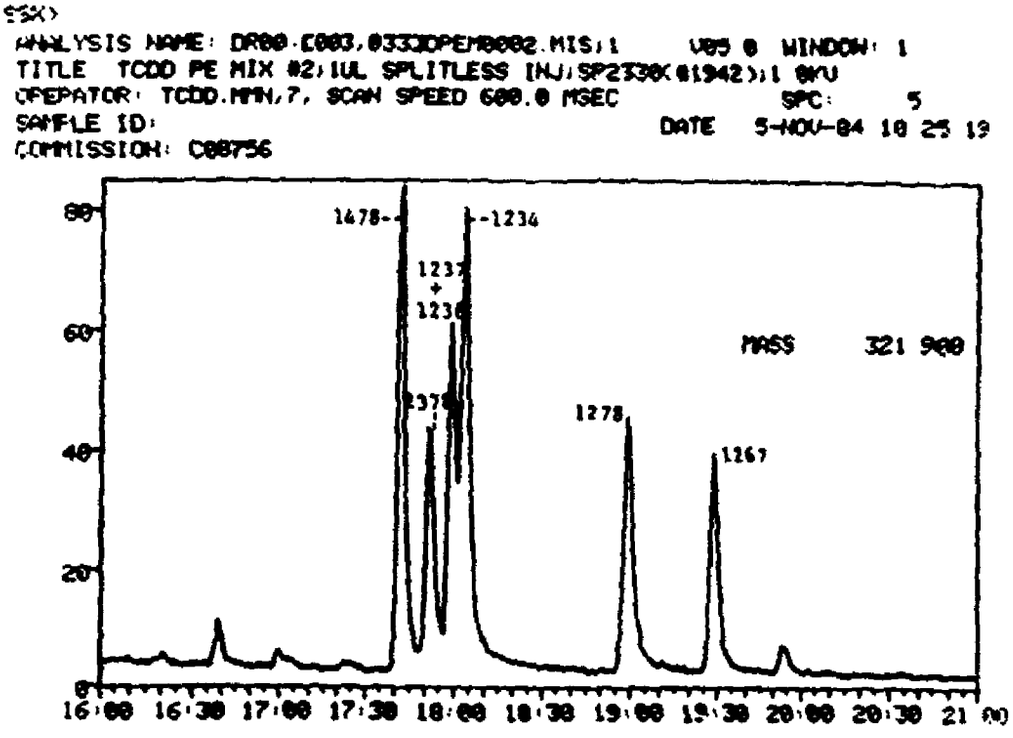

Figure 2-2. Selected ion current profile for mass 322 from GC/MS analysis of performance check solution containing TCDDs as noted in the plot, using a 60 m SP-2330 fused silica capillary column.

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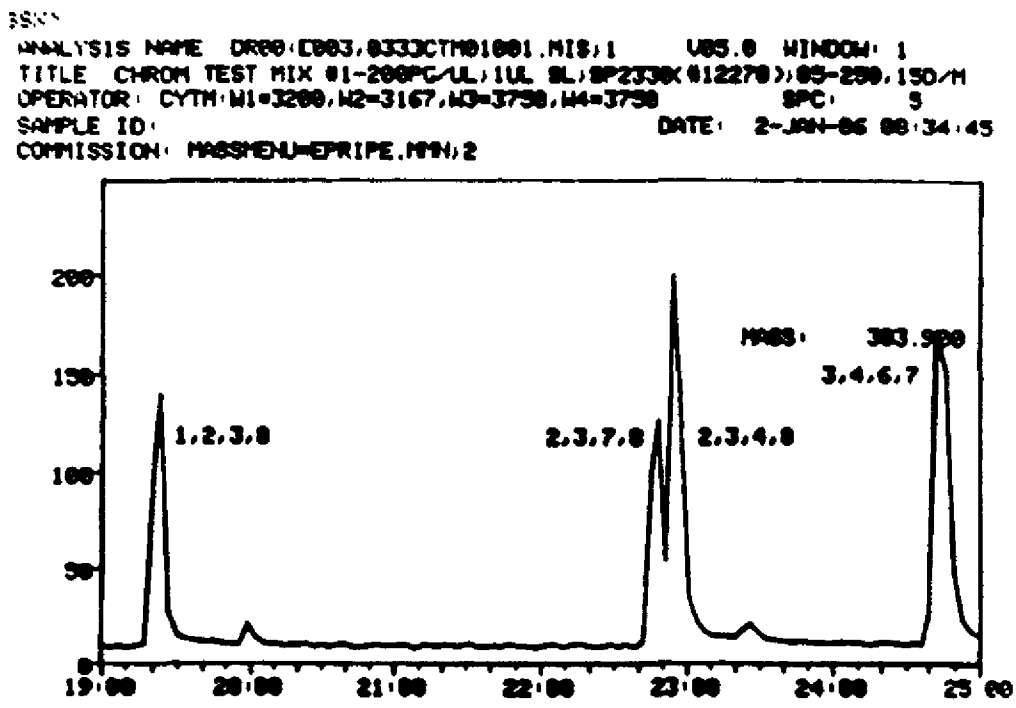

Figure 2-3. Selected ion current profile for mass 304 from GC/MS analysis of performance check solution containing TCDFs as noted on the plot, using a 60 m SP-2330 fused-silica capillary column.

Table 2-1

ANALYTICAL SEQUENCE IN GC/MS DETERMINATION OF PCDFs AND PCDDs

Time Window	Start (min)	Stop (min)	GC Column Temp. (°C)	Temp. Prog Rate (°C/min)	Cycle Time (ms)	Dwell Time (ms)	Compounds Monitored	Ions Monitored (m/z) Mass 1	Mass 2	Isotope Ratio (Mass 1/ Mass 2)
1	18:00	26:00	85	15	3200	197	TCDF	303.9	305.9	0.77
							^{13}C-TCDF	315.9	317.9	0.77
							TCDD	319.9	321.9	0.77
							^{13}C-TCDD	331.9	333.9	0.77
							PnCDF	337.9	339.9	0.61
							^{13}C-PnCDF	349.9	351.9	0.61
							PnCDD	355.9	357.9	1.54
							HxDPE[a]	373.8	--	--
							HpDPE[a]	407.8	--	--
2	26:00	35.30	250	--	3167	195	PnCDF	337.9	339.9	0.61
							PnCDF[b]	274.9	--	--
							PnCDD	355.9	357.9	1.54
							PnCDD[b]	290.9	--	--
							HxCDF	373.8	375.8	1.23
							^{13}C-HxCDF	385.9	387.9	1.23
							HxCDF[b]	310.9	--	--
							HxCDD	389.8	391.8	1.23
							HxCDD[b]	326.9	--	--
							HpDPE[a]	407.8	--	--
							ODPE[a]	443.8	--	--
3	35:30	56:00	250	--	3750	372	HxCDF	373.8	375.8	1.23
							HxCDD	389.9	391.8	1.23
							HpCDF	407.8	409.8	1.03
							HpCDD	423.8	425.8	1.03
							ODPE[a]	443.8	--	--
							NDPE[a]	477.7	--	--
4	56:00	66:00	250	--	3750	534	OCDF	441.7	443.7	0.88
							OCDD	457.7	459.7	0.88
							^{13}C-OCDD	469.8	471.8	0.88
							ODPE[a]	511.7	--	--

[a] HxDPE, HpDPE, ODPE, NDPE, ODPE designate hexa-, hepta-, octa-, nona-, and decachlorodiphenyl ethers, respectively.

[b] Mass monitored to identify fragment ion (M-COCl).

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some of the ion masses were included in more than one window to ensure that all isomers from a particular congener class were monitored.

Three major criteria were used to confirm the presence of specific PCDFs/PCDDs in the samples analyzed:

- correct retention times for each PCDF/PCDD of interest relative to the appropriate isotopically labeled internal standard(s)
- intensity ratio for $M^+/(M+2)^+$ within 10% of the theoretically expected ratio (see Table 2-1)
- signal-to-noise response for each PCDF/PCDD of interest greater than 2.5:1 for both ion masses monitored.

Quantification. Ideally, each of the 210 separate isomers of PCDF and PCDD should be quantified using the instrument response of the corresponding labeled internal standard as a reference. Since only a limited number of these standards are available in practice, the approach generally followed is to use an appropriate set of internal standards that includes representative isomers from each chlorinated class of PCDFs and PCDDs, and further assume that the data obtained for these are representative of all isomers in each group.

Relative response factors were determined from the analysis of standard solutions containing the internal standards and isomers representative of each chlorination class. Response factors were calculated from the following equation:

$$RF = Ax(Qis/Ais)Qx \qquad (2\text{-}1)$$

where Ax = sum of the integrated ion abundances of the masses for the unlabeled compound

Ais = sum of the integrated ion abundances of the masses for the appropriate labeled compound

Qis = amount of the appropriate labeled compound, ng

Qx = amount of the unlabeled compound, ng.

The PCDFs and PCDDs in the sample extract are quantified by calculating the ratios of the mass spectral responses obtained for the ions characteristic of the labeled

PCDFs/PCDDs to those of the appropriate internal standards, corrected for differences in response factor. The equation used for quantification was:

$$\text{Concentration (ng/g)} = \frac{Ax \cdot Qis}{Ais \cdot W \cdot RF} \qquad (2\text{-}2)$$

where W = weight of sample, g
RF = response factor.

Because the labeled internal standard was added before the sample was extracted and analyzed, and the internal standard was quantified at the same time as the native components, any losses of PCDD/PCDF incurred during the analysis were accounted for by the above approach.

Detection limits, i.e., the minimum detectable concentrations required to produce a signal 2.5 times the average background signal, were calculated for each PCDF/PCDD congener class. For each class, the average width of the baseline noise-band for the native compounds and the peak height for a known concentration of the associated ^{13}C-labeled analog were measured manually. Measurements of the noise band were made in a region of the selected ion current profile that was free of interferences and as close as practicable in the plot to the peak for the corresponding ^{13}C-labeled compound. The detection limit, DL, was calculated using the relationship:

$$DL = \frac{(2.5)\ (Ax \cdot Qis)}{Ais \cdot RF \cdot W} \qquad (2\text{-}3)$$

where Ax = height of the noise band of the selected mass for the unlabeled compound
Ais = height of the peak corresponding to the labeled compound of the same congener class.

Section 3

RESULTS AND DISCUSSION

PHASE I

Calibration and Quality Assurance Data

Before using the SP-2330 GC column to generate response factors and analyze the baseline and in-service samples, the column performance was evaluated in terms of its ability to resolve the isomers of interest and to cover the entire tetra- through octa- range of compounds. The resolution of the column for the highly toxic 2,3,7,8-TCDD and TCDF with respect to closely eluting isomers is shown in Figures 2-2 and 2-3. Figure 3-1 shows the separation of the tetra- through octa-congeners in a total analysis time of about 1 hour, using the temperature program given earlier. The ion masses used to monitor the PCDFs and PCDDs are indicated on the plots, along with the identity of the specific components detected.

The response factors generated using the standard "Radian PCDF/TCDD Cocktail" solution described earlier are listed in Table 3-1. The solution, which was analyzed in triplicate, did not contain either the OCDF or OCDD components. OCDF was, however, included in the "Rappe Toxic Cocktail," which was also mixed with equal amounts of the ^{13}C-labeled standards. Analysis of this solution gave an average response factor of 0.92 ±0.13 for OCDF with respect to ^{13}C-OCDD. The response factors used to calculate the concentrations of the other PCDFs and PCDDs of interest in the Phase I baseline and in-service samples are marked with asterisks in Table 3-1.

Baseline Samples

To test the various procedures, the five baseline samples were extracted and analyzed in duplicate for the native spikes listed in Figure 3-2, and for total PCDFs and PCDDs. The results obtained for the analysis of the baseline fluids are summarized in Tables 3-2 through 3-6. It should be noted that the values reported for the isomer pairs 1,2,3,7,8-/1,2,3,4,8-PnCDF and 1,2,3,4,7,8-/1,2,3,4,7,9-HxCDF are shown as composite amounts, since these isomers cannot be resolved using the

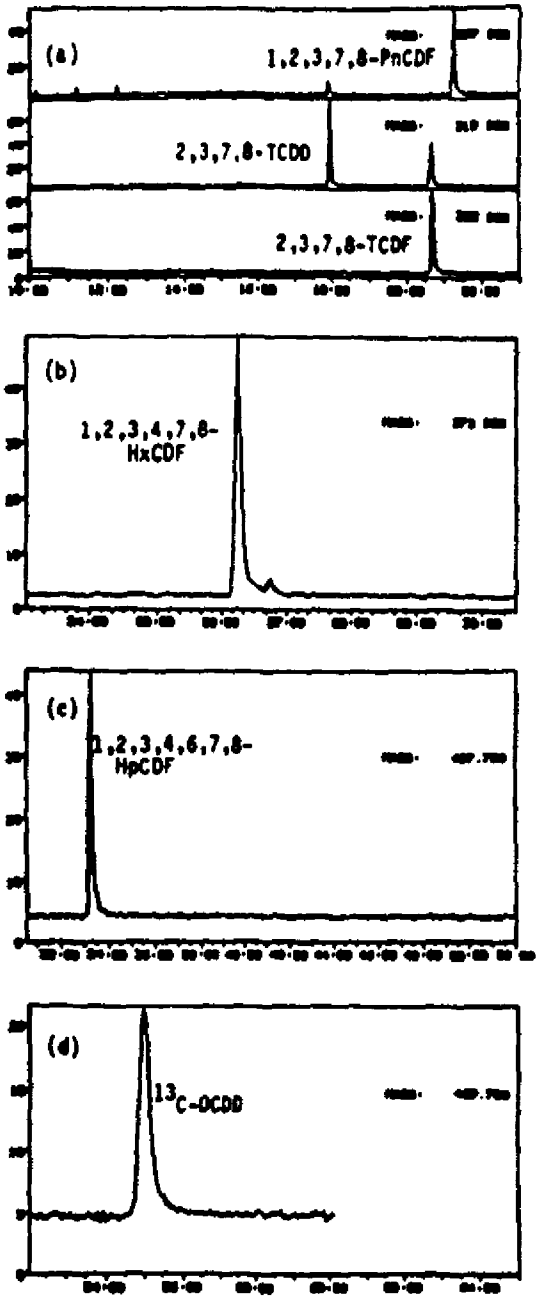

Figure 3-1. Selected ion current profiles of chromatography performance solution using SP-2330 capillary column. (a) TCDF/TCDD/PnCDF components in 1st time window; (b) HxCDF component in 2nd time window; (c) HpCDF component in 3rd time window; (d) OCDD in 4th time window.

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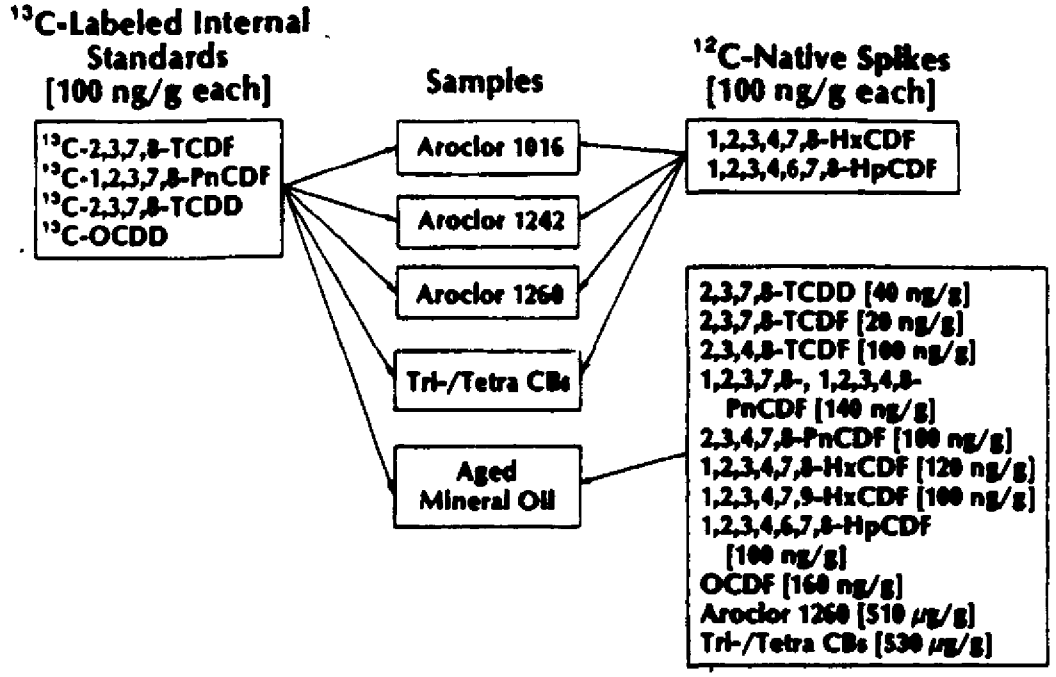

Figure 3-2. Summary of Baseline Samples and Spikes (Phase I)

Table 3-1

AVERAGE RESPONSE FACTORS FOR PCDD/PCDF CALIBRATION COMPOUNDS (PHASE 1)

Compound	Average Response Factor			
	^{13}C-2,3,7,8-TCDD	^{13}C-2,3,7,8-TCDF	^{13}C-1,2,3,7,8-PnCDF	^{13}C-OCDD
2,3,7,8-TCDD	0.98 ±0.03*	0.86 ±0.07		
2,3,7,8-TCDF	1.39 ±0.12	1.21 ±0.01*		
1,2,3,7,8-PnCDF	1.04 ±0.08	0.91 ±0.02	1.24 ±0.03*	
1,2,3,4,7,8,-HxCDF	0.95 ±0.04	0.84 ±0.06	1.13 ±0.03*	1.40 ±0.06
1,2,3,4,6,7,8-HpCDF	1.24 ±0.11	1.09 ±0.14	1.48 ±0.14*	1.79 ±0.68*

*Response factors used to calculate concentrations in samples.

SP-2330 capillary column. In the case of the partially overlapping 2,3,7,8-/2,3,4,8-TCDF peaks, the amounts of each present in the samples were estimated from the relative areas of the peaks. These areas were determined by dropping a perpendicular line from the valley between the two peaks to the baseline.

Aroclor 1016 (Radian I.D. E729-09-01). The Aroclor 1016 sample was extracted and analyzed in triplicate (Table 3-2) instead of duplicate, largely because of the marked differences observed for several of the component concentrations in the first two determinations. In fact, the results show that far better agreement was observed between the second and third determinations; we are unable to explain the values obtained in the first determination.

In terms of the second and third determinations, the data in Table 3-2 show that the Aroclor 1016 fluid does not contain any native PCDFs or PCDDs other than those that were spiked into the sample before analysis. The values obtained for the spiked components, 1,2,3,4,7,8-/1,2,3,4,7,9-HxCDF and 1,2,3,4,6,7,8-HpCDF, are roughly 50% of the expected concentrations. The reason for these low recoveries is not clear, but may be due to an adverse matrix effect.

Table 3-2

PCDF/PCDD CONCENTRATIONS IN BASELINE SAMPLE: AROCLOR 1016
(Radian I.D. E729-09-01)

Components	Concentration (ng/g) Spiked	Measured Det. 1	Det. 2	Det. 3	Ave.
PCDF/PCDD					
Total Tetra-CDF		90			
Total Penta-CDF		125			
Total Hexa-CDF		158	63	56	92
Total Hepta-CDF		152	45	45	81
Octa-CDF		59			
Total Tetra-CDD					
Octa-CDD					
Compound					
2,3,7,8-Tetra-CDD					
2,3,7,8-Tetra-CDF		15			
2,3,4,8-Tetra-CDF		8			
1,2,3,7,8-Penta-CDF*		34			
1,2,3,4,8-Penta-CDF*					
2,3,4,7,8-Penta-CDF					
1,2,3,4,7,8-Hexa-CDF*	100	109	63	56	76
1,2,3,4,7,9-Hexa-CDF*					
1,2,3,7,8,9-Hexa-CDF					
1,2,3,6,7,8-Hexa-CDF					
2,3,4,6,7,8-Hexa-CDF					
1,2,3,4,6,7,8-Hepta-CDF	100	83	45	45	58

* Isomers coelute on SP-2330 column.

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Aroclor 1242 (Radian I.D. E729-10-01). Two extractions and analyses were performed on the Aroclor 1242 sample (Table 3-3). In general, a larger number of PCDFs and PCDDs was observed at significantly higher levels than in the Aroclor 1016 sample. The first determination gave very good agreement between the spiked and observed levels of HxCDF and HpCDF components. The measured values, however, were much lower for the second determination. By contrast, the values obtained for the other tetra- and penta- CDFs of interest showed good agreement with one another.

Table 3-3

PCDF/PCDD CONCENTRATIONS IN BASELINE SAMPLE: AROCLOR 1242
[Radian I.D. E729-10-01]

	Concentration (ng/g)			
		Measured		
Components	Spiked	Det. 1	Det. 2	Ave.
PCDF/PCDD				
Total Tetra-CDF		854	878	866
Total Penta-CDF		382	323	353
Total Hexa-CDF		152	58	105
Total Hepta-CDF		144	74	109
Octa-CDF		120	134	127
Total Tetra-CDD				
Octa-CDD				
Compound				
2,3,7,8-Tetra-CDD				
2,3,7,8-Tetra-CDF		70	69	70
2,3,4,8-Tetra-CDF		153	161	157
1,2,3,7,8-Penta-CDF*		47	36	42
1,2,3,4,8-Penta-CDF*				
2,3,4,7,8-Penta-CDF		67	34	51
1,2,3,4,7,8-Hexa-CDF*	100	100	25	63
1,2,3,4,7,9-Hexa-CDF*				
1,2,3,7,8,9-Hexa-CDF				
1,2,3,6,7,8-Hexa-CDF				
2,3,4,6,7,8-Hexa-CDF				
1,2,3,4,6,7,8-Hepta-CDF	100	110	44	77

* Isomers coelute on SP-2330 column.

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Aroclor 1260 (Radian I.D. E729-11-01). The Aroclor 1260 sample (Table 3-4) showed a rather complex mixture of PCDFs at significantly increased levels in comparison with either Aroclor 1016 or Aroclor 1242. Here, the agreement between the two determinations was generally very good. The values obtained for the two spiked HxCDF and HpCDF components are six to seven times higher than the expected values, probably as a result of the levels of these compounds which, together with the other PCDFs listed in the table, are present as contaminants in the Aroclor 1260. These data emphasize the point that the Aroclors, especially Aroclor 1260,

Table 3-4

PCDF/PCDD CONCENTRATIONS IN BASELINE SAMPLE: AROCLOR 1260
[Sample No. E729-11-01]

Components	Concentration (ng/g) Spiked	Measured Det. 1	Det. 2	Ave.
PCDF/PCDD				
Total Tetra-CDF		629	595	612
Total Penta-CDF		1039	1034	1037
Total Hexa-CDF		1372	1493	1433
Total Hepta-CDF		1810	2159	1985
Octa-CDF		3833	4474	4154
Total Tetra-CDD				
Octa-CDD			2	
Compound				
2,3,7,8-Tetra-CDD				
2,3,7,8-Tetra-CDF		145	144	145
2,3,4,8-Tetra-CDF		48	47	48
1,2,3,7,8-Penta-CDF*		236	225	231
1,2,3,4,8-Penta-CDF*				
2,3,4,7,8-Penta-CDF		89	86	88
1,2,3,4,7,8-Hexa-CDF*	100	568	634	601
1,2,3,4,7,9-Hexa-CDF*				
1,2,3,7,8,9-Hexa-CDF				
1,2,3,6,7,8-Hexa-CDF				
2,3,4,6,7,8-Hexa-CDF				
1,2,3,4,6,7,8-Hepta-CDF	100	626	742	684

* Isomers coelute on SP-2330 column.

contain considerable amounts of PCDFs, despite the fact that they were "fresh" fluids that had not seen any service in electric utility equipment.

Tri-/tetrachlorobenzenes (Radian I.D. E729-12-01). Both measurements of the PCDFs and PCDDs in the tri-/tetrachlorobenzene sample gave values that were in excellent agreement with each other and with the amounts of the HxCDF and HpCDF components spiked into the fluid (Table 3-5). The results suggest that the polychlorinated benzene matrix is relatively "clean" and does not have a negative influence on the extraction and analysis of PCDFs and PCDDs using our procedure.

Table 3-5

PCDF/PCDD CONCENTRATIONS IN BASELINE SAMPLE: CHLOROBENZENES
[Radian I.D. E729-12-01]

	Concentration (ng/g)			
		Measured		
Components	Spiked	Det. 1	Det. 2	Ave.
PCDF/PCDD				
Total Tetra-CDF				
Total Penta-CDF				
Total Hexa-CDF		105	100	103
Total Hepta-CDF		101	95	98
Octa-CDF				
Total Tetra-CDD				
Octa-CDD				
Compound				
2,3,7,8-Tetra-CDD				
2,3,7,8-Tetra-CDF				
2,3,4,8-Tetra-CDF				
1,2,3,7,8-Penta-CDF*				
1,2,3,4,8-Penta-CDF*				
2,3,4,7,8-Penta-CDF				
1,2,3,4,7,8-Hexa-CDF*	100	105	100	103
1,2,3,4,7,9-Hexa-CDF*				
1,2,3,7,8,9-Hexa-CDF				
1,2,3,6,7,8-Hexa-CDF				
2,3,4,6,7,8-Hexa-CDF				
1,2,3,4,6,7,8-Hepta-CDF	100	101	95	98

* Isomers coelute on SP-2330 column.

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Aged Mineral Oil (Radian I.D. E729-08-01). The aged mineral oil sample was chosen to simulate a complex real-world situation, as illustrated in Figure 3-2. The data in Table 3-6 show reasonably good agreement between the two determinations. In some cases, such as for 2,3,7,8-TCDD and 2,3,7,8-TCDF, both the repeatability and accuracy were almost 100%, while in others, notably 2,3,4,8-TCDF and 1,2,3,4,7,8-/1,2,3,4,7,9-HxCDF, the agreement between the two determinations was poor. Furthermore, for 2,3,4,7,9-PnCDF and 1,2,3,4,6,7,8-HpCDF, the measured

Table 3-6

PCDF/PCDD CONCENTRATIONS IN BASELINE SAMPLE: MINERAL OIL
[Radian I.D. E729-08-01]

Components	Concentration (ng/g) Spiked**	Measured Det. 1	Det. 2	Avg.
PCDF/PCDD				
Total Tetra-CDF		88	52	70
Total Penta-CDF		172	158	165
Total Hexa-CDF		130	284	207
Total Hepta-CDF		24	56	40
Octa-CDF	160	430	355	393
Total Tetra-CDD		41	43	42
Octa-CDD				
Compound				
2,3,7,8-Tetra-CDD	40	41	41	41
2,3,7,8-Tetra-CDF	20	22	20	21
2,3,4,8-Tetra-CDF	100	66	32	49
1,2,3,7,8-Penta-CDF*	140	113	111	112
1,2,3,4,8-Penta-CDF*				
2,3,4,7,8-Penta-CDF	100	59	45	52
1,2,3,4,7,8-Hexa-CDF*	120	130	281	206
1,2,3,4,7,9-Hexa-CDF*	100			
1,2,3,7,8,9-Hexa-CDF				
1,2,3,6,7,8-Hexa-CDF				
2,3,4,6,7,8-Hexa-CDF				
1,2,3,4,6,7,8-Hepta-CDF	100	24	52	38

* Isomers coelute on SP-2330 column.

** In addition, sample spiked with 510 µg/g Aroclor 1260 and 530 µg/g tri-/tetrachlorobenzenes.

values were markedly lower than the expected concentrations. No clearcut reasons can be offered for these large discrepancies.

In-Service Samples

Three of the participating laboratories undertook a preliminary round-robin study using four dielectric fluids taken from in-service transformers and capacitors. Because this represented our first attempt at characterizing the PCDF and PCDD constituents of in-service equipment, the only speciation performed was for the 2,3,7,8-TCDF and TCDD. For the rest, only total congener class concentrations were measured. All of the samples were extracted and analyzed in duplicate. The results obtained are discussed in the following sections.

Oil-Filled Substation Distribution Transformer (Battelle I.D. ISL-4-O). Sample ISL-4-O, a mineral oil fluid containing 100 µg/g PCBs, was taken from a substation distribution transformer. The transformer had failed in service as a result of major arcing. Analysis of this sample did not reveal the presence of any PCDFs or PCDDs (Table 3-7).

Table 3-7

PCDF/PCDD CONCENTRATIONS IN IN-SERVICE SAMPLE:
OIL-FILLED TRANSFORMER
[Battelle I.D. ISL-4-O]

Components	Concentration (ng/g) Det. 1	Det. 2	Ave.	Detection Limit (ng/g)
PCDF/PCDD				
Total Tetra-CDF	nd	nd	nd	10
Total Penta-CDF	nd	nd	nd	18
Total Hexa-CDF	nd	nd	nd	22
Total Hepta-CDF	nd	nd	nd	7
Octa-CDF	nd	nd	nd	33
Total Tetra-CDD	nd	nd	nd	10
Octa-CDD	nd	nd	nd	33
Compound				
2,3,7,8-Tetra-CDD	nd	nd	nd	
2,3,7,8-Tetra-CDF	nd	nd	nd	

nd = not detected

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Askarel Capacitor (Battelle I.D. ISL-1-A). Sample ISL-1-A was taken from a capacitor containing Aroclor 1242 which had failed in service. It had bulged but did not rupture, and showed evidence of burnt paper on the inside. Again, analysis of the fluid did not reveal the presence of detectable levels of PCDFs or PCDDs (Table 3-8).

Table 3-8

PCDF/PCDD CONCENTRATIONS IN IN-SERVICE SAMPLE:
ASKAREL CAPACITOR
[Battelle I.D. ISL-1-A]

Components	Concentration (ng/g) Det. 1	Det. 2	Ave.	Detection Limit (ng/g)
PCDF/PCDD				
Total Tetra-CDF	nd	nd	nd	1
Total Penta-CDF	nd	nd	nd	10
Total Hexa-CDF	nd	nd	nd	9
Total Hepta-CDF	nd	nd	nd	6
Octa-CDF	nd	nd	nd	4
Total Tetra-CDD	nd	nd	nd	1
Octa-CDD	nd	nd	nd	4
Compound				
2,3,7,8-Tetra-CDD	nd	nd	nd	
2,3,7,8-Tetra-CDF	nd	nd	nd	

nd = not detected

Askarel Load Center Network Transformer (Battelle I.D. ISL-2-A). Sample ISL-2-A was taken from a load center network transformer that had been in service for 20 years, and contained typical proportions of Aroclor 1260 and tri-/tetrachlorobenzenes. The results of the analysis (Table 3-9) revealed substantial concentrations (ug/g-levels) of all of the congener classes, especially HxCDFs. Furthermore, the agreement observed between the two sets of data was quite satisfactory

and did not indicate any analytical difficulties that could be ascribed to the matrix. The values shown here are similar to those obtained earlier for the "fresh" sample of Aroclor 1260 (Table 3-4), which had not seen any electric utility service.

Askarel Load Center Network Transformer (Battelle I.D. ISL-3-A). Sample ISL-3-A contained 70% Aroclor 1260, 29% trichlorobenzenes, and 1% tetrachlorobenzenes. The fluid was taken from a transformer that had been in service for 31 years. Here, the concentrations for the PCDFs (Table 3-10) were significantly higher than for the previous Aroclor 1260-containing transformer (ISL-2-A), especially with respect to the hexa-, hepta-, and octa-CDFs. This transformer had been in service for 11 years longer than ISL-2-A.

Table 3-9

PCDF/PCDD CONCENTRATIONS IN IN-SERVICE SAMPLE:
ASKAREL LOAD CENTER NETWORK TRANSFORMER
[Battelle I.D. ISL-2-A]

Components	Concentration (ng/g) Det. 1	Det. 2	Ave.	Detection Limit (ng/g)
PCDF/PCDD				
Total Tetra-CDF	962	549	756	3
Total Penta-CDF	2163	921	1542	2
Total Hexa-CDF	3247	1436	2342	3
Total Hepta-CDF	1341	1844	1593	1
Octa-CDF	162	962	562	7
Total Tetra-CDD	nd	nd	nd	3
Octa-CDD	nd	48		7
Compound				
2,3,7,8-Tetra-CDD	nd	nd	nd	
2,3,7,8-Tetra-CDF	281	141	211	

nd = not detected

MONS 215449

Table 3-10

PCDF/PCDD CONCENTRATIONS IN IN-SERVICE SAMPLE:
ASKAREL LOAD CENTER NETWORK TRANSFORMER
(Battelle I.D. ISL-3-A)

Components	Concentration (ng/g) Det. 1	Det. 2	Ave.	Detection Limit (ng/g)
PCDF/PCDD				
Total Tetra-CDF	210	68	139	1
Total Penta-CDF	2,949	716	1,833	1
Total Hexa-CDF	10,965	3,967	7,466	2
Total Hepta-CDF	12,931	11,484	12,208	1
Octa-CDF	5,723	6,893	6,308	6
Total Tetra-CDD	nd	nd	nd	1
Octa-CDD	nd	10		6
Compound				
2,3,7,8-Tetra-CDD	nd	nd	nd	
2,3,7,8-Tetra-CDF	13	8	11	

nd = not detected

Conclusions

The results obtained in the Phase I pilot study for the analysis of the five baseline and four in-service samples suggested that the extraction and analysis methods developed for PCDFs and PCDDs in dielectric fluids are compound-specific and sufficiently sensitive. However, indications were that the precision attainable with these methods could possibly be improved by attention to some aspects of the extraction and sample concentration procedure. These were addressed at the start of the Phase II study.

Analysis of the baseline samples gave reasonable agreement with expected values in those cases where comparisons were possible, i.e., in those samples in which the native levels of the PCDF-contaminants did not mask the components that were spiked into the samples. In the case of the in-service samples, significant quantities of PCDFs were found in 20- and 31-year-old transformers containing Aroclor 1260.

PHASE II

Upon completion of the Phase I study, several changes were made to the sample extraction and concentration procedures in an effort to improve the overall precision and efficiency of the methodology. These changes, which are incorporated in the method summary, were based on the work of Albro et al. [13] and included the following:

1. Investigate the effect of reducing the length of the A-540 basic alumina column, because elution through this column was found to be the most time-consuming step. Investigate the effect of increasing the size of the EM-1078 acid alumina column--the least time-consuming step--in an effort to improve overall cleanup efficiency.

2. Include propylene glycol as a "keeper" and 2,3,7-tri-CDD as a "carrier" to minimize losses during evaporation of solvents and on glass surfaces.

3. Replace isooctane with toluene as the final solvent to reduce losses during sample concentration due to the strong adherence of some congeners to the glass walls.

4. Investigate the efficacy of the roto-evaporator for all sample concentration steps.

5. Include ions in the GC/MS analysis mass-menu to indicate the presence of polychlorinated diphenylether interferences.

Most of these steps proved to be beneficial and were incorporated into the sample extraction protocol that was used in Phase II of the study.

Quality Assurance and Calibration Data

Column Performance. Before undertaking the Phase II stage of the investigation, the performance of the SP-2330 GC column was checked to evaluate its ability to resolve the isomers of interest and to cover the entire congener range of interest. Figures 2-3 and 2-4 show the resolution obtained with this column for 2,3,7,8-TCDD and TCDF from their closely eluting isomers.

Figure 3-3 shows the plots obtained for the chromatography performance standard, which was prepared at Battelle, to further evaluate the system and establish the order of elution on the SP-2330 fused-silica column. To this mixture we added several more 2,3,7,8-substituted PCDF/PCDD isomers (denoted below with an asterisk) in order to establish their elution times as well. The performance

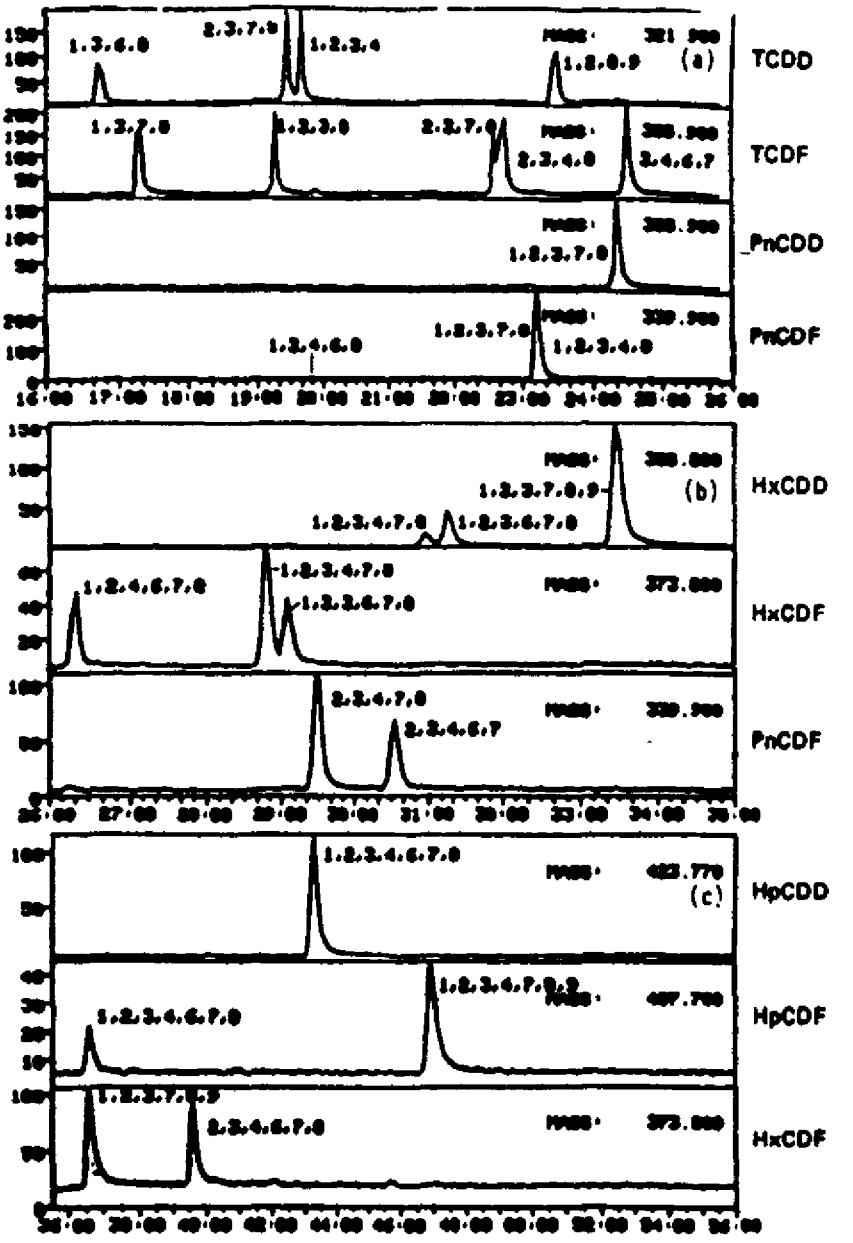

Figure 3-3. Selected ion current profiles of chromatography performance solution using SP-2300 capillary column. (a) TCDD/TCDF/PnCDD/PnCDF components in 1st time window; (b) HxCDD/HxCDF/PnCDF components in 2nd time window; (c) HpCDD/HpCDF/HxCDF components in 3rd time window.

mixture was prepared with the following compounds at a concentration of about 200 pg/μL each in n-decane, and the order of elution is shown below.

Isomer	Elution Order
1,3,6,8-TCDD	First tetra-CDD eluter
1,2,3,4-TCDD	Co-eluter
2,3,7,8-TCDD	
1,2,8,9-TCDD	Last eluter
1,3,7,8-TCDF	Second tetra-CDF eluter
2,3,4,8-TCDF	Co-eluter
1,2,3,8-TCDF	Co-eluter?
2,3,7,8-TCDF	
3,4,6,7-TCDF	Second-last tetra-CDF eluter
1,2,3,7,8-PnCDD*	
1,2,4,6,8-PnCDF	Second penta-CDF eluter
1,2,3,4,8-PnCDF	Co-eluter
1,2,3,7,8-PnCDF	Co-eluter
2,3,4,7,8-PnCDF	
2,3,4,6,7-PnCDF	Last penta-CDF eluter
1,2,3,4,7,8-HxCDD*	
1,2,3,6,7,8-HxCDD*	
1,2,3,7,8,9-HxCDD*	Second last eluter
1,2,4,6,7,8-HxCDF	Second hexa-CDF eluter
1,2,3,4,7,8-HxCDF	
1,2,3,6,7,8-HxCDF	
1,2,3,7,8,9-HxCDF*	
2,3,4,6,7,8-HxCDF	Last hexa-CDF eluter
1,2,3,4,6,7,8-HpCDD*	Last eluter
1,2,3,4,6,7,8-HpCDF*	First eluter
1,2,3,4,7,8,9-HpCDF*	Last eluter.

Calibration Data. The calibration standards prepared by Radian were used to generate five sets of calibration curves and response factors for the compounds of interest. For example, the selected ion current profiles obtained for the injection of a 2 μL aliquot of the 150 ng/mL standard solution are shown in Appendix A (Figure A-1), along with a listing of the raw data for each mass, time centroid, concentration, and corresponding peak area. The masses used to monitor for the components of interest as well as the measured peak areas are shown on the plots.

The calibration curves are shown in Appendix B, Figures B-1 through B-9. No data were obtained for the 2.5 ng/mL and 7,500 ng/mL standards, since they gave responses that fell outside the working range of our GC/MS system. The results in Figures B-1 through B-9 indicate that all of the experimental data are well approximated by straight lines, the correlation coefficients for linear regressions ranging between 0.9920 and 0.9997.

Response factors for the compounds of interest were calculated according to Eq. 2-1. The response factors generated in this way are listed in Table 3-11, along with the mean of replicate determinations (Ave.), the standard deviation (SD), the percent relative standard deviation (RSD, %), and the number of replicate measurements performed (n). In general, the precision obtained for the individual compounds at each concentration is highly satisfactory, and is less than 10% RSD for all of the compounds except OCDF. Because of chromatographic limitations, OCDF did not give measurable peak areas for the 10 and 40 ng/mL standards, and the RSD for the higher native concentrations ranged between 7.8% and 16.0%.

It is interesting to note that the response factors listed in Table 3-11 for 1,2,3,7,8-PnCDF and 2,3,4,7,8-PnCDF agree very closely with one another throughout the concentration range. This agreement is expected on theoretical grounds. On the other hand, the response factors for 1,2,3,4,7,8-HxCDF and 2,3,4,6,7,8-HxCDF differ from one another by almost a factor of two. The reason for this is that they were measured in adjacent time windows, with significantly different dwell-time characteristics. The 1,2,3,4,7,8-HxCDF and its isotopic analog occur in the second time window; although the 2,3,4,6,7,8-HxCDF isomer appears in the third window, its response factor is still calculated with respect to the labeled HxCDF in the second window. Thus, the response factor for the former is closer to the theoretically expected value. According to the analytical scheme shown in Table 2-1, the dwell time for window 3 is 1.91 times greater than that for window 2. This ratio is sufficient to account fully for the apparent difference in response factors for the two HxCDF isomers shown in Table 3-11. In practice, this difference between the two values is of no real consequence since the baseline and in-service samples were analyzed under the same experimental conditions that were used to generate the response factors.

Table 3-12 gives the average response factors for the compounds of interest over the entire range of concentrations measured for each analyte. The overall precision varies between 3.7% and 6.5% for all compounds, except for OCDF for which the relative standard deviation is 16.5%. Again, this reflects the fact that this compound exhibited severe tailing on the SP-2330 column, thus decreasing the signal levels attainable and the reproducibility.

Response Factor Verification Data. In order to verify the constancy of the response factors with time, the standard solutions were analyzed at regular intervals throughout the study, and the response factors compared with the values

Table 3-11

RESPONSE FACTORS FOR PCDD/PCDF CALIBRATION COMPOUNDS (page 1 of 2)

Concentration of ^{13}C-Compounds	Response Factors							
	2,3,7,8-TCDD	2,3,7,8-TCDF	1,2,3,7,8-PnCDF	2,3,4,7,8-PnCDF	1,2,3,4,7,8-HxCDF	2,3,4,6,7,8-HxCDF	1,2,3,4,6,7,8-HpCDF	OCDF[b]
10 ng/mL	1.04	1.09	1.30	1.23	1.10	1.84	1.30	
	1.05	1.16	1.11	1.23	1.13	2.14	1.17	
	1.00	1.16	1.21	1.16	0.99	2.16	1.15	
	0.93	1.08	1.08	1.13	0.98	1.93	1.26	
	0.91	1.15	1.17	1.16	1.00	2.13	1.24	
Ave[c]	0.99	1.13	1.17	1.18	1.04	2.04	1.22	
SD	0.06	0.04	0.09	0.05	0.07	0.15	0.06	
RSD (%)	6.4	3.5	7.4	3.8	6.7	7.3	5.1	
n	5	5	5	5	5	5	5	0
40 ng/mL	1.01	1.10	1.11	1.13	1.07	1.94	1.04	
	0.88	1.13	1.20	1.19	1.04	1.79	1.09	
	1.04	1.19	1.17	1.18	1.03	1.77	1.22	
	0.88	1.14	1.11	1.16	1.12	2.17	1.24	
	0.92	1.08	1.11	1.10	1.14	2.07	1.23	
Ave[c]	0.95	1.12	1.14	1.15	1.08	1.95	1.16	
SD	0.07	0.05	0.04	0.04	0.05	0.17	0.09	
RSD (%)	7.9	4.3	3.7	3.2	4.5	8.9	7.9	
n	5	5	5	5	5	5	5	0
150 ng/mL	0.90	1.11	1.25	1.24	1.14	1.93	1.28	
	0.92	1.13	1.22	1.20	1.15	2.08	1.33	
	0.84	1.19	1.14	1.11	1.12	1.89	1.26	
	0.97	1.18	1.11	1.08	1.14	2.05	1.22	
	0.90	1.10	1.15	1.15	1.12	2.05	1.24	0.18
								0.17
								0.15
								0.16
Ave[c]	0.91	1.14	1.17	1.16	1.13	2.00	1.27	0.17
SD	0.05	0.04	0.06	0.07	0.01	0.08	0.04	0.01
RSD (%)	5.2	3.6	5.0	5.6	1.2	4.2	3.3	7.8
n	5	5	5	5	5	5	5	4

Table 3-11

RESPONSE FACTORS FOR PCDD/PCDF CALIBRATION COMPOUNDS (page 2 of 2)

Concentration of ^{12}C-Compounds	Response Factors							
	2,3,7,8-TCDD	2,3,7,8-TCDF	1,2,3,7,8-PeCDF	2,3,4,7,8-PeCDF	1,2,3,4,7,8-HxCDF	2,3,4,6,7,8-HxCDF	1,2,3,4,6,7,8-HpCDF[a]	OCDF[b]
500 ng/mL	0.87	1.08	1.24	1.24	1.05	1.91	1.22	
	0.92	1.10	1.21	1.22	1.15	2.07	1.26	
	0.96	1.17	1.19	1.20	1.09	2.05	1.27	0.16
	0.99	1.14	1.20	1.21	1.08	2.06	1.26	0.20
	0.98	1.13	1.19	1.15	1.14	2.14	1.27	0.19
								0.14
Ave[c]	0.94	1.14	1.21	1.20	1.10	2.05	1.26	0.17
SD	0.05	0.04	0.02	0.03	0.04	0.08	0.02	0.03
RSD (%)	5.2	3.5	1.7	2.8	3.4	4.1	1.7	16.0
n	5	5	5	5	5	5	5	4
2,500 ng/mL	0.92	1.10	1.09	1.13	1.10	1.97	1.25	
	0.89	1.24	1.26	1.27	1.16	2.10	1.25	
	0.98	1.17	1.16	1.15	1.14	2.07	1.32	
	0.92	1.13	1.21	1.18	1.17	2.08	1.29	
	0.84	1.15	1.17	1.17	1.10	2.11	1.25	0.19
								0.19
								0.23
								0.24
Ave[c]	0.88	1.16	1.18	1.18	1.13	2.07	1.27	0.21
SD	0.03	0.05	0.06	0.05	0.03	0.08	0.03	0.03
RSD (%)	3.7	4.5	5.3	4.6	2.9	2.7	2.5	12.4
n	5	5	5	5	5	5	5	4

[a] Response factor calculated with respect to ^{13}C-1,2,3,4,7,8-HxCDF.

[b] Response factor calculated with respect to ^{13}C-OCDD (assumed ^{13}C-OCDD Radian Corp., private communication). All others calculated with respect to ^{13}C-labeled analogs.

[c] Ave = average value; SD = standard deviation; RSD = relative standard deviation; n = number of deviations.

Table 3-12

AVERAGE RESPONSE FACTORS OVER ENTIRE CONCENTRATION RANGE FOR PCDD/PCDF CALIBRATION COMPOUNDS

Components	Ave.	SD	RSD (%)	n
2,3,7,8-TCDD	0.94	0.06	6.5	25
2,3,7,8-TCDF	1.14	0.04	3.7	25
1,2,3,7,8-PnCDF	1.17	0.06	4.9	25
2,3,4,7,8-PnCDF	1.17	0.05	4.1	25
1,2,3,4,7,8-HxCDF	1.10	0.05	4.9	25
2,3,4,6,7,8-HxCDF	2.02	0.12	5.8	25
1,2,3,4,6,7,8-HpCDF*	1.24	0.07	5.3	25
OCDF**	0.18	0.03	16.5	12

* Response factor calculated with respect to ^{13}C-1,2,3,4,7,8-HxCDF.

** Response factor calculated with respect to ^{13}C-OCDD (assumed ^{13}C-OCDD concentration = 300 ng/mL; Alan Nichols, Radian Corp., private communication). All other response factors calculated with respect to their ^{13}C-labeled analogs.

obtained during the calibration phase. The results are summarized in Table 3-13 and may be compared with the average values mentioned above. At no time did the values obtained in the verification experiments differ from the average response factors by more than a few percentage points. This high degree of consistency indicates that the GC/MS system remained very stable and reproducible in terms of signal detectability and response throughout the study.

Baseline Samples

The three spiked baseline samples (Aroclor 1016, Aroclor 1260, and aged mineral oil) were extracted and analyzed in triplicate, using the average response factors given in Table 3-12. The results obtained are summarized in Tables 3-15 through 3-17. Each table also shows the amounts of the various PCDFs and PCDDs that were

Table 3-13

RESPONSE FACTORS FROM VERIFICATION RUNS

Components	Response Factors from Calibration Data		Daily Response Factors per Concentration of ^{13}C Compounds (ng/mL)				
	Ave.	SD	150	150	2500	2500	500
2,3,7,8-TCDD	0.94	0.06	0.88	0.92	NC	NC	0.86
2,3,7,8-TCDF	1.14	0.04	1.09	1.12	1.18	1.11	1.12
1,2,3,7,8-PnCDF	1.17	0.06	1.18	1.19	1.21	1.22	1.21
2,3,4,7,8-PnCDF	1.17	0.05	1.15	1.19	1.22	1.21	1.18
1,2,3,4,7,8-HxCDF	1.10	0.05	1.10	1.05	1.15	1.08	1.14
2,3,4,6,7,8-HxCDF	2.02	0.12	2.04	1.98	2.15	1.97	2.07
1,2,3,4,6,7,8-HpCDF*	1.24	0.07	1.22	1.18	1.28	1.27	1.26
OCDF**	0.18	0.03	0.17	0.15	0.19	0.23	0.14

* Response factor calculated with respect to ^{13}C-1,2,3,4,7,8-HxCDF.

** Response factor calculated with respect to ^{13}C-OCDD (assumed ^{13}C-OCDD concentration = 300 ng/mL; Alan Nichols, Radian Corp., private communication). All other response factors calculated with respect to their ^{13}C-labeled analogs.

NC = Not calculated due to interferences in 2,3,7,8-TCDD.

spiked into the samples before analysis, as well as the average measured values and the detection limits estimated using Eqs. 2-2 and 2-3.

Analytical data tiers, which identify data groups, have been used to evaluate the data and compare the measured results with the spiked values. Specific analytes that have been quantified using a spiked, labeled calibration standard of the same isomeric compound are expected to have a higher inherent reliability and accuracy than, say, the summed congener results. The defined tiers are listed in Table 3-14.

Table 3-14

ANALYTICAL DATA CONFIDENCE TIERS

Tier	Description	Example
1	Unambiguous; all isomers fully resolved, and identical labeled standard used	2,3,7,8-TCDD OCDD
2	Compounds for which labeled isomeric analogs used for quantification; not fully resolved	2,3,7,8-TCDF 1,2,3,7,8-PnCDF
3	2,3,7,8-substituted compounds for which no labeled analogs are available	2,3,4,6,7,8-HxCDF
4	Summed congener classes	All HxCDF

Aroclor 1016 (Radian I.D. E729-53-02). Triplicate extractions and analyses of the Aroclor 1016 baseline sample gave high levels of precision for almost all of the compounds of interest, except 1,2,3,4,6,7,8-HpCDF (Table 3-15). The agreement between the spiked and measured concentrations for the Tier 1 compound 2,3,7,8-TCDD was excellent, and the agreement for the Tier 2 compounds was almost as good. Overall, it is clear that the unspiked Aroclor 1016 fluid contained virtually no chlorinated furans, since the concentrations measured in this sample are adequately explained in terms of the levels spiked in before analysis. Furthermore, the recoveries obtained for the labeled analogs also support the view that the Aroclor 1016 matrix is satisfactorily handled by our extraction and analysis procedures.

Aroclor 1260 (Radian I.D. E729-53-03). The Aroclor 1260 sample (Table 3-16) showed significantly higher levels of PCDFs than were found for the Aroclor 1016. The same trend--increasing levels of PCDF contaminants with degree of chlorination--was observed in the earlier Phase I analysis of these Aroclors. In general, the reproducibility of the values is almost as good as was the case with the less complex Aroclor 1016. One of the measurements of the Tier 1 compound 2,3,7,8-TCDD was based on the ^{13}C-2,3,7,8-TCDF as the internal standard. This was necessary because the ^{13}C-2,3,7,8-TCDD peaks were unusable due to interferences. Nevertheless, the average measured concentration for 2,3,7,8-TCDD was in good agreement with the expected value. The average values obtained for the two Tier 2

Table 3-15

PCDF/PCDD CONCENTRATIONS IN BASELINE SAMPLE: AROCLOR 1016
(Radian I.D. E729-53-02)

Components	PCDF/PCDD (ng/g) Spiked	Det. 1	Det. 2	Det. 3	Ave.	SD	RSD (%)	Detection Limit ng/g
PCDF/PCDD								
Total Tetra-CDF		81	62	81	81	1	1	
Total Penta-CDF		311	310	314	312	2	1	
Total Hexa-CDF		224	232	222	226	5	2	
Total Hepta-CDF		593	589	404	529	108	20	
Octa-CDF	132	197	136	73	135	62	46	24
Total Tetra-CDD		93	93	95	94	1	2	
Octa-CDD								5.2
Compound								
2,3,7,8-Tetra-CDD	93	93	93	95	94	1	2	0.5
2,3,7,8-Tetra-CDF	93	81	82	81	81	1	1	0.7
2,3,4,8-Tetra-CDF								
1,2,3,7,8-Penta-CDF*	158	181	168	168	164	3	2	0.7
1,2,3,4,8-Penta-CDF*								
2,3,4,7,8-Penta-CDF	158	149	144	148	147	3	2	
1,2,3,4,7,8-Hexa-CDF*		2	1	2	2	1	35	1.0
1,2,3,4,7,9-Hexa-CDF*								
1,2,3,7,8,9-Hexa-CDF								
1,2,3,6,7,8-Hexa-CDF	93	62	81	64	62	2	2	
2,3,4,8,7,8-Hexa-CDF	132	160	170	157	162	7	4	
1,2,3,4,8,7,8-Hepta-CDF	526	583	589	404	529	108	20	2.9
		Percent Recovery**						
^{13}C-Labeled Compound								
^{13}C-2,3,7,8-TCDF		98	93	100	97	4	4	
^{13}C-1,2,3,7,8-PCDF		103	95	100	99	4	4	
^{13}C-1,2,3,4,7,8-HxCDF		85	72	75	77	7	9	
^{13}C-OCDD		86	75	42	68	23	34	

* Isomers coelute on SP-2330 column.

** Percent recovery determined from the response of the ^{13}C-internal standards vs. ^{13}C-2,3,7,8-TCDD.

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Table 3-16

PCDF/PCDD CONCENTRATIONS IN BASELINE SAMPLE: AROCLOR 1260
[Radian I.D. E729-53-03]

Components	Spiked	PCDF/PCDD (ng/g) Det. 1	Det. 2	Det. 3	Ave.	SD	RSD (%)	Detection Limit* (ng/g)
PCDF/PCDD								
Total Tetra-CDF		1950	1647	1583	1593	98	3	
Total Penta-CDF		1114	1217	1093	1141	66	6	
Total Hexa-CDF		2338	2283	2242	2288	48	2	
Total Hepta-CDF		1209	1072	880	1047	178	17	
Octa-CDF	222	3618	2530	1989	2712	830	31	92
Total Tetra-CDD		107**	89	97	98	9	9	
Octa-CDD								9.9
Compound								
2,3,7,8-Tetra-CDD	111	107**	89	97	98	9	9	0.5
2,3,7,8-Tetra-CDF	833	853	808	881	847	36	4	1.1
2,3,4,8-Tetra-CDF	194	268	338	254	287	45	18	
1,2,3,7,8-Penta-CDF*	111	323	346	322	330	14	4	1.1
1,2,3,4,8-Penta-CDF*								
2,3,4,7,8-Penta-CDF	111	266	275	252	264	12	4	
1,2,3,4,7,8-Hexa-CDF*	900	987	921	942	950	34	4	3.4
1,2,3,4,7,9-Hexa-CDF*								
1,2,3,7,8,9-Hexa-CDF								
1,2,3,6,7,9-Hexa-CDF	278	361	395	371	382	12	3	
2,3,4,8,7,8-Hexa-CDF	56	318	280	298	302	14	5	
1,2,3,4,8,7,8-Hepta-CDF	111	567	511	444	507	62	12	2.0
		Percent Recovery***						
^{13}C-Labeled Compound								
^{13}C-2,3,7,8-TCDF		NC	93	101	97			
^{13}C-1,2,3,7,8-PCDF		NC	83	82	83			
^{13}C-1,2,3,4,7,8-HxCDF		NC	89	52	61			
^{13}C-OCDD		NC	37	14	26			

* Isomers coelute on SP-2330 column.

** Concentration calculated with respect to ^{13}C-2,3,7,8-TCDF.

*** Percent recovery determined from the response of the ^{13}C-internal standards vs. ^{13}C-2,3,7,8-TCDD.

NC = Not calculated due to interferences in ^{13}C-2,3,7,8-TCDD.

compounds, 2,3,7,8-TCDF and 1,2,3,7,8-PnCDF, however, were considerably higher than the expected values. Although neither of these peaks was fully resolved from neighboring isomers, it is more likely that this discrepancy was due to the compounds present in Aroclor 1260 as contaminants. Examination of the values obtained for the remaining compounds of interest, along with the total tetra- through octa-CDFs in Table 3-16, indicates that the same conclusion applies here as well. Despite the relative complexity of the Aroclor 1260 matrix, the recoveries obtained for all of the labeled analogs, except ^{13}C-OCDD, were quite satisfactory.

Mineral Oil (Radian I.D. E729-53-01). The data in Table 3-17 for the aged mineral oil sample show a high degree of reproducibility throughout, and excellent agreement between measured and expected values for all compounds of interest. This applies not only to the Tier 1 and 2 compounds but also to those in Tiers 3 and 4. The reason for this lies in the fact that the compounds spiked into the mineral oil were not subject to any interferences during the analysis because of a total absence of PCDF contaminants from the sample. Although the measured precision and accuracy were very good for the mineral oil, the recoveries based on the labeled PCDFs were much higher than expected, except for the ^{13}C-2,3,7,8-TCDF, which was 64%. We are unable to account for this discrepancy at present.

In-Service Samples

The seven samples of dielectric fluids taken from in-service transformers and capacitors were extracted and analyzed in triplicate in the same way as the three baseline samples. The results obtained are discussed in the following sections.

Askarel Load Center Network Transformer: Sample 41159-11-11 (Battelle I.D. ISL-03-A). Sample 41159-11-11 was the same transformer fluid that was analyzed in Phase I as Sample ISL-3-A. It consisted of 70% Aroclor 1260, 29% trichlorobenzenes, and 1% tetrachlorobenzenes. The transformer had been in service for 31 years when the fluid was removed. The analytical results are shown in Table 3-18.

A cursory examination of the data shows that the precision obtained was somewhat lower than for the three baseline samples. This presumably reflects the increase in complexity of the sample matrix. Despite this, the recoveries obtained for the labeled compounds were generally satisfactory for the congener classes measured.

Table 3-17

PCDF/PCDD CONCENTRATIONS IN BASELINE SAMPLE: MINERAL OIL
(Radian I.D. E729-53-01)

Components	Spiked	PCDF/PCDD (ng/g) Det. 1	Det. 2	Det. 3	Ave.	SD	RSD (%)	Detection Limit (ng/g)
PCDF/PCDD								
Total Tetra-CDF		174	150	147	157	15	9	
Total Penta-CDF		293	295	310	299	9	3	
Total Hexa-CDF		471	462	487	467	5	1	
Total Hepta-CDF		322	400	377	366	40	11	
Octa-CDF								54
Total Tetra-CDD		24	17	21	21	4	17	
Octa-CDD								10
Compound								
2,3,7,8-Tetra-CDD	25	24	17	21	21	4	17	1.5
2,3,7,8-Tetra-CDF	100	100	82	84	89	10	11	5.0
2,3,4,8-Tetra-CDF	100	74	66	63	68	6	8	
1,2,3,7,8-Penta-CDF*	150	151	150	156	152	3	2	0.8
1,2,3,4,8-Penta-CDF*								
2,3,4,7,8-Penta-CDF	150	142	145	154	147	6	4	
1,2,3,4,7,8-Hexa-CDF*	250	241	238	240	240	2	1	1.5
1,2,3,4,7,8-Hexa-CDF*								
1,2,3,7,8,9-Hexa-CDF								
1,2,3,6,7,8-Hexa-CDF	50	62	62	62	62	0	0	
2,3,4,6,7,8-Hexa-CDF	175	168	163	165	165	3	2	
1,2,3,4,6,7,8-Hepta-CDF	400	322	400	377	366	40	11	1.7
		Percent Recovery**						
^{13}C-Labeled Compound								
^{13}C-2,3,7,8-TCDF		68	67	58	64	6	9	
^{13}C-1,2,3,7,8-PCDF		114	202	219	177	55	31	
^{13}C-1,2,3,4,7,8-HxCDF		103	272	305	227	108	48	
^{13}C-OCDD		77	282	282	214	118	55	

* Isomers coelute on SP-2330 column.

** Percent recovery determined from the response of the ^{13}C-internal standards vs. ^{13}C-2,3,7,8-TCDD.

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Table 3-18

PCDF/PCDD CONCENTRATIONS IN IN-SERVICE SAMPLE:
LOAD CENTER NETWORK TRANSFORMER ASKAREL
(Sample 41159-11-11; Battelle I.D. ISL-03-A)

Components	PCDF/PCDD (ng/g) Det. 1	Det. 2	Det. 3	Ave.	SD	RSD (%)	Detection Limit (ng/g)
PCDF/PCDD							
Total Tetra-CDF	103	99	87	96	8	9	
Total Penta-CDF	1601	1911	1649	1720	167	10	
Total Hexa-CDF	5449	6789	7194	6477	913	14	
Total Hepta-CDF	7035	7798	10095	8309	1593	19	
Octa-CDF	29722	33265	46148	36378	8644	24	60
Total Tetra-CDD							
Octa-CDD	17	20	15	17	3	15	5
Compound							
2,3,7,8-Tetra-CDD							0.5
2,3,7,8-Tetra-CDF	26	10	9	15	10	64	0.5
2,3,4,8-Tetra-CDF	29	16	18	21	7	33	
1,2,3,7,8-Penta-CDF*	867	984	926	926	59	6	1
1,2,3,4,8-Penta-CDF*							
2,3,4,7,8-Penta-CDF	118	105	112	112	7	6	
1,2,3,4,7,8-Hexa-CDF*	3130	3953	4086	3723	518	14	1
1,2,3,4,7,9-Hexa-CDF*							
1,2,3,7,8,9-Hexa-CDF							
1,2,3,6,7,8-Hexa-CDF	401	545	595	514	101	20	
2,3,4,6,7,8-Hexa-CDF	87	67	83	79	11	13	
1,2,3,4,6,7,8-Hepta-CDF	3212	3925	4609	3915	699	18	1
	Percent Recovery**						
^{13}C-Labeled Compound							
^{13}C-2,3,7,8-TCDF	85	89	100	91	8	9	
^{13}C-1,2,3,7,8-PCDF	124	129	106	120	12	10	
^{13}C-1,2,3,4,7,8-HxCDF	136	127	90	118	24	21	
^{13}C-OCDD	91	76	69	79	11	14	

* Isomers coelute on SP-2330 column.

** Percent recovery determined from the response of the ^{13}C-internal standards vs. ^{13}C-2,3,7,8-TCDD.

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In general, the levels of PCDFs measured here were relatively high and, except for OCDF, were in quite good agreement with the amounts found in the Aroclor 1260 baseline sample and in the ISL-3-A sample analyzed in Phase I. This lends added support to an earlier comment that most of the PCDFs observed in such in-service samples may be accounted for in terms of the PCDFs present as contaminants in the original Aroclor.

The differences between the two OCDF concentrations in Phase I and Phase II can be explained largely in terms of the response factors used to calculate the concentrations. In Phase I, the OCDF/^{13}C-OCDD response factor was calculated from the "Rappe Cocktail." However, some of the response factors determined from this mixture were suspect due to the manner in which the mixture had been prepared for transport and distribution to the participating laboratories. The Phase II calibration standards, which contained well-defined amounts of OCDF, yielded an OCDF/^{13}C-OCDD response factor roughly one-fifth that obtained from the "Rappe Cocktail." The high detection limit listed for this compound and OCDD, however, is in large measure due to the poor chromatographic behavior of these compounds on the capillary column used in these analyses, and may account to some extent for the differences noted.

Askarel Load Center Network Transformer: Sample 41159-11-12 (Battelle I.D. ISL-08-A). Sample 41159-11-12 was taken from a load center network transformer that had been in service for 28 years, and contained 67% Aroclor 1260, 30% trichlorobenzenes, and 2% tetrachlorobenzenes. Inspection of the fluid at the time that the sample was taken indicated the presence of carbon throughout the askarel.

Generally, the precision attained in the triplicate analysis of this sample was relatively high, and was significantly better than that obtained for the previous sample (Table 3-19).

Although this sample appeared to share most of the major characteristics of Sample 41159-11-11, the levels of most of the PCDFs of interest were somewhat lower. This may be due to the presence of the carbon particles mentioned above, which may have acted as an absorbent and thus reduced the measurable amount of the PCDFs in the extractable portion of the fluid. As in the previous case, the recoveries measured in terms of the labeled compounds were very good and do not indicate unusual matrix effects.

Table 3-19

PCDF/PCDD CONCENTRATIONS IN IN-SERVICE SAMPLE:
LOAD CENTER NETWORK TRANSFORMER ASKAREL
[Sample No. 41159-11-12; Battelle I.D. ISL-08-A]

Components	PCDF/PCDD (ng/g) Det. 1	Det. 2	Det. 3	Ave.	SD	RSD (%)	Detection Limit (ng/g)
PCDF/PCDD							
Total Tetra-CDF	136	125	125	129	6	5	
Total Penta-CDF	329	339	309	326	15	5	
Total Hexa-CDF	939	1002	1002	981	36	4	
Total Hepta-CDF	1511	1504	2106	1707	346	20	
Octa-CDF	7617	7702	9475	8265	1049	13	66
Total Tetra-CDD							
Octa-CDD		22	17	20	3	16	7
Compound							
2,3,7,8-Tetra-CDD							1
2,3,7,8-Tetra-CDF	31	25	27	28	3	11	0.5
2,3,4,8-Tetra-CDF	10	13	14	12	2	17	
1,2,3,7,8-Penta-CDF*	110	115	121	115	6	5	1
1,2,3,4,8-Penta-CDF*							
2,3,4,7,8-Penta-CDF	43	43	51	46	5	10	
1,2,3,4,7,8-Hexa-CDF*	501	549	571	540	36	7	1
1,2,3,4,7,9-Hexa-CDF*							
1,2,3,7,8,9-Hexa-CDF							
1,2,3,6,7,8-Hexa-CDF	80	87	79	82	4	5	
2,3,4,6,7,8-Hexa-CDF	13	15	19	16	3	20	
1,2,3,4,6,7,8-Hepta-CDF	569	563	772	635	119	19	2
	Percent Recovery**						
^{13}C-Labeled Compound							
^{13}C-2,3,7,8-TCDF	80	91	106	92	13	14	
^{13}C-1,2,3,7,8-PCDF	127	110	113	117	9	8	
^{13}C-1,2,3,4,7,8-HxCDF	109	91	116	105	13	12	
^{13}C-OCDD	57	46	101	68	29	43	

* Isomers coelute on SP-2330 column.

** Percent recovery determined from the response of the ^{13}C-internal standards vs. ^{13}C-2,3,7,8-TCDD.

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Capacitor: Sample 41159-11-13 (Battelle I.D. ISL-27-A). Sample 41159-11-13 was taken from a capacitor, the composition and age of which were unknown. The results of the analysis of this sample are summarized in Table 3-20. The results indicate much lower levels for the PCDFs of interest than found in the previous two askarel transformer fluids. As noted earlier, poor chromatographic behavior in the time window corresponding to OCDD and OCDF resulted in much higher detection limits for these compounds than for the remaining compounds of interest. In this context, it is interesting to note that, although a peak was observed for OCDD, the value reported in the table is just below the estimated detection limit, and thus should probably be ignored. Once again, the recoveries estimated from the labeled compounds were quite satisfactory, and suggest that the sample matrix was compatible with our extraction method.

Precipitator Transformer: Sample 41159-11-14 (Battelle I.D. ISL-17-A). Sample 41159-11-14 was taken from a 27-year-old 50 KVA precipitator transformer. The analytical results obtained are listed in Table 3-21. For this sample, the precision attained was generally of the same order as was seen for the three baseline samples. Concentrations of the PCDFs of interest in this sample were highest for the penta- and hexa-CDFs in contrast to the previous Aroclor 1260-containing in-service samples (41159-11-11 and 41159-11-12), in which the maxima for the total-CDFs were "skewed" towards the hepta- and octa-CDFs.

Sample 41159-11-14 also showed a value for OCDD that was approximately equal to the estimated detection limit. As in the previous case, this indicates that the measured value for this compound should be disregarded. Once again, the recoveries calculated from the ^{13}C-labeled analogs were not exceptionally high in this sample.

Mineral Oil Arc Furnace Transformer: Sample 41159-11-15 (Battelle I.D. ISL-23-0). Sample 41159-11-15 was a mineral oil drawn from an arc furnace transformer that had undergone heavy electrical service for eight years. According to the data in Table 3-22, the sample was essentially free of all PCDF and PCDD components, except for small amounts of HpCDF (including 1,2,3,4,6,7,8-HpCDF) and OCDD. Because of the very low levels encountered, the reproducibility of the data was quite poor. The average recoveries obtained for the ^{13}C-labeled analogs varied between 69% and 209%, indicating an unusual matrix effect for this sample.

Table 3-20

PCDF/PCDD CONCENTRATIONS IN IN-SERVICE SAMPLE: CAPACITOR AROCLOR
(Sample No. 41159-11-13; Battelle I.D. ISL-27-A)

Components	PCDF/PCDD (ng/g) Det. 1	Det. 2	Det. 3	Ave.	SD	RSD (%)	Detection Limit (ng/g)
PCDF/PCDD							
Total Tetra-CDF	572	473	461	502	61	12	
Total Penta-CDF	276	253	222	250	27	11	
Total Hexa-CDF	54	52	83	63	17	28	
Total Hepta-CDF	17	15	30	21	8	39	
Octa-CDF							42
Total Tetra-CDD							
Octa-CDD	9	8	8	8	1	7	10
Compound							
2,3,7,8-Tetra-CDD							0.5
2,3,7,8-Tetra-CDF	27	27	28	27	1	2	1
2,3,4,8-Tetra-CDF	78	72	80	77	4	5	
1,2,3,7,8-Penta-CDF*	23	22	20	22	2	7	0.5
1,2,3,4,8-Penta-CDF*							
2,3,4,7,8-Penta-CDF	63	59	67	63	4	6	
1,2,3,4,7,8-Hexa-CDF*	19	18	27	21	5	23	1
1,2,3,4,7,9-Hexa-CDF*							
1,2,3,7,8,9-Hexa-CDF							
1,2,3,6,7,8-Hexa-CDF	6	7	10	8	2	27	
2,3,4,6,7,8-Hexa-CDF	3	3	5	4	1	31	
1,2,3,4,6,7,8-Hepta-CDF	9	7	13	10	3	32	1
	Percent Recovery**						
^{13}C-Labeled Compound							
^{13}C-2,3,7,8-TCDF	85	85	88	86	2	2	
^{13}C-1,2,3,7,8-PCDF	117	132	121	123	8	6	
^{13}C-1,2,3,4,7,8-HxCDF	138	141	106	128	19	15	
^{13}C-OCDD	132	104	88	108	22	21	

* Isomers coelute on SP-2330 column.

** Percent recovery determined from the response of the ^{13}C-internal standards vs. ^{13}C-2,3,7,8-TCDD.

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Table 3-21

PCDF/PCDD CONCENTRATIONS IN IN-SERVICE SAMPLE:
PRECIPITATOR TRANSFORMER AROCLOR
[Sample No. 41159-11-14; Battelle I.D. ISL-17-A]

Components	PCDF/PCDD (ng/g) Det. 1	Det. 2	Det. 3	Ave.	SD	RSD (%)	Detection Limit (ng/g)
PCDF/PCDD							
Total Tetra-CDF	970	617	576	721	217	30	
Total Penta-CDF	9236	6589	6002	7276	1723	24	
Total Hexa-CDF	10598	9918	10666	10394	414	4	
Total Hepta-CDF	1725	2196	2254	2058	290	14	
Octa-CDF	293	626	374	431	174	40	37
Total Tetra-CDD							
Octa-CDD	8	13	5	9	4	47	8
Compound							
2,3,7,8-Tetra-CDD							0.5
2,3,7,8-Tetra-CDF	151	132	141	141	10	7	1
2,3,4,8-Tetra-CDF	146	116	141	134	16	12	
1,2,3,7,8-Penta-CDF*	1115	1039	1023	1059	49	5	1
1,2,3,4,8-Penta-CDF*							
2,3,4,7,8-Penta-CDF	1772	1584	1726	1694	98	6	
1,2,3,4,7,8-Hexa-CDF*	3802	3711	3775	3763	47	1	2
1,2,3,4,7,9-Hexa-CDF*							
1,2,3,7,8,9-Hexa-CDF	174	187	233	198	31	16	
1,2,3,6,7,8-Hexa-CDF	1195	1155	1137	1162	30	3	
2,3,4,6,7,8-Hexa-CDF	387	472	509	456	63	14	
1,2,3,4,6,7,8-Hepta-CDF	728	905	884	839	97	12	1
	Percent Recovery**						
^{13}C-Labeled Compound							
^{13}C-2,3,7,8-TCDF	101	79	103	94	13	14	
^{13}C-1,2,3,7,8-PCDF	110	183	133	142	37	26	
^{13}C-1,2,3,4,7,8-HxCDF	115	230	102	149	70	47	
^{13}C-OCDD	77	238	91	135	89	66	

* Isomers coelute on SP-2330 column.

** Percent recovery determined from the response of the ^{13}C-internal standards vs. ^{13}C-2,3,7,8-TCDD.

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Table 3-22

PCDF/PCDD CONCENTRATIONS IN IN-SERVICE SAMPLE:
ARC FURNACE TRANSFORMER MINERAL OIL
[Sample No. 41159-11-15; Battelle I.D. ISL-23-0]

Components	PCDF/PCDD (ng/g) Det. 1	Det. 2	Det. 3	Ave.	SD	RSD (%)	Detection Limit (ng/g)
PCDF/PCDD							
Total Tetra-CDF							
Total Penta-CDF		16					
Total Hexa-CDF							
Total Hepta-CDF	13	5		9	5	54	
Octa-CDF							31
Total Tetra-CDD							
Octa-CDD	13	10	8	10	3	24	3
Compound							
2,3,7,8-Tetra-CDD							1
2,3,7,8-Tetra-CDF							3
2,3,4,8-Tetra-CDF							
1,2,3,7,8-Penta-CDF*							0.5
1,2,3,4,8-Penta-CDF*							
2,3,4,7,8-Penta-CDF		7					
1,2,3,4,7,8-Hexa-CDF*							1
1,2,3,4,7,9-Hexa-CDF*							
1,2,3,7,8,9-Hexa-CDF							
1,2,3,6,7,8-Hexa-CDF							
2,3,4,6,7,8-Hexa-CDF							
1,2,3,4,6,7,8-Hepta-CDF	5	2		4	2	52	0.5
	Percent Recovery**						
^{13}C-Labeled Compound							
^{13}C-2,3,7,8-TCDF	72	68	67	69	3	4	
^{13}C-1,2,3,7,8-PCDF	137	217	274	209	69	33	
^{13}C-1,2,3,4,7,8-HxCDF	152	199	265	205	57	28	
^{13}C-OCDD	109	127	176	137	35	25	

* Isomers coelute on SP-2330 column.

** Percent recovery determined from the response of the ^{13}C-internal standards vs. ^{13}C-2,3,7,8-TCDD.

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Substation Distribution Transformer: Sample 41159-11-16 (Battelle I.D. ISL-4-0). Sample 41159-11-16 was taken from a substation distribution transformer that contained 100 ppm of either Aroclor 1254 or Aroclor 1260, and had undergone major arcing and in-service failure. The results obtained from the triplicate extraction and analysis of this sample are summarized in Table 3-23. The data in the table show relatively large coefficients of variance for almost all compounds of interest. The reasons for this lack of reproducibility are not clear, and suggest that the concentrations obtained for this sample should be treated with some caution. Recoveries here, measured in terms of the labeled analogs, also vary widely, suggesting that the analysis of this matrix was not as successful as some of the other samples discussed earlier.

Askarel Load Center Network Transformer: Sample 41159-11-17 (Battelle I.D. ISL-2-A). This was the same sample that was analyzed in Phase I as ISL-2-A, and was taken from a transformer that had been in service for 20 years and contained typical proportions of Aroclor 1260 and tri-/tetrachlorobenzenes. The results obtained are shown in Table 3-24 and may be compared with the results obtained aarlier (Table 3-9). In general, agreement is very good except in the case of OCDF. The discrepancy between the Phase I and Phase II OCDF concentrations can again be explained by the response factors used to calculate the concentrations (see earlier discussion). Overall, the precision attained in the most recent measurement was quite satisfactory, as were the measured recoveries across the congener range.

Table 3-23

PCDF/PCDD CONCENTRATIONS IN IN-SERVICE SAMPLE:
SUBSTATION DISTRIBUTION TRANSFORMER OIL
[Sample No. 41159-11-16; Battelle I.D. ISL-4-0]

Components	PCDF/PCDD (ng/g) Det. 1	Det. 2	Det. 3	Ave.	SD	RSD (%)	Detection Limit (ng/g)
PCDF/PCDD							
Total Tetra-CDF							
Total Penta-CDF	358	87	215	220	136	62	
Total Hexa-CDF	619	191	381	397	214	54	
Total Hepta-CDF	114	33	62	70	41	59	
Octa-CDF							37
Total Tetra-CDD							
Octa-CDD	25	23	28	25	3	10	5
Compound							
2,3,7,8-Tetra-CDD							3
2,3,7,8-Tetra-CDF							5
2,3,4,8-Tetra-CDF							
1,2,3,7,8-Penta-CDF*	72	19	40	44	27	61	0.5
1,2,3,4,8-Penta-CDF*							
2,3,4,7,8-Penta-CDF	111	29	65	68	41	60	
1,2,3,4,7,8-Hexa-CDF*	243	65	144	151	89	59	1
1,2,3,4,7,9-Hexa-CDF*							
1,2,3,7,8,9-Hexa-CDF	15	4	8	9	6	62	
1,2,3,6,7,8-Hexa-CDF	87	21	46	51	33	65	
2,3,4,6,7,8-Hexa-CDF	32	11	19	21	11	51	
1,2,3,4,6,7,8-Hepta-CDF	43	15	23	27	14	53	0.5
	Percent Recovery**						
^{13}C-Labeled Compound							
^{13}C-2,3,7,8-TCDF	48	68	73	63	13	21	
^{13}C-1,2,3,7,8-PCDF	228	212	196	212	16	8	
^{13}C-1,2,3,4,7,8-HxCDF	260	125	165	183	69	38	
^{13}C-OCDD	182	87	90	120	54	45	

* Isomers coelute on SP-2330 column.

** Percent recovery determined from the response of the ^{13}C-internal standards vs. ^{13}C-2,3,7,8-TCDD.

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Table 3-24

PCDF/PCDD CONCENTRATIONS IN IN-SERVICE SAMPLE:
LOAD CENTER NETWORK TRANSFORMER ASKAREL
[Sample No. 41159-11-17; Battelle I.D. ISL-02-A]

Components	PCDF/PCDD (ng/g) Det. 1	Det. 2	Det. 3	Ave.	SD	RSD (%)	Detection Limit (ng/g)
PCDF/PCDD							
Total Tetra-CDF	431	344	275	350	78	22	
Total Penta-CDF	1221	887	810	973	218	22	
Total Hexa-CDF	2311	2006	1745	2021	283	14	
Total Hepta-CDF	1912	2273	1430	1872	423	23	
Octa-CDF	6046	6846	5801	6231	547	9	32
Total Tetra-CDD							
Octa-CDD	22	23	13	19	6	28	8
Compound							
2,3,7,8-Tetra-CDD							0.5
2,3,7,8-Tetra-CDF	102	103	71	92	18	20	2
2,3,4,8-Tetra-CDF	50	39	27	39	12	30	
1,2,3,7,8-Penta-CDF*	320	292	237	283	42	15	0.5
1,2,3,4,8-Penta-CDF*							
2,3,4,7,8-Penta-CDF	180	176	139	165	23	14	
1,2,3,4,7,8-Hexa-CDF*	1218	1131	920	1090	153	14	0.5
1,2,3,4,7,9-Hexa-CDF*							
1,2,3,7,8,9-Hexa-CDF							
1,2,3,6,7,8-Hexa-CDF	119	115	119	118	2	2	
2,3,4,6,7,8-Hexa-CDF	74	81	55	70	13	19	
1,2,3,4,6,7,8-Hepta-CDF	1095	1270	776	1047	250	24	1
	Percent Recovery**						
^{13}C-Labeled Compound							
^{13}C-2,3,7,8-TCDF	99	79	77	85	12	14	
^{13}C-1,2,3,7,8-PCDF	115	138	120	124	12	10	
^{13}C-1,2,3,4,7,8-HxCDF	110	139	98	116	21	18	
^{13}C-OCDD	77	124	59	87	34	39	

* Isomers coelute on SP-2330 column.

** Percent recovery determined from the response of the ^{13}C-internal standards vs. ^{13}C-2,3,7,8-TCDD.

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Section 4

CONCLUSIONS

The method that we have developed for the sensitive and compound-specific measurement of PCDFs and PCDDs in PCB-contaminated dielectric fluids has proven to be reliable when applied to a variety of matrices and over a wide range of concentrations. The study was designed to characterize the PCDF/PCDD content of the samples, and to assess the precision and accuracy of the procedure under carefully controlled experimental conditions. As the sample matrix increases in complexity, there is a concomitant decrease in the overall precision attainable. Furthermore, the precision obtained for the individual isomers is generally significantly better than for the total congener classes.

The results obtained for the baseline Aroclor samples show a strong increase in PCDF content as the weight percent of chlorine in the formulation increases. Thus, Aroclor 1016 gives no measurable levels of PCDF, whereas Aroclor 1260 shows significant concentrations, especially for the higher congener classes. Some of the Aroclor 1260-containing in-service samples also have significant levels of PCDF contaminants, but it is difficult to establish a strong correlation because the composition of several of the in-service fluids is not known with any degree of certainty. Nevertheless, in some instances, it appears that the concentrations of PCDFs in the in-service fluids may be explained in terms of the levels present in the original Aroclor 1260 fluid.

If this observation is generally valid, it suggests that askarels that have been in use in electrical equipment do not contain higher levels of PCDFs than unused fluids. Rather, the PCDFs present may be due to the original synthesis techniques used to manufacture the askarels. Although the data generated in the current study provide some indications that this may be the case, we do not have enough information to draw definitive conclusions. Further work is clearly needed. This should focus on characterizing the PCDF composition of several more PCB-contaminated electric fluids taken from in-service equipment, as well as unused

higher-chlorinated Aroclors, such as Aroclor 1254 and 1260, as a function of age. Once this information is available, it may be possible to estimate the level of PCDF contamination in electrical utility equipment on the basis of known composition and usage without the need to perform analyses on individual units each time.

Section 5

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Appendix A

SELECTED ION CURRENT PROFILES FOR CALIBRATION SOLUTION E729-55-05

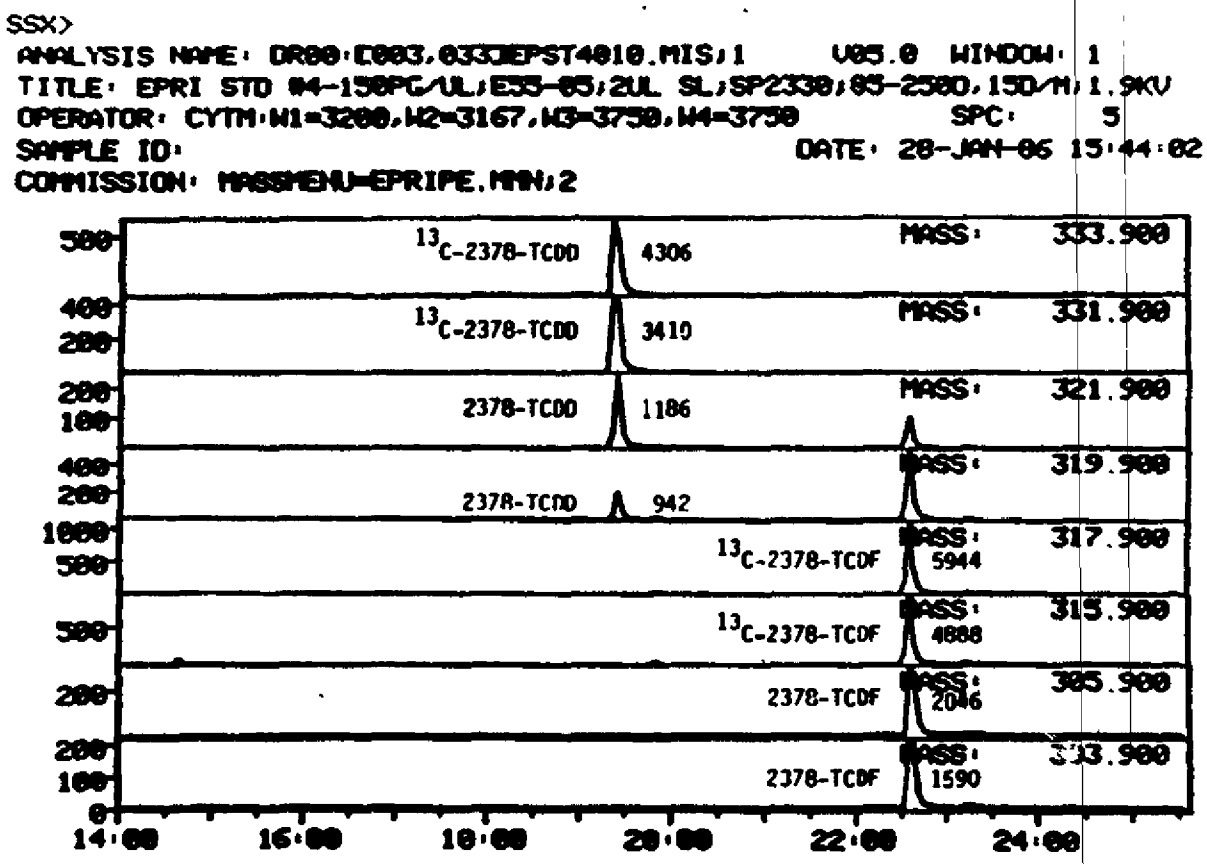

Figure A1. Selected ion current profiles for masses corresponding to PCDF and PCDD labeled and native compounds present in calibration solution E729-55-05. Concentration of labeled compounds = 500 ng/mL each; concentration of unlabeled compounds = 150 ng/mL each. Peaks of interest and measured peak areas (in arbitrary units) are indicated on the plots.

SSX>
ANALYSIS NAME: DR88:C883.633EPST4010.MIS;1 V85.0 WINDOW: 1
TITLE: EPRI STD 84-150PG/UL;E55-85;2UL SL;SP2330;85-250D,15D/M;1.9KV
OPERATOR: CYTH:M1=3280,M2=3167,M3=3750,M4=3750 SPC: 5
SAMPLE ID: DATE: 20-JAN-86 15:44:02
COMMISSION: MASSMENU=EPRIPE.MAN;2

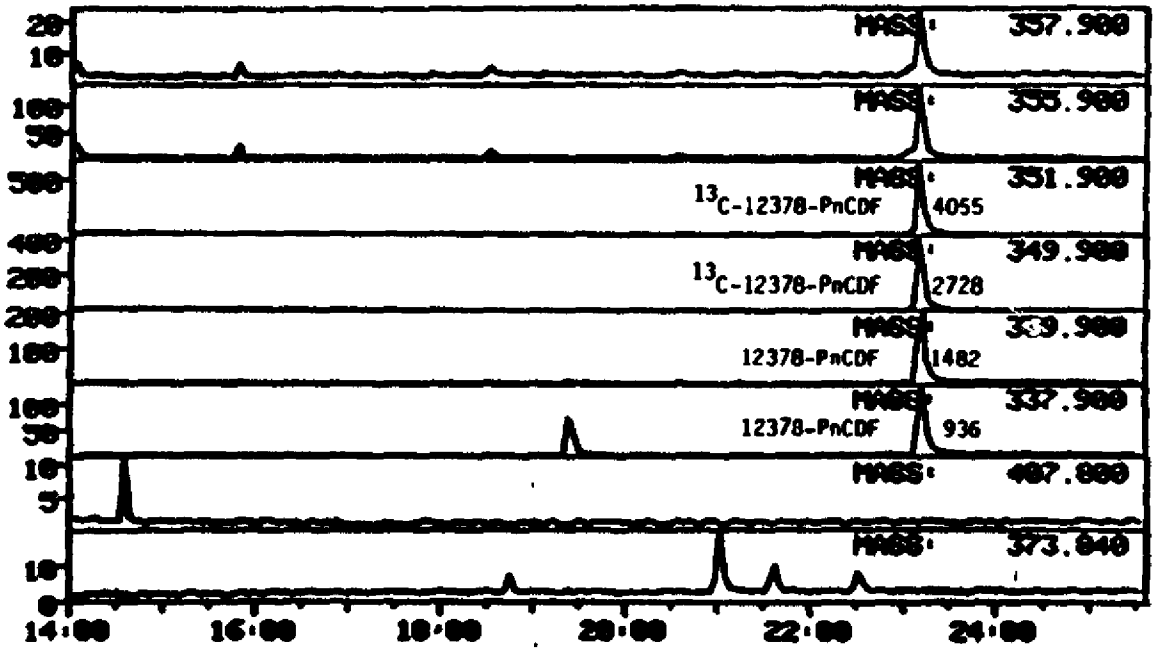

Figure A1. (continued)

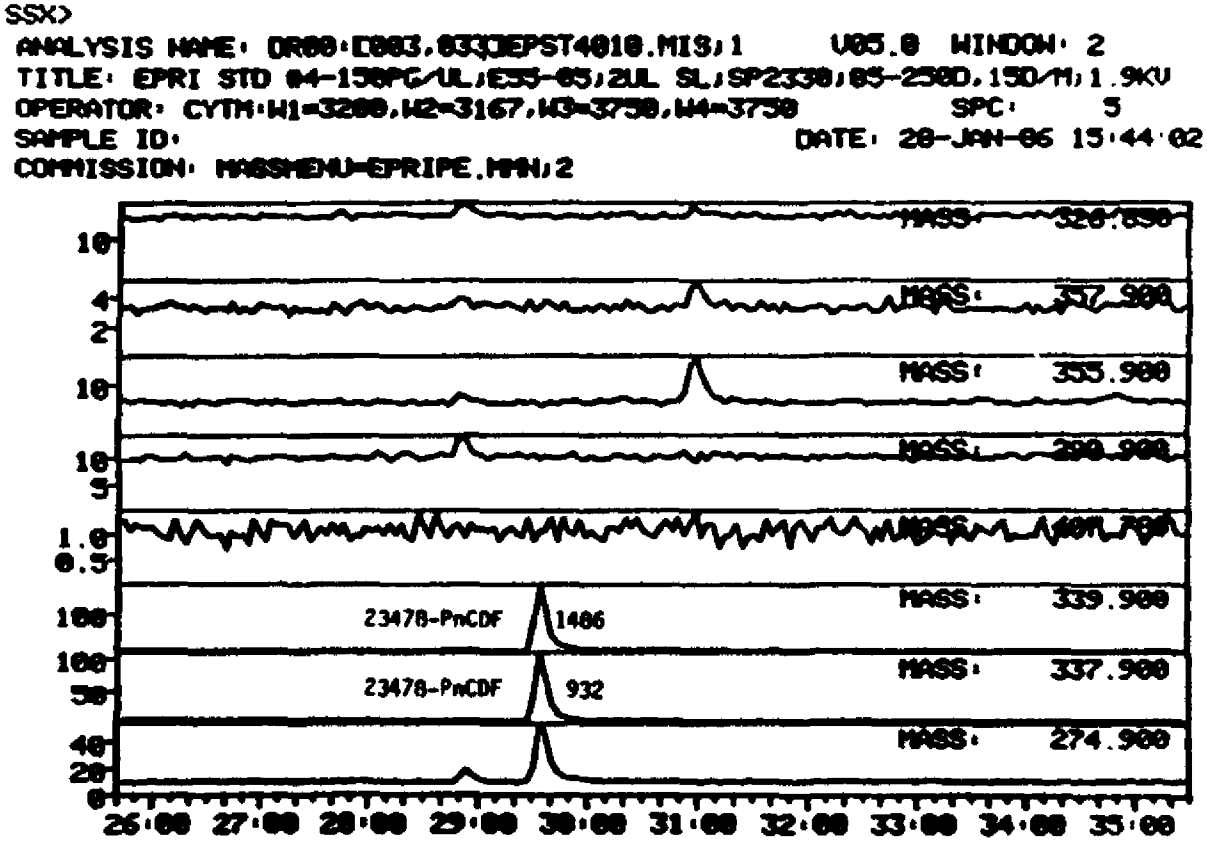

Figure A1. (continued)

SSX>
ANALYSIS NAME: DR80:C003,0333EPST4010.MIS;1 V05.0 WINDOW: 2
TITLE: EPRI STD 04-150PG/UL;E55-65;2UL SL;SP2330;65-250D,150/M;1.9KV
OPERATOR: CYTM:M1=3200,M2=3167,M3=3750,M4=3750 SPC: 5
SAMPLE ID: DATE: 28-JAN-86 15:44:02
COMMISSION: MASSMENU=EPRIPE.MAN;2

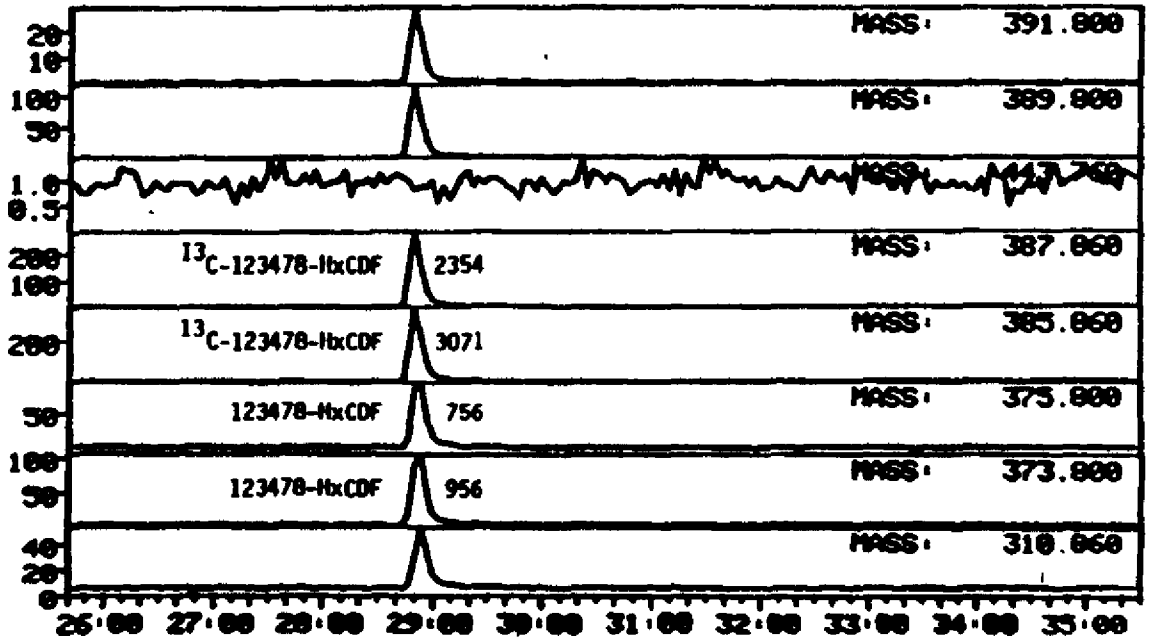

Figure A1. (continued)

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SSX>
ANALYSIS NAME: DR00:[003,033]EPST4010.MIS;1 V05.0 WINDOW: 3
TITLE: EPRI STD #4-130PG/UL;E35-65;2UL SL;SP2330;85-250D,15D/M;1.9KV
OPERATOR: CYTH:W1=3200,W2=3167,W3=3750,W4=3750 SPC: 5
SAMPLE ID: DATE: 28-JAN-86 15:44:02
COMMISSION: MASSMENU=EPRIPE.MAN;2

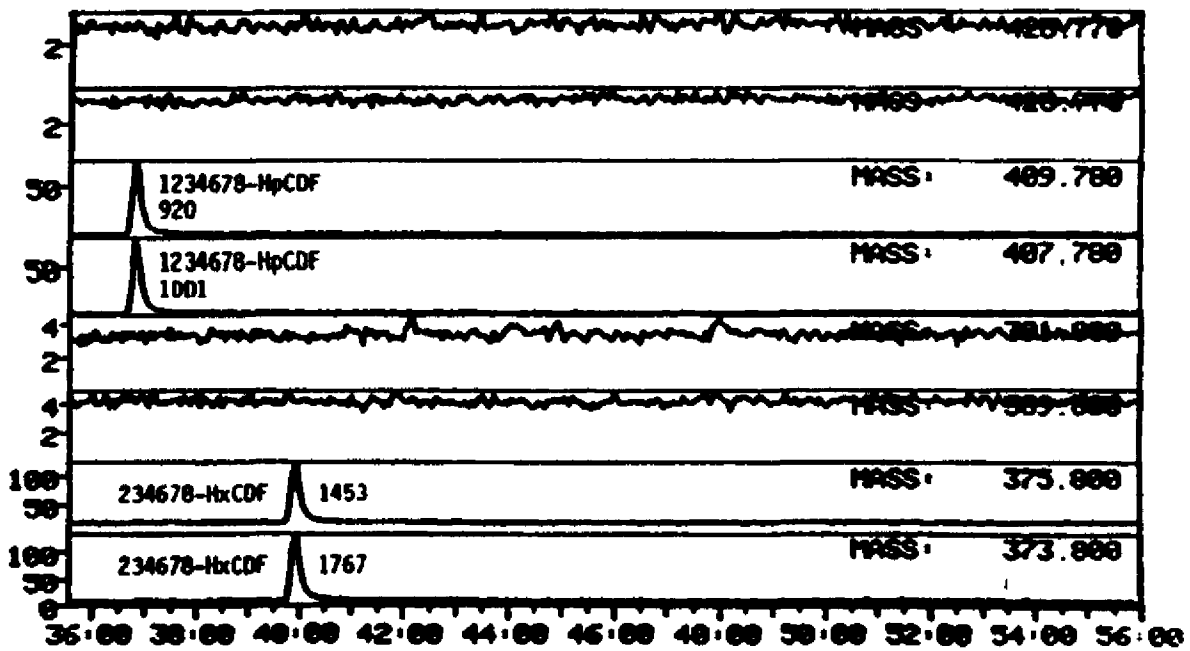

Figure A1. (continued)

SSX>
ANALYSIS NAME: DR00:D003.033DEPST4010.MIS;1 V05.0 WINDOW: 4
TITLE: EPRI STD 04-130PC/UL;E55-65;2UL SL;SP2330;65-2500,150/M;1.9KV
OPERATOR: CYTH:W1=3200,W2=3167,W3=3750,W4=3750 SPC: 5
SAMPLE ID: DATE: 20-JAN-06 15:44:02
COMMISSION: MASSMENU-EPRIPE.MAN;2

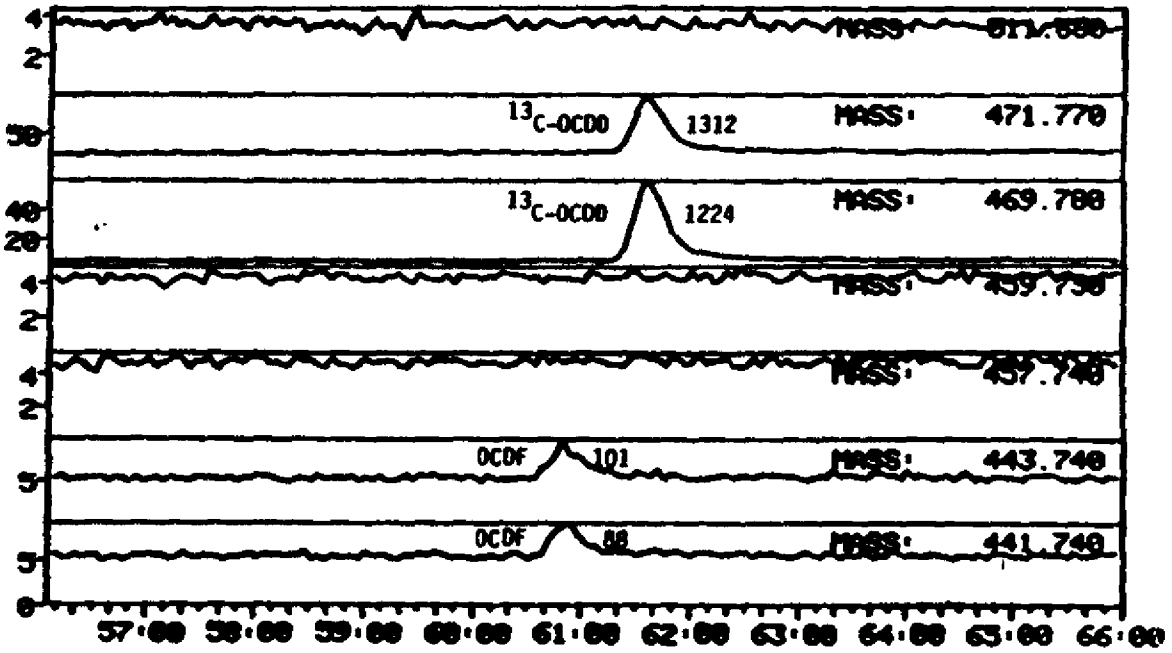

Figure A1. (continued)

SSX: PLIST OF DR00:[003,033]EPST4010.PEC;1
MAR 31 86 15:58:30 VERSION V05.0 PAGE: 1

CONC. = 1.7303E-01 * AREA + 2.3824E+02
R^2 VALUE FOR AREA = 5.5041E-01

CONC. = 7.7686E-01 * HEIGHT + 3.5365E+02
R^2 VALUE FOR HEIGHT = 4.0603E-01

MASS	TIME CENTROID	AREA	HEIGHT	AREA CONC.	HT. CONC.	SOURCE/ TYPE
303.9000	22:38	1.5304E+03	212	3.0000E+02	3.0000E+02	K/MM
305.9000	22:38	2.0464E+03	293	3.0000E+02	3.0000E+02	K/MM
315.9000	22:37	4.0004E+03	936	1.0000E+03	1.0000E+03	K/MM
317.9000	22:37	5.9439E+03	1132	1.0000E+03	1.0000E+03	K/MM
319.9000	19:27	9.4283E+02	282	3.0000E+02	3.0000E+02	K/MM
321.9000	19:27	1.1855E+03	246	3.0000E+02	3.0000E+02	K/MM
331.9000	19:27	3.4102E+03	442	1.0000E+03	1.0000E+03	K/MM
333.9000	19:27	4.3864E+03	639	1.0000E+03	1.0000E+03	K/MM
337.9000	23:15	9.3640E+02	134	3.0000E+02	3.0000E+02	K/MM
337.9000	29:37	9.3237E+02	186	3.0000E+02	3.0000E+02	K/MM
339.9000	23:14	1.4815E+03	286	3.0000E+02	3.0000E+02	K/MM
339.9000	29:37	1.4868E+03	174	3.0000E+02	3.0000E+02	K/MM
349.9000	23:13	2.7277E+03	432	1.0000E+03	1.0000E+03	K/MM
351.9000	23:13	4.0555E+03	661	1.0000E+03	1.0000E+03	K/MM
373.8000	28:54	9.3568E+02	183	3.0000E+02	3.0000E+02	K/MM
373.8000	40:00	1.7667E+03	128	3.0000E+02	3.0000E+02	K/MM
373.8000	28:54	7.5644E+02	79	3.0000E+02	3.0000E+02	K/MM
373.8000	40:00	1.4335E+03	185	3.0000E+02	3.0000E+02	K/MM
385.8000	28:54	3.8715E+03	361	1.0000E+03	1.0000E+03	K/MM
387.8000	28:54	2.3542E+03	281	1.0000E+03	1.0000E+03	K/MM

Figure A2. Computer-generated summary report of peaks selected and measured in sample file EPST4010.MIS;1 (Figure A1) from calibration solution E729-55-05. Peaks are listed in order of increasing mass, and are marked either "K/MM" or "U/MM", where K indicates peaks of known concentration (standards), U indicates peaks of unknown concentration, and MM shows that the peaks were manually selected for processing.

SSX> PLIST OF DR00:[003,033]EPST4010.PEC;1
MAR 31 86 15:58:38 VERSION V05.0 PAGE: 2

MASS	TIME CENTROID	AREA	HEIGHT	AREA CONC.	HT. CONC.	SOURCE/ TYPE
467.7000	36:55	1.0007E+03	76	3.0000E+02	3.0000E+02	K/MM
469.7000	36:54	9.1963E+02	70	3.0000E+02	3.0000E+02	K/MM
441.7400	60:57	8.8351E+01	4	3.0000E+02	3.0000E+02	K/MM
443.7400	60:57	1.0142E+02	5	3.0000E+02	3.0000E+02	K/MM
469.7000	61:41	1.2242E+03	55	1.0000E+03	1.0000E+03	K/MM
471.7700	61:40	1.3124E+03	60	1.0000E+03	1.0000E+03	K/MM

**** PLIST PROCESSING COMPLETE ****

SSX>

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Figure A2. (continued)

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Appendix B

CALIBRATION CURVES

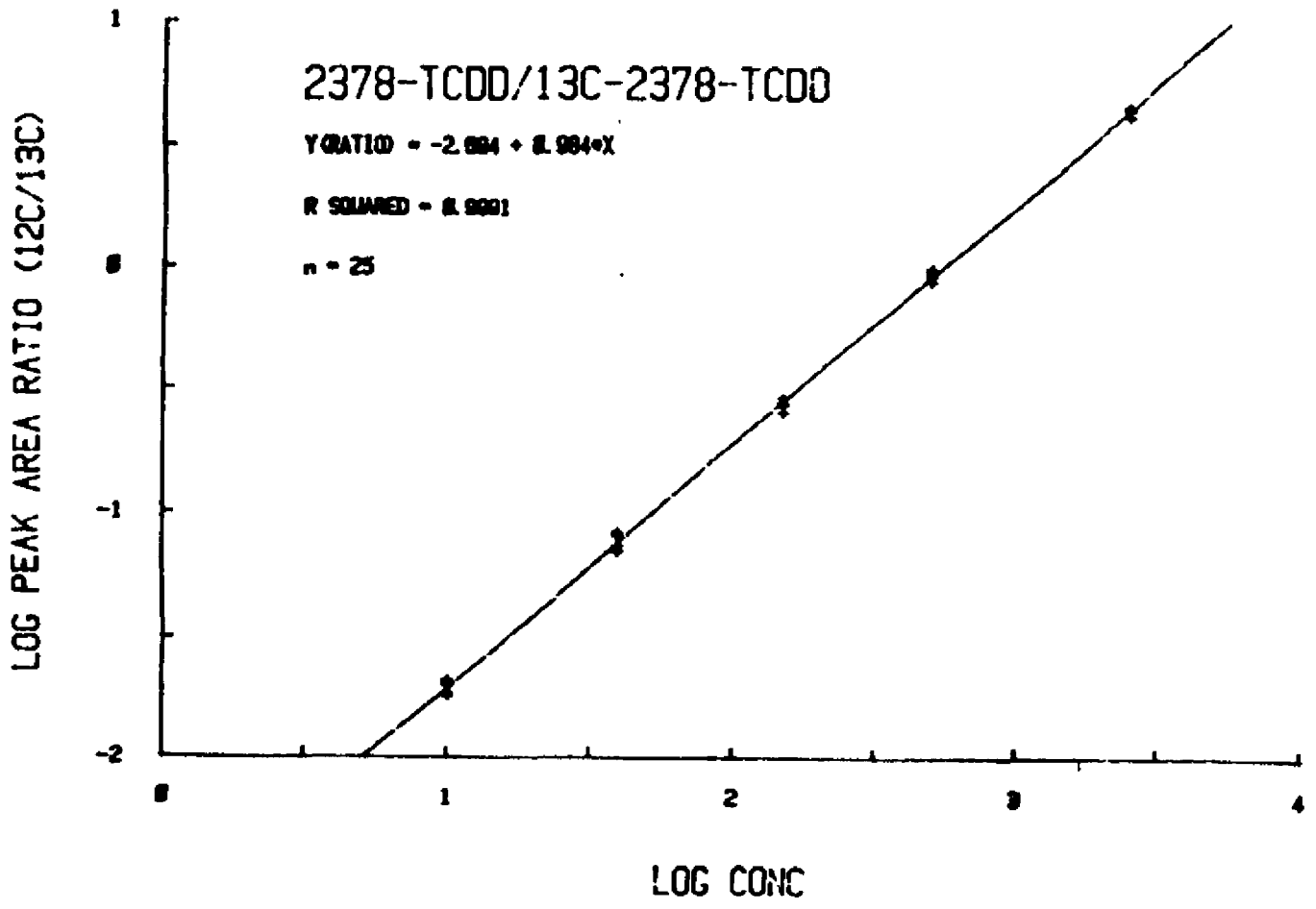

Figure 81. Calibration Curve for 2,3,7,8-TCDD with Respect to ^{13}C-2,3,7,8-TCDD

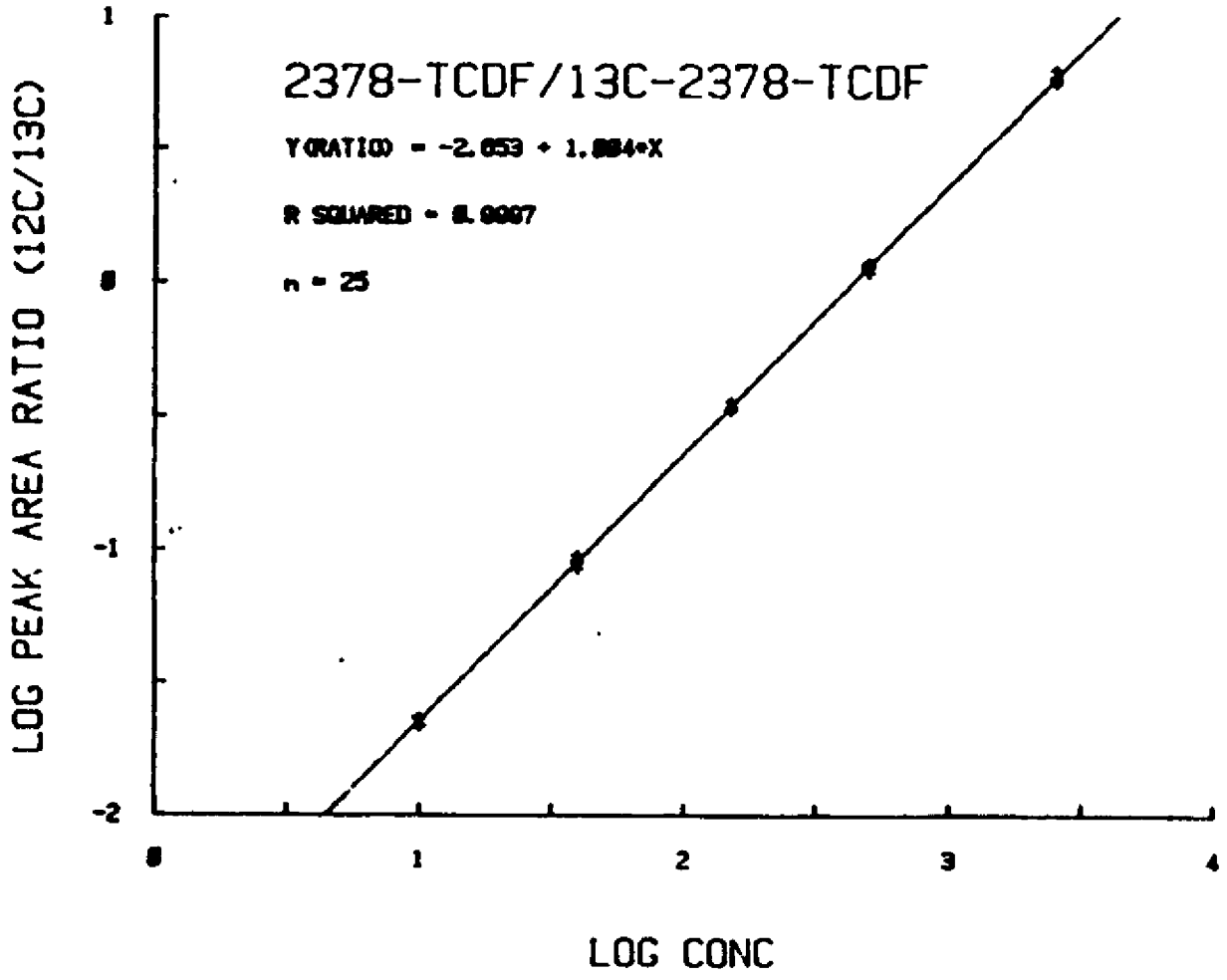

Figure B2. Calibration Curve for 2,3,7,8-TCDF with Respect to ^{13}C-2,3,7,8-TCDF

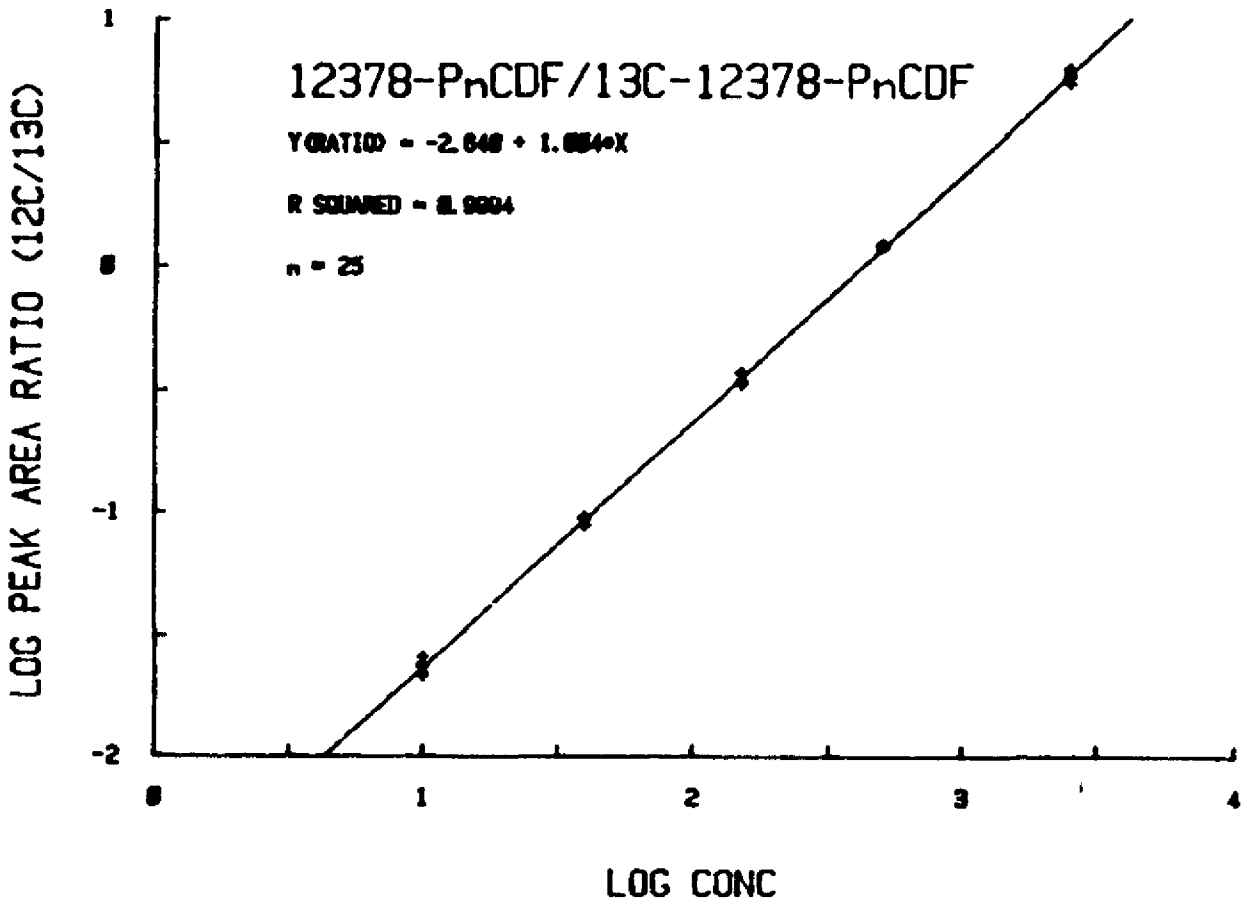

Figure B3. Calibration Curve for 1,2,3,7,8-PnCDF with Respect to ^{13}C-1,2,3,7,8-PnCDF

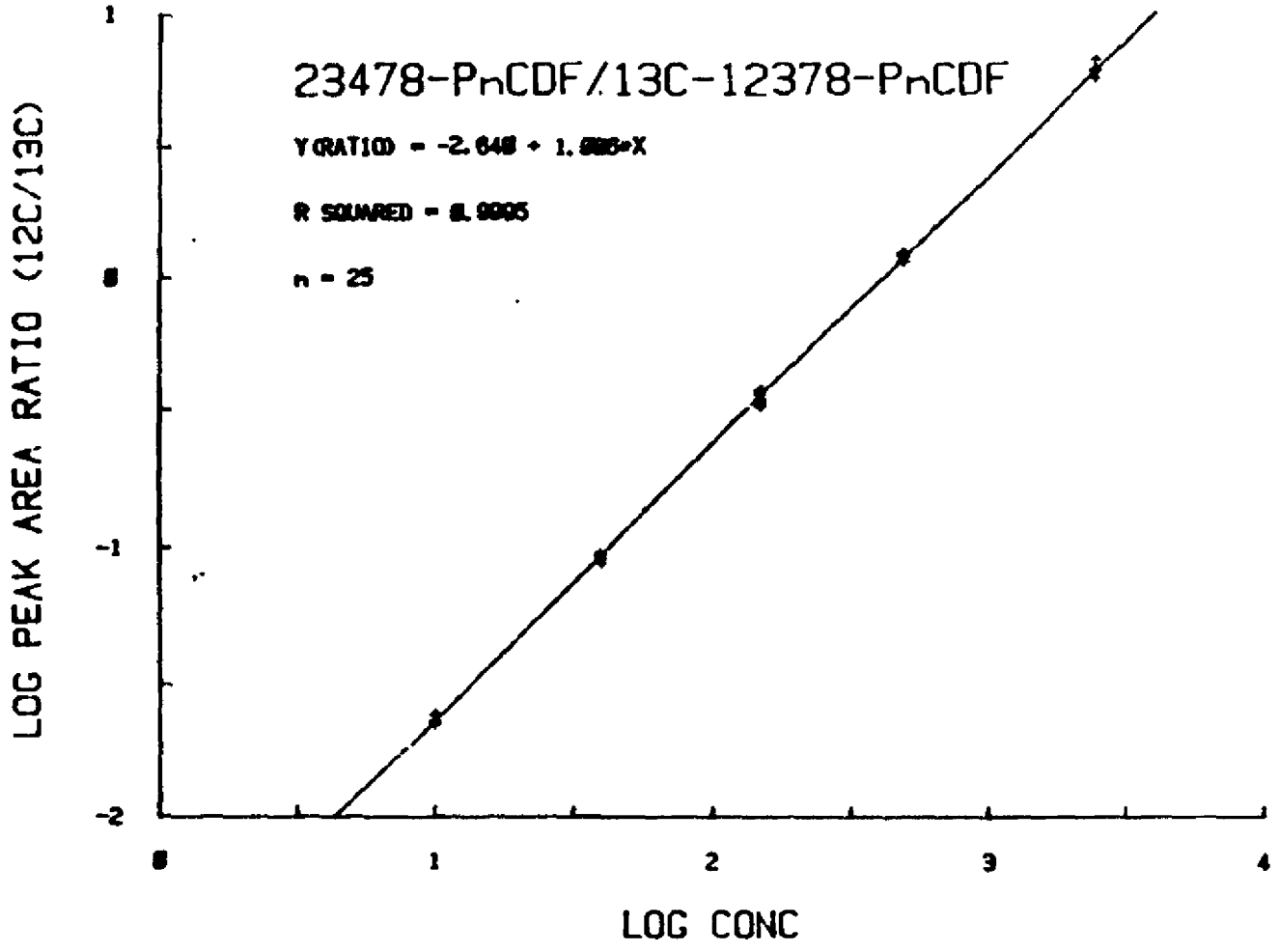

Figure B4. Calibration Curve for 2,3,4,7,8-PnCDF with Respect to ^{13}C-1,2,3,7,8-PnCDF

...with Respect to ^{13}C-1,2,3,4,7,8-HxCDF

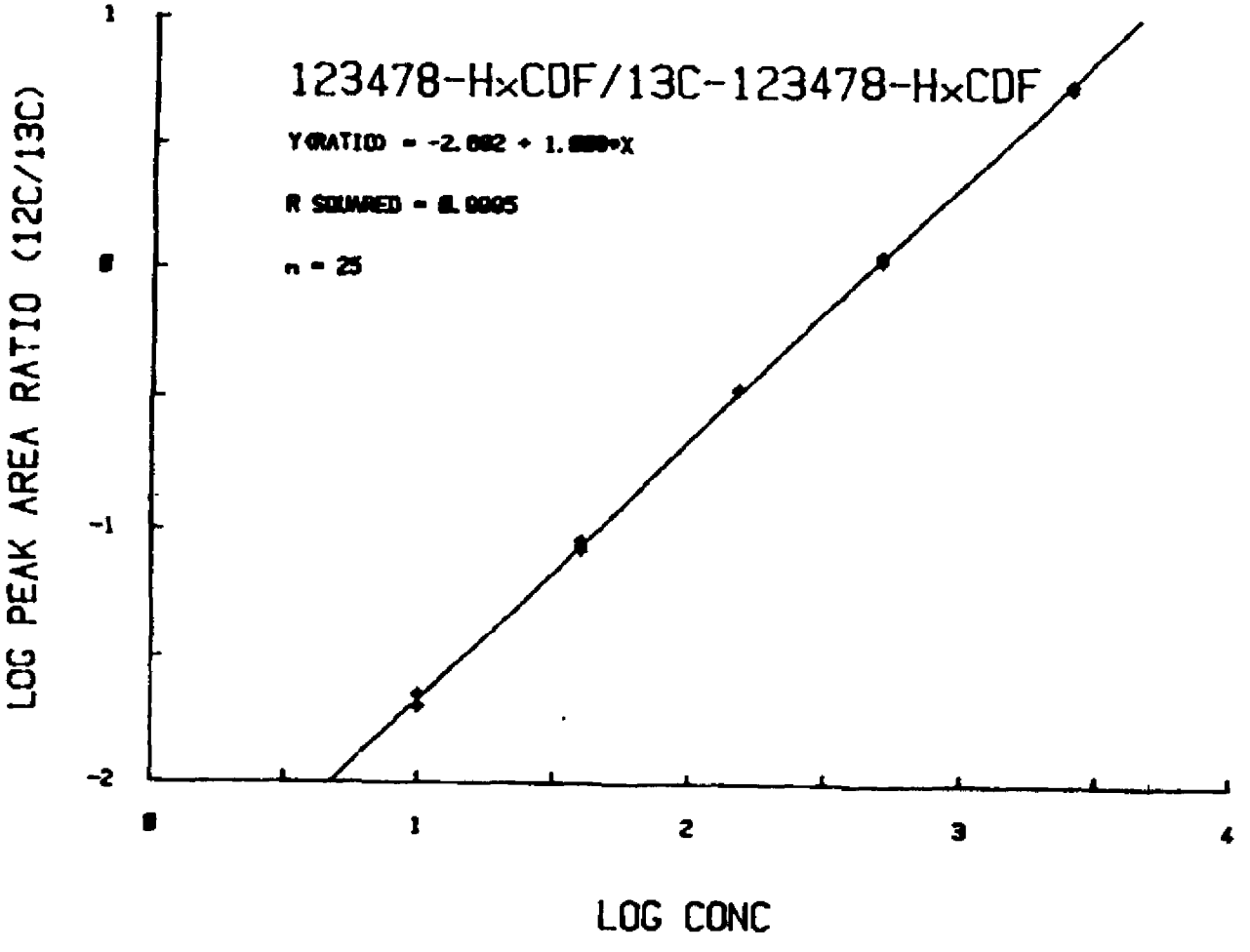

Figure 85. Calibration Curve for 1,2,3,4,7,8-HxCDF with Respect to ^{13}C-1,2,3,4,7,8-HxCDF

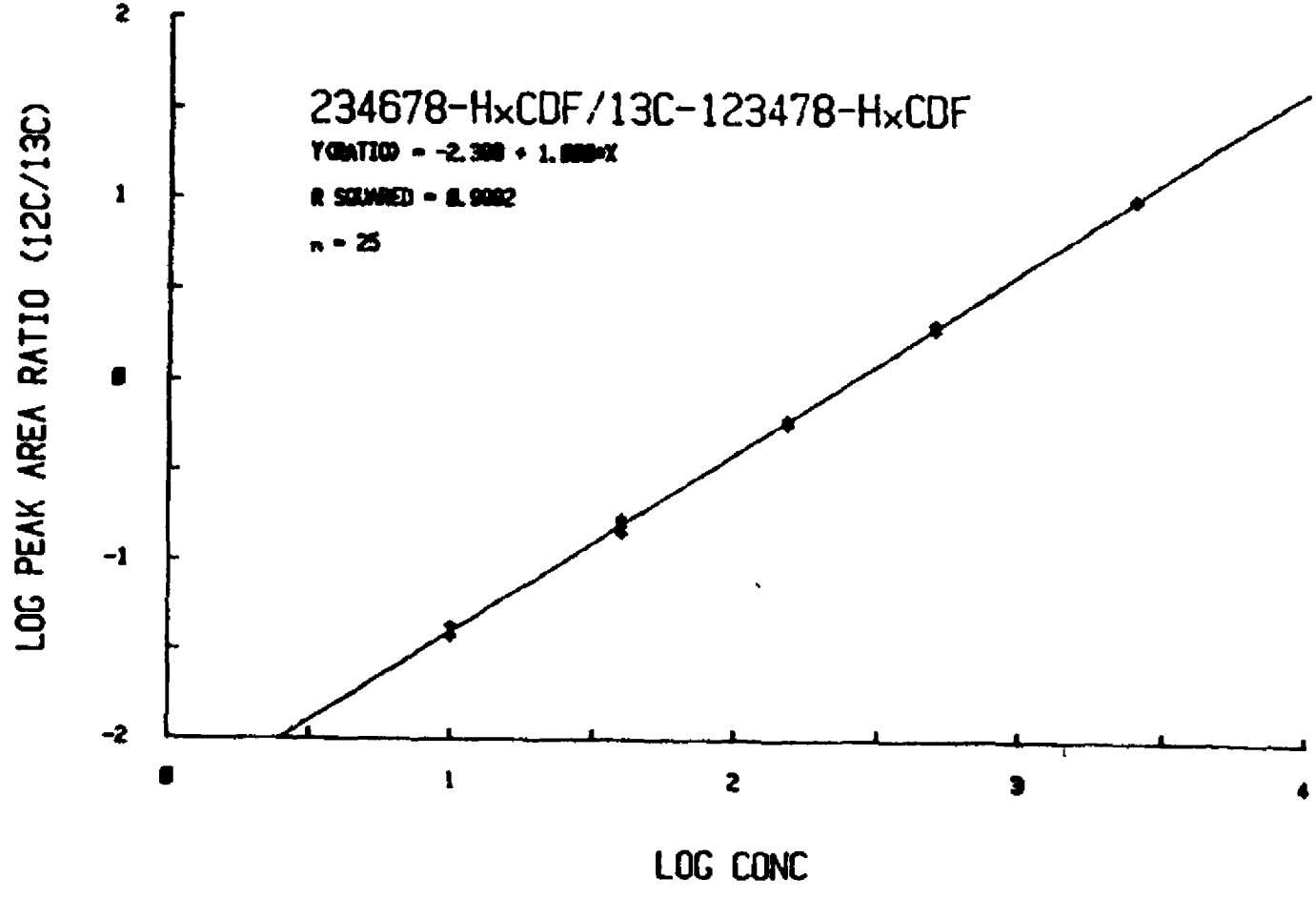

Figure 86. Calibration Curve for 2,3,4,7,8-HxCDF with Respect to ^{13}C-1,2,3,4,7,8-HxCDF

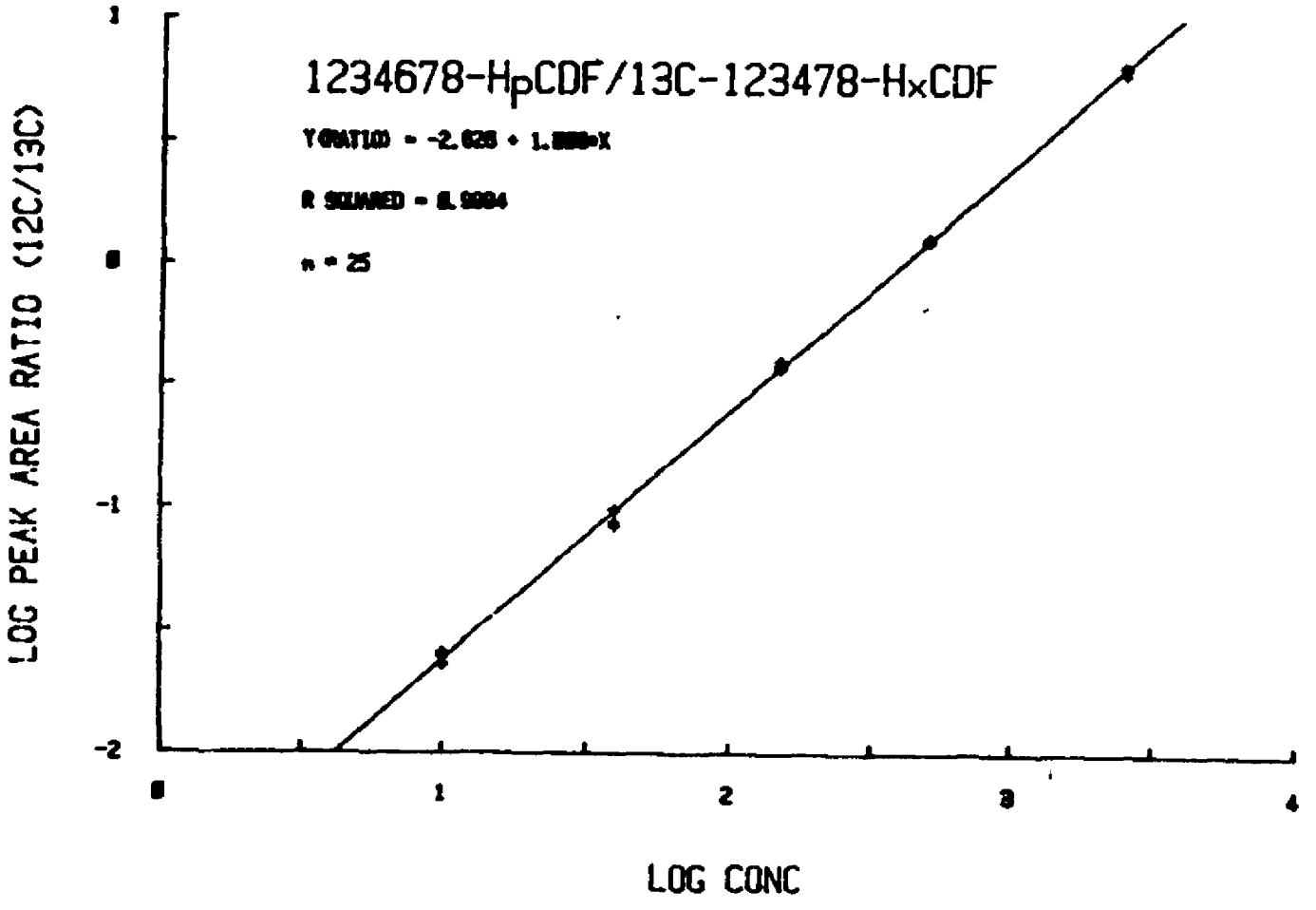

Figure 87. Calibration Curve for 1,2,3,4,6,7,8-HpCDF with Respect to ^{13}C-1,2,3,4,7,8-HxCDF

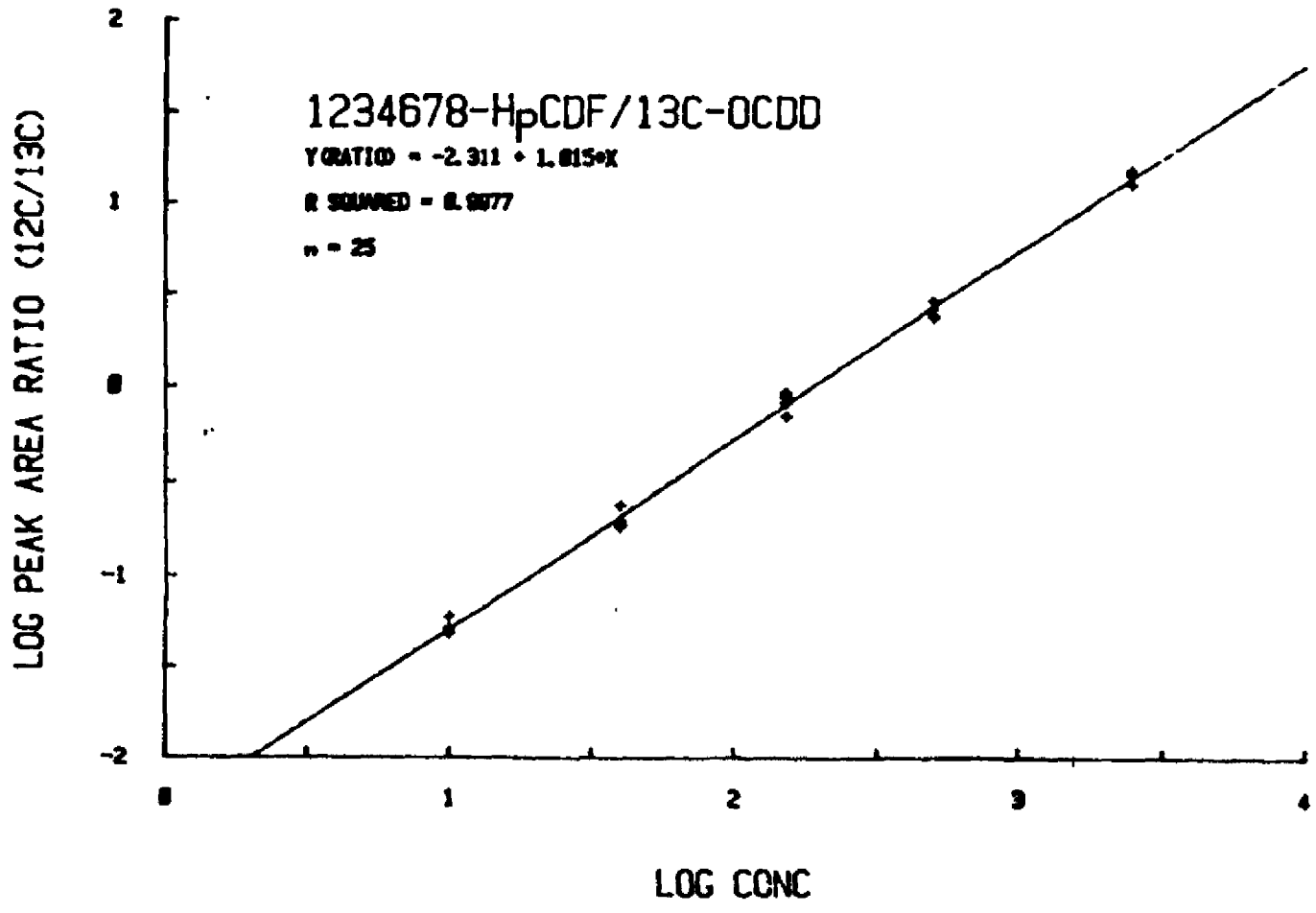

Figure B8. Calibration Curve for 1,2,3,4,6,7,8-HpCDF with Respect to ^{13}C-OCDD

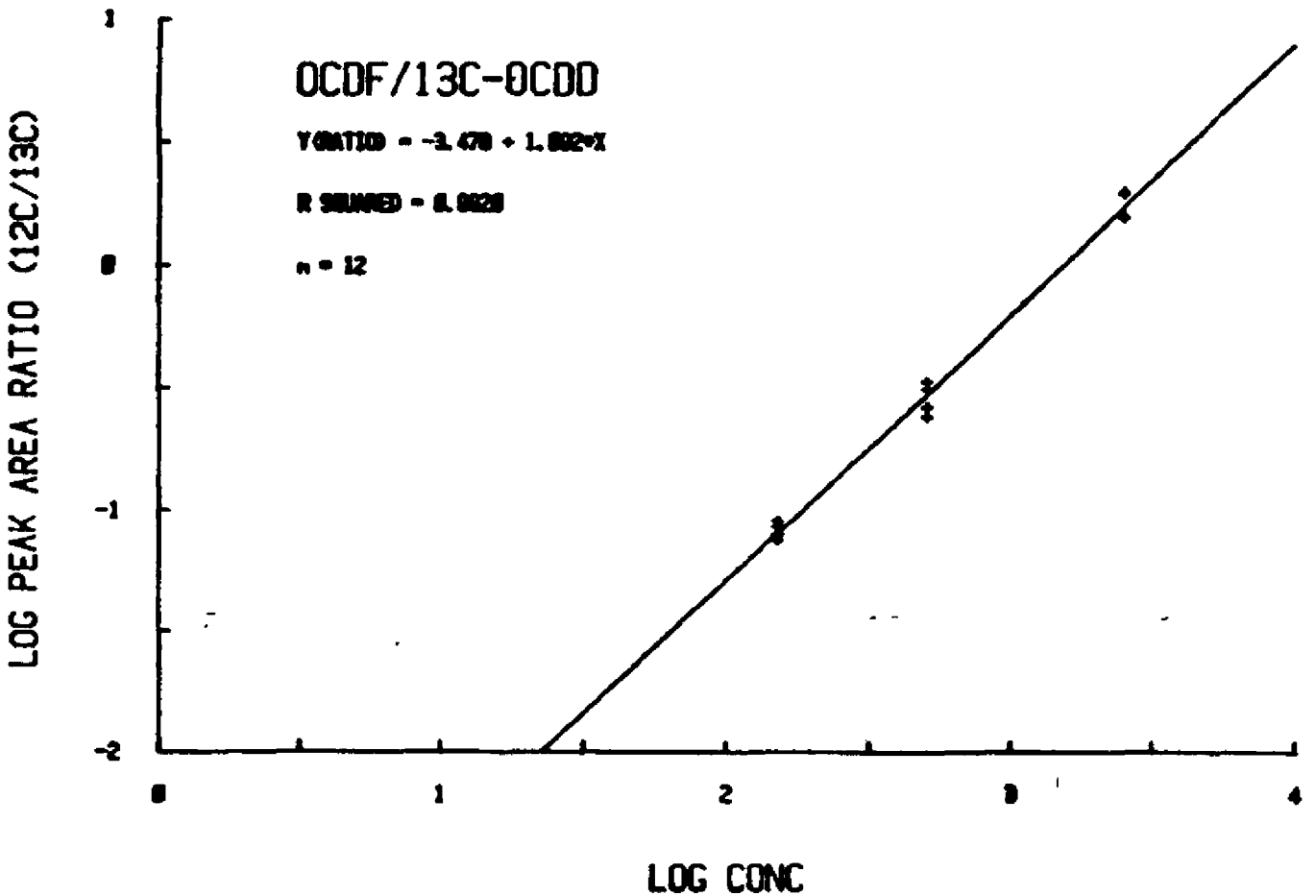

Figure 89. Calibration Curve for OCDF with Respect to ^{13}C-OCDD