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EPRI EL-EA-5443
Volume 3
Project 2028-10
Final Report
June 1988



Analysis of Polychlorinated Dibenzofurans and Polychlorinated Dibenzo-*p*-Dioxins in Transformers and Capacitors

Volume 3: Summary and Statistical Analysis of the Round-Robin Test

Prepared by
Research Triangle Institute
Research Triangle Park, North Carolina

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REPORT SUMMARY

SUBJECTS: Hazardous and toxic waste management / Transmission substation design and operation / Distribution substations

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

AUDIENCE: Environmental managers / Distribution engineers

Analysis of Polychlorinated Dibenzofurans and Polychlorinated Dibenzo-*p*-Dioxins in Transformers and Capacitors

Volumes 1–3

PCDF and PCDD—by-products of PCB pyrolysis and combustion—apparently cause many of the health effects originally attributed to PCB. In parallel and round-robin studies, independent laboratories found that normal equipment operation and arcing failure cause little if any oxidation and do not significantly modify PCB fluids.

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 had not matured prior to this study. Information had also been insufficient on the quantity and types of PCDF and PCDD in as-manufactured PCB and on the formation of these by-products during normal operation or arcing failure in utility equipment. Because of these uncertainties, utilities and regulators have assumed the worst-case PCDF-PCDD formation when there is a PCB-related accident, thereby overstating the potential toxicity. EPRI report EL/EA-4858 describes portions of the research performed in these projects.

OBJECTIVE: To improve techniques for measuring PCDF/PCDD in the presence of PCB.

APPROACH: Five laboratories (including two whose studies are discussed in report EL/EA-4858) 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 the laboratory results.

RESULTS: These three volumes report the second group of PCDF–PCDD analyses. Results from all participating laboratories correlated remarkably well. Some of the results follow.

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• Use of the ^{13}C compounds allowed successful separation of the components in several closely eluting pairs of physiologically active PCDF and less-active compounds.

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

Volumes 1 and 2 describe several analytic techniques, with the appendix of Volume 2 including a report on the analysis by the University of Umeå in Sweden, as well. Volume 3 summarizes all the laboratory techniques, presents comprehensive statistical analyses, and provides an executive summary.

EPRI PERSPECTIVE

This research is 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 high correlation of results from several laboratories indicates that researchers can exercise great flexibility in selecting techniques and developing facilities. In addition, new work has started (EPRI project RP2028-21) in which the best features of each of the five analytic methods will be assembled to provide a single recommended method.

PROJECTS

RP2028-6, RP2028-7, RP2028-10
EPRI Project Managers: Gil Addis; Jacques Guertin
Electrical Systems Division; Environment Division
Contractors: New York State Department of Health; Battelle Columbus Laboratories; Research Triangle Institute

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EL/EA-5443, Volume 3
Research Project 2028-10

Final Report, June 1988

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ABSTRACT

An interlaboratory study involving five independent laboratories was conducted to quantitatively assess accuracy and precision of polychlorinated dibenzo-p-dioxin (PCDD) and polychlorinated dibenzofuran (PCDF) congener analysis in three spiked and seven in-service utility fluids. Data was obtained using capillary gas chromatography/mass spectrometry for 16 different PCDD and PCDF compounds. Five different ^{13}C-labeled internal standards were added to the samples and the samples were purified prior to analysis. Each laboratory's generated calibrations for the individual compounds were linear for concentrations over four orders of magnitude. Analyses were performed in triplicate on an extract to provide insight to instrumental reproducibility.

The median and range of percent accuracy for four of the five laboratories was 102 and 56-146, respectively, across all chemicals measured in the two spiked samples. The fifth laboratory had a median and range of 107 and 8-3939, respectively.

The median and range of percent reproducibility (coefficients of variation) for three of the four laboratories was 8.2 and 0-46, respectively, across all 10 synthetic and in-service samples and all compounds measured. The fourth laboratory had a median and range of 30 and 2-159, respectively. The fifth laboratory did not report replicate analyses on each extract and thus reproducibility for instrumental analysis could not be calculated.

The largest variability (accuracy and precision) was attributed to the different types of samples (>90%) in three of the four laboratories while the fourth had as much as 63.1% variability from the sample type analyzed and as much as 36.9% due to instrumental measurement error.

At the approximate 95% prediction intervals, the analysis of these 10 samples by any one of the five laboratories would be expected to produce variability in the results for each PCDD or PCDF congener measured ranging from a factor of two to 300.

Of the five participating laboratories, the analytical method employed by Lab-E gave for the most part the best accuracy and precision while Lab-C was the poorest.

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ACKNOWLEOGMENTS

The authors extend their sincere appreciation to the EPRI technical management team led by Or. G. Addis and his colleagues, Dr. J. Guertin, and Dr. R. Komai who provided adroit guidance to this program and encouragement to all the participants. Dr. T. Rouse (General Electric Company) is thanked for his contributions concerning utility use of dielectric liquids.

We would like to also thank our research comrades who contributed the analytical data for this interlaboratory collaborative study. They are Dr. S. Gordon (Illinois Institute of Technology Research Institute), Drs. G. Eadon and Dr. Hilker (New York State Department of Health), Dr. M. Kilpatrick (Radian Corp.), Dr. M. Cooke (Battelle Columbus Div.), and Dr. C. Rappe (U. of Umeå).

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SUMMARY

EPRI has sponsored a four-year research program to evaluate the analysis of selected individual compounds of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in dielectric fluids. These are impurities often associated with askarel mixtures of polychlorinated biphenyls (PCBs) and tri/tetrachlorobenzene (TCB). They have been known to form either in the PCB manufacturing process or as a result of excessive heat (fires). This program included the synthesis of new natural (^{12}C) and isotopically labeled (^{13}C) PCDD and PCDF analytical standards. Standards and spiked test samples were prepared by one of the laboratories and distributed to the four other participating laboratories as part of a round robin study. The samples were then analyzed as unknowns. The impetus for the studies has been the wide range of toxicities (4-5 orders of magnitude) seen for the individual compounds in animal tests and the difficulty of quantitatively analyzing for some of these chemically similar compounds of dissimilar toxicity, often in the presence of a great excess of PCBs. PCBs themselves are a group of compounds with chemical behavior relatively similar to PCDF/PCDD during sample cleanup stages.

It should be remembered that the major object of the study was to evaluate and upgrade methods of analysis; analysis of field samples was an important secondary output. The study involving five participating laboratories, was conducted in two phases. Phase I was designed to located glaring discrepancies in the techniques, and Phase II to statistically improve results of the different laboratories on a series of unknown samples.

Phase I involved the analysis of PCDFs and PCDDs in five spiked basic samples: Aroclor-1016, Aroclor-1242, Aroclor-1260, a tri- and tetrachlorobenzene mixture, and aged mineral oil; and four in-service dielectric fluids. Each participating laboratory used its best available in-house extraction and analysis techniques (Gas Chromatography/Mass Spectrometry, GC/MS). Since validated analytical methods did not exist before this program was initiated, this phase of the program was necessary to assess any deficiencies and optimize the analytical methodology.

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The isotopically labeled standards were needed to calibrate the efficiency of cleanup and to determine the sensitivity (response) of the MS for the various individual compounds of PCDF and PCDD being analyzed.

After evaluating the results of Phase I and implementing several improvements to the methodology, Phase II was initiated. Phase II was designed to provide quantitative data on PCDF and PCDD compounds in selected in-service dielectric fluids and to make a statistical interlaboratory comparison of these data. The specific aims were 1) to determine the accuracy of analysis by each participating laboratory for a selected list of PCDFs and PCDDs in spiked samples, 2) to determine the precision of analysis by each laboratory for PCDFs and PCDDs in spiked and in-service utility samples, 3) to perform an interlaboratory comparison and thus a comparison of methods employed for accuracy and precision, and finally 4) to measure the levels of PCDFs and PCDDs in a few selected in-service utility samples.

This study suggests that there is no strongly preferred analytical procedure (among those using a combination of extraction/chemical cleanup, gas chromatography, and mass spectrometry) for measuring compound specific concentrations of PCDF and PCDD. For spiked samples, originally free of PCDF and PCDD, five different methods (corresponding to five different participating laboratories) yielded concentrations accurate to within ±20% (except one laboratory measured 2,3,4,6,7,8-hexachlorinated dibenzofuran [2,3,4,6,7,8-H_6-CDF] with an order of magnitude error).

Since standards for all 150 PCDF and PCDD compounds were not available, it was not possible to know the accuracy of measurement on the unknown field samples. Only the precision of measurement could be ascertained.

Considerable variation in measurement precision was observed between laboratory procedures. For example, measurement of very low concentrations (1 to 10 ng/g range) showed an order of magnitude variation, whereas measurement in higher concentration range (100 to 10,000 ng/g) were considerably more precise. Again, a specific H_6CDF measurement was an exception, having as much as four orders of magnitude variation. For total individual congener classes, concentration measurements had only one order of magnitude variation.

What range of concentrations were found in the field samples? The maximum concentration for 2,3,7,8-Tetra-CDD was 32 ng/g and the maximum concentration of 2,3,7,8-tetra-CDF + 2,3,4,8-tetra-CDF was 459 ng/g. The highest concentration found was for one sample of the much less critical octachlorinated dibenzofuran - 65,000 ng/g. These concentrations are reported with a statistical 95% confidence level.

SECTION 1
INTRODUCTION

Because of the concerns about the health effects of polychlorinated biphenyls (PCBs) their production was banned and regulation instituted in 1976 by the Toxic Substance Control Act (TSCA), PL 94-469. Certain totally enclosed electrical uses of PCBs are allowed for the remainder of the useful life of existing electrical equipment. Many of these adverse health effects appear to be attributable to trace contaminants such as polychlorinated dibenzofurans (PCDF) and polychlorinated dibenzo-p-dioxins (PCDD) in the PCBs.

The Electric Power Research Institute (EPRI) inititated a program to investigate the chemistry of PCDF and PCDD as they may relate to use of Askarel, a dielectric fluid, which contains PCBs and potential trace contamination of PCDF/PCDD. This program had three primary objectives: (1) to develop and optimize analytical methods and quantitatively characterize these methods for measuring PCDF/PCDD in dielectric fluids, (2) to apply these methods to measurement of PCDF/PCDD levels in typical dielectric fluids used in utility operations, and (3) to investigate possible PCDF/PCDD formation in simulated transformer events.

As part of the objective to evaluate methodology, the program included the synthesis of native and isotopically labeled PCDD and PCDF analytical standards (1) to allow for analysis of selected individual congeners of PCDDS and PCDFs. Analytical standards and spiked matrix samples were prepared by a contract laboratory and then distributed to four other participating laboratories as part of a round robin study. These samples were analyzed blind by five independent contract laboratories - Illinois Institute of Technology Research Institute (IITRI), New York State Department of Health (NYSDOH), Radian Corp., Battelle, Columbus Division, and U. Umea.

The method evaluation study was conducted in two phases. Phase I involved the analysis of PCDF's and PCDD's in five spiked baseline samples; for example, Aroclor-1016, Aroclor-1242, Aroclor-1260, tri- and tetrachlorobenzene mixture, aged mineral oil, and four in-service dielectric fluids (1-4). Each participating laboratory used their best available in-house extraction and analysis techniques (1-4). Since validated methods for PCDD and PCDF analysis did not exist before this program was initiated, this phase was necessary to assess any deficiencies and to optimize the analytical methodology. After Phase I results were evaluated and

several improvements were implemented, then Phase II was undertaken. This report covers the effort under Phase II.

Phase II was designed to yield quantitative data on PCDD and PCDF congeners in selected in-service dielectric fluids and to make a statistical interlaboratory comparison on these data. The specific aims were (1) to determine the accuracy of analysis by each participating laboratory for a selected list of PCDD's and PCDF's in spiked samples, (2) to determine the precision of analysis by each laboratory for PCDF's and PCDD's in spiked and in-service utility samples, (3) to perform an interlaboratory comparison of methods for accuracy and precision, and finally (4) to measure the levels of PCDF's and PCDD's in a few selected in-service utility samples.

Although this report primarily addresses the statistical analysis of PCDD and PCDF congener data from the five laboratories, a section on chemical methodology is included to allow the reader to examine the similarities and differences in the analytical procedures employed by each laboratory. These procedures are also described in more detail in the reports from the five individual laboratories (1-4).

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SECTION 2
CHEMICAL METHODOLOGY

SELECTION OF SAMPLES FROM ELECTRICAL EQUIPMENT FOR PCDF AND PCDD ANALYSIS

The rationale for the selection of transformers and capacitors to be sampled for PCDF and PCDD analysis was previously developed and reported elsewhere (5). Since the analysis is time consuming and difficult, the intention was to choose a small number of samples, which would yield the greatest amount of information about the large population of equipment in use. Also, the samples were chosen to provide a potentially wide spectrum of challenge to the analytical methodology which was being statistically evaluated in the Round Robin Study.

ACQUISITION OF IN-SERVICE SAMPLES

The acquisition of in-service samples was performed by one of the participating laboratories and the procedures employed have been reported (4).

The samples selected for use in the Round Robin Study are shown in Table 2. Two baseline samples were spiked with a selected number of congeners at known concentrations into mineral oil and Aroclor 1016, respectively. A third sample, Aroclor 1260, was spiked at known levels with these same congeners but it also contained endogenous PCBF's and PCDD's. Samples 11-17 (Table 2) were in-service utility samples that were selected to represent the various types of utility uses (5). In some cases the dielectric was Aroclor 1260, or mineral oil containing PCBs. Dielectric fluids from transformers, capacitors, or precipitators were selected for this Round Robin Study. Some of the devices had been in use for many years (Table 2).

SYNTHESIS OF STANDARDS

Because ^{13}C isotope is present in a natural abundance of 1.1%, synthetically enriched compounds can be prepared for use as analytical internal standards. Isotopically enriched compounds can be clearly distinguished from native substances by mass spectrometry. For this reason, Radian Corporation prepared ^{13}C-labeled and unlabeled (native) PCDD and PCDF congeners as analytical standards for use by all laboratories participating in the Round Robin Study (1). Subsequently, analytical standard solutions were also prepared of these authentic PCDD and PCDF congeners and distributed by Radian Corp.

Standard Materials

Radian synthesized the following materials (1):

1,2,3,7,8-Pentachlorodibenzofuran (PnCDF)
1,2,3,4,7,8-Hexachlorodibenzofuran (HxCDF)
1,2,3,4,6,7,8-Heptachlorodibenzofuran (HpCDF)
2,3,7,8-Tetrachlorodibenzofuran-$^{13}C_{12}$ (TCDF-^{13}C)
1,2,3,7,8-Pentachlorodibenzofuran-$^{13}C_{12}$ (PnCDF-^{13}C)
1,2,3,4,7,8-Hexachlorodibenzofuran-$^{13}C_{12}$ (HxCDF-^{13}C)

Several congeners in Radian's PCDF/PCDD Standards Inventory were also donated to the program. These congeners were:

2,3,7,8-Tetrachlorodibenzo-p-dioxin
2,3,7,8-Tetrachlorodibenzo-p-dioxin-$^{13}C_{12}$
2,3,7,8-Tetrachlorodibenzofuran
Octachlorodibenzo-p-dioxin-$^{13}C_{12}$
2,3,4,8-Tetrachlorodibenzofuran
2,3,4,7,8-Pentachlorodibenzofuran
1,2,3,6,7,8-Hexachlorodibenzofuran
2,3,4,6,7,8-Hexachlorodibenzofuran
Octachlorodibenzofuran

A mixture of congeners was obtained from Professor Christoffer Rappe of the University of Umea, Sweden. This semi-quantitative mixture, the "toxic cocktail", contained the following isomers:

1,3,4-Trichlorodibenzofuran
2,3,4,8-Tetrachlorodibenzofuran
2,3,4,7,8-Pentachlorodibenzofuran
1,2,3,4,8-Pentachlorodibenzofuran
1,2,3,4,7,8-Hexachlorodibenzofuran
1,2,3,4,6,7,8-Heptachlorodibenzofuran
Octachlorodibenzofuran

All the compounds prepared or obtained by Radian were made up as stock spiking solutions at 50 μg/mL or 100 μg/mL. These solutions were further diluted to produce standard solutions for distribution to the participating analytical laboratories. Table 15 lists the standards provided by Radian.

Baseline Liquids

To determine the accuracy and precision of PCDD/PCDF measurements, a selection of baseline liquids were re-analyzed in the Round Robin Analysis portion of the program (1). The Baseline liquids (Table 16) were dissolved in hexane at levels of 0.18 - 0.20 grams/mL and spiked with measured levels of ^{13}C-labeled congeners. In this instance, however, a selection of native congeners were spiked "blind" at levels known only to the person performing the spiking. Additionally, a set of samples were prepared with no native congener spikes in order to determine background PCDD/PCDF levels. Table 17 describes these samples and reveals the spiking levels. The seven "In-Service" Liquids were spiked with ^{13}C-labeled

TABLE 15. STANDARD SOLUTIONS[a]

I.D. No.	Description	Concentration
E729-14-02	2,3,7,8-Tetrachlorodibenzofuran (TCDF)-^{13}C	100 ng/mL
E729-06-04	2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD)-^{13}C	100 ng/mL
E729-15-02	1,2,3,7,8-Pentachlorodibenzofuran (PnCDF)-^{13}C	100 ng/mL
E729-16-02	Octachlorodibenzo-p-dioxin (OCDD)-^{13}C	40 ng/mL
E729-05-04	2,3,7,8-Tetrachlorodibenzofuran	100 ng/mL
E729-06-02	2,3,7,8-Tetrachlorodibenzo-p-dioxin	100 ng/mL
E729-05-01	1,2,3,7,8-Pentachlorodibenzofuran	100 ng/mL
E729-05-02	1,2,3,4,7,8-Hexachlorodibenzofuran (HxCDF)	100 ng/mL
E729-05-03	1,2,3,4,6,7,8-Heptachlorodibenzofuran (HpCDF)	100 ng/mL
E729-06-01	Radian PCDF/TCDD Mixture	
	2,3,7,8-TCDF	100 ng/mL
	2,3,7,8-TCDD	100 ng/mL
	1,2,3,7,8-PnCDF	100 ng/mL
	1,2,3,4,7,8-HxCDF	100 ng/mL
	1,2,3,4,6,7,8-HpCDF	100 ng/mL
E729-07-02	Professor Rappe's "Toxic Cocktail"	
	1,2,4-TrCDF	~116 ng/mL
	2,3,4,8-TCDF	~100 ng/mL
	2,3,4,7,8-PnCDF	~100 ng/mL
	1,2,3,4,8-PnCDF	~100 ng/mL
	1,2,3,4,7,9-HxCDF	~100 ng/mL
	1,2,3,4,6,7,8-HpCDF	~100 ng/mL
	OCDF	~160 ng/mL
E729-55-01	Calibration Mixture I	
	Native Congeners	
	2,3,7,8-TCDD	7.5 µg/mL
	2,3,7,8-TCDF	7.5 µg/mL
	1,2,3,7,8-PnCDF	7.5 µg/mL
	2,3,4,7,8-PnCDF	7.5 µg/mL
	1,2,3,4,7,8-HxCDF	7.5 µg/mL
	2,3,4,6,7,8-HxCDF	7.5 µg/mL
	1,2,3,4,6,7,8-HpCDF	7.5 µg/mL
	OCDF	7.5 µg/mL
	Labeled Congeners	
	2,3,7,8-TCDD-$^{13}C_{12}$	300 ng/mL
	2,3,7,8-TCDF-$^{13}C_{12}$	300 ng/mL

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TABLE 15 (cont'd.)

I.D. No.	Description	Concentration
	1,2,3,7,8-PnCDF-$^{13}C_{12}$	500 ng/mL
	1,2,3,4,7,8-HxCDF-$^{13}C_{12}$	500 ng/mL
	OCDD-$^{13}C_{12}$	200 ng/mL
E729-55-03	Calibration Mixture II	
	Native Congeners	
	2,3,7,8-TCDD	2.5 µg/mL
	2,3,7,8-TCDF	2.5 µg/mL
	1,2,3,7,8-PnCDF	2.5 µg/mL
	2,3,4,7,8-PnCDF	2.5 µg/mL
	1,2,3,4,7,8-HxCDF	2.5 µg/mL
	2,3,4,6,7,8-HxCDF	2.5 µg/mL
	1,2,3,4,6,7,8-HpCDF	2.5 µg/mL
	OCDF	2.5 µg/mL
	Labeled Congeners	
	2,3,7,8-TCDD-$^{13}C_{12}$	500 ng/mL
	2,3,7,8-TCDF-$^{13}C_{12}$	500 ng/mL
	1,2,3,7,8-PnCDF-$^{13}C_{12}$	500 ng/mL
	1,2,3,4,7,8-HxCDF-$^{13}C_{12}$	500 ng/mL
	OCDD-$^{13}C_{12}$	200 ng/mL
E729-55-04	Calibration Mixture III	
	Native Congeners	
	2,3,7,8-TCDD	500 ng/mL
	2,3,7,8-TCDF	500 ng/mL
	1,2,3,7,8-PnCDF	500 ng/mL
	2,3,4,7,8-PnCDF	500 ng/mL
	1,2,3,4,7,8-HxCDF	500 ng/mL
	2,3,4,6,7,8-HxCDF	500 ng/mL
	1,2,3,4,6,7,8-HpCDF	500 ng/mL
	OCDF	500 ng/mL
	Labeled Congeners	
	2,3,7,8-TCDD-$^{13}C_{12}$	500 ng/mL
	2,3,7,8-TCDF-$^{13}C_{12}$	500 ng/mL
	1,2,3,7,8-PnCDF-$^{13}C_{12}$	500 ng/mL
	1,2,3,4,7,8-HxCDF-$^{13}C_{12}$	500 ng/mL
	OCDD-$^{13}C_{12}$	200 ng/mL

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TABLE 15 (cont'd.)

I.D. No.	Description	Concentration
E729-55-05	Calibration Mixture IV	
	Native Congeners	
	2,3,7,8-TCDD	150 ng/mL
	2,3,7,8-TCDF	150 ng/mL
	1,2,3,7,8-PnCDF	150 ng/mL
	2,3,4,7,8-PnCDF	150 ng/mL
	1,2,3,4,7,8-HxCDF	150 ng/mL
	2,3,4,6,7,8-HxCDF	150 ng/mL
	1,2,3,4,6,7,8-HpCDF	150 ng/mL
	OCDF	150 ng/mL
	Labeled Congeners	
	2,3,7,8-TCDD-$^{13}C_{12}$	500 ng/mL
	2,3,7,8-TCDF-$^{13}C_{12}$	500 ng/mL
	1,2,3,7,8-PnCDF-$^{13}C_{12}$	500 ng/mL
	1,2,3,4,7,8-HxCDF-$^{13}C_{12}$	500 ng/mL
	OCDD-$^{13}C_{12}$	200 ng/mL
E729-55-06	Calibration Mixture V	
	Native Congeners	
	2,3,7,8-TCDD	40 ng/mL
	2,3,7,8-TCDF	40 ng/mL
	1,2,3,7,8-PnCDF	40 ng/mL
	2,3,4,7,8-PnCDF	40 ng/mL
	1,2,3,4,7,8-HxCDF	40 ng/mL
	2,3,4,6,7,8-HxCDF	40 ng/mL
	1,2,3,4,6,7,8-HpCDF	40 ng/mL
	OCDF	40 ng/mL
	Labeled Congeners	
	2,3,7,8-TCDD-$^{13}C_{12}$	500 ng/mL
	2,3,7,8-TCDF-$^{13}C_{12}$	500 ng/mL
	1,2,3,7,8-PnCDF-$^{13}C_{12}$	500 ng/mL
	1,2,3,4,7,8-HxCDF-$^{13}C_{12}$	500 ng/mL
	OCDD-$^{13}C_{12}$	200 ng/mL
E729-56-01	Calibration Mixture VI	
	Native Congeners	
	2,3,7,8-TCDD	10 ng/mL
	2,3,7,8-TCDF	10 ng/mL

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TABLE 15 (cont'd.)

I.D. No.	Description	Concentration
	1,2,3,7,8-PnCDF	10 ng/mL
	2,3,4,7,8-PnCDF	10 ng/mL
	1,2,3,4,7,8-HxCDF	10 ng/mL
	2,3,4,6,7,8-HxCDF	10 ng/mL
	1,2,3,4,6,7,8-HpCDF	10 ng/mL
	OCDF	10 ng/mL
	Labeled Congeners	
	2,3,7,8-TCDD-$^{13}C_{12}$	500 ng/mL
	2,3,7,8-TCDF-$^{13}C_{12}$	500 ng/mL
	1,2,3,7,8-PnCDF-$^{13}C_{12}$	500 ng/mL
	1,2,3,4,7,8-HxCDF-$^{13}C_{12}$	500 ng/mL
	OCDD-$^{13}C_{12}$	200 ng/mL
E729-56-D2	Calibration Mixture VII	
	Native Congeners	
	2,3,7,8-TCDD	2.5 ng/mL
	2,3,7,8-TCDF	2.5 ng/mL
	1,2,3,7,8-PnCDF	2.5 ng/mL
	2,3,4,7,8-PnCDF	2.5 ng/mL
	1,2,3,4,7,8-HxCDF	2.5 ng/mL
	2,3,4,6,7,8-HxCDF	2.5 ng/mL
	1,2,3,4,6,7,8-HpCDF	2.5 ng/mL
	DCDF	2.5 ng/mL
	Labeled Congeners	
	2,3,7,8-TCDD-$^{13}C_{12}$	500 ng/mL
	2,3,7,8-TCDF-$^{13}C_{12}$	500 ng/mL
	1,2,3,7,8-PnCDF-$^{13}C_{12}$	500 ng/mL
	1,2,3,4,7,8-HxCDF-$^{13}C_{12}$	500 ng/mL
	OCDD-$^{13}C_{12}$	200 ng/mL

[a]See Ref. 1. for details.

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TABLE 16. BASELINE FLUID SAMPLES - GC/MS CROSSCHECK[a]

ID No.	Description	Spike	Spiking Level
E729-09-01	Aroclor 1016	2,3,7,8-TCDF-^{13}C	100 ng/g
		1,2,3,7,8-PnCDF-^{13}C	100 ng/g
		2,3,7,8-TCDD-^{13}C	100 ng/g
		OCDD-^{13}C	40 ng/g
		1,2,3,4,7,8-HxCDF	100 ng/g
		1,2,3,4,6,7,8-HpCDF	100 ng/g
E729-10-0	Aroclor 1242	2,3,7,8-TCDF-^{13}C	100 ng/g
		1,2,3,7,8-PnCDF-^{13}C	100 ng/g
		2,3,7,8-TCDD-^{13}C	100 ng/g
		OCDD-^{13}C	40 ng/g
		1,2,3,4,7,8-HxCDF	100 ng/g
		1,2,3,4,6,7,8-HpCDF	100 ng/g
E729-11-01	Aroclor 1260	2,3,7,8-TCDF-^{13}C	100 ng/g
		1,2,3,7,8-PnCDF-^{13}C	100 ng/g
		2,3,7,8-TCDD-^{13}C	100 ng/g
		OCDD-^{13}C	40 ng/g
		1,2,3,4,7,8-HxCDF	100 ng/g
		1,2,3,4,6,7,8-HpCDF	100 ng/g
E729-12-01	Tri-Tetrachlorobenzenes	2,3,7,8-TCDF-^{13}C	100 ng/g
		1,2,3,7,8-PnCDF-^{13}C	100 ng/g
		2,3,7,8-TCDD-^{13}C	100 ng/g
		OCDD-^{13}C	40 ng/g
		1,2,3,4,7,8-HxCDF	100 ng/g
		1,2,3,4,6,7,8-HpCDF	100 ng/g
E729-08-01	Aged Mineral Oil	2,3,7,8-TCDF-^{13}C	100 ng/g
		1,2,3,7,8-PnCDF-^{13}C	100 ng/g
		2,3,7,8-TCDD-^{13}C	100 ng/g
		OCDD-^{13}C	40 ng/g
		2,3,7,8-TCDD	40 ng/g
		2,3,7,8-TCDF	20 ng/g
		1,2,3,7,8-PnCDF	40 ng/g
		1,2,3,4,7,8-HxCDF	120 ng/g
		1,2,3,4,6,7,8-HpCDF	0 ng/g
	Professor Rappe's "Toxic Cocktail"		
E729-08-01	Aged Mineral Oil	OCDF	~160 ng/g
		1,2,3,4,7,9-HxCDF	~100 ng/g
		2,3,4,7,8-PnCDF	~100 ng/g
		1,2,3,4,8-PnCDF	~100 ng/g
		2,3,4,8-TCDF	~100 ng/g
		1,3,4-TrCDF	~116 ng/g
		Aroclor 1260	510 µg/g
		Tri-Tetrachlorobenzenes	530 µg/g

[a]See Ref. 1 for details.

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TABLE 17. BASELINE FLUID SAMPLES - ROUND RD8IN ANALYSIS[a]

ID No.	Description	Spike	Spiking Level
E729-53-01	Mineral Oil	Aroclor 1260	640 µg/g
		Tri/Tetrachlorobenzenes	1250 µg/g
		2,3,7,8-TCDD-^{13}C	100 ng/g
		2,3,7,8-TCDF-^{13}C	100 ng/g
		1,2,3,7,8-PnCDF-^{13}C	100 ng/g
		1,2,3,4,7,8-HxCDF-^{13}C	100 ng/g
		OCDD-^{13}C	40 ng/g
		2,3,7,8-TCDD	25 ng/g
		2,3,7,8-TCDF	100 ng/g
		2,3,4,8-TCDF	100 ng/g
		1,2,3,7,8-PnCDF	150 ng/g
		2,3,4,7,8-PnCDF	150 ng/g
		1,2,3,4,7,8-HxCDF	250 ng/g
		1,2,3,6,7,8-HxCDF	50 ng/g
		2,3,4,6,7,8-HxCDF	175 ng/g
		1,2,3,4,6,7,8-HpCDF	400 ng/g
		OCDF	0 ng/g
E729-53-02	Aroclor 1016	2,3,7,8-TCDD-^{13}C	100 ng/g
		2,3,7,8-TCDF-^{13}C	100 ng/g
		1,2,3,7,8-PnCDF-^{13}C	100 ng/g
		1,2,3,4,7,8-HxCDF-^{13}C	100 ng/g
		OCDD-^{13}C	40 ng/g
		2,3,7,8-TCDD	53 ng/g
		2,3,7,8-TCDF	53 ng/g
		2,3,4,8-TCDF	0 ng/g
		1,2,3,7,8-PnCDF	158 ng/g
		2,3,4,7,8-PnCDF	158 ng/g
		1,2,3,4,7,8-HxCDF	0 ng/g
		1,2,3,6,7,8-HxCDF	53 ng/g
		2,3,4,6,7,8-HxCDF	132 ng/g
		1,2,3,4,6,7,8-HpCDF	526 ng/g
		OCDF	132 ng/g
E729-53-03	Aroclor 1260	2,3,7,8-TCDD-^{13}C	100 ng/g
		2,3,7,8-TCDF-^{13}C	100 ng/g
		1,2,3,7,8-PnCDF-^{13}C	100 ng/g
		1,2,3,4,7,8-HxCDF-^{13}C	100 ng/g
		OCDD-^{13}C	40 ng/g
		2,3,7,8-TCDD	111 ng/g
		2,3,7,8-TCDF	833 ng/g
		2,3,4,8-TCDF	194 ng/g
		1,2,3,7,8-PnCDF	111 ng/g
		2,3,4,7,8-PnCDF	111 ng/g
		1,2,3,4,7,8-HxCDF	500 ng/g
		1,2,3,6,7,8-HxCDF	278 ng/g
		2,3,4,6,7,8-HxCDF	56 ng/g
		1,2,3,4,6,7,8-HpCDF	111 ng/g
		OCDF	222 ng/g
		Aroclor 1260	680 µg/g
		Tri/Tetrachlorobenzenes	1320 µg/g

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TABLE 17 (cont'd.)

ID No.	Description	Spike	Spiking Level
E729-54-02	Mineral Oil	2,3,7,8-TCDD-^{13}C	100 ng/g
		2,3,7,8-TCDF-^{13}C	100 ng/g
		1,2,3,7,8-PnCDF-^{13}C	100 ng/g
		1,2,3,4,7,8-HxCDF-^{13}C	100 ng/g
		OCDD-^{13}C	40 ng/g
E729-54-03	Aroclor 1260	2,3,7,8-TCDD-^{13}C	100 ng/g
		2,3,7,8-TCDF-^{13}C	100 ng/g
		1,2,3,7,8-PnCDF-^{13}C	100 ng/g
		1,2,3,4,7,8-HxCDF-^{13}C	100 ng/g
		OCDD-^{13}C	40 ng/g
E729-54-04	Aroclor 1016	2,3,7,8-TCDD-^{13}C	100 ng/g
		2,3,7,8-TCDF-^{13}C	100 ng/g
		1,2,3,7,8-PnCDF-^{13}C	100 ng/g
		1,2,3,4,7,8-HxCDF-^{13}C	100 ng/g
		OCDD-^{13}C	40 ng/g

[a]See Ref. 1 for details.

congeners at Battelle Memorial Institute, Columbus, Ohio, using stock solutions provided by Radian Corporation (4).

PREPARATION OF PCDD AND PCDF STANDARDS

Calibration Standards)

PCDD and PCDF standard compounds including ^{13}C-labelled standard compounds, dissolved in solvent, were received at each laboratory sealed in glass vials. The seven vials each contained all of the following compounds:

2,3,7,8-TCDD	1,2,3,4,6,7,8,9-OCDF
2,3,7,8-TCDF	2,3,7,8-TCDD-$^{13}C_{12}$
1,2,3,7,8-PnCDF	2,3,7,8-TCDF-$^{13}C_{12}$
2,3,4,7,8-PnCDF	1,2,3,7,8-PnCDF-$^{13}C_{12}$
1,2,3,4,7,8-HxCDF	1,2,3,4,7,8-HxCDF-$^{13}C_{12}$
2,3,4,6,7,8-HxCDF	1,2,3,4,6,7,8,9-OCDD-$^{13}C_{12}$

Each vial contained all of the native compounds at one of the following concentration levels:

7,500 ng/mL
2,500 ng/mL
500 ng/mL
150 ng/mL
40 ng/mL
10 ng/mL
2.5 ng/mL

Each standard solution contained all of the ^{13}C compounds at 500 ng/mL each.

Baseline Samples

Three baseline samples (Aroclor 1016, Aroclor 1260, and aged mineral oil) 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 13C-compounds listed above. Each sample was also spiked with "blind" amounts of the following unlabeled compounds:

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

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

In-Service Samples

Seven in-service samples were fluids consisting 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.

SAMPLE EXTRACTION AND EXTRACT PREPARATIONS

For this Round Robin Study each participating laboratory employed their best available in-house extraction and analysis techniques which are shown in Table 1. Because the methods varied between the laboratories, a parameter being statistically tested in the Round Robin Study, a detailed description of each is presented here.

Procedures Employed by NYSDOH (3)

The volume of a portion of samples of electric insulating fluids and mineral oil was measured and extracted by adding 25 mL of acetone and mixing thoroughly. Hexane (25 mL) was added and the sample was stirred and extracted for a minimum of 1 h. To remove PCBs and nonplanar aromatics and to isolate one fraction containing all tetra- to OCDFs and OCDDs the sample extract was chromatographed on acid alumina, PX-21 carbon and neutral alumina. A preprogrammed Hamilton valve control system designed at NYSDOH was used to reproducibly select solvents and chromatographic columns (3). The recovery of all tetra- to OCDFs and OCDDs (as verified with available standards) from an individual chromatographic column was >95%.

The sample extract was applied to an activated acidic alumina column, followed by 30 mL of 3% CH_2Cl_2 in hexane. The CDF/CDD fraction was eluted with 70 mL of 50% CH_2Cl_2 in hexane onto a carbon column followed by 50 mL of 10% benzene in hexane. The CDF/CDD fraction was eluted in the reverse direction with 30 mL of 50% xylene in hexane onto a neutral alumina column (replaces xylene with a volatile solvent) followed by 30 mL of 3% CH_2Cl_2 in hexane. The final purified CDF/CDD fraction was eluted with 70 mL of easily volatilized 50% CH_2Cl_2 in hexane and concentrated with first boiling water and then vacuum to 4-10 μL (3). Extracts were stored in the dark for GC/MS in sealed 150 μL borosilicate capillary tubes.

Procedures Employed by IITRI (2)

The extraction and cleanup procedure which was employed was based on the general method described by Albro and coworkers (2) for the fractionation and cleanup determination of complex mixtures of chlorinated aromatic compounds. An overview is shown in Figure 1. Briefly, the procedure consisted of the following major steps.

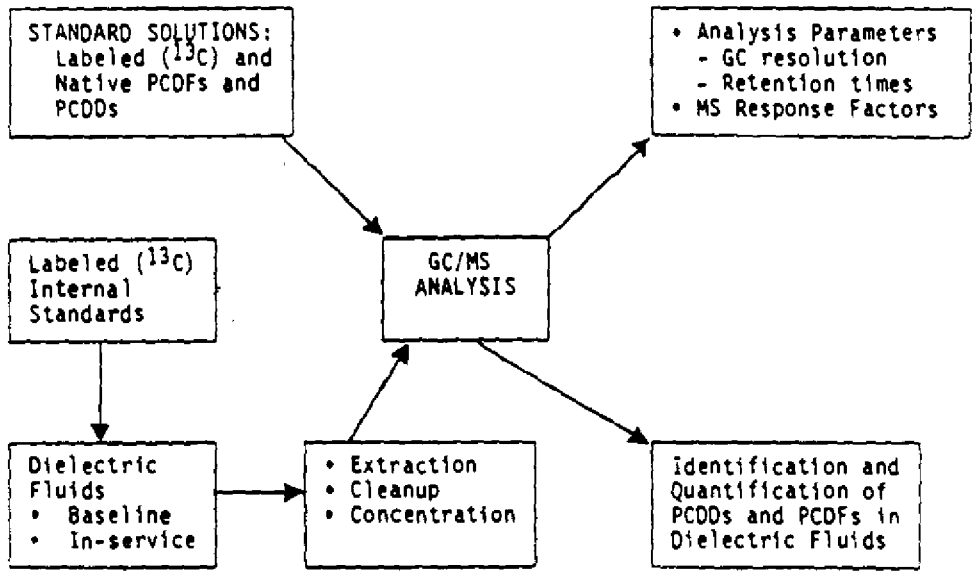

Figure 1. Overview of Analytical Protocol (Ref. 2)

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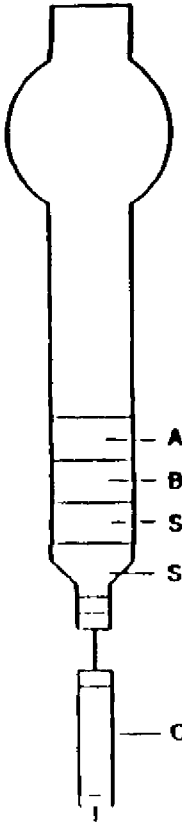
1. To the sample (ca. 0.1 g), spiked with a mixture of ^{13}C-labeled PCDF and/or PCDD internal standards, about 30 ng of 2,3,7-tri-CDD was added to serve as a "carrier" compound.
2. The sample was chromatographed on a gel permeation column (20 g Sephadex LH-20), eluting with 50% methylene chloride-in-methanol and collecting the 60-150 mL fraction, to separate halogenated aromatic compounds from any alphatics present.
3. About 10 µL of propylene glycol were added as a "keeper" compound, to prevent sample loss during roto-evaporation.
4. After roto-evaporation, the halogenated aromatic fraction was chromatographed on an A-540 basic alumina column (20 grams topped with a layer of anhydrous sodium sulfate), eluting with 180 mL of 2% methylene chloride-in-hexane, to elute the PCB fraction.
5. Congeners eluted with 20% methylene chloride-in-hexane (200-220 mL), to recover PCDFs, PCDDs, polychlorinated quadriphenyls, and less chlorinated PCBs.
6. About 10 µL of propylene glycol were added, then the fraction was 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 was discarded.
7. The purified PCDF/PCDD fraction was eluted with 20% methylene chloride-in-hexane (120 mL).
8. The extract was concentrated to 25 µL immediately before analysis using toluene.
9. When necessary, the extract was 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 was reversed and 8 mL of toluene were collected.

Procedures Employed by Radian (1)

The extraction technique used by Radian for the Round Robin analysis phase of this study was a modified Smith-Stallings/EPA Region VII clean-up (1). Figure 2 describes the clean-up procedure used for these dielectric samples.

An aliquot of the sample (approximately 0.25 g) was transferred to a column consisting of 2.5 cm sodium sulfate (on bottom), 5 g silica gel type 60, (70-230 mesh), 6 g basic silica gel (35% potassium hydroxide), and 10 g acid silica gel (40% sulfuric acid). This column was eluted with 170 mL 1:1 methylene chloride:cyclohexane directly onto a 5.0 cm column of 1-9 µm carbon (PX-2) on glass fibers. The silica gel was discarded and the carbon column washed with 25 mL 1:1

Part 1
Modified Smith-Stallings Clean-Up



150 mL 1:1 Methylene chloride: cyclohexane
Discard silica gel
25 mL 1:1 Methylene chloride: cyclohexane
50 mL 75:20:5 Methylene chloride: methanol: benzene
Invert carbon column
50 mL Toluene (collect)

Acid silica gel 10g
Basic silica gel 6g
Silica gel 5g
Sodium sulfate 1"

Carbon/glass fibers

Part 2
"Region 7" Clean-Up



Acid silica gel 5g
Silica gel 1g
Acid alumina 6g

Solvent exchange the toluene to hexane
Transfer hexane extract to silica gel column
60 mL hexane
Discard silica gel
20 mL hexane
20 mL 20% methylene chloride: hexane (collect)
Concentrate

[illegible] Sample Clean-up Procedures: Round Robin Analysis (Ref. 1)

methylene chloride:cyclohexane and 50 mL 75:20:5 methylene chloride:methanol: benzene. The eluted solvents were discarded. The PCDDs and PCDFs were eluted from the carbon column with 50 mL toluene. The toluene was evaporated to dryness on a rotary evaporator. The dried extract was redissolved in hexane and transferred to a column of 5 g acid-impregnated silica gel and 1 g silica gel (lower layer). This column was eluted with 60 mL hexane directly onto a 6 g acid alumina (AG 4, 100-200 mesh) column. The silica gel was discarded and the acid alumina was washed with another 20 mL hexane. The eluted hexane was discarded. The PCDDs and PCDFs were eluted off the alumina with 20 mL 20% methylene chloride/hexane. The volume of this eluate was reduced to 1-2 mL with a stream of nitrogen. The extract was transferred to a 1 mL conical vial and taken to dryness. Each sample was processed in triplicate (this was the only lab which performed sample processing in replicate).

Procedures Employed by Battelle (4)

One milliliter aliquots (containing ~250 mg of the original fluid) of each sample was transferred to separatory funnels and diluted with 49 mL of hexane. The hexane solutions were washed with 10 mL portions of concentrated sulfuric acid until the washes were only slightly colored. A maximum of five acid washes were used. Following the acid washes, each oil was washed with 20 mL of distilled water to remove any residual acid. The hexane solutions were transferred to glass collection tubes and concentrated to approximately 2 mL using gentle streams of nitrogen gas.

The hexane solutions were transferred to multilayered silica gel columns containing activated silica gel, 44 percent concentrated sulfuric acid on silica gel, and 33 percent 1M sodium hydroxide on silica gel. The PCDD/PCDF isomers were eluted from the columns using 70 mL of hexane and the entire eluates, including the original sample volume, were collected.

The eluates from the multilayered silica gel columns were concentrated to approximately 1 mL using gentle streams of nitrogen and transferred to the top of columns containing 5 g of activated basic alumina. These columns were eluted using hexane, hexane/methylene chloride (97:3, v/v) and hexane/methylene chloride (1:1, v/v) as elution solvents. The 1:1 hexane/methylene chloride eluates were collected, solvent exchanged into hexane, and transferred to the top of alumina columnns containing approximately 2 g of activated basic alumina. These columns were eluted with hexane, hexane/methylene chloride (97:3, v/v), and hexane/methylene chloride (1:1, v/v). The 1:1 hexane/methylene chloride eluates were collected, concentrated to near dryness with nitrogen gas, and spiked with 10 ng of 1,2,3,4-TCDD-$^{13}C_{12}$. These solutions were stored at 0°C until they were analyzed.

For samples still too contaminated with interferences to be analyzed, they (41159-11-12,13,14,17 and E729-53-02,03) were chromatographed through florisil columns to provide additional analyte enrichment. Each of the florisil columns was prepared using 5 g of activated florisil (60-100 mesh) which was slurry packed with hexane. The sample solutions were diluted with approximately 5 mL of hexane and transferred to the florisil columns. The columns were eluted with hexane, hexane/ethyl ether (94:6, v/v), and hexane/methylene chloride (25:75, v/v). The 25:75 hexane/methylene chloride fraction was collected and concentrated to approximately 20 µL. These solutions were stored at 0°C until they were analyzed.

CAPILLARY GAS CHROMATOGRAPHY/MASS SPECTROMETRY ANALYSIS

Procedures Used by NYSDOH (3)

Low Resolution Mass Spectrometry--

All sample extracts were analyzed with a Hewlett-Packard 5970 Mass Selective Detector. A portion of each extract was injected into the split-splitless injection port (250°C) and eluted through a 50 m (.25 mm i.d.; .33 µm film thickness) Hewlett-Packard 5% phenyl methyl silicone fused silica capillary column. The following temperature program was used:

H-P 5890 Temperature Program

Level	Initial Temp.	Initial Time	Rate (°C/min)	Final Temp.	Final Time	Total Time
1	190	1.00	5.0	220	16.00	23.00
2			5.0	235	7.00	33.00
3			5.0	250	18.00	54.00
4			5.0	270	7.00	65.00
5			5.0	300	24.00	95.00

The gas chromatograph is interfaced directly to the source of the mass selective detector and the transfer line and ion source are heated to 275°C and 150°C respectively. The mass selective detector was operated in the selective ion monitoring (SIM) mode. The m/z values characteristic of native TCDD, TCDF, PnCDF, HxCDF, OCDF, and OCDD and TCDD-$^{13}C_{12}$, TCDF-$^{13}C_{12}$, PnCDF-$^{13}C_{12}$, HxCDF-$^{13}C_{12}$ and OCDD-$^{13}C_{12}$ were monitored at various times during the ninety-five (95) minute runs. The time window used for monitoring the different congener classes (TCDD, TCDF, etc.) were determined by the previous injection of either window standards (TCDD) or a mixture of combusted PCB. Raw data was collected into and processed by an H-P Quicksilver data system. The data system was used to generate electronic copies o:

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reports of retention times and areas at each m/z value monitored. Additional custom software was used to identify GC peaks and quantitate analyte levels. This software was written by NYSDOH staff and processed on an IBM PC or XT. The H-P reports were input in ASCII and transferred by using a customized H-P Pascal operating system (sender) and the program called Kermit (receiver). Each sample extract was instrumentally analyzed in triplicate.

High Resolution Mass Spectrometry--

Some extracts were analyzed with a Kratos MS-50 High Resolution GC/MS/DS. In this system portions of the extracts were injected into the on-column injection port of a Carlo-Erba 4160 high resolution gas chromatograph and eluted through a 50 m (.20 mm i.d.; .33 μm film thickness) Hewlett-Packard 5% methyl phenol silicone fused capillary column. The oven was temperature programmed as follows:

H-P 5890 Temperature Program

Level	Initial Temp.	Initial Time	Rate (°C/min)	Final Temp.	Final Time	Total Time
1	190°C	1.0	5.0	220	16.00	23.00
2			5.0	235	7.00	33.00
3			5.0	300	50.00	86.00

The gas chromatograph is interfaced to the MS-50 through a direct line heated to 250°C. The ion source temperature was 250°C. The high resolution mass spectrometry was operated in either of two SIM type modes. In normal multiple peak monitoring peak (NMPM) the m/x values of a particular analyte and its corresponding internal standard were observed at 10,000 RP (10% valley) by integrating all the signal detected within 50 ppm of their exact mass values. In high resolution multiple peak monitoring mode (HRMPM) the mass spectrometry is operated at the same high resolving power but the analyte and internal standard exact masses are profiled. The data system adjusts the accelerating and electric sector voltages to focus a mass slightly below the mass of interest. The computer then triggers a 0.3 sec analog scan through a 300 ppm section of the mass range which includes the exact mass of the ion of interest (3). In both ion monitoring modes the raw data was acquired into and processed by the Kratos DS-55 data system. Quantitation was done manually by calculating concentrations using peak areas obtained from the DS-55 output.

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Procedures Used by IITRI (2)

Samples and standards were analyzed using combined capillary column gas chromatography/low-resolution mass spectrometry (HRGC/LRMS or GC/MS). Figure 3 summarizes the major elements of their analysis protocol.

The gas chromatograph, a Varian 3700, was equipped with a 60 m x 0.25 mm i.d. fused-silica SP-2330 (Supelco) column. Samples were injected in the splitless mode, with the column programmed limit for 60 minutes. The SP-2330 column had 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 (2). However, it was 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 (2).

An example of the chromatographic resolution obtained using the SP-2330 column is shown in Figure 4 for 2,3,7,8-TCDD and several closely-eluting tetradioxin isomers. The plot clearly shows that this column was isomer-specific for 2,3,7,8-TCDD. Figure 5 shows the separation obtained between the 2,3,7,8- and 2,3,4,8-TCDF isomers. Here the resolution was not as good as in the previous case, but it 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 which 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 (2). The presence of these compounds could give rise to fragment ions with the same masses as those monitored for the PCFs. 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".

A listing of the masses that were monitored, along with the theoretical isotope ratios, is given in Table 18. In order to obtain maximum sensitivity and selectivity during an experiment, the run was divided into 4 adjoining time windows. Each window contained up to 16 ion masses (for specific native and labeled PCDFs and PCDDs, and chlorinated diphenyl ethers), and the sample dwell times and interchannel delay times were chosen to give the most sensitive and fast 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 windows, some of the ion masses were included in more than one window to ensure that all isomers from a particular congener class were monitored.

GC/MS ANALYSIS
(IITRI)

- 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

Figure 3. Summary of Major Elements of IITRI's GC/MS Analysis Protocol (Ref. 2).

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SSX>
ANALYSIS NAME: DR00:C003,033JOPEM0002.MIS;1 V05.0 WINDOW: 1
TITLE: TCDD PE MIX #2;1UL SPLITLESS INJ;SP2330(#1942);1.9KV
OPERATOR: TCDD.MAN;7, SCAN SPEED 600.0 MSEC SPC: 5
SAMPLE ID: DATE: 5-NOV-84 10:25:19
COMMISSION: C08756

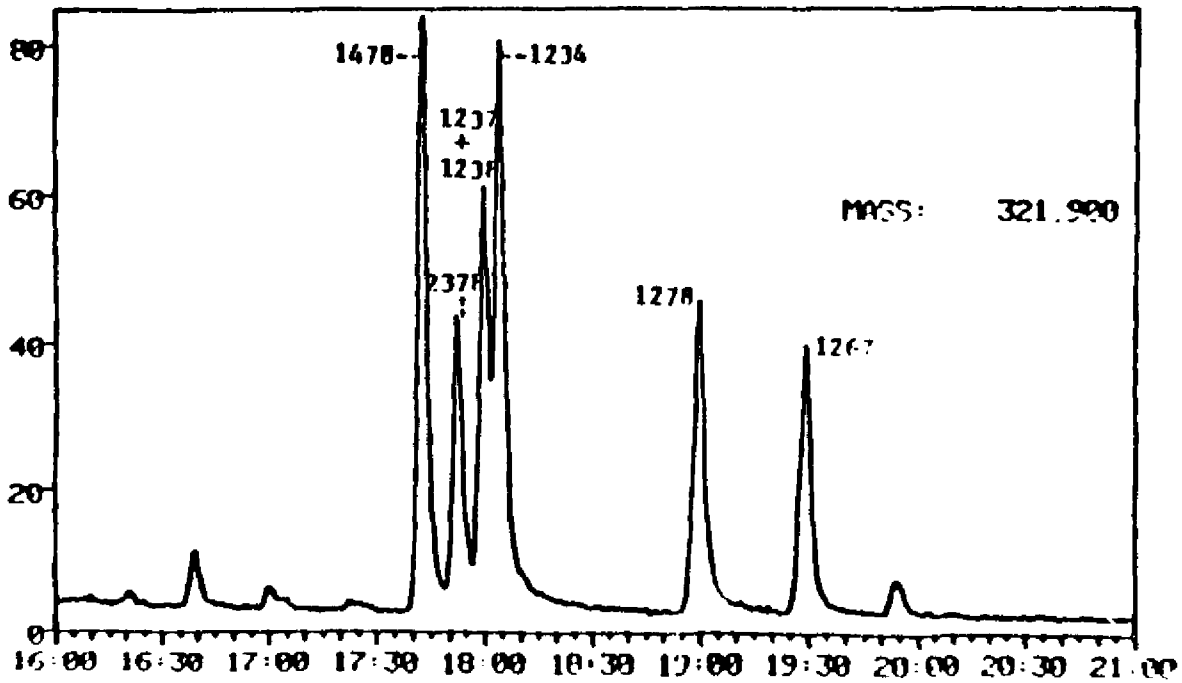

Figure 1. Selected ion current profile for mass 322 from GC/MS analysis of performance check solution containing 4 CDDs as noted on the plot, using a 60 m SP-2330 fused silica capillary column (DB-5).

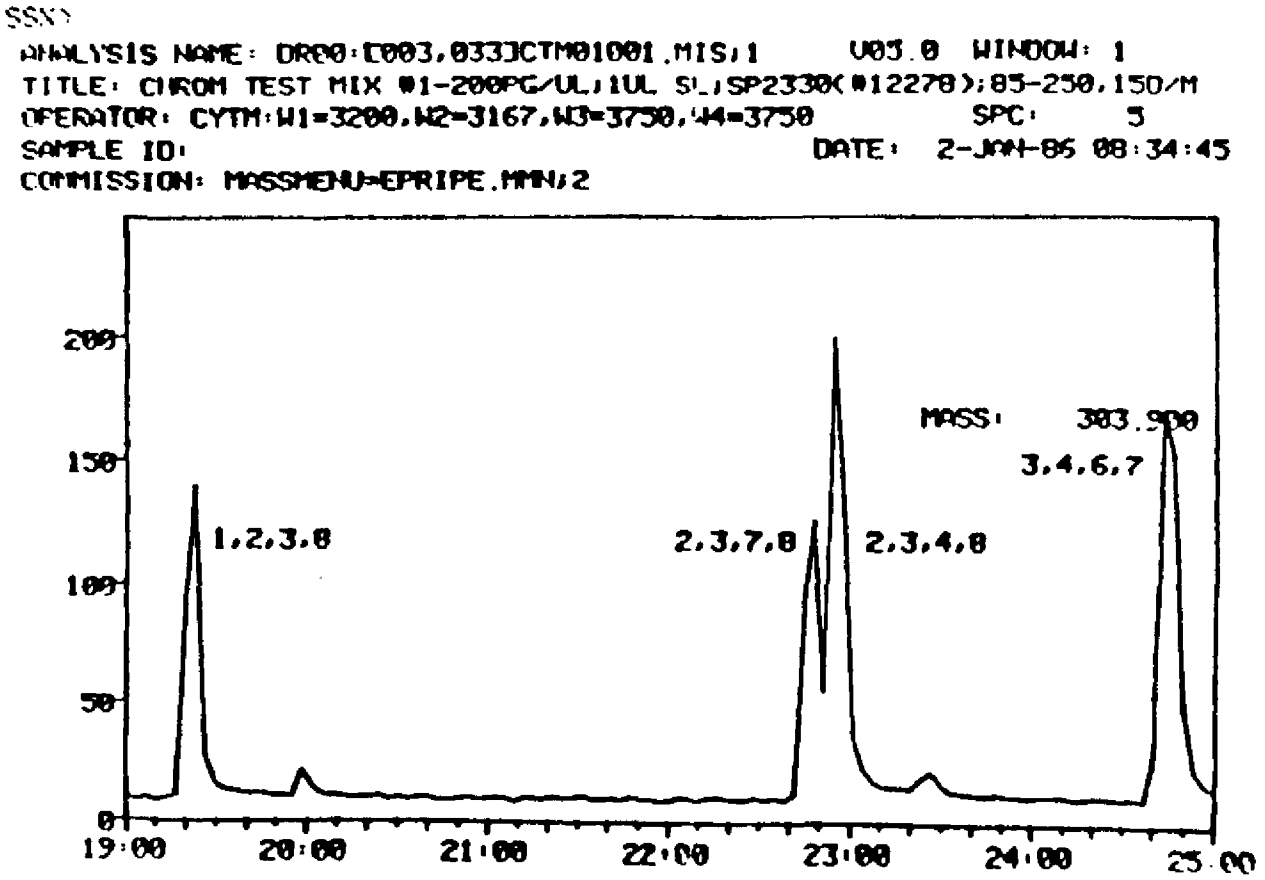

Figure 5. Selected ion current profile for mass 304 from GC/MS analysis of performance check solution containing TCDFs as noted on the plot, using a 60 m SP-2330 fused silica capillary column (Ref. 2).

TABLE 18. ANALYTICAL SEQUENCE IN GC/MS DETERMINATION OF PCDFs AND PCDDs[a]

Time Window	Start (min)	Stop (min)	GC Column Temp (C)	Temp Prog Rate (C/min)	Cycle Time (ms)	Dwell Time (ms)	Compounds Monitored[b]	Ions Monitored[c] (m/z) Mass 1	Mass 2	Isotope Ratio (Mass 1/Mass 2)
1	14:00	26:00	85	15	3200	197	TCDF	303.9	305.9	0.77
							13C-TCDF	315.9	317.9	0.77
							TCDD	319.9	321.9	0.77
							13C-TCDD	331.9	333.9	0.77
							PnCDF	337.9	339.9	0.61
							13C-PnCDF	349.9	351.9	0.61
							PnCDD	355.9	357.9	1.54
							HxDPE[d]	373.8	--	--
							HpDPE[d]	407.8	--	--
2	26:00	35:30	250	--	3157	185	PnCDF	337.9	339.9	0.61
							PnCDF[e]	274.9	--	--
							PnCDD	355.9	357.9	1.54
							PnCDD[e]	290.9	--	--
							HxCDF	373.8	375.8	1.23
							13C-HxCDF	385.9	387.9	1.23
							HxCDF[e]	310.9	--	--
							13C-HxCDF	389.8	391.8	1.23
							HxCDF[e]	310.9	--	--
							HxCDD	389.9	391.8	1.23
							HxCDD[e]	326.9	--	--
							HpDPE[d]	407.8	--	--
							ODPE[d]	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[d]	443.8	--	--
							NDPE[d]	477.7	--	--
4	56:00	66:00	250	--	3750	534	OCDF	441.7	443.7	0.88
							OCDD	457.7	459.7	0.88
							13C-OCDD	469.8	471.8	0.88
							ODPE[d]	511.7	--	--

[a] See Ref. 2.

[b] HxPE, HpDPE, ODPE, NDPE, DDPE designate hexa-, hepta-, octa-, nona-, and decachlorobiphenyl ethers resp.

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

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The major criteria which were used for confirming the presence of specific PCDFs/PCDDs in the samples analyzed were the following: (1) correct retention times for each PCDF/PCDD of interest relative to the appropriate isotopically-labeled internal standard(s), (2) intensity ratio for $(M)^+/(M+2)^+$ within 10% of theoretically-expected ratio (Table 18), and (3) signal-to-noise response of each PCDF/PCDD of interest greater than 2.5:1 for both ion masses monitored. Each sample extract was instrumentally analyzed in triplicate.

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 were available in practice, the approach generally followed was to use an appropriate set of internal standards which included representative isomers from each chlorinated class of PCDFs and PCDDs, and further assumed that the data obtained for these was representative of all isomers in each group.

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

$$RF = A_X Q_{IS} / A_{IS} Q_X$$

where A_X = sum of the integrated ion abundances of the masses for the unlabeled compound
A_{IS} = sum of the integrated ion abundances of the masses for the appropriate labeled compound
Q_{IS} = amount of the appropriate labeled compound (ng)
Q_X = amount of the labeled compound (ng)

Quantification of PCDFs and PCDDs in the sample extract was achieved 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:

$$\text{Concentration (ng/g)} = (A_X \times Q_{IS}) / A_{IS} \times W \times R_F$$

where W = weight of sample (g)
R_F = response factor

Because the labeled internal standard was added prior to sample extraction and analysis, 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:

$$DL = (2.5)\ (A_X \times Q_{IS})/A_{IS} \times R_F \times W)$$

where A_X = height of the noise band of the selected mass for the unlabeled compound

A_{IS} = height of the peak corresponding to the labeled compound of the same congener class.

Procedures Used by Radian (1)

GC/MS analysis of the sample extracts was performed on a Hewlett-Packard 5985/87 in the selected ion monitoring mode for quantitation and identification of PCDD/PCDFs. Each sample was extracted in triplicate and each extract was instrumentally analyzed in triplicate yielding nine determinations on each sample. The first series of extracts were run on a Hewlett-Packard 50 m, Ultra-2 column (a methylphenyl silicone coating equivalent to DB-5). On the Ultra-2 column, an initial temperature of 80°C was used. The second and third determinations were performed using a J&W 60 m, 0.32 mm I.D., I μm film, DB-5 column. The GC/MS conditions are shown on Table I9. Dried sample extracts were dissolved in 50 μL of hexane and a 1.0 μL volume was injected onto a cool SGE on-column injector.

Each of the three extracts was analyzed a fourth time using a Supelco SP-2331, 60 m, 0.32 mm I.D., 0.2 μm film capillary column to separate 2,3,7,8-TCDF and 2,3,4,8-TCDF. For this separation, samples were evaporated to dryness and then reconstituted with 40 μL of nonane. A two-stage temperature program of 170°-200° at 20°/min followed by 200°-275° at 4°/min was used.

Chromatographic Test Mixture

Part of this project involved separating the more toxic PCDD/PCDF isomers from coeluters. The chromatographic test mixture prepared at Battelle Memorial Institute contained the following analytes at 200 ng/L each:

1,3,6,8-TCDD	1,2,3,4,8-PnCDF
1,2,8,9-TCDD	1,2,4,6,8-PnCDF
1,2,3,4-TCDD	2,3,4,6,7-PnCDF
2,3,7,8-TCDD	1,2,3,7,8-PnCDF
1,3,7,8-TCDD	2,3,4,7,8-PnCDF
3,4,6,7-TCDF	1,2,4,6,7,8-HxCDF
2,3,4,8-TCDF	2,3,4,6,7,8-HxCDF
1,2,3,8-TCDF	1,2,3,4,7,8-HxCDF
2,3,7,8-TCDF	1,2,3,6,7,8-HxCDF

This test mixture was run daily to evaluate the chromatography. Chromatograms of all the analytes in the test mixture are shown on Figures 6 through 9 for DB-

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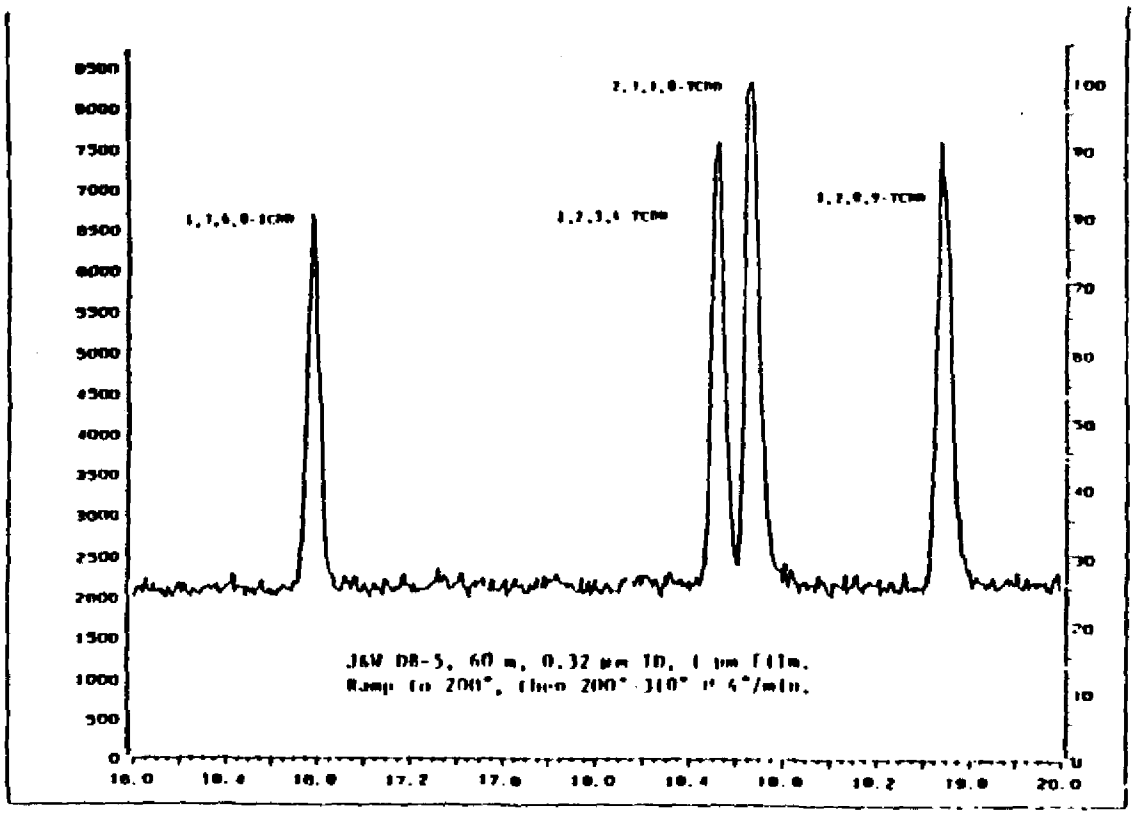

Figure 6. TCDD Test Mixture Chromatogram on DB-5 (Ref. 1)

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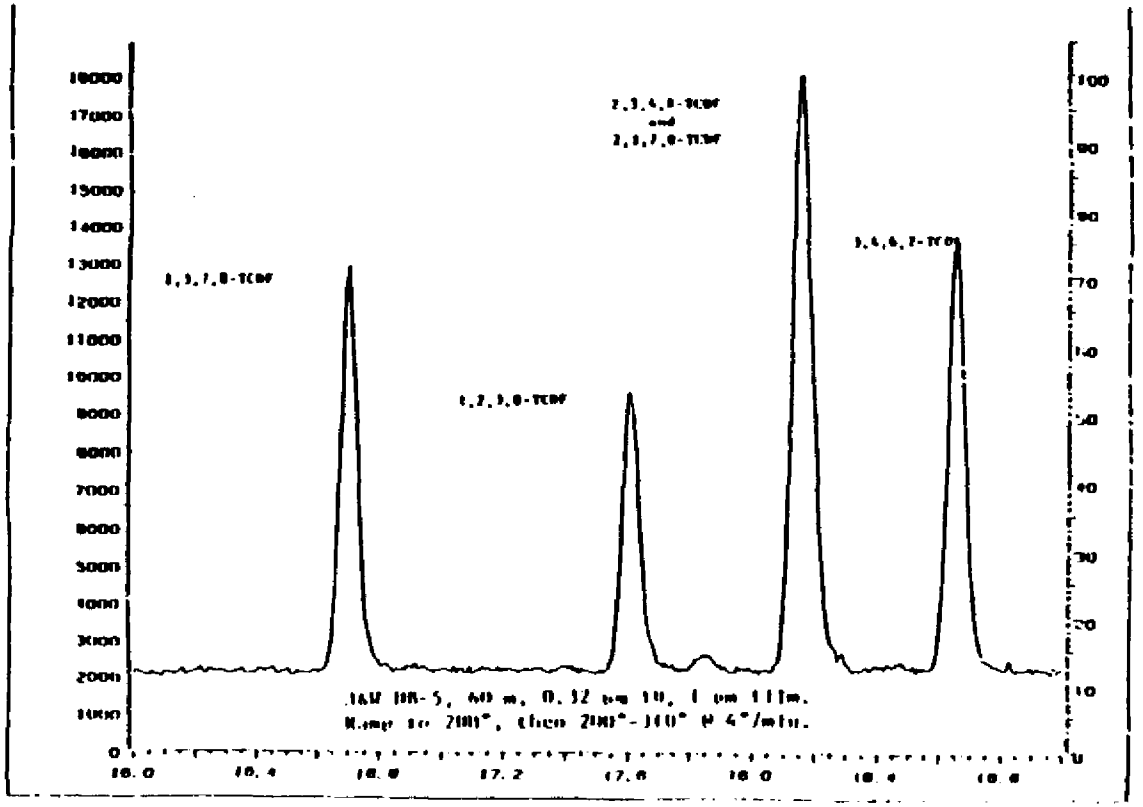

Figure 7. TCDF Test Mixture Chromatogram on DB-5 (Ref. 1)

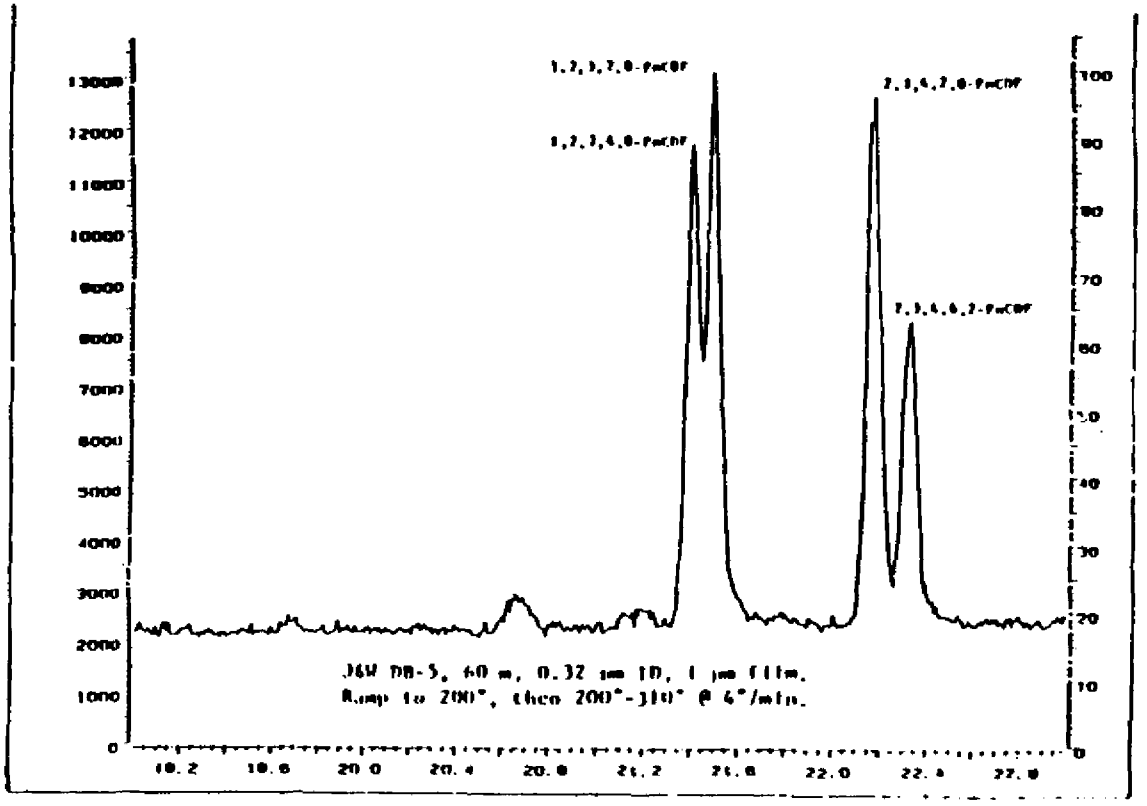

Figure 8. PnCDF Test Mixture Chromatogram on DB-5 (Ref. 1)

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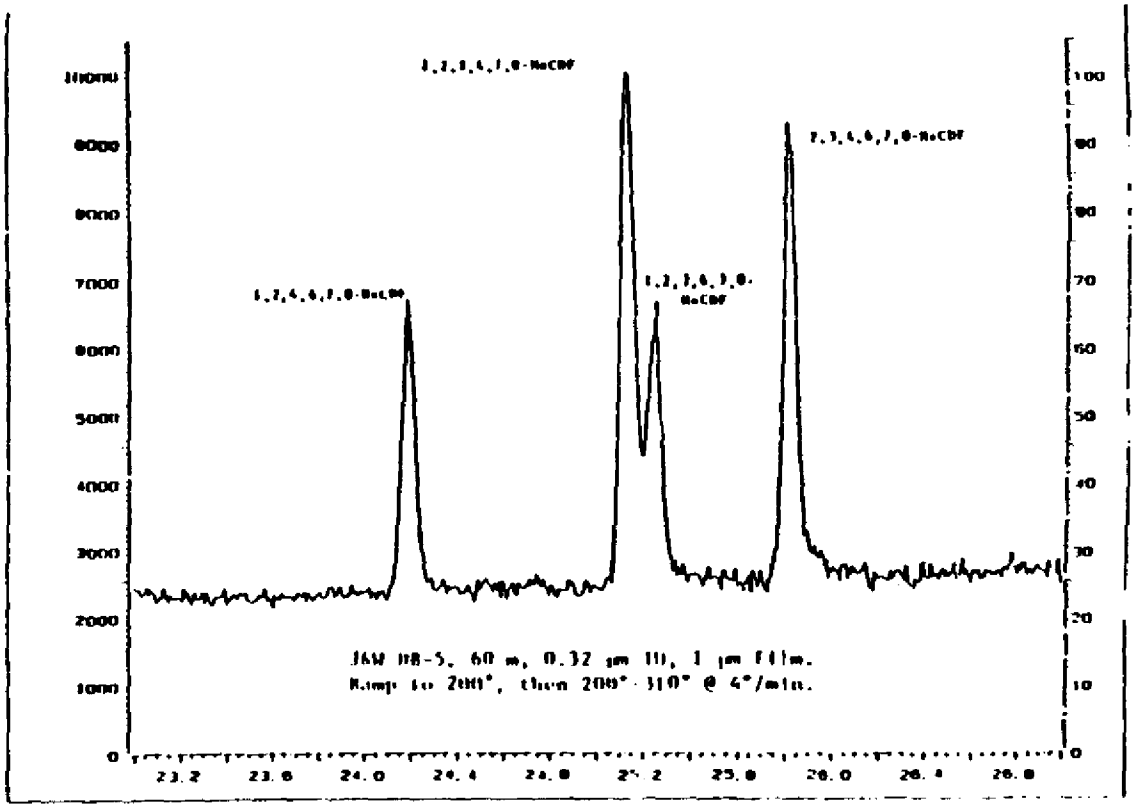

Figure 9. HxCDF Test Mixture Chromatogram on DB-5 (Ref. 1)

MONS 218560

TABLE 19. HRGC-MS ANALYTICAL CONDITIONS[a]

Mass Spectrometer:	Hewlett-Packard 5985 with 5987 Upgrade
Data System:	HP1000 RTE/6
Source Temperature:	250°C
Internal Source Pressure:	3×10^{-5} Torr
Mode:	Electron Impact
Electron Energy:	70 eV
Electron Multiplier Voltage:	2650-2800 volts
Resolution:	Unit
Interface Temperature:	275°C
Scan Mode:	Selected Ion Monitoring
Cycle Time:	0.5 sec
Column:	60 meters x 0.32 mm I.D., J&W DB-5 fused silica capillary column, 1.0 μm film
Carrier Gas:	Hydrogen at 5 psi
Carrier Linear Velocity:	35 cm/sec
Injector:	Cool On-column (65°C)
Interface to MS:	SGE Source Coupling at 275°C
GC Program:	Initial hold of 0.5 min at 65°C then 65°-200° at 30°/min, then 200°-310° at 4°/min
Injection Volume:	1 μL
Tailing Factor:	0.7-2.0

[a]Ref. 1.

Figures 10 through 13 for SP-2331. One analyte, 1,2,4,6,8-PnCDF, could not be found in the chromatographic test mixture. On DB-5, 2,3,7,8-TCDF and 2,3,4,8-TCDF were not resolved, but on SP-2331 this pair could be separated with a 65% valley. On SP-2331, 1,2,3,4,8-PnCDF and 1,2,3,7,8-PnCDF could not be resolved, but on DB-5 this pair could be separated with a 55% valley.

Actual samples were more difficult to resolve than the chromatographic test mixture. The analytes 1,2,3,4,8-PnCDF and 1,2,3,7,8-PnCDF could not be resolved in many cases, particularly when the 1,2,3,4,8-PnCDF concentration was much higher than the 1,2,3,7,8-PnCDF concentration. In one sample (41159-11-14), the

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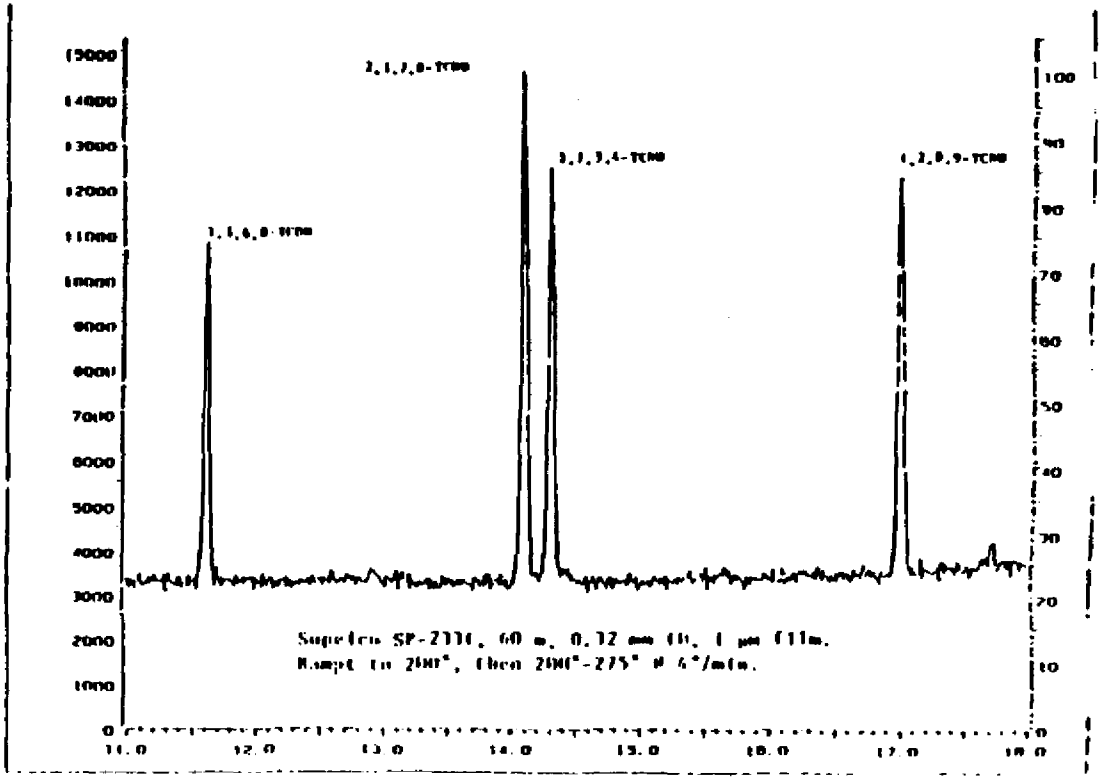

Figure 10. TCDD Test Mixture Chromatogram on SP-2331 (Ref. 1)

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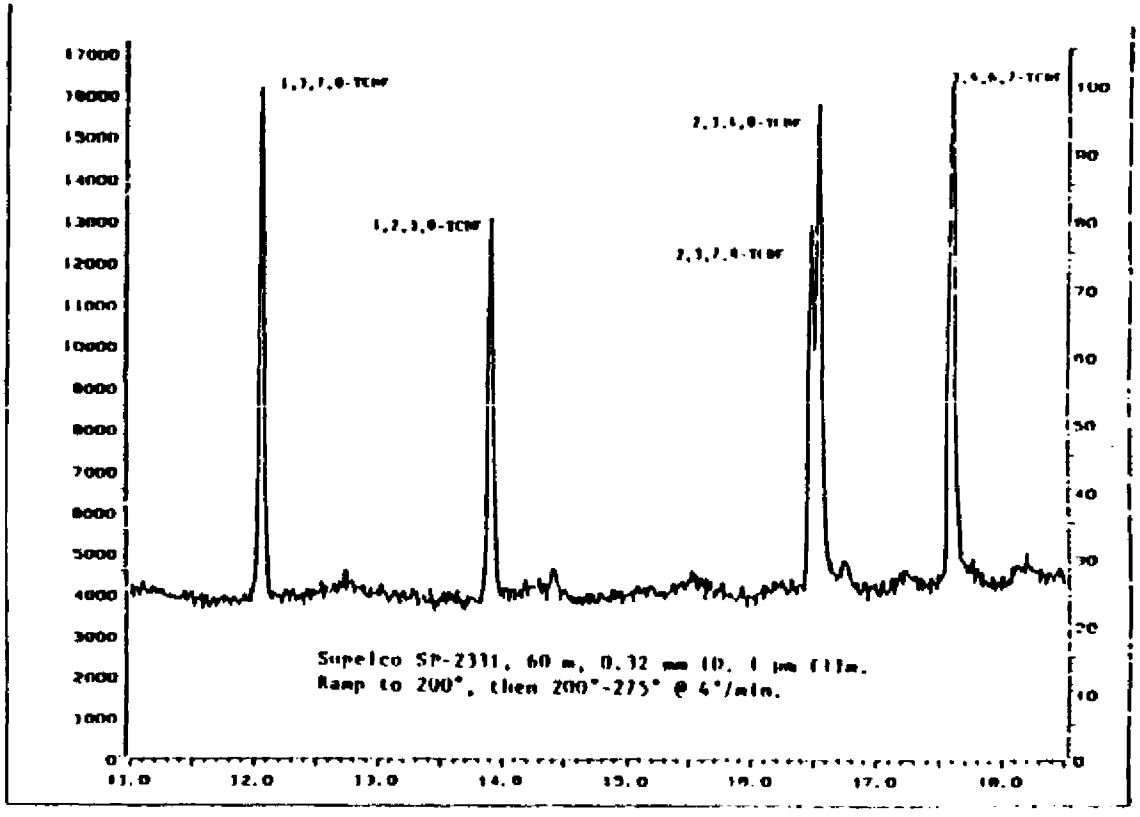

Figure 11. TCDF Test Mixture Chromatogram on SP-2331 (Ref. 1)

MONS 218563

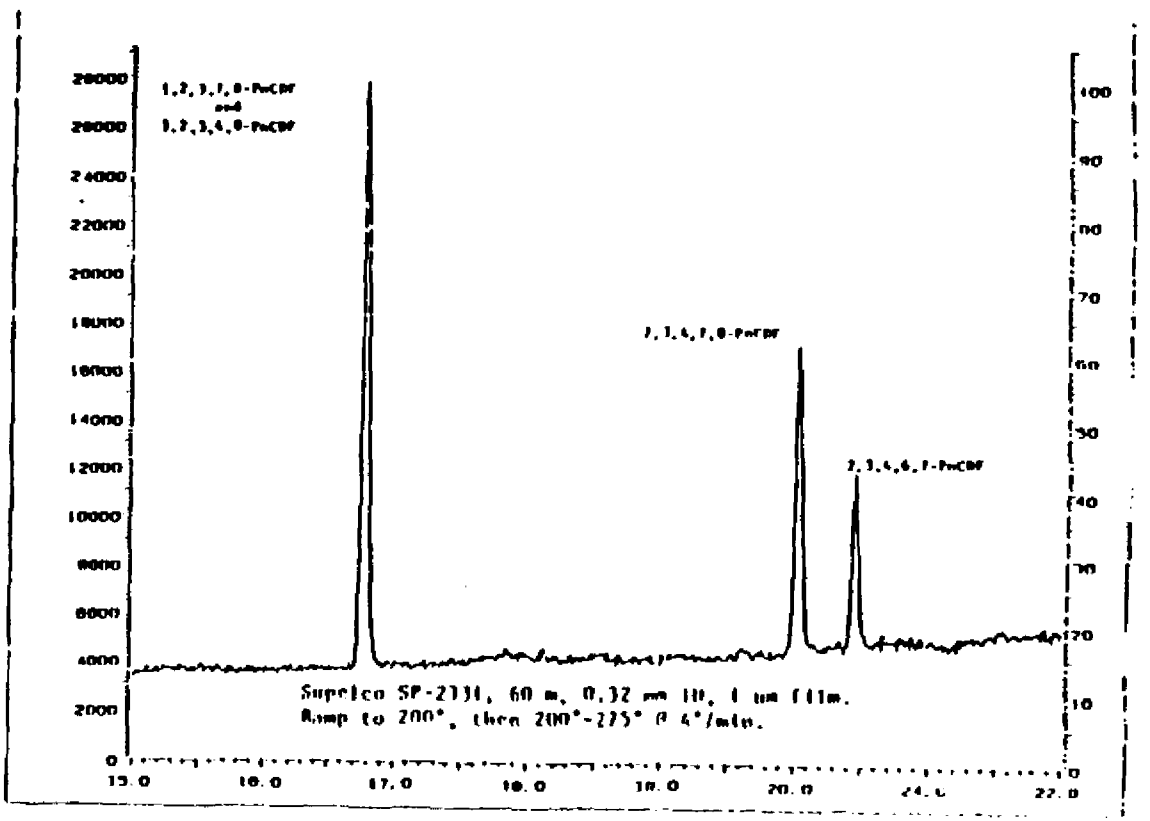

Figure 12. PeCDF Test Mixture Chromatogram on SP-2331 (Ref. 1)

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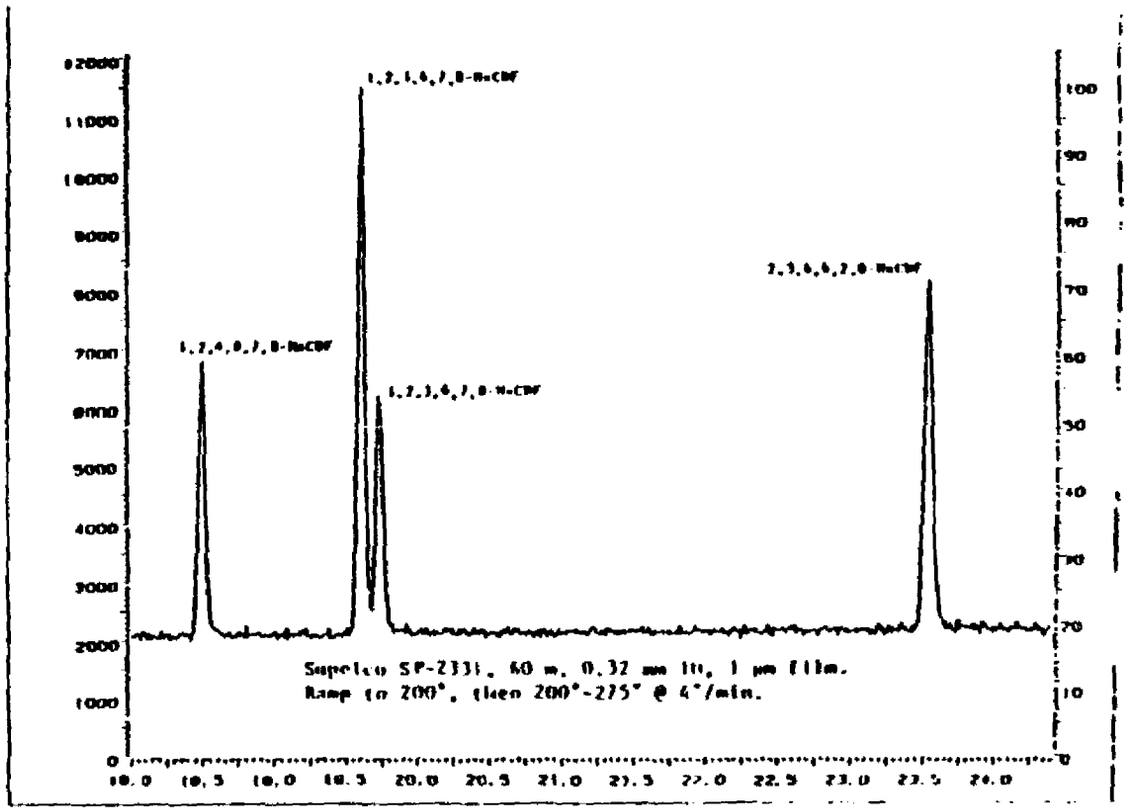

Figure 13. HxCDF Test Mixture Chromatogram on SP-2331 (Ref. 1)

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2,3,7,8-TCDF and 2,3,4,8-TCDF pair could not be resolved accurately due to a coeluting interference. Several of the in-service liquid extracts were reported by Radian to be very complex and required the removal of 12 to 18 inches of the front of the column after every injection to give adequate resolution for subsequent samples. Column degradation for DB-5 and SP-2331 could be observed from the daily test mixture chromatograms over the course of this work.

Calibration

Four C^{12}/C^{13} area ratio calibration curves were generated during this study, the first on Ultra-2, the second and third on DB-5 and the fourth on SP-2331. Concentrations of 40, 150, 500, 2500, and 7500 ng/mL were calibrated for the first three calibration curves with each calibration point being the average of three determinations. The fourth calibration curve on SP-2331 also was determined in triplicate for concentrations of 40, 150, 500, and 2500 ng/mL. Calibration curves were generated and statistical analysis performed for the following analyte/C^{13} internal standard sets:

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

Identification of PCDD/PCDFs

Identification of native PCDFs and PCDDs was performed by measuring chlorine isotope ratios and monitoring the presence of the fragment ions from loss of COCl. For PCDFs, two chlorine isotope peaks were monitored in addition to the quantitating ion. Only the most abundant chlorine isotope peak was monitored in the first series of extracts. The acceptance criteria for PCDD/PCDF positive identification required agreement better than ±10% between the theoretical and experimentally determined chlorine isotope ratios. The presence of either a second chlorine isotope peak or a M-COCl peak also was necessary for positive identification.

In the few cases where there was substantial interference in the ion pair for the largest chlorine isotope peak, the second largest chlorine isotope peak was used for evaluation of the isotope ratio acceptance criteria. In a few cases, a ±15% chlorine isotope ratio was accepted. If a peak was not within ±10% of the criteria on one determination but was within ±10% on previous determinations, the determination was accepted.

Quantitation

Quantitation was performed by isotope dilution using the ^{13}C-labeled internal standards added before extraction. Concentrations were determined from C^{12}/C^{13} ratios of sample analyte to internal standard and a linear fit to the five-point calibration curves. A separate calibration curve was generated for 2,3,4,7,8-PnCDF. All other PnCDFs were quantitated from the 1,2,3,7,8-PnCDF calibration curve. A separate calibration curve was produced for 2,3,4,6,7,8-HxCDF. All other HxCDFs and HpCDFs were quantitated from the 1,2,3,4,7,8-HxCDF calibration curve. OCDD and OCDF were quantitated from the OCDD-^{13}C calibration curve. Congener class total concentrations were calculated by summing concentrations of each peak which passed the identification criteria for the congener class. Surrogate recoveries were determined using the mean 500 ng/mL response factor from the calibration checks made at the start and end of the analyses.

One sample (41159-11-13), had a severe interference which coeluted with the TCDF-^{13}C peaks. TCDFs in this sample were quantitated verus the area of the PnCDF-^{13}C quantitating ion with a normalization factor of 1.1 (the average ratio of TCDF-^{13}C to PnCDF-^{13}C response).

Detection Limits

Instrumental detection limits were defined as the analyte concentration which gave a 3:1 signal-to-noise ratio. Method detection limits for all analytes were approximately 3 ng/g except OCDF and OCDD which were 10 ng/g due to peak broadening at the later retention times. The lowest point on the calibration curves, 40 ng/mL, corresponds to a sample concentration of 8 ng/g.

Procedures Used by Battelle (4)

Analysis--

The sample extracts were instrumentally analyzed in triplicate and quantified for PCDD/PCDF using combined capillary column gas chromatography/high resolution mass spectrometry (HRGC/HRMS). The HRGC/HRMS consisted of a Carlo Erba Model 4160 Gas Chromatograph interfaced directly into the ion source of a VG Model 7070 high resolution mass spectrometer. The chromatographic column was a 60 M DB-5 fused silica column using helium carrier gas at a flow velocity of 30 cm/sec. The mass spectrometer was operated in the electron impact (EI) ionization mode at a mass resolution of 9000-12000 (M/ΔM, 10 percent valley definition). All HRGC/HRMS data were acquired by multiple-ion-detection (MID) using a VG Model 2035 Data System.

Recovery of Internal Standards--

The recoveries of the internal standards were calculated by comparison to an external standard, 1,2,3,4-TCDD-$^{13}C_{12}$ which was added following the column cleanup steps. Relative response factors were determined from triplicate analyses of a

standard mixture containing the labelled internal standards and the 1,2,3,4-TCDD-$^{13}C_{12}$. The equation used to calculate the recoveries was:

$$\text{Recovery (\%)} = \frac{A_{is} \times Q_{rs} \times 100}{A_{rs} \times Q_{is} \times R_f}$$

Where:

A_{is} = Sum of integrated areas for internal standard;
Q_{rs} = Quantity of recovery standard in ng;
Q_{is} = Quantity of internal standard in ng;
A_{rs} = Sum of integrated areas for recovery standard; and
R_f = Response factor.

Quantification

The PCDD/PCDF isomers and congener class concentrations were determined by comparing the sum of the two ion masses monitored for each class to the sum of the two ion masses monitored for the corresponding internal standard. It was assumed that the response factors for each of the individual isomers in a class were the same as the response factors calculated for the specific isomers present in the standard solutions. The response factors were calculated from six replicate analyses of standard solutions at four concentrations. The sum of the two most intense ion masses in the molecular ion region of each isomer were used to generate the response factors.

The formula used for quantifying the PCDD/PCDF isomers was:

$$\text{Quantity/Sample (ng/g)} = \frac{A_c \times Q_{is}}{A_{is} \times R_f \times W}$$

Where:

Quantity = Total quantity in ng of target isomer or congener class
A_c = Sum of integrated areas for the target isomer or congener class
Q_{is} = Quantity of internal standard in ng
A_{is} = Total integrated areas for the internal standard
R_f = Response factor.

Each pair of resolved peaks in the selected-ion-current chromatograms was evaluated manually to determine if it met the criteria for a PCDD or PCDF isomer. By examining each pair of peaks separately, quantitative accuracy was improved over what is obtained when all of the peaks in a selected chromatographic window are averaged. When averaged data are used, it is possible for pairs of peaks with high and low chlorine isotope ratios to produce averaged data that meet the chlorine isotope ratio criterion. For example, two pairs of peaks having chlorine isotope ratios of 0.56 and 0.96, both outside of the acceptable range, would have an average ratio of 0.76. By checking the isotope ratio of these peaks separately, they would be eliminated from the class total.

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Quantitation

Quantitation was performed by isotope dilution using the ^{13}C-labeled internal standards added before extraction. Concentrations were determined from C^{12}/C^{13} ratios of sample analyte to internal standard and a linear fit to the five-point calibration curves. A separate calibration curve was generated for 2,3,4,7,8-PnCDF. All other PnCDFs were quantitated from the 1,2,3,7,8-PnCDF calibration curve. A separate calibration curve was produced for 2,3,4,6,7,8-HxCDF. All other HxCDFs and HpCDFs were quantitated from the 1,2,3,4,7,8-HxCDF calibration curve. OCDD and OCDF were quantitated from the OCDD-^{13}C calibration curve. Congener class total concentrations were calculated by summing concentrations of each peak which passed the identification criteria for the congener class. Surrogate recoveries were determined using the mean 500 ng/mL response factor from the calibration checks made at the start and end of the analyses.

One sample (41159-11-13), had a severe interference which coeluted with the TCDF-^{13}C peaks. TCDFs in this sample were quantitated verus the area of the PnCDF-^{13}C quantitating ion with a normalization factor of 1.1 (the average ratio of TCDF-^{13}C to PnCDF-^{13}C response).

Detection Limits

Instrumental detection limits were defined as the analyte concentration which gave a 3:1 signal-to-noise ratio. Method detection limits for all analytes were approximately 3 ng/g except OCDF and OCDD which were 10 ng/g due to peak broadening at the later retention times. The lowest point on the calibration curves, 40 ng/mL, corresponds to a sample concentration of 8 ng/g.

Procedures Used by Battelle (4)

Analysis--

The sample extracts were instrumentally analyzed in triplicate and quantified for PCDD/PCDF using combined capillary column gas chromatography/high resolution mass spectrometry (HRGC/HRMS). The HRGC/HRMS consisted of a Carlo Erba Model 4160 Gas Chromatograph interfaced directly into the ion source of a VG Model 7070 high resolution mass spectrometer. The chromatographic column was a 60 M DB-5 fused silica column using helium carrier gas at a flow velocity of 30 cm/sec. The mass spectrometer was operated in the electron impact (EI) ionization mode at a mass resolution of 9000-12000 (M/ΔM, 10 percent valley definition). All HRGC/HRMS data were acquired by multiple-ion-detection (MID) using a VG Model 2035 Data System.

Recovery of Internal Standards--

The recoveries of the internal standards were calculated by comparison to an external standard, 1,2,3,4-TCDD-$^{13}C_{12}$ which was added following the column cleanup steps. Relative response factors were determined from triplicate analyses of a

standard mixture containing the labelled internal standards and the 1,2,3,4-TCDD-$^{13}C_{12}$. The equation used to calculate the recoveries was:

$$\text{Recovery (\%)} = \frac{A_{is} \times Q_{rs} \times 100}{A_{rs} \times Q_{is} \times R_f}$$

Where:

A_{is} = Sum of integrated areas for internal standard;
Q_{rs} = Quantity of recovery standard in ng;
Q_{is} = Quantity of internal standard in ng;
A_{rs} = Sum of integrated areas for recovery standard; and
R_f = Response factor.

Quantification

The PCDD/PCDF isomers and congener class concentrations were determined by comparing the sum of the two ion masses monitored for each class to the sum of the two ion masses monitored for the corresponding internal standard. It was assumed that the response factors for each of the individual isomers in a class were the same as the response factors calculated for the specific isomers present in the standard solutions. The response factors were calculated from six replicate analyses of standard solutions at four concentrations. The sum of the two most intense ion masses in the molecular ion region of each isomer were used to generate the response factors.

The formula used for quantifying the PCDD/PCDF isomers was:

$$\text{Quantity/Sample (ng/g)} = \frac{A_c \times Q_{is}}{A_{is} \times R_f \times W}$$

Where:

Quantity = Total quantity in ng of target isomer or congener class
A_c = Sum of integrated areas for the target isomer or congener class
Q_{is} = Quantity of internal standard in ng
A_{is} = Total integrated areas for the internal standard
R_f = Response factor.

Each pair of resolved peaks in the selected-ion-current chromatograms was evaluated manually to determine if it met the criteria for a PCDD or PCDF isomer. By examining each pair of peaks separately, quantitative accuracy was improved over what is obtained when all of the peaks in a selected chromatographic window are averaged. When averaged data are used, it is possible for pairs of peaks with high and low chlorine isotope ratios to produce averaged data that meet the chlorine isotope ratio criterion. For example, two pairs of peaks having chlorine isotope ratios of 0.56 and 0.96, both outside of the acceptable range, would have an average ratio of 0.76. By checking the isotope ratio of these peaks separately, they would be eliminated from the class total.

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The criterion that were used to identify PCDD and PCDF isomers were:

1. Simultaneous responses at both ion masses.
2. Chlorine isotope ratio within +/-15% of the theoretical value.
3. Chromatographic retention times within windows determined from analyses of standard mixtures.
4. Signal-to-noise ratio equal to or greater than 2.5 to 1.0.

The individual isomers for which a isotopically labelled analog was available included the additional criterion that they eluted within 2 seconds of the internal standard.

The limit of detection (LOD) was calculated for samples in which isomers of a particular chlorine congener class were not detected. The formula used for calculating the LOD was:

$$LOD/g\ (ng) = \frac{H_c \times Q_{is} \times 2.5}{H_{is} \times R_f \times W}$$

Where:

LDD = Single isomer limits of detection for a congener class in ng;
H_c = Height of congener class isomer;
Q_{is} = Quantity of internal standard in ng;
H_{is} = Peak height of internal standard;
R_f = Response factor; and
W = Weight in grams of sample.

Calibration Curve

Calibration curves were generated for each of the native/isotopically labelled isomer pairs. The calibration standards were analyzed at least five times at each of four concentration levels between 0.04 and 2.5 parts-per-million (ppm). The repsonse factors were calculated by dividing the sum of the areas for the two most abundant ion masses in the molecular ion cluster of each native PCDD/PCDF isomer by the sum of the areas for the corresponding ion masses from the isotopically labelled standard. The isomer pairs for which response factors were calculated included:

2,3,7,8-TCDD vs 2,3,7,8-TCDD-$^{13}C_{12}$
2,3,7,8-TCDF vs 2,3,7,8-TCDF-$^{13}C_{12}$
OCDD vs OCDD-$^{13}C_{12}$
OCDF vs OCDD-$^{13}C_{12}$
1,2,3,7,8-Penta-CDF vs 1,2,3,7,8-Penta-CDF-$^{13}C_{12}$
2,3,4,7,8-Penta-CDF vs 1,2,3,7,8-Penta-CDF-$^{13}C_{12}$
1,2,3,4,7,8-Hexa-CDF vs 1,2,3,4,7,8-Hexa-CDF-$^{13}C_{12}$
2,3,4,6,7,8-Hexa-CDF vs 1,2,3,4,7,8-Hexa-CDF-$^{13}C_{12}$
1,2,3,4,6,7,8-Hepta-CDF vs OCDD-$^{13}C_{12}$

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It was assumed that each of the isomers of a particular chlorine congener class had the same response factor.

Detection Limits

Detection limits were calculated for samples that did not contain PCDD/PCDF isomers in a particular class. These detection limits were calculated using the quantification equation with the addition of a factor of 2.5 to account for the signal-to-noise criterion.

The noise level was measured as the average of the peak-to-peak noise that occurred in the baseline of the particular MID channel. If at all possible, the noise was measured at the retention time of the isotopically labelled internal standard. The height of the internal standard peak was measured to the average of the noise that occurred on the peak top. The reported limits of detection are for single PCDD/PCDF isomers and have been corrected for recovery losses during sample workup.

Baseline Analyses--

The three baseline samples, Aroclor 1260, Aroclor 1254, and Aroclor 1016 were analyzed using the methodology described above. The Aroclor 1016 presented the greatest analytical problem due to the relatively high amount of the sample that passed through the column cleanup steps. Even after the four column cleanup steps, a noticeable polychlorinated biphenyl (PCB) background was evident in the single ion current chromatograms.

In-Service Analyses--

The seven in-service samples were also analyzed using the methodology described above.

QUALITY CONTROL

Each participating laboratory followed their own extensive quality control program which has been previously reported (1-4).

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SECTION 3
RESULTS AND DISCUSSION OF STATISTICAL ANALYSIS

EVALUATION OF CALIBRATION MODEL

The calibration data from four of the five participating laboratories in the Round Robin Study was evaluated in terms of the regressions employed, i.e. their appropriateness and linearity over the range of interest for PCDD and PCDF congener analysis (data from Lab C was not available for regression analysis).

For each of the labs, the calibration model is:

$$LOG_{10}\ (y) = a + b\ LOG_{10}\ (x)$$

Where x = concentration

$$y = \begin{cases} \text{response ratio for LAB-A} \\ \text{peak area ratio for LAB-B} \\ \text{area ratios for LAB-D} \\ \text{normalized counts for LAB-E} \end{cases}$$

Exponentiating, the model becomes

$$y = 10^a \cdot x^b$$

Since b is approximately equal to one for each lab and compound, the model can be simplified to

$$y = CX$$

where $C = 10^a$

Tables 20 to 24 give the estimates of C for each lab and compound.

Where

$$C = \frac{y}{x}$$

The intercepts in Tables 21 through 24, except for 2,3,7,8-TCDF (Table 24) were all significantly different from zero at the 0.01 level. Thus, if laboratories employed regression models using a zero intercept, considerable error in the calibration would result. For example, the regression model used by Lab-E was inappropriate (See Appendix A). Discussions with the Lab-E Project Director at this laboratory indicated that the isotopic response ratios of $^{13}C/^{12}C$-PCDF and PCDD congeners were used for quantification, thus, the results reported did not employ the reported regressions. All other laboratories used regression models in which the regression was not forced through the zero intercept.

TABLE 20. CONVERSION FACTORS

	LAB-A	LAB-B	LAB-D	LAB-E
2,3,7,8-TCDD	0.002227	0.003117	0.001994	0.6901
2,3,7,8-TCDF	0.001916	0.003795	0.002293	1.0950
1,2,3,7,8-PNCDF	0.001661	0.003915	0.002513	0.8904
2,3,4,7,8-PNCDF	0.001713	0.003916	0.002601	0.7414
1,2,3,4,7,8-HXCDF	0.001947	0.003657	0.002211	0.6701
2,3,4,6,7,8-HXCDF	0.002217	0.006736	0.002275	0.4082
1,2,3,4,6,7,8-HPCDF	0.002677	0.004121	0.001679	0.3281
OCDF	0.0009404	0.000611	0.001395	0.0469

TABLE 21. CALIBRATION CURVES: LAB-A

$$Y = LOG_{10}\left(\frac{\text{Average Response Factor} \times \text{Concentration}}{500}\right)$$

$$X = LOG_{10}\ (\text{Concentration})$$

	NUMBER OF OBSERVATIONS	INTERCEPT	SLOPE	R^2
2,3,7,8-TCDD	5	-2.704**	1.020**	0.9994
2,3,7,8-TCDF	6	-2.731**	1.005**	0.9997
1,2,3,7,8-PNCDF	6	-2.819**	1.016**	0.9999
2,3,4,7,8-PNCDF	6	-2.702**	0.973**	0.9996
1,2,3,4,7,8-HXCDF	6	-2.769**	1.023**	0.9999
2,3,4,6,7,8-HXCDF	6	-2.632**	0.991**	0.9998
1,2,3,4,6,7,8-HPCDF	6	-2.600**	1.011**	0.9998
OCDF	6	-2.906**	0.949**	0.9980

**Significantly different from zero at .01 level.

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TABLE 22. CALIBRATION CURVES: LAB-B

$$Y = LOG_{10}\left(\frac{\text{Average Response Factor} \times \text{Concentration}}{300}\right)$$

$$X = LOG_{10}\ (\text{Concentration})$$

	NUMBER OF OBSERVATIONS	INTERCEPT	SLOPE	R^2
2,3,7,8-TCDO	25	-2.475**	0.985**	0.9991
2,3,7,8-TCDF	25	-2.432**	1.005**	0.9997
1,2,3,7,8-PNCDF	25	-2.418**	1.005**	0.9994
2,3,4,7,8-PNCDF	25	-2.414**	1.003**	0.9996
1,2,3,4,7,8-HXCDF	25	-2.468**	1.014**	0.9996
2,3,4,6,7,8-HXCDF	25	-2.184**	1.006**	0.9991
1,2,3,4,6,7,8-HPCDF	25	-2.410**	1.011**	0.9994
OCDF	25	-3.470**	1.091**	0.9918

* Significantly different from zero at .05 level.

** Significantly different from zero at .01 level.

TABLE 23. CALIBRATION CURVES: LAB-D

$$Y = LOG_{10}\ (\text{Average Area Ratio})$$
$$X = LOG_{10}\ (\text{Concentration})$$

	NUMBER OF OBSERVATIONS	INTERCEPT	SLOPE	R^2
2,3,7,8-TCDD	4	-2.691**	0.996**	0.9993
2,3,7,8-TCDF	4	-2.609**	0.988**	0.9999
1,2,3,7,8-PNCDF	4	-2.600**	1.000**	0.9999
2,3,4,7,8-PNCDF	4	-2.636**	1.020**	0.9998
1,2,3,4,7,8-HXCDF	4	-2.634**	0.991**	0.9999
2,3,4,6,7,8-HXCDF	4	-2.617**	0.989**	0.9999
1,2,3,4,6,7,8-HPCDF	4	-2.778**	1.001**	0.9999
OCDF	3	-2.762**	0.966**	0.9995

* Significantly different from zero at .05 level.

** Significantly different from zero at .01 level.

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TABLE 24. CALIBRATION CURVES: LAB-E

$Y = LOG_{10}$ (Raw Counts)
$X = LOG_{10}$ (Concentration)

	NUMBER OF OBSERVATIONS	INTERCEPT	SLOPE	R^2
2,3,7,8-TCDD	18	-0.286**	1.047**	0.9945
2,3,7,8-TCDF	18	0.004	1.014**	0.9994
1,2,3,7,8-PNCDF	18	-0.144**	1.037**	0.9977
2,3,4,7,8-PNCDF	18	-0.230**	1.038**	0.9960
1,2,3,4,7,8-HXCDF	18	-0.259**	1.032**	0.9958
2,3,4,6,7,8-HXCDF	18	-0.547**	1.058**	0.9893
1,2,3,4,6,7,8-HPCDF	18	-0.668**	1.067**	0.9875
OCDF	18	-1.762**	1.142	0.9779

* Significantly different from zero at .05 level.

** Significantly different from zero at .01 level.

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The slopes were very nearly unity and the R^2 of the regression indicated excellent linearity over the three orders of magnitude concentration range used for calibrating the instrumentation (Tables 21-24).

RESULTS OF ROUND ROBIN

Statistical analysis of the PCDD and PCDF concentration data first required the establishment of a standard reporting format for all of the laboratories. To satisfy this requirement, the following data conversions were performed:

1) For LAB-C 1,2,3,6,7,8-HXCDF was excluded because it was not reported separately but in combination with 1,2,3,4,7,8-HXCDF.
2) If measured amounts were not reported, then detection limits were substituted, if available.
3) For those labs which separately reported 2,3,7,8- and 2,3,4,8- TCDF, or 1,2,3,7,8- and 1,2,3,4,8-PCDF, or 1,2,3,4,7,8- and 1,2,3,4,7,9-HXCDF, the reported concentrations of the pairs were added together (in order to conform with the reporting format of the other laboratories).

Table 8-1 in Appendix 8 gives a listing of the data. Measured concentrations (ng/g) for each of the individual instrumental determinations of a single extract are shown, along with the means and standard deviations of the determinations, by laboratory, sample, and compound. Since LAB-E reported only one instrumental determination of a single extract for each sample and compound, only that measured concentration is given. LAB-D reported results for three extracts for each sample with three instrumental determinations for each extract. These extract results are listed separately. LAB-A reported six determinations for OCDD in sample 11 and 1,2,3,7,8,9-HXCDF in sample 12. Large ranges in concentrations are evident -- for example, by comparing the means among compounds within a sample 1 for LAB-A 1,2,3,4,6,7,8-HPCDF has an average concentration of 354 while OCDD has an average concentration of 2.08. Also, the standard deviations (precision) show great variation in magnitude. Because of this variation in standard deviations, equal variances could not be assumed. Since the standard deviations tended to increase as the concentration levels increased, basic data transformations of taking logarithms and square roots were tried. These, unfortunately, did not correct the problem. This limited the types of statistical tests that could be performed since many depend on the equality of variances.

The coefficients of variations (CVs) which represents precision of the analytical methods for the labs, excluding LAB-E, are given in Table 25. Only those concentrations reported as measured amounts rather than detection limits were included in the calculations. There appears to be little relation between the measured concentration and the CV, i.e., the CV does not tend to increase or decrease as the measured concentration increases. These CVs are summarized in

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TABLE 25. COEFFICIENTS OF VARIATION BY COMPOUND, LAB, AND SAMPLE

Sample	LAB-A	LAB-B	LAB-C	LAB-D-1	LAB-D-2	LAB-D-3
COMPOUND = TOTAL TCDF						
1	16.1	9.4	15.8	5.6	6.5	1.9
2	3.8	0.9	8.7	2.4	4.2	1.0
3	1.3	3.1	27.0	6.6	4.4	1.3
11	47.0	8.6	61.0	13.7	12.0	6.2
12	58.9	4.9	27.7	6.8	3.1	18.3
13	18.5	12.1	26.0	11.3	11.5	12.6
14	23.9	30.0	30.1	10.5	3.6	2.1
15	27.6	.[a]	.	.	.	.
16	21.7	.	.	.	.	.
17	4.3	22.3	22.2	11.9	9.4	0.6
COMPOUND = TOTAL PNCDF						
1	10.8	3.1	41.5	7.6	3.6	20.9
2	10.2	0.7	13.9	0.8	2.7	1.1
3	2.0	5.8	8.3	11.8	10.6	5.0
11	6.9	9.7	50.4	15.4	2.0	0.2
12	19.2	4.7	56.9	13.6	2.6	2.3
13	3.2	10.8	10.2	17.5	6.5	6.1
14	2.9	23.7	31.5	28.5	3.1	1.2
15	10.9	.	.	.	.	.
16	8.8*	61.6	.	.	.	.
17	3.1	22.5	10.8	12.1	11.1	8.8
COMPOUND = TOTAL HXCDF						
1	13.1	1.0	137.1	1.3	1.0	1.7
2	5.8	2.3	83.3	1.7	0.9	4.8
3	3.5	2.1	64.6	10.9	30.3	1.9
11	2.6	14.1	99.3	11.9	1.8	1.8
12	4.6	3.7	20.3	8.5	5.7	5.1
13	14.6	27.5	10.7	22.5	18.4	25.9
14	1.9	4.0	55.3	12.4	6.2	1.0
15	36.2	.	.	44.1	5.6	24.1
16	16.8	54.0	.	47.0	.	.
17	1.7	14.0	42.0	9.2	1.3	0.3
COMPOUND = TOTAL HPCDF						
1	4.4	10.9	96.2	9.7	5.1	2.4
2	11.8	20.4	76.1	3.2	4.3	6.3
3	3.6	16.8	65.6	2.7	6.6	7.1
11	8.6	19.2	52.2	18.3	0.8	3.1
12	14.3	20.2	28.6	13.9	5.3	4.2
13	21.4	39.4	62.4	.	3.5	.
14	2.6	14.1	21.9	19.4	18.2	1.9
15	56.2	62.9*	.	38.7	12.8	10.2
16	.	58.9	.	70.1	.	.
17	6.5	22.6	18.3	15.1	5.4	1.2

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TABLE 25 (cont'd.)

Sample	LAB-A	LAB-B	LAB-C	LAB-D-1	LAB-D-2	LAB-D-3
COMPOUND = TOTAL OCDF						
1	7.9	.	.	26.5*	.	.
2	10.8	45.8	.	1.6	4.1	5.5
3	3.3	30.6	32.6	2.9	6.0	5.4
11	5.7	23.8	14.4	13.6	8.5	5.0
12	8.8	12.7	10.8	12.2	2.4	4.1
13	10.7	.	60.7	39.0	4.4	4.2
14	2.5	40.3	20.0	4.5	11.8	16.8
15	34.1	.	.	4.8	2.6	4.7
16	.	.	.	47.8	27.4	.
17	8.9	8.8	8.5	12.3	3.6	2.1
COMPOUND = TOTAL TCDD						
1	11.8	17.0	.	2.3	4.0	4.3
2	16.0	2.2	2.5	3.0	2.3	3.1
3	3.3	9.2	15.8	1.7	5.3	1.6
14	56.6*	.	.	.	.	.
16	43.9*	.	.	.	.	.
COMPOUND = OCDD						
11	25.1**	14.5	91.7	.	.	.
12	.	18.1	.	.	.	.
13	19.0	6.9	.	.	.	.
14	3.0	46.6	.	.	.	.
15	11.5	24.4	.	.	.	.
16	12.2	9.9	11.8	.	8.3	.
17	20.5	28.5	30.1	.	.	.
COMPOUND = 2,3,7,8-TCDD						
1	11.8	17.0	11.4	2.3	4.0	4.3
2	16.0	2.2	2.5	3.0	2.3	3.1
3	3.3	9.2	15.8	1.7	5.3	1.6
COMPOUND = 2,3,7,8 + 2,3,4,8-TCDF						
1	15.5	9.4	15.8	5.6	6.5	1.9
2	4.5	0.9	8.7	2.4	4.2	1.0
3	0.8	1.0	19.5	1.1	3.8	2.2
11	24.3	45.7	16.4	9.6	0.0	2.9
12	21.1	4.3	24.7	11.5	5.4	15.9
13	16.5	4.4	15.6	9.9	5.6	2.2
14	16.3	9.1	6.7	9.7	2.1	1.2
15	9.3	.	.	.	.	.
16	16.4		.	.	.	.
17	3.7	22.0	15.6	14.5	6.4	1.1

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TABLE 25 (cont'd.)

Sample	LAB-A	LAB-B	LAB-C	LAB-D-1	LAB-D-2	LAB-D-3
COMPOUND = 1,2,3,7,8 + 1,2,3,4,8-PNCDF						
1	12.0	2.1	11.5	1.4	3.0	0.7
2	11.5	1.8	3.1	1.3	2.1	1.0
3	0.9	4.1	13.6	4.0	6.8	3.7
11	12.9	6.3	31.6	10.4	2.1	2.2
12	26.1	4.8	23.1	16.6	4.5	2.9
13	8.4	7.1	12.8	6.3	7.5	0.0
14	3.8	4.6	7.3	15.6	17.3	5.7
15	11.7	.	.	.	.	.
16	.	61.1	.	.	.	.
17	4.0	14.9	2.2	11.5	18.4	4.5
COMPOUND = 2,3,4,7,8-PNCDF						
1	11.1	4.2	60.1	13.8	2.1	2.1
2	15.3	1.8	23.4	0.4	3.3	1.4
3	2.9	4.4	37.8	0.7	5.2	2.8
11	2.9	5.8	9.4	32.4	3.7	2.7
12	22.2	10.1	5.1	22.0	3.2	5.3
13	8.7	6.3	17.2	10.9	1.8	2.5
14	1.4	5.8	14.8	20.1	1.3	1.9
15	11.0	.	.	.	.	.
16	14.1*	60.1	.	.	.	.
17	7.2	13.7	7.3	22.0	4.9	4.9
COMPOUND = 1,2,3,4,7,8 + 1,2,3,4,7,9-HXCDF						
1	13.2	0.6	36.7	1.3	2.4	3.7
2	40.2	34.6	.	.	.	.
3	3.2	3.5	8.6	1.9	2.0	3.0
11	2.1	13.9	100.9	8.0	1.7	1.7
12	1.9	6.6	16.0	10.1	0.6	4.7
13	17.0	23.1	38.6	7.5	2.3	3.4
14	0.6	1.2	30.8	9.9	16.3	3.4
15	35.8	.	.	57.3	4.3	27.2
16	5.8	59.2	.	38.6	.	19.2
17	5.4	14.1	43.0	10.3	0.8	0.9
COMPOUND = 1,2,3,7,8,9-HXCDF						
3	5.4	.	80.9	4.7	5.1	1.3
11	.	.	82.3	11.0	4.4	2.3
12	27.1**	.	20.3	6.9	5.4	1.5
13	33.2	.	36.5	.	24.1	15.7*
14	4.8	15.7	88.5	14.0	26.9	1.1
15	42.4	.	.	.	.	.
16	.	61.9	.	.	.	.
17	.	.	53.3	4.8	2.3	4.4

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TABLE 25 (cont'd.)

Sample	LAB-A	LAB-B	LAB-C	LAB-D-1	LAB-D-2	LAB-D-3
COMPOUND = 1,2,3,6,7,8-HXCDF						
1	14.9	0.0	.	4.1	5.9	8.1
2	3.4	2.5	.	5.3	2.7	7.6
3	4.0	3.2	.	5.2	9.3	2.0
11	1.0	19.6	.	7.0	20.8	1.3
12	2.7	5.3	.	8.1	7.9	27.6
13	12.3	27.2	.	.	10.2	.
14	1.7	2.6	.	7.6	14.7	16.0
15	34.9	.	.	.	.	.
16	.	64.9	.	.	.	.
17	3.0	2.0	.	7.9	22.5	8.7
COMPOUND = 2,3,4,5,7,8-HXCDF						
1	6.2	1.5	159.1	2.2	1.6	1.3
2	7.3	4.2	86.9	0.4	0.4	3.7
3	4.8	4.7	80.9	1.2	11.4	2.1
11	12.7	13.4	121.3	15.3	4.0	0.5
12	25.0	19.5	30.6	21.7	3.2	5.4
13	8.8	31.5	41.2	.	10.2	23.6
14	5.2	13.7	125.1	11.2	26.2	2.0
16	.	51.3	.	.	.	.
17	12.3	19.2	52.7	5.8	1.6	5.5
COMPOUND = 1,2,3,4,6,7,8-HPCDF						
1	4.0	10.9	96.2	9.7	5.1	2.4
2	11.7	20.4	76.1	3.2	4.3	6.3
3	4.1	12.1	144.9	1.4	5.4	5.7
11	10.3	17.8	58.9	17.6	0.7	4.0
12	9.9	18.7	36.9	14.9	5.5	4.9
13	21.1	31.6	60.9	.	7.5	.
14	1.6	11.5	39.9	20.4	17.6	1.2
15	.	60.6*	.	21.7	6.7	10.3
16	.	53.4	.	57.4	.	.
17	3.4	23.9	29.2	14.9	4.8	1.6

* Based on two rather than three determinations.

** Based on six rather than three determinations.

a. * No measurable value reported, i.e., not detected, therefore no CV was calculated.

Table 26 showing the minimum, median, and maximum CVs over all compounds by laboratory and sample. Overall, Lab-C shows the largest median and maximum values for CVs, but there is also variation among the other laboratories.

TABLE 26. MINIMUM, MEDIAN, AND MAXIMUM CVs BY LAB AND SAMPLE OVER ALL COMPOUNDS

	Sample							
	1	2	3	11	12	13	14	17
MINIMUM								
LAB-A	4.01	3.45	0.83	0.99	1.90	3.25	0.57	1.71
LAB-B	0.00	0.67	1.02	5.83	3.71	4.41	1.24	1.96
LAB-C	11.36	2.55	8.33	9.36	5.13	10.20	6.68	2.16
LAB-D-1	1.25	0.40	0.74	6.97	6.84	6.25	4.48	4.64
LAB-D-2	0.98	0.41	2.04	0.00	0.58	1.75	1.28	0.83
LAB-D-3	0.71	0.96	1.31	0.17	1.55	0.00	0.98	0.14
MEDIAN								
LAB-A	11.78	11.15	3.26	8.63	19.21	15.54	2.86	4.34
LAB-B	4.25	2.25	4.56	14.10	6.62	17.63	12.62	19.22
LAB-C	41.53	13.87	29.82	58.92	23.94	31.23	30.49	22.18
LAB-D-1	4.85	2.44	2.68	13.60	12.22	11.08	12.39	11.91
LAB-D-2	4.00	2.70	5.39	2.08	4.54	7.83	14.61	[illegible]
LAB-D-3	2.40	3.08	2.21	2.53	4.92	8.24	1.93	2.07
MAXIMUM								
LAB-A	16.06	40.29	5.42	46.96	58.89	33.18	58.57	20.47
LAB-B	16.99	45.81	30.59	45.73	20.24	39.41	46.63	23.49
LAB-C	159.06	86.90	144.88	121.26	56.85	62.39	125.10	53.75
LAB-D-1	26.52	5.30	11.82	32.44	22.05	39.04	28.47	22.04
LAB-D-2	6.53	4.29	30.30	20.80	7.86	24.12	26.89	22.61
LAB-D-3	20.86	7.64	7.11	6.21	27.56	26.91	16.84	8.34

The spiked versus measured amounts in samples 1 and 2 are compared in Tables 27 and 28. The percent accuracy by compound, lab, and sample for the arithmetic mean, the geometric mean, the minimum, and the maximum are given in Table 27. The percent accuracy was determined by calculating the summary statistic, dividing by the spiked amount, then multiplying by 100. For example,

$$\% \text{ accuracy mean} = \frac{\text{mean}}{\text{spike}} \times 100$$

With the exception of Total PNCDF; Total HXCDF; 2,3,4,7,8-PNCDF; 2,3,4,6,7,8-HXCDF, and 1,2,3,4,6,7,8-HPCDF for LAB-C, these numbers generally fall in the 50 to 150 range.

To summarize the percent found, Table 28 gives the minimum, median, and maximum percent found by laboratory. Percent found expresses each determination as a percentage of the spiked amount similar to the formula above. LAB-C had the

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TABLE 27. PERCENT ACCURACY FOR SPIKED SAMPLES BY COMPOUND, SAMPLE, AND LAB

Lab	Sample 1				Sample 2			
	Arithmetic Mean	Geometric Mean	Minimum	Maximum	Arithmetic Mean	Geometric Mean	Minimum	Maximum
COMPOUND = TOTAL HCDF								
Lab A	89.0	88.2	72.5	97.5	118.9	119.0	114.7	123.0
Lab B	78.5	78.3	73.9	87.0	115.7	115.7	115.1	117.0
Lab C	95.0	94.2	88.0	110.0	129.5	119.2	107.5	126.4
Lab D Ext 1	88.0	88.3	84.0	94.0	118.2	118.2	115.1	120.0
Lab D Ext 2	92.3	92.5	88.0	99.5	112.0	112.5	107.5	117.0
Lab D Ext 3	92.7	92.7	93.0	94.5	113.0	113.0	113.2	115.1
Lab E	95.0	95.0	95.0	95.0	117.0	117.0	117.0	117.0
COMPOUND = TOTAL PNCDF								
Lab A	94.0	93.6	83.7	104.0	98.7	98.4	87.3	106.3
Lab B	99.0	99.7	97.7	102.3	98.6	98.6	98.1	99.4
Lab C	124.4	118.0	86.7	183.3	164.6	163.5	145.6	189.9
Lab D Ext 1	96.0	96.6	88.3	106.0	95.1	95.3	94.3	95.9
Lab D Ext 2	102.3	102.3	98.3	105.1	98.2	98.2	96.5	101.3
Lab D Ext 3	97.0	96.4	88.1	99.3	96.2	96.2	94.9	96.0
Lab E	106.7	106.7	106.7	106.7	117.3	117.3	117.3	117.5
COMPOUND = TOTAL HXCDF								
Lab A	84.3	83.0	73.7	95.0	114.4	114.3	108.6	123.6
Lab B	98.2	98.2	91.3	99.2	122.2	122.3	120.0	125.4
Lab C	510.2	253.7	82.1	1389.5	1527.9	1152.3	473.0	2910.9
Lab D Ext 1	102.3	102.3	101.5	103.0	102.9	102.9	101.6	104.9
Lab D Ext 2	101.7	101.7	100.0	107.3	105.9	105.9	104.9	106.5
Lab D Ext 3	99.0	99.0	91.9	101.1	105.2	105.1	99.5	108.6
Lab E	103.2	103.2	103.2	103.2	81.1	81.1	81.1	81.1
COMPOUND = TOTAL HPCDF								
Lab A	88.9	88.9	85.3	93.0	119.2	118.7	108.9	135.4
Lab B	91.6	91.2	80.5	100.0	108.5	99.0	74.0	112.7
Lab C	65.3	39.2	8.3	132.5	35.2	20.3	12.4	64.6
Lab D Ext 1	107.9	102.6	97.0	134.5	108.4	104.3	102.5	108.2
Lab D Ext 2	108.4	108.3	102.0	113.0	114.1	114.1	109.7	119.6
Lab D Ext 3	91.0	93.0	91.5	96.0	99.5	99.7	98.3	106.7
Lab E	112.5	112.5	112.5	112.5	119.0	119.0	119.0	119.0
COMPOUND = OCDF								
Lab A	--[a]	--	--	--	91.2	90.0	81.1	100.0
Lab B	--	--	--	--	102.5	94.7	55.3	149.2
Lab C	--	--	--	--	--	--	--	--
Lab D Ext 1	--	--	--	--	96.0	96.0	34.7	97.7
Lab D Ext 2	--	--	--	--	92.9	92.9	89.4	97.0
Lab D Ext 3	--	--	--	--	97.0	96.9	91.7	103.0
Lab E	--	--	--	--	42.4	42.4	42.4	42.4

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TABLE 21 (cont'd.)

Lab	Sample 1				Sample 2			
	Arithmetic Mean	Geometric Mean	Minimum	Maximum	Arithmetic Mean	Geometric Mean	Minimum	Maximum
COMPOUND - TOTAL TCDD								
Lab A	75 3	75 0	60 0	85 2	90 9	90 1	74 1	102 0
Lab B	92 7	81 9	60 0	96 0	101 3	101 2	100 0	101 0
Lab C	10 4	10 4	10 4	10 4	85 5	85 5	83 0	86 0
Lab D Ext 1	90 1	90 6	86 0	100 0	95 6	95 6	92 5	98 1
Lab D Ext 2	100 0	99 9	96 0	104 0	95 6	95 6	94 3	98 1
Lab D Ext 3	92 0	83 1	56 0	96 0	93 7	93 2	90 6	96 2
Lab E	56 0	56 0	56 0	56 0	71 7	71 7	71 1	71 7
COMPOUND - OCDD								
Lab A	--	--	--	--	--	--	--	--
Lab B	--	--	--	--	-	--	--	--
Lab C	--	--	--	--	--	--	--	--
Lab D Ext 1	--	--	--	--	--	--	--	--
Lab D Ext 2	--	--	--	--	--	--	--	--
Lab D Ext 3	--	--	--	--	--	--	--	--
Lab E	--	--	--	--	--	--	--	--
COMPOUND - 1,3,7,8-TCDD								
Lab A	75 3	75 0	60 0	85 2	90 9	90 1	74 1	102 0
Lab B	82 1	81 9	60 0	96 0	101 3	101 2	100 0	101 0
Lab C	81 3	81 0	75 0	92 0	85 5	85 5	83 0	86 0
Lab D Ext 1	90 7	90 6	86 0	100 0	95 6	95 6	92 5	98 1
Lab D Ext 2	100 0	99 9	96 0	104 0	95 6	95 6	94 3	98 1
Lab D Ext 3	92 0	91 9	86 0	96 0	93 2	93 2	90 6	96 2
Lab E	56 0	56 0	56 0	56 0	71 3	71 2	71 7	71 7
COMPOUND - 1,2,7,8 + 1,3,4,8-TCDF								
Lab A	88 8	88 7	73 0	97 5	117 5	117 4	114 2	123 6
Lab B	78 5	78 3	73 5	87 0	115 2	115 2	115 1	117 0
Lab C	95 0	94 2	80 0	110 0	119 5	119 2	102 5	126 4
Lab D Ext 1	88 8	88 7	84 0	94 0	118 2	118 2	115 1	120 0
Lab D Ext 2	92 1	92 5	86 0	99 5	112 6	112 5	102 5	117 0
Lab D Ext 3	92 3	92 1	91 0	94 5	113 0	113 0	113 2	115 2
Lab E	94 5	94 5	94 5	94 5	110 5	110 5	110 5	110 5
COMPOUND - 2,3,7,8 + 1,2,3,7,8 PeCDF								
Lab A	90 3	89 8	80 7	107 0	100 9	100 4	87 5	110 3
Lab B	101 5	101 5	100 0	101 0	104 0	104 0	101 9	105 1
Lab C	100 0	99 6	97 3	103 3	126 0	116 0	113 9	120 3
Lab D Ext 1	97 6	97 5	96 0	98 7	99 4	99 3	98 1	100 1
Lab D Ext 2	91 6	91 6	89 3	93 7	97 0	97 0	95 6	98 4
Lab D Ext 3	94 3	94 3	92 7	96 0	98 5	98 5	97 5	99 4
Lab E	106 7	106 7	106 7	106 7	120 3	120 3	120 3	120 3

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TABLE 27 (cont'd.)

Lab	Sample 1				Sample 2			
	Arithmetic Mean	Geometric Mean	Minimum	Maximum	Arithmetic Mean	Geometric Mean	Minimum	Maximum
COMPOUND = 2,3,4,7,8-PNCDF								
Lab-A	94.0	91.6	84.7	105.3	93.7	92.8	77.2	103.2
Lab-B	98.0	97.9	96.2	102.2	93.0	93.0	91.1	94.3
Lab-C	148.2	130.0	88.0	246.7	206.0	203.1	164.6	259.5
Lab-B Ext 1	98.0	95.0	88.7	104.0	98.9	98.9	98.5	31.1
Lab-B Ext 2	108.7	109.7	102.3	111.3	99.4	99.3	97.5	102.2
Lab-B Ext 3	104.0	104.0	102.0	106.0	93.9	93.9	92.6	94.9
Lab-E	106.7	106.2	105.7	106.7	113.9	113.9	113.9	113.9
COMPOUND = 1,2,3,4,7,8 + 1,2,3,6,7,9-HXCDF								
Lab-A	91.0	90.5	79.6	103.6	--	--	--	--
Lab-B	95.9	95.9	95.7	96.4	--	--	--	--
Lab-C	104.0	98.0	60.0	120.0	--	--	--	--
Lab-B Ext 1	106.0	105.0	104.0	107.2	--	--	--	--
Lab-B Ext 2	102.1	101.0	100.0	105.2	--	--	--	--
Lab-B Ext 3	104.0	104.0	100.0	107.2	--	--	--	--
Lab-E	116.0	116.0	116.0	116.0	--	--	--	--
COMPOUND = 1,2,3,7,8,9-HXCDF								
Lab-A	--	--	--	--	--	--	--	--
Lab-B	--	--	--	--	--	--	--	--
Lab-C	--	--	--	--	--	--	--	--
Lab-B Ext 1	--	--	--	--	--	--	--	--
Lab-B Ext 2	--	--	--	--	--	--	--	--
Lab-B Ext 3	--	--	--	--	--	--	--	--
Lab-E	--	--	--	--	--	--	--	--
COMPOUND = 1,2,3,6,7,8-HXCDF								
Lab-A	91.3	82.8	70.2	94.8	106.7	100.6	203.8	110.8
Lab-B	124.8	124.8	124.8	124.8	111.6	117.6	115.1	120.8
Lab-B Ext 1	102.2	102.6	98.8	106.8	100.8	100.7	103.8	125.2
Lab-B Ext 2	97.3	97.2	94.8	104.8	106.9	106.9	103.8	209.4
Lab-B Ext 3	96.8	85.8	82.8	94.8	113.2	113.8	103.8	126.8
Lab-E	62.8	62.8	62.8	62.8	35.5	35.5	35.5	35.5
COMPOUND = 2,3,4,6,7,8-HXCDF								
Lab-A	91.6	91.5	85.7	92.1	114.1	113.9	106.1	122.7
Lab-B	94.5	94.5	93.1	96.8	123.8	122.9	118.9	129.8
Lab-C	3104.6	313.5	88.8	3372.4	2015.2	2478.8	515.2	3939.4
Lab-B Ext 1	98.1	98.1	96.6	100.6	100.9	100.9	100.8	100.8
Lab-B Ext 2	101.3	101.1	99.8	102.3	105.6	105.6	105.3	106.1
Lab-B Ext 3	98.7	98.7	97.1	99.4	102.8	102.8	97.2	104.5
Lab-E	97.1	97.1	97.1	97.1	83.3	83.3	83.3	83.3

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TABLE 22 (cont'd.)

Lab	Sample 1				Sample 2			
	Arithmetic Mean	Geometric Mean	Minimum	Maximum	Arithmetic Mean	Geometric Mean	Minimum	Maximum
COMPOUND = 1,2,3,4,6,7,8-HPCDF								
Lab-A	88.4	86.4	85.3	92.3	110.9	110.4	109.3	134.0
Lab-B	93.6	91.2	88.5	100.0	100.5	99.0	76.9	112.3
Lab-C	95.3	39.2	9.3	132.5	35.2	26.3	12.1	64.0
Lab-D Ext 1	102.9	102.6	97.0	114.5	108.4	104.3	102.5	108.2
Lab-D Ext 2	108.0	108.3	102.0	113.0	111.1	111.1	109.7	113.4
Lab-D Ext 3	93.0	93.0	91.5	96.0	99.9	99.7	94.3	106.7
Lab-E	112.5	112.5	112.5	112.5	319.0	319.0	319.4	119.0

*Below limit of detection.

TABLE 28. MINIMUM, MEDIAN, AND MAXIMUM PERCENT FOUND (ACCURACY) FOR ALL PCDF AND PCDD CONGENERS IN SPIKED SAMPLES 1 AND 2

	Sample 1			Sample 2		
LAB	Minimum	Median	Maximum	Minimum	Median	Maximum
LAB-A	68.0	87.8	105.3	74.7	106.8	135.4
LAB-B	68.0	96.0	124.0	55.3	112.0	149.2
LAB-C	8.2	94.2	3371.4	12.4	120.3	3939.4
LAB-D	80.7	98.7	114.5	90.5	100.8	120.8
LAB-D	88.0	100.8	113.8	89.4	104.9	119.4
LAB-D	66.7	94.5	107.2	90.6	98.7	120.8
LAB-E	56.0	103.2	116.0	42.4	113.9	120.2

the largest ranges. Among the other laboratories, LAB-B had the highest maximum values, while LAB-E had the lowest minimums.

To provide a better comparison of the analytical method performance among the laboratories, the following steps were taken:

1) Samples 15 and 16 were dropped from further analysis because few compounds were found above the detection limit.
2) To eliminate the missing data for LABS-B and C caused by nonreporting of detection limits, the following values, based upon detection limits reported by LAB-D, were imputed:

Compound	Limit of Detection (ng/g)
Total TCDD	3
OCDD	10
2,3,7,8-TCDD	3
2,3,4,7,8-PCDF	3

Analyses of variance were then run on the altered data to determine the sources of variation. Table 29 gives the total variance by compounds for each laboratory and then breaks it down into sample (different types analyzed) and error (instrumental measurement) variances. Since LAB-E reported only one observation per compound and sample, its variance could not be broken down, but the total variance can be compared with the other labs. Generally, the TCDF, PNCDF, and OCDD compounds showed smaller variances, while OCDF showed the largest variances. There was some variability among laboratories in amount of total variance with LAB-E having a tendency to be higher, but no clear cut patterns emerge. Lab-C had the largest measurement error for almost every congener. The greatest percent of variation, however, was due to sample differences as reflected in comparing percent sample variance with percent measurement error variance.

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TABLE 29. VARIANCE COMPONENTS BY COMPOUND AND LAB

	Variance Components			As Percent of Total	
	Total	Sample	Measurement Error	Sample	Measurement Error
TOTAL TCDF					
LAB-A	1.23	1.14	0.09	93.0	7.0
LAB-B	1.24	1.22	0.02	98.3	1.7
LAB-C	1.33	1.22	0.12	91.1	8.9
LAB-D Ext.-1	1.52	1.51	0.01	99.4	0.6
LAB-D Ext.-2	1.31	1.30	0.01	99.5	0.5
LAB-D Ext.-3	1.37	1.36	0.01	99.5	0.5
LAB-E	1.66	-[a]	-	-	-
TOTAL PNCDF					
LAB-A	1.55	1.54	0.01	99.4	0.6
LAB-B	1.37	1.36	0.02	98.9	1.1
LAB-C	1.57	1.42	0.15	90.3	9.7
LAB-D Ext.-1	1.71	1.68	0.02	98.6	1.4
LAB-D Ext.-2	1.55	1.55	0.00	99.7	0.3
LAB-D Ext.-3	1.60	1.59	0.01	99.5	0.5
LAB-E	1.90	-	-	-	-
TOTAL HXCDF					
LAB-A	3.34	3.33	0.01	99.8	0.2
LAB-B	2.96	2.94	0.01	99.5	0.5
LAB-C	3.50	2.86	0.65	81.6	18.4
LAB-D Ext.-1	4.42	4.41	0.01	99.7	0.3
LAB-D Ext.-2	3.18	3.16	0.02	99.4	0.6
LAB-D Ext.-3	3.38	3.36	0.01	99.7	0.3
LAB-E	4.20	-	-	-	-
TOTAL HPCDF					
LAB-A	4.20	4.19	0.01	99.7	0.3
LAB-B	3.19	3.15	0.05	98.5	1.5
LAB-C	4.65	4.06	0.59	87.3	12.7
LAB-D Ext.-1	6.06	6.04	0.02	99.7	0.3
LAB-D Ext.-2	3.76	3.75	0.01	99.8	0.2
LAB-D Ext.-3	5.55	5.49	0.06	98.9	1.1
LAB-E	5.35	-	-	-	-
OCDF					
LAB-A	10.94	10.93	0.01	99.9	0.1
LAB-B	6.50	6.43	0.07	98.9	1.1
LAB-C	6.46	6.30	0.16	97.5	2.5
LAB-D Ext.-1	8.52	8.48	0.04	99.5	0.5
LAB-D Ext.-2	6.41	6.40	0.00	99.9	0.1
LAB-D Ext.-3	8.19	8.19	0.00	99.9	0.1
LAB-E	9.86	-	-	-	-

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TABLE 29 (cont'd.)

	Variance Components			As Percent of Total	
	Total	Sample	Measurement Error	Sample	Measurement Error
TOTAL TCDD					
LAB-A	5.61	4.34	1.27	77.4	22.6
LAB-B	2.22	2.22	0.00	99.8	0.2
LAB-C	2.24	2.24	0.00	99.8	0.2
LAB-D Ext.-1	2.25	2.25	0.00	99.9+	0.0
LAB-D Ext.-2	2.30	2.30	0.00	99.9+	0.0
LAB-D Ext.-3	2.19	2.19	0.00	99.9+	0.0
LAB-E	7.52	-	-	-	-
OCDD					
LAB-A	2.73	2.15	0.58	78.7	21.3
LAB-B	0.24	0.15	0.09	63.1	36.9
LAB-C	0.59	0.53	0.06	89.2	10.8
LAB-D Ext.-1	-	-	-	-	-
LAB-D Ext.-2	-	-	-	-	-
LAB-D Ext.-3	-	-	-	-	-
LAB-E	0.84	-	-	-	-
2,3,7,8-TCDD					
LAB-A	8.05	6.87	1.18	85.4	14.6
LAB-B	5.46	5.45	0.00	99.9	0.1
LAB-C	2.12	2.12	0.00	99.8	0.2
LAB-D Ext.-1	2.25	2.25	0.00	99.9+	0.0
LAB-D Ext.-2	2.30	2.30	0.00	99.9+	0.0
LAB-D Ext.-3	2.19	2.19	0.00	99.9+	0.0
LAB-E	7.52	-	-	-	-
2,3,7,8 + 2,3,4,8-TDCF					
LAB-A	1.13	1.11	0.02	98.0	2.0
LAB-B	1.32	1.29	0.03	97.6	2.4
LAB-C	1.70	1.67	0.03	98.4	1.6
LAB-D Ext.-1	1.57	1.56	0.01	99.5	0.5
LAB-D Ext.-2	1.43	1.42	0.00	99.8	0.2
LAB-D Ext.-3	1.43	1.43	0.00	99.8	0.2
LAB-E	1.65	-	-	-	-
1,2,3,7,8 + 1,2,3,4,8-PNCDF					
LAB-A	1.70	1.69	0.02	99.0	1.0
LAB-B	1.54	1.54	0.00	99.7	0.3
LAB-C	2.10	2.08	0.03	98.8	1.2
LAB-D Ext.-1	1.94	1.93	0.01	99.5	0.5
LAB-D Ext.-2	1.92	1.91	0.01	99.5	0.5
LAB-D Ext.-3	1.65	1.65	0.00	99.9	0.1
LAB-E	2.02	-	-	-	-

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TABLE 29 (cont'd.)

	Variance Components			As Percent of Total	
	Total	Sample	Measurement Error	Sample	Measurement Error
2,3,4,7,8-PNCDF					
LAB-A	1.27	1.26	0.01	98.9	1.1
LAB-B	1.20	1.20	0.01	99.5	0.5
LAB-C	1.65	1.58	0.08	95.4	4.6
LAB-D Ext.-1	1.30	1.26	0.04	97.0	3.0
LAB-D Ext.-2	1.32	1.32	0.00	99.9	0.1
LAB-D Ext.-3	1.29	1.29	0.00	99.9	0.1
LAB-E	1.76	-	-	-	-
1,2,3,4,7,8 + 1,2,3,4,7,9-HXCDF					
LAB-A	6.47	6.44	0.03	99.6	0.4
LAB-B	7.25	7.22	0.03	99.6	0.4
LAB-C	4.48	4.24	0.24	94.6	5.4
LAB-D Ext.-1	5.93	5.93	0.01	99.9	0.1
LAB-D Ext.-2	5.69	5.69	0.00	99.9	0.1
LAB-D Ext.-3	5.78	5.78	0.00	99.9+	0.0
LAB-E	8.71	-	-	-	-
1,2,3,7,8,9-HXCDF					
LAB-A	7.86	7.48	0.38	95.2	4.8
LAB-B	3.50	3.50	0.00	99.9	0.1
LAB-C	4.68	4.04	0.65	86.2	13.8
LAB-D Ext.-1	4.88	4.86	0.02	99.7	0.3
LAB-D Ext.-2	4.46	4.44	0.02	99.6	0.4
LAB-D Ext.-3	4.86	4.85	0.01	99.8	0.2
LAB-E	6.06	-	-	-	-
1,2,3,6,7,8-HXCDF					
LAB-A	2.99	2.99	0.01	99.8	0.2
LAB-B	2.48	2.46	0.01	99.4	0.6
LAB-C	-	-	-	-	-
LAB-D Ext.-1	3.01	3.00	0.00	99.9	0.1
LAB-D Ext.-2	2.32	2.30	0.02	99.2	0.8
LAB-D Ext.-3	2.85	2.83	0.02	99.3	0.7
LAB-E	3.79	-	-	-	-
2,3,4,6,7,8-HXCDF					
LAB-A	3.27	3.25	0.01	99.5	0.5
LAB-B	2.62	2.59	0.03	99.0	1.0
LAB-C	4.53	3.18	1.38	69.6	30.4
LAB-D Ext.-1	3.11	3.10	0.01	99.6	0.4
LAB-D Ext.-2	1.77	1.76	0.01	99.2	0.8
LAB-D Ext.-3	1.85	1.84	0.01	99.5	0.5
LAB-E	4.27	-	-	-	-

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TABLE 29 (cont'd.)

	Variance Components			As Percent of Total	
	Total	Sample	Measurement Error	Sample	Measurement Error
1,2,3,4,6,7,8-HPCDF					
LAB-A	4.05	4.04	0.01	99.8	0.2
LAB-B	3.01	2.97	0.04	98.7	1.3
LAB-C	3.97	3.10	0.87	78.1	21.9
LAB-D Ext.-1	4.43	4.41	0.02	99.6	0.4
LAB-D Ext.-2	3.32	3.32	0.01	99.8	0.2
LAB-D Ext.-3	4.00	3.94	0.06	98.5	1.5
LAB-E	5.28	-	-	-	-

[a]Below limit of detection.

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For LAB-D, the variance component for repetitive extraction of the same sample could be included because data for three extracts was reported (see Table 30). Here as before, at least 95% of the variance was in the samples with extract and instrumental measurement error contributing little.

To gain further understanding of the differences in variance, Table 31 gives the standard deviations (the square root of the variances) by compound, sample, and laboratory (recalling that each lab used different analytical procedures as described in Section 2.0). The laboratories were then ranked by compound and sample according to the size of the standard deviation, i.e. for TCDF in Sample 1, LAB-D-3 had the smallest standard deviation while LAB-C had the largest. Generally, LAB-C had larger standard deviations (and therefore poorer accuracy and precision from their analytical method). While the other laboratories, excluding LAB-C, show no large differences, LAB-D tended to be lower (and therefore the best accuracy and precision from their analytical method). Also shown are the results of Bartlett's tests for homogeneity of variance among laboratories, by compound and sample (6). Here again, there is variability in the results. For some of the compound-sample combinations, the labs were significantly different at the .01 level while for other combinations the labs were not significantly different at the .05 level.

Table 32 gives the results of Levene's test for homogeneity of variance among laboratories (over samples), by compound (6). For every compound, the laboratories were significantly different from one another at the .05 level, and for all but one compound (1,2,3,6,7,8-HXCDF), they were significantly different from one another at the .01 level.

Table 33 provides approximate 95-percent prediction intervals of levels reported from future analyses of the samples. The seven laboratories (LAB-D included three times) were treated as a random sample from a large population of laboratories, and a variance component, denoted as VL, of the log concentrations due to laboratories (and therefore analytical method used) was thus estimated. A measurement error variance component, VM, was also estimated. This component is the within-extract variance of the log concentrations. Data from the LAB-E were not used in determining this component of variance, since there were no replicate observations. The two components were used to calculate the prediction intervals via the following formula:

$$\exp\{x \pm 2V\},$$

where

x = mean of the log concentrations (across laboratories and extracts), and

V = square root of (VL + VM).

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TABLE 30. VARIANCE COMPONENTS BY COMPOUND FOR LAB-D

Compounds	Variance Components				As Percent of Total		
	Total	Sample	Extract	Error	Sample	Extract	Error
Total TCDF	1.40	1.38	0.01	0.01	98.9	0.6	0.5
Total PNCDF	1.62	1.61	0.00	0.01	99.2	0.0	0.8
Total HXCDF	3.66	3.59	0.05	0.01	98.3	1.3	0.4
Total HPCDF	5.13	5.00	0.09	0.03	97.6	1.8	0.6
OCDF	7.73	7.41	0.30	0.02	95.9	3.9	0.2
Total TCDD	2.25	2.25	0.00	0.00	99.9+	0.0	0.0
OCDD	0.00	0.00	0.00	0.00	99.9+	0.0	0.0
2,3,7,8-TCDD	2.25	2.25	0.00	0.00	99.9+	0.0	0.0
2,3,7,8 + 2,3,4,8-TCDF	1.48	1.47	0.00	0.00	99.5	0.2	0.3
1,2,3,7,8 + 1,2,3,4,8-PNCDF	1.84	1.82	0.01	0.01	99.2	0.4	0.4
2,3,4,7,8-PNCDF	1.31	1.30	0.00	0.01	98.9	0.0	1.1
1,2,3,4,7,8 + 1,2,3,4,7,9-HXCDF	5.80	5.80	0.00	0.00	99.9	0.0	0.1
1,2,3,7,8,9-HXCDF	4.73	4.71	0.01	0.01	99.5	0.2	0.3
1,2,3,6,7,8-HXCDF	2.73	2.69	0.02	0.01	98.6	0.8	0.5
2,3,4,6,7,8-HXCDF	2.25	2.16	0.08	0.01	96.1	3.4	0.5
1,2,3,4,6,7,8-HPCDF	3.92	3.87	0.02	0.03	98.7	0.5	0.7

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TABLE 31. STANDARD DEVIATIONS, THEIR RANKS, AND BARTLETT'S TEST BY COMPOUND AND SAMPLE

	Standard Deviations							Ranks					
Sample	LAB-A	LAB-B	LAB-C	LAB-D-1	LAB-D-2	LAB-D-3	BT	LAB-A	LAB-B	LAB-C	LAB-D-1	LAB-D-2	LAB-D-3
COMPOUND = TOTAL TCDF													
1	28.56	14.80	30.00	10.02	12.10	3.51		5	4	6	2	3	1.0
2	2.36	0.58	5.51	1.93	2.52	0.56		4	1	6	3	5	2
3	20.82	49.32	366.82	99.15	65.51	20.89	**	2	3	6	5	4	1
11	108.01	9.33	85.08	19.87	20.31	10.44	*	6	1	5	3	4	2
12	182.17	6.35	20.61	4.58	3.06	19.60	**	6	3	5	2	1	4
13	143.93	60.92	130.00	97.12	92.47	109.61		4	1	5	3	2	6
14	263.04	216.61	217.03	92.49	30.75	16.45	*	6	4	5	3	2	1
17	23.39	16.12	85.06	59.87	39.55	3.21	*	2	6	5	4	3	1
COMPOUND = TOTAL PNCDF													
1	30.51	9.29	155.03	21.94	11.14	84.93	*	4	1	6	3	2	5
2	31.75	2.08	72.11	2.52	8.39	3.46	**	5	1	6	2	4	3
3	26.46	46.37	100.00	166.96	194.52	67.88		1	2	4	6	5	3
11	123.42	166.86	960.31	312.68	41.87	3.52	**	3	4	6	5	2	1
12	74.91	15.26	177.30	42.45	7.09	7.23	**	5	3	6	4	1	2
13	11.53	27.10	25.17	46.48	20.84	26.51		1	5	3	6	2	4
14	300.00	1722.66	2542.31	2889.85	278.13	123.15	**	3	4	5	6	2	1
17	35.12	214.48	84.29	181.04	131.23	108.53		1	6	2	5	4	3
COMPOUND = TOTAL HXCDF													
1	52.63	4.51	3504.8	6.08	4.72	7.94	**	5	1	6	3	2	4
2	12.22	5.28	2354.6	3.21	1.13	9.29	**	5	3	6	2	1	4
3	86.22	48.17	7689.8	271.01	622.22	42.15	**	3	2	6	4	5	1
11	172.14	913.30	24055.4	828.67	126.26	131.05	**	3	5	6	4	1	2
12	43.02	14.37	257.8	65.04	49.90	44.66		2	4	6	5	4	3
13	6.49	17.35	15.3	3.61	9.45	11.63		2	6	5	1	3	4
14	200.00	413.63	12765.5	1217.54	590.93	96.11	**	2	3	6	5	4	1
17	30.55	283.29	6600.9	206.65	30.23	6.08	**	2	5	6	4	2	1
COMPOUND = TOTAL HPCDF													
1	15.57	40.00	251.02	40.19	22.03	9.02	**	2	4	6	5	3	1
2	23.90	107.96	140.80	17.32	25.77	32.86	**	4	5	6	1	2	3
3	85.44	175.86	1172.40	64.84	147.14	148.19	**	2	5	6	1	3	4
11	793.67	1592.60	4638.73	1855.80	92.60	546.43	**	3	4	6	5	1	2
12	295.01	343.56	600.00	332.56	125.01	95.04		3	5	6	4	2	1
13	2.16	8.14	12.40	0.00	0.56	4.04	*	3	5	6	1	2	4
14	52.82	290.13	787.11	397.56	310.24	40.78		2	3	6	5	4	1
17	107.84	422.94	905.51	322.10	139.41	28.04	*	2	6	4	5	3	1
COMPOUND = OCDF													
1	0.27	0.00	.	4.58	0.59	0.00	**	3	1.5		5	4.5	1.5
2	13.01	62.00	.	2.06	5.03	7.00	**	4	5.0		1	2.0	3.0
3	168.33	829.67	1357.69	314.04	221.20	228.29	**	2	6.0	4	1	3.0	5.0
11	2562.53	9644.25	3484.10	3897.22	879.17	1420.07		3	6.0	4	5	1.0	2.0
12	945.66	1049.04	493.29	817.92	127.80	232.46		4	6.0	3	5	1.0	2.0
13	1.61	0.00	20.23	6.51	1.15	1.15	**	4	1.0	5	3	1.5	1.5
14	4.96	171.66	36.06	8.62	21.74	36.67	*	1	6.0	4	2	3.0	5.0
17	137.66	546.51	404.15	598.67	14.29	89.69		3	5.0	4	6	1.0	2.0

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TABLE 31 (cont'd.)

	Standard Deviations							Ranks					
Sample	LAB-A	LAB-B	LAB-C	LAB-D-1	LAB-D-2	LAB-D-3	ST	LAB-A	LAB-B	LAB-C	LAB-D-1	LAB-D-2	LAB-D-3
COMPOUND = TOTAL TCDD													
1	2.22	3.51		0.58	1.00	1.00		4	5		1	2.5	2.5
2	7.70	1.15	1.15	1.53	1.15	1.53	*	6	3	1.5	5	1.5	4.0
3	2.09	8.02	15.28	1.73	5.51	1.53	*	3	5	6.0	2	4.0	1.0
11	34.97	0.00	0.00	0.00	0.00	0.00		6	3	3.0	3	3.0	3.0
12	3.37	0.00	0.00	0.00	0.00	0.00		6	3	3.0	3	3.0	3.0
13	0.34	0.00	0.00	0.00	0.00	0.00		6	3	3.0	3	3.0	3.0
14	0.47	0.00	0.00	0.00	0.00	0.00		6	3	3.0	3	3.0	3.0
17	0.24	0.00	0.00	0.00	0.00	0.00		6	3	3.0	3	3.0	3.0
COMPOUND = OCDD													
1	2.61	0.00	.	0	0	0		5	2.5	6	3.5	2.5	2.5
2	2.14	0.00	.	0	0	0		5	2.5	.	2.5	2.5	2.5
3	4.66	0.00	.	0	0	0		5	2.5	.	2.5	2.5	2.5
11	3.03	2.52	4.16	0	0	0		5	4.0	6.0	2.0	2.0	2.0
12	9.40	7.64	0.00	0	0	0	**	5	6.0	2.5	2.5	2.5	2.5
13	0.44	0.58	0.00	0	0	0	*	5	6.0	2.5	2.5	2.5	2.5
14	0.03	4.04	4.62	0	0	0	*	4	6.0	6.0	2.0	2.0	2.0
17	4.68	5.51	4.62	0	0	0		5	6.0	4.0	2.0	2.0	2.0
COMPOUND = 2,3,7,8-TCDD													
1	2.22	3.51	2.31	0.58	1.00	1.00		4	6	5.0	1	2.5	3.5
2	1.70	1.15	1.15	1.53	1.15	1.53	*	6	3	1.5	5	1.5	4.0
3	2.09	8.02	15.28	1.73	5.51	1.53	*	3	5	6.0	2	4.0	1.0
11	34.24	0.00	0.00	0.00	0.00	0.00		6	3	3.0	3	3.0	3.0
12	1.11	0.00	0.00	0.00	0.00	0.00		6	3	3.0	3	3.0	3.0
13	0.34	0.00	0.00	0.00	0.00	0.00		6	3	3.0	3	3.0	3.0
14	0.04	0.00	0.00	0.00	0.00	0.00		6	3	3.0	3	3.0	3.0
17	0.24	0.00	0.00	0.00	0.00	0.00		6	3	3.0	3	3.0	3.0
COMPOUND = 2,3,7,8 + 2,3,4,6-TCDF													
1	27.47	14.80	30.00	10.02	12.10	3.51		5	4.0	6	2	3.0	1
2	2.80	0.56	5.51	1.53	2.52	0.58		5	1.0	6	3	4.0	2
3	10.00	11.59	219.38	12.22	42.03	25.42	**	1	2.0	6	3	5.0	4
11	12.84	18.46	5.51	3.46	0.00	1.15		5	6.0	4	2	1.0	2
12	15.50	1.23	9.27	3.06	1.73	5.51		6	1.5	5	3	1.5	4
13	38.35	4.58	41.63	25.01	12.06	5.77		5	1.0	6	4	3.0	2
14	68.46	25.11	25.17	32.15	2.09	4.00		6	3.0	4	5	2.0	1
17	7.00	28.72	28.46	27.51	17.02	2.00	*	2	6.0	4	5	3.0	1
COMPOUND = 1,2,3,7,8 + 1,2,3,4,6-PNCDF													
1	16.27	3.21	17.32	2.08	4.16	1.00	**	5	3	6	2	4	1
2	18.29	2.89	5.77	2.00	3.21	1.53	**	6	3	5	2	4	1
3	2.06	13.56	32.15	12.74	20.23	12.17		1	4	6	3	5	2
11	105.71	58.50	11.58	104.41	21.13	22.81	*	6	4	1	5	2	3
12	25.20	5.51	6.24	19.66	4.56	3.00	*	6	3	4	5	2	1
13	1.51	1.53	1.12	1.00	1.15	0.00		5	6	3	2	4	1
14	42.12	49.15	62.45	221.59	210.79	56.04		2	3	4	6	5	1
17	51.06	42.23	1.53	37.40	49.00	14.47		3	2	1	4	6	5

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TABLE 31 (cont'd.)

Sample	Standard Deviations						BT	Ranks					
	LAB-A	LAB-B	LAB-C	LAB-D-1	LAB-D-2	LAB-D-3		LAB-A	LAB-B	LAB-C	LAB-D-1	LAB-D-2	LAB-D-3
COMPOUND = 2,3,4,7,8-PNCDF													
1	15.72	6.24	132.29	18.92	3.48	3.21	**	4	3	6	5	2	1
2	22.81	2.65	78.38	0.56	5.20	2.08	**	5	3	6	1	4	2
5	8.50	11.58	237.14	2.06	14.01	8.06	**	3	4	6	1	5	2
11	3.06	6.51	11.55	34.82	4.00	3.06	**	1	4	5	6	3	2
12	11.79	4.62	2.00	7.94	1.15	2.08		6	4	2	5	1	3
13	5.80	4.00	11.36	8.51	1.00	1.53		4	3	6	5	1	2
14	26.46	89.00	331.46	312.67	21.13	33.05	**	2	4	6	5	1	3
17	11.83	22.61	20.82	44.66	9.64	9.29		3	5	4	6	2	1
COMPOUND = 1,2,3,4,7,8 + 1,2,3,4,7,8-HXCDF													
1	30.12	1.53	85.4	3.46	8.11	8.64	**	5	1	6	2	3	4
2	1.71	0.58	.	0.00	0.00	0.00		5	4	.	2	2	2
3	39.45	33.73	152.6	22.74	23.86	35.23		5	3	6	1	2	4
11	99.90	517.84	13519.3	394.71	80.89	83.53	**	3	5	6	4	1	2
12	11.88	35.60	120.5	67.96	3.06	25.67	*	2	4	6	5	1	3
13	3.12	4.93	10.6	1.53	0.58	2.88	*	4	5	6	2	1	3
14	25.02	86.74	1644.2	419.82	680.20	148.33	**	1	2	6	4	5	3
17	56.20	253.24	2294.2	145.23	11.53	13.32	**	3	5	6	4	1	2
COMPOUND = 1,2,3,7,8,9-HXCDF													
1	0.27	.	.	0.00	0.00	0.00		4	.	.	2	2	2
2	0.24	.	.	0.00	0.00	0.00		4	.	.	2	2	2
3	2.05	.	559.84	1.53	1.73	0.58	**	4	.	5	2	3	1
11	1.36	0	847.88	28.62	11.88	8.81	**	2	1	3	3	6	3
12	8.11	0	9.48	2.52	2.08	0.58	**	5	1	6	4	2	2
13	0.09	0	6.93	1.15	1.53	1.00		2	1	6	4	5	3
14	9.14	31	3985.86	173.14	288.83	15.72	**	1	3	6	4	5	2
17	0.58	0	1024.30	2.88	1.53	4.51	**	2	1	8	4	3	5
COMPOUND = 1,2,3,6,7,8-HXCDF													
1	8.17	0.00	.	2.08	2.89	3.46		5	1	.	2	3	4
2	1.85	1.53	.	3.06	1.53	4.58		3	2	.	4	1	5
3	13.32	72.08	.	15.72	27.30	8.00		3	2	.	4	5	1
11	9.81	100.72	.	22.28	64.49	4.04	**	1	3	.	7	4	2
12	1.18	4.36	.	3.00	3.51	8.08	*	1	4	.	2	3	5
13	0.49	2.08	.	0.00	0.58	0.58		2	5	.	1	3	4
14	17.32	29.68	.	93.66	110.39	110.53		1	2	.	3	4	5
17	1.84	2.31	.	4.51	18.61	6.03	*	1	2	.	3	5	4
COMPOUND = 2,3,4,6,7,8-HXCDF													
1	10.02	2.52	3308.35	3.79	2.89	2.31	**	5	2	6	4	3	1
2	11.02	6301	2311.45	0.58	0.58	4.93		5	4	6	2	1	3
3	14.36	14.29	4658.68	3.78	38.58	8.49	**	4	3	6	1	5	2
11	5.67	10.58	908.45	20.05	9.06	1.00	**	2	4	6	5	3	1
12	3.05	3.06	31.72	5.00	1.15	2.08		3	4	6	5	1	2
13	0.78	1.15	11.14	0.00	1.73	2.52		2	4	6	3	1	5
14	20.43	82.55	3481.89	105.72	227.28	19.73	**	2	3	6	4	5	1
17	7.27	13.45	1457.17	9.03	1.53	6.00	**	4	5	6	3	1	2

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TABLE 31 (cont'd.)

	Standard Deviations							Ranks					
Sample	LAB-A	LAB-B	LAB-C	LAB-D-1	LAB-D-2	LAB-D-3	BT	LAB-A	LAB-B	LAB-C	LAB-D-1	LAB-D-2	LAB-D-3
COMPOUND = 1,2,3,4,6,7,8-HPCDF													
1	14.19	40.06	261.07	40.33	22.03	8.03	**	2	4	6	5	3	1
2	72.95	107.98	140.80	17.32	25.77	32.98	**	4	5	6	1	2	3
3	34.64	61.58	460.74	10.69	47.67	42.03	**	2	3	6	1	4	5
11	384.32	698.55	1709.90	672.92	25.02	166.79	**	3	5	6	4	1	2
12	60.82	119.97	200.33	101.36	33.00	31.87		3	5	6	4	2	1
13	0.61	3.06	3.53	0.00	0.58	4.04		3	4	5	1	2	6
14	11.02	96.70	370.05	132.06	119.83	8.72	**	2	6	4	5	6	1
17	27.16	250.47	70.85	153.66	99.37	37.93	*	2	6	4	5	3	1

* Bartlett's test shows significant difference at the .05 level.
** Bartlett's test shows significant difference at the .01 level.

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TABLE 32. LEVENE'S TEST OF DIFFERENCES AMONG LABS BY COMPOUND OVER SAMPLES

Compound	F-Value	Degrees of Freedom
Total TCDF	8.89**	5
Total PNCDF	11.15**	5
Total HXCDF	23.12**	5
Total HPCDF	17.39**	5
OCDF	6.97**	5
Total TCDD	17.82**	5
OCDD	12.81**	5
2,3,7,8-TCDD	14.96**	5
2,3,7,8 and 2,3,4,8-TCDF	6.60**	5
1,2,3,7,8 and 1,2,3,4,8-PNCDF	4.39**	5
2,3,4,7,8-PNCDF	9.76**	5
1,2,3,4,7,8 and 1,2,3,4,7,9-HXCDF	17.80**	5
1,2,3,7,8,9-HXCDF	16.10**	5
1,2,3,6,7,8-HXCDF	2.96*	4
2,3,4,6,7,8-HXCDF	39.93**	5
1,2,3,4,6,7,8-HPCDF	22.80**	5

* Significantly different at the .05 level.
** Significantly different at the .01 level.

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TABLE 33. APPROXIMATE 95 PERCENT PREDICITON INTERVALS BY COMPOUND AND SAMPLE[a]

Compound	Sample							
	1	2	3	11	12	13	14	17
Total TCDF	144 222	57 67	1046 2321	57 362	37 321	389 1247	532 1389	249 729
Total PNCDF	206 431	220 517	1004 1682	1125 3079	143 590	179 442	5849 13417	562 1999
Total HXCDF	155 1862	40 2118	798 10654	3041 21535	726 1320	11 198	5897 21657	610 13977
Total HPCDF	103 1105	137 1532	819 4341	1581 41116	1467 3090	2 52	1391 3486	242 11063
OCDF	2 89	67 208	2280 6436	9641 64743	3822 10453	7 75	96 457	442 24465
Total TCDD	6 60	40 60	63 132	<1 21	<1 14	<1 15	<1 20	<1 10
OCDD	1 59	1 40	2 32	7 19	5 30	<1 70	1 43	5 32
2,3,7,8-TCDD	15 30	40 60	63 132	<1 25	<1 20	<1 13	<1 32	<1 11
2,3,7,8 + 1,2,3,4,8-PNCDF	144 221	57 67	977 1355	24 61	15 81	90 459	251 459	119 241
1,2,3,7,8 + 1,2,3,4,8-PNCDF	123 168	138 193	226 425	41 7913	27 264	8 30	742 1577	74 746
2,3,4,7,8-PNCDF	99 248	90 321	164 618	84 145	28 59	46 80	1324 2389	136 403
1,2,3,4,7,8 + 1,2,3,4,7,9-HXCDF	182 347	1 15	825 1838	2138 12579	447 809	13 36	3144 5860	486 5023
1,2,3,7,8,9-HXCDF	<1 34	<1 25	2 965	1 8869	4 167	<1 61	64 7800	<1 6136
1,2,3,6,7,8-HXCDF	31 72	45 72	254 412	218 603	20 97	2 10	561 1385	43 134
2,3,4,6,7,8-HXCDF	40 1041	24 1912	55 3975	26 879	9 68	1 51	196 2882	10 2237
1,2,3,4,6,7,8-HPCDF	103 1104	137 1530	96 3258	580 16405	418 976	1 17	482 1130	79 5652

[a]Values are in ppb.

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With about 95 percent confidence of being correct (i.e. 1 our of 20 measurements having a chance of being cutside of this range), each of the reported intervals is expected to cover a future laboratory's analytical results for the given compound and sample. This assumes that the concentrations are log normally distributed. Note that the data are not adequate for assessing this assumption; also the data for generating these intervals are extremely limited and can be sensitive to spurious observations. Many of the intervals are so wide that they are likely to be of little use. If the analytical method used by Lab-C was omitted, these intervals would improve, but a quantitative estimate of this improvement would be difficult to determine since the amount of data for statistical analysis would be insufficient.

SECTION 4
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APPENDIX A
EVALUATION OF CALIBRATION REGRESSION USED BY U. UMEÅ

RESEARCH TRIANGLE INSTITUTE

Center for Medical Environmental and Energy Statistics

September 2, 1986

MEMORANDUM

TO: Edo Pellizzari

FROM: Andy Clayton

SUBJECT: Problems with Calibration of Dioxin/Furan Data

REFERENCE: Analys results EPRI-prodjekt 2028 (6/23/86)

Two problems with the calibration procedure used by the Umeå Universitet laboratory are noted. These are the following:

1. The regression of x on y is performed, where x is the (injected) amount of dioxin/furan, and y is the (observed) normalized count. Although there has been much controversy over the past 20-25 years concerning whether it is more appropriate to regress x on y or y on x, I believe that most statisticians agree that regressing y on x is the preferred approach.

2. Ordinary least squares (OLS) is used to fit the calibration curve (assumed to be a straight line). This is a much more serious problem. OLS is appropriate when the magnitude of the measurement errors is approximately the same across the entire range of concentrations of interest. This is clearly not the situation here. As an example, consider the data for 2378-TCDF. When x=7500, the y values range from 8593.7 to 8037.3, a difference of 443.6. On the other hand, when x=10, the range of observed counts is only 2.8. Clearly, the measurement error increases with increasing concentration, so that OLS is inappropriate. The severity of the problem is demonstrated by the estimates obtained for 2378-TCDF. Using the values of a and b from the referenced document, it is seen that a normalized count of 10 units will yield a predicted concentration of (.853)(10) + 29.89 = 38.42 pg. Examination of the calibration data indicates that the true concentration should be roughly 10 pg. For lower concentrations (say, less than 200 pg), OLS has thus produced a curve that (in this case) results in a significant overestimation of the true concentration. It is precisely in this range where the transformer data occur.

One solution to the above problems is to perform the calibration ourselves and to apply the new calibration to normalized counts obtained from the reported concentrations and the reported curve parameter estimates. Some imprecision will occur due to the fact that the concentrations are reported to only two significant digits. Alternatively, we can request the raw (normalized count) data, perform an appropriate calibration, and re-estimate the concentrations for the transformers.

Post Office Box 12194 Research Triangle Park, North Carolina 27709 Telephone 919 541-6000

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APPENDIX B
DATA USED IN COMPARISONS BETWEEN LABS

TABLE B-1. DATA USED IN COMPARISONS BETWEEN LABS

Sample	Lab	Compound	Det. 1	Det 2	Det 3	Mean	Std Dev
1	MVSDOH	TOTAL TCDF	245.00	189 00	184.00	172 00	28 60
		TOTAL PNCDF	351.00	312.00	295 00	286 00	30 50
		TOTAL HXCDF	398 00	455 00	380 00	400 00	52 60
		TOTAL HPCDF	359 00	341.00	372 00	358 00	13 60
		OCDF	3.48	3 55	3 85	3 37	0 27
		TOTAL TCDD	17 00	21.50	18 20	18 80	2 22
		OCDD	3 88	0 19	0 87	2 00	1 61
		2,3,7,8-TCDD	17 00	21.50	18 20	18 80	2 32
		2,3,7,8 + 2,3,4,8-TCDF	245.00	185 00	192 00	174 00	27 50
		1,2,3,7,8 + 1,2,3,4,8-PNCDF	321 00	353 00	132 00	135 00	46 30
		2,3,4,7,8-PNCDF	127.00	130.00	158.00	141 00	15 70
		1,2,3,4,7,8 + 1,2,3,4,7,8-HXCDF	223 00	836 00	199 00	226 00	30 10
		1,2,3,7,8,9-HXCDF	0.83	0.07	0.05	0 23	0 27
		1,2 3,6,7,8-HXCDF	48.10	47.00	38 10	41 30	5 17
		2,3 4,6,7,8-HXCDF	150.00	181.00	170 00	160 00	10 00
		1,2,3,4,6,7,8-HPCDF	931.00	362.00	350.00	334 00	14 20
2	MVSDOH	TOTAL TCDF	58.80	82.70	83.50	41 00	8 38
		TOTAL PNCDF	276.00	258.00	324.00	212 00	31 70
		TOTAL HXCDF	201.00	800.00	265.00	212 00	12 20
		TOTAL HPCDF	270.00	712.00	891.00	827 00	73 80
		OCDF	133.00	107 00	121.00	120 00	13 00
		TOTAL TCDD	39.40	90 40	56 50	45 20	7 70
		OCDD	1 44	0.41	4 32	2 12	2 14
		2,3,7,8-TCDD	58.80	80.40	54 30	46 20	7 70
		2,3,7,8 + 2,3 4,8-TCDF	60.80	80.80	65 30	62 30	2 80
		1,2,3,7,8 + 1,2,3,4,8-PNCDF	138.00	171.00	168 00	158 00	18 30
		2,3 4,7,8-PNCDF	188.00	158.00	183 00	148 00	22 60
		1,2,3 8,7,8 + 1,2,3,4,7,8-HXCDF	8.77	3.83	0.12	4 24	1 71
		1,2,3,7,8,9-HXCDF	0.21	0 05	0 52	0 26	0 24
		1,2,3,6,7,8-HXCDF	58.30	54 60	54 30	54.30	3 83
		2,3,4,6,7,8-HXCDF	140.00	100 00	102 00	151 00	11 00
		1,2,3,4,6,7,8-HPCDF	578.00	708 00	301 00	625 00	95 00
3	MVSDOH	TOTAL TCDF	1630.00	1650 00	1580.00	1613 00	29 80
		TOTAL PNCDF	1350.00	1250.00	1340.00	1320.00	38 50
		TOTAL HXCDF	2480 00	2500.00	2350.00	2473 00	88 20
		TOTAL HPCDF	2470.00	2300.00	2400.00	2350.00	85 40
		OCDF	4830 00	8090.00	8170 00	3037 00	161 00
		TOTAL TCDD	85.30	65.30	81 70	64 10	2 09
		OCDD	3.73	0.75	5 89	4 76	4 68
		2,3,7,8-TCDD	85.10	65.50	61.70	64.10	2 09
		2,3,7,8 + 2,3,4,8-TCDF	1210.00	1270 00	1200 00	1210 00	10 00
		1,2,8,7,8 + 1,2,3,4,8-PNCDF	338.00	342.00	346 00	345 00	3 06
		2,3,4,7,8-PNCDF	304.00	288.00	291.00	294 00	8 50
		1,2,3,4,7,8 + 1,2,3,4,7,8-HXCDF	1220.00	1200.00	1255.00	1241 00	29 40
		1,2,3,7,8,9-HXCDF	37.80	35 80	35 80	37 80	1 05
		1,2,3,6,7,8-HXCDF	320.00	351.00	347 00	336 00	13 30
		2,3,4,6,7,8-HXCDF	313.00	290.00	281.00	297 00	14 40
		1,2,3,4,6,7,8-HPCDF	885.00	805.00	865 00	845 00	34 80

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TABLE B-1 (cont'd.)

Sample	Lab	Compound	Det. 1	Det. 2	Det. 3	Mean	Std. Dev.
11	NYSDOH	TOTAL TCDF	232.00	121.00	337.00	230.00	106.00
		TOTAL PNCDF	1930.00	1690.00	1780.00	1783.00	121.00
		TOTAL HXCDF	8840.00	8370.00	8520.00	8643.00	172.00
		TOTAL HPCDF	10100.00	8610.00	9080.00	9197.00	784.00
		OCDF	39000.00	37700.00	42100.00	38600.00	3201.00
		TOTAL TCDD	1.55	82.60	2.78	22.20	33.00
		OCDD	11.60	0.00	14.50	12.10	3.03
			10.00	10.48	17.00		
		2,3,7,8-TCDD	1.32	82.20	2.78	22.10	34.70
		2,3,7,8 + 2,3,4,8-TCDF	40.80	48.00	87.70	53.50	12.90
		1,2,3,7,8 + 1,2,3,4,8-PNCDF	838.00	736.00	780.00	830.00	100.00
		2,3,4,7,8-PNCDF	101.00	107.00	103.00	104.00	3.00
		1,2,3,4,7,8 + 1,2,3,6,7,8-HXCDF	4708.00	4614.00	4823.00	4677.00	88.80
		1,2,3,7,8,9-HXCDF	2.34	6.14	8.00	5.82	1.36
		2,3,4,7,8-HXCDF	350.00	367.00	362.00	363.00	3.01
		2,3,4,6,7,8-HXCDF	31.20	48.40	40.80	46.70	5.87
		1,2,3,4,6,7,8-HPCDF	3840.00	3290.00	3090.00	3780.00	384.00
12	NYSDOH	TOTAL TCDF	228.00	188.00	918.00	308.00	137.00
		TOTAL PNCDF	430.00	342.00	439.00	369.00	74.80
		TOTAL HXCDF	883.00	807.00	956.00	930.00	43.00
		TOTAL HPCDF	2400.00	2040.00	1830.00	2063.00	295.00
		OCDF	8500.00	8000.00	7810.00	7170.00	641.00
		TOTAL TCDD	0.55	0.49	7.10	2.83	3.87
		OCDD	37.40	80.80	87.10	37.00	0.60
		2,3,7,8-TCDD	0.05	0.12	2.00	0.72	1.13
		2,3,7,8 + 2,3,4,8-TCDF	80.00	81.10	90.00	73.50	15.50
		1,2,3,7,8 + 1,2,3,4,8-PNCDF	110.00	60.80	101.00	90.10	25.10
		2,3,4,7,8-PNCDF	80.80	38.80	89.40	53.20	11.90
		1,2,3,4,7,8 + 1,2,3,4,7,8-HXCDF	821.00	898.00	812.00	810.00	31.80
		1,2,3,7,8,9-HXCDF	97.90	17.78	36.10	29.90	8.11
			39.80	22.20	31.30		
		1,2,3,6,7,8-HXCDF	43.00	44.00	42.30	42.30	1.10
		2,3,4,6,7,8-HXCDF	15.20	9.10	12.30	12.20	3.05
		1,2,3,4,6,7,8-HPCDF	802.00	540.00	631.00	612.00	88.80
13	NYSDOH	TOTAL TCDF	888.00	780.00	942.00	770.00	144.00
		TOTAL PNCDF	368.00	381.00	340.00	383.00	11.50
		TOTAL HXCDF	39.70	81.00	47.00	44.30	6.48
		TOTAL HPCDF	8.30	12.30	9.61	10.10	2.16
		OCDF	12.40	15.30	10.80	15.10	1.41
		TOTAL TCDD	0.16	0.38	0.85	0.46	0.36
		OCDD	1.10	0.36	0.20	0.58	0.44
		2,3,7,8-TCDD	0.10	0.50	0.63	0.48	0.34
		2,3,7,8 + 2,3,4,8-TCDF	167.00	226.00	273.00	232.00	38.40
		1,2,3,7,8 + 1,2,3,4,8-PNCDF	16.80	17.30	17.10	18.10	1.51
		2,3,4,7,8-PNCDF	81.30	81.80	71.10	84.60	5.40
		1,2,3,4,7,8 + 1,2,3,4,7,8-HXICDF	10.80	21.90	18.30	16.30	2.12
		1,2,3,7,8,9-HXICDF	0.36	0.36	0.24	0.28	0.09
		1,2,3,6,7,8-HXICDF	3.60	4.38	3.94	3.90	0.48
		2,3,4,6,7,8-HXICDF	1.70	2.00	1.75	1.82	0.18
		1,2,3,4,6,7,8-HPCDF	3.60	4.00	3.38	3.86	0.81

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TABLE B-1 (cont'd.)

Sample	Lab	Compound	Det. 1	Det. 2	Det. 3	Mean	Std Dev
14	HYDON	TOTAL TCDF	1500.00	853 00	1100 00	1184 00	233 00
		TOTAL PNCDF	10300.00	10300.00	10800 00	10100 00	300 00
		TOTAL HXCDF	10500.00	19000 00	10700 00	10700.00	300 00
		TOTAL HPCDF	2000.00	2030.00	2100 00	2040 00	32 90
		OCDF	186.00	187.00	181.00	184 00	4 58
		TOTAL TCDD	0.00	0.42	0 05	0 48	0 47
		OCDD	1.04	0.05	1.01	1.01	0 03
		1,3,7,8-TCDD	0.00	0 02	0 05	0.05	0 04
		2,3,7,8 + 2,3,4 8-TCDF	480 00	349.00	381 00	408 00	66 50
		1,2,3,7,8 + 1,2 3,4,8-PNCDF	1100 00	1032.00	1135 00	1098 00	42 10
		2,3,4,7,8-PNCDF	1030.00	1050.00	1070.00	1060 00	28 50
		1,2,3,4,7,8 + 1,2,3,6,7,8-HXCDF	4413.00	4432.00	4382 00	4409.00	25 00
		1,2,3,7,8,9-HXCDF	162.00	177.00	173.00	171 00	8 18
		1,3,3,8,7,8-HXCDF	1030.00	1030.00	1000.00	1020 00	17 30
		2,3,4,8,7,8-HXCDF	360.00	404.00	390 00	389 00	20 40
		1,2,3,4,6,7,8-HPCDF	600.00	870.00	700.00	699 00	11 00
15	HYDON	TOTAL TCDF	0.03	0.36	0.21	0.41	0 11
		TOTAL PNCDF	1.72	1.84	2 14	1 93	0 21
		TOTAL HXCDF	1.70	1.34	2 43	1.78	0 45
		TOTAL HPCDF	0.01	0 03	0 10	0 31	0 17
		OCDF	0.40	0.30	0 44	0 33	0 51
		TOTAL TCDD	0.00	0.00	30.00	4 72	11 50
		OCDD	2.02	3.30	5 80	3.40	0 38
		2,3,7,8-TCDD	0.00	0.00	30 00	8 72	11 30
		2,3,7,8 + 2,3,4 8-TCDF	0.20	0 24	0 23	0.22	0 02
		1,2,3,7,8 + 1,3 3,4,8-PNCDF	0.37	0.39	0 21	0.36	0 04
		2,3,4,7,8-PNCDF	0.40	0.21	0 41	0.46	0 03
		1,2,3,4,7,8 + 1 2,3,4,7,8-HXCDF	1.20	0.60	1 10	1 01	0 38
		1,2,3,7,8,9-HXCDF	0.12	0.11	0 20	0.20	0 09
		1,2,3,6,7,8-HXCDF	0.25	0.13	0 27	0.22	0 08
		2,3,4,6,7,8-HXCDF	0.21	0.14	0 07	0 14	0 07
		1,2,3,4,6,7,8-HPCDF	0.26	0.09	0 09	0 15	0 11
16	HYSDON	TOTAL TCDF	0.15	0.10	0 23	0.10	0 04
		TOTAL PNCDF	0.34	0.00	0 33	0 49	0 13
		TOTAL HXCDF	0.60	0 32	0 71	0 00	0 10
		TOTAL HPCDF	0.00	0.23	0 21	0 38	0 25
		OCDF	0.63	2.40	3 00	2 20	1 38
		TOTAL TCDD	0.01	0.16	0 10	0 30	0 27
		OCDD	20.00	10 00	17 10	18 20	2 23
		2,3,7,8-TCDD	0.60	0 12	0 00	0 27	0 29
		2,3,7,8 + 2,3,4 8-TCDF	0.15	0.10	0 13	0 15	0 03
		1,2,3,7,8 + 1,2 3,4,8-PNCDF	0.00	0.10	0 14	0 33	0 20
		2,3,4,7,8-PNCDF	0.34	0 00	0 11	0 18	0 14
		1,2,3,4,7,8 + 1 2,3,4,7,8-HXCDF	0.77	0.71	0.00	0 72	0 04
		1,2,3,7,8,9-HXCDF	0.21	0.10	0.10	0.19	0 03
		1,2,3,6,7,8-HXCDF	0.21	0.10	0.10	0 18	0 03
		2,3,4,6,7,8-HXCDF	0.32	0 20	0 10	0 23	0 08
		1,2,3,4,6,7,8-HPCDF	0.00	0.23	0.21	0 36	0 25

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TABLE B-1 (cont'd.)

Sample	Lab	Compound	Det. 1	Det. 2	Det. 3	Mean	S.D.	Conc.
17	MYSDOR	TOTAL TCDF	833.00	992.00	812.00	938.00	23.00	[illegible]
		TOTAL PNCDF	1170.00	1130.00	1180.00	1193.00	15.00	[illegible]
		TOTAL HXCDF	1700.00	1700.00	1820.00	1707.00	30.00	[illegible]
		TOTAL HPCDF	1780.00	1300.00	1810.00	1837.00	134.00	[illegible]
		OCDF	3982.00	4410.00	4734.00	4369.00	184.00	[illegible]
		TOTAL TCDD	1.10	0.82	0.71	0.00	0.00	[illegible]
		OCDD	10.70	24.20	28.40	23.80	9.28	[illegible]
		2,3,7,8-TCDD	1.10	0.82	0.71	0.00	0.00	[illegible]
		2,3,7,8 + 2,3,4,8-TCDF	193.00	184.00	183.00	187.00	7.00	[illegible]
		1,2,3,7,8 + 1,2,3,4,8-PNCDF	288.00	277.00	287.00	278.00	11.00	[illegible]
		2,3,4,7,8-PNCDF	170.00	151.00	193.00	163.00	14.00	[illegible]
		1,2,3,4,7,8 + 1,2,3,4,7,8-HXCDF	1001.00	1031.00	1111.00	1047.00	58.70	[illegible]
		1,2,3,7,8,9-HXCDF	0.00	0.00	0.00	0.78	0.00	[illegible]
		1,2,3,6,7,8-HXCDF	84.00	85.20	61.70	83.00	1.00	[illegible]
		2,3,4,6,7,8-HXCDF	70.00	58.00	58.00	61.30	7.57	[illegible]
		1,2,3,4,6,7,8-HPCDF	818.00	761.00	784.00	787.00	27.10	[illegible]
1	[ITRI	TOTAL TCDF	174.00	150.00	147.00	157.00	14.00	[illegible]
		TOTAL PNCDF	293.00	285.00	310.00	290.00	9.29	[illegible]
		TOTAL HXCDF	471.00	468.00	469.00	467.00	4.51	[illegible]
		TOTAL HPCDF	382.00	400.00	377.00	380.00	40.00	[illegible]
		OCDF	84.00	84.00	84.00	84.00	0.00	[illegible]
		TOTAL TCDD	24.00	17.00	21.00	20.70	3.51	[illegible]
		OCDD	10.00	10.00	10.00	10.00	0.00	[illegible]
		2,3,7,8-TCDD	24.00	17.00	21.00	20.70	3.51	[illegible]
		2,3,7,8 + 2,3,4,8-TCDF	174.00	180.00	147.00	157.00	14.00	[illegible]
		1,2,3,7,8 + 1,2,3,4,8-PNCDF	181.00	130.00	158.00	132.00	3.61	[illegible]
		2,3,4,7,8-PNCDF	142.00	145.00	154.00	147.00	5.24	[illegible]
		1,2,3,4,7,8 + 1,2,3,4,7,8 HXCDF	241.00	230.00	240.00	240.00	1.54	[illegible]
		1,2,3,7,8,9-HXCDF						
		1,2,3,6,7,8-HXCDF	82.00	82.00	82.00	82.00	0.00	[illegible]
		2,3,4,6,7,8-HXCDF	100.00	105.00	105.00	103.00	2.52	[illegible]
		1,2,3,4,6,7,8-HPCDF	382.00	400.00	377.00	386.00	40.10	[illegible]
2	[ITRI	TOTAL TCDF	81.00	82.00	81.00	81.30	0.58	[illegible]
		TOTAL PNCDF	311.00	310.00	314.00	312.00	2.08	[illegible]
		TOTAL HXCDF	224.00	232.00	222.00	226.00	5.29	[illegible]
		TOTAL HPCDF	503.00	009.00	484.00	520.00	113.00	[illegible]
		OCDF	197.00	138.00	73.00	135.00	62.00	[illegible]
		TOTAL TCDD	53.00	52.00	55.00	53.70	1.15	[illegible]
		OCDD	8.20	3.20	5.20	5.30	0.00	[illegible]
		2,3,7,8-TCDD	03.00	53.00	55.00	52.70	1.15	[illegible]
		2,3,7,8 + 2,3,4,8-TCDF	81.00	82.00	61.00	81.30	0.58	[illegible]
		1,2,3,7,8 + 1,2,3,4,8-PNCDF	101.00	100.00	105.00	104.00	2.65	[illegible]
		2,3,4,7,8-PNCDF	149.00	144.00	148.00	147.00	2.52	[illegible]
		1,2,3,4,7,8 + 1,2,3,4,7,8-HXCDF	2.00	1.00	2.00	1.87	0.58	[illegible]
		1,2,3,7,8,9-HXCDF						
		1,2,3,6,7,8-HXCDF	82.00	81.00	84.00	82.30	1.53	[illegible]
		2,3,4,6,7,8-HXCDF	100.00	170.00	137.00	102.00	5.01	[illegible]
		1,2,3,4,6,7,8-HPCDF	552.00	500.00	404.00	520.00	110.00	[illegible]

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TABLE B-1 (cont'd.)

Sample	Lab	Compound	Det 1	Det 2	Det 3	Mean	Std Dev
9	11TR1	TOTAL TCDF	1650.00	1647.00	1583.00	1593.00	68.30
		TOTAL PNCDF	1114.00	1217.00	1093.00	1141.00	88.48
		TOTAL HXCDF	2338.00	2283.00	2241.00	2288.00	48.38
		TOTAL HPCDF	1209.00	1072.00	886.00	1047.00	176.00
		OCDF	5818.00	5530.00	5906.00	5718.00	830.00
		TOTAL TCDD	107.00	98.00	97.00	97.70	6.02
		OCDD	9.00	8.00	9.00	8.80	0.00
		2,3,7,8-TCDD	107.00	98.00	97.00	97.70	6.01
		2,3,7,8 + 2,3,4,8-TCDF	1121.00	1144.00	1135.00	1133.00	11.80
		1,2,3,7,8 + 1,2,3,4,8-PNCDF	329.00	348.00	322.00	330.00	13.40
		2,3,4,7,8-PNCDF	286.00	275.00	232.00	264.00	11.60
		1,2,3,4,7,8 + 1,2,3,4,7,8-HXCDF	987.00	881.00	842.00	950.00	33.70
		1,2,3,7,8,9-HXCDF					
		1,2,3,6,7,8-HXCDF	381.00	363.00	371.00	382.00	12.10
		2,3,4,6,7,8-HXCDF	310.00	286.00	289.00	282.00	14.30
		1,2,3,4,6,7,8-HPCDF	567.00	511.00	484.00	587.00	61.60
11	11TR1	TOTAL TCDF	103.00	96.00	97.00	96.30	6.33
		TOTAL PNCDF	1601.00	1911.00	1948.00	1720.00	167.00
		TOTAL HXCDF	8466.00	6788.00	7384.00	6477.00	813.00
		TOTAL HPCDF	7835.00	7768.00	10095.00	8300.00	1381.00
		OCDF	28722.00	33263.00	46148.00	38378.00	8646.00
		TOTAL TCDD					
		OCDD	17.00	20.00	15.00	17.50	2.32
		2,3,7,8-TCDD	0.50	0.50	0.50	0.50	0.00
		2,3,7,8 + 2,3,4,6-TCDF	35.00	26.00	27.00	30.00	10.50
		1,2,3,7,8 + 1,2,3,4,8-PNCDF	887.00	984.00	828.00	836.00	58.30
		2,3,4,7,8-PNCDF	110.00	103.00	112.00	112.00	5.51
		1,2,3,4,7,8 + 1,2,3,4,7,8-HXCDF	3130.00	3033.00	4006.00	3723.00	514.15
		1,2,3,7,8,9-HXCDF					
		1,2,3,6,7,8-HXCDF	401.00	543.00	503.00	314.00	101.00
		2,3,4,6,7,8-HXCDF	87.00	87.00	83.00	79.00	10.80
		1,2,3,4,6,7,8-HPCDF	3212.00	3023.00	4300.00	3015.00	809.00
12	11TR1	TOTAL TCDF	130.00	125.00	129.00	128.00	6.33
		TOTAL PNCDF	326.00	939.00	308.00	328.00	13.30
		TOTAL HXCDF	936.00	1008.00	1002.00	981.00	54.48
		TOTAL HPCDF	1911.00	1306.00	2108.00	1707.00	348.00
		OCDF	7617.00	7708.00	9478.00	8265.00	1069.00
		TOTAL TCDD					
		OCDD	7.00	22.00	17.00	15.30	7.64
		2,3,7,8-TCDD	1.00	1.00	1.00	1.00	0.00
		2,3,7,8 + 2,3,4,8-TCDF	41.00	38.00	41.00	40.00	1.73
		1,2,3,7,8 + 1,2,3,4,8-PNCDF	110.00	115.00	121.00	115.00	5.51
		2,3,4,7,8-PNCDF	43.00	43.00	51.00	42.70	4.62
		1,2,3,4,7,8 + 1,2,3,4,7,8-HXCDF	501.00	540.00	371.00	540.00	35.80
		1,2,3,7,8,9-HXCDF					
		1,2,3,6,7,8-HXCDF	80.00	87.00	78.00	82.00	4.36
		2,3,4,6,7,8-HXCDF	13.00	13.00	10.00	15.70	3.06
		1,2,3,4,6,7,8-HPCDF	389.00	383.00	773.00	635.00	159.00

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TABLE B-1 (cont'd.)

Sample	Lab	Compound	Det. 1	Det. 2	Det. 3	Mean	Std Dev
13	11TR1	TOTAL TCDF	572.00	473.00	461.00	502.00	65.90
		TOTAL PNCDF	278.00	233.00	221.00	350.00	27.10
		TOTAL HXCDF	84.00	82.00	63.00	83.00	17.30
		TOTAL HPCDF	17.00	13.00	30.00	20.79	8.14
		OCDF	42.00	42.00	42.00	42.00	0.00
		TOTAL TCDD	.	.	.	.	
		OCDD	9.00	9.00	9.00	9.33	0.56
		2,3,7,8-TCDD	0.50	0.50	0.50	0.50	0.00
		2,3,7,8 + 2,3,4,8-TCDF	103.00	98.00	105.00	104.00	4.39
		1,2,3,7,8 + 1,2,3,4,8-PNCDF	23.00	23.00	20.00	21.70	1.53
		2,3,4,7,8-PNCDF	83.00	89.00	67.00	65.00	4.00
		1,2,3,4,7,8 + 1,2,3,4,7,9-HXCDF	16.00	18.00	27.00	31.30	6.53
		1,2,3,7,8,9-HXCDF	.	.	.	.	
		1,2,3,6,7,8-HXCDF	6.00	7.00	10.00	7.67	2.06
		2,3,4,6,7,8-HXCDF	2.00	3.00	5.00	2.67	1.15
		1,2,3,4,6,7,8-HPCDF	8.00	7.00	13.00	9.67	3.08
14	11TR1	TOTAL TCDF	870.00	837.00	870.00	721.00	217.00
		TOTAL PNCDF	6138.00	6380.00	6002.00	7276.00	1721.00
		TOTAL HXCDF	10388.00	9916.00	10869.00	10384.00	414.00
		TOTAL HPCDF	1725.00	2190.00	2234.00	3038.00	290.00
		OCDF	383.00	626.00	374.00	431.00	174.00
		TOTAL TCDD	.	.	.	.	
		OCDD	4.00	13.00	5.00	6.67	4.04
		2,3,7,8-TCDD	0.50	0.50	0.50	0.20	0.00
		2,3,7,8 + 2,3,4,8-TCDF	287.00	248.00	282.00	278.00	25.10
		1,2,3,7,8 + 1,2,3,4,8-PNCDF	1116.00	1039.00	1023.00	1059.00	49.20
		2,3,4,7,8-PNCDF	1772.00	1594.00	1726.00	1694.00	96.00
		1,2,3,4,7,8 + 1,2,3,4,7,9-HXCDF	3902.00	3711.00	3775.00	3383.00	46.70
		1,2,3,7,8,9-HXCDF	174.00	187.00	233.00	186.00	31.00
		1,2,3,6,7,8-HXCDF	1193.00	1169.00	1137.00	1162.00	29.70
		2,3,4,6,7,8-HXCDF	387.00	472.00	509.00	438.00	62.60
		1,2,3,4,6,7,8-HPCDF	738.00	805.00	884.00	839.00	96.70
15	11TR1	TOTAL TCDF	.	.	.	.	.
		TOTAL PNCDF	.	18.00	.	18.00	.
		TOTAL HXCDF	.	.	.	.	.
		TOTAL HPCDF	13.00	8.00	.	9.00	3.85
		OCDF	31.00	31.00	31.00	31.00	0.00
		TOTAL TCDD	.	.	.	.	.
		OCDD	13.00	10.00	8.00	10.30	2.52
		2,3,7,8-TCDD	1.00	1.00	1.00	1.00	0.00
		2,3,7,8 + 2,3,4,8-TCDF	3.00	3.00	3.00	3.00	0.00
		1,2,3,7,8 + 1,2,3,4,8-PNCDF	0.00	0.50	0.50	0.50	0.00
		2,3,4,7,8-PNCDF	.	7.00	.	7.00	.
		1,2,3,4,7,8 + 1,2,3,4,7,9-HXCDF	1.00	1.00	1.00	1.00	0.00
		1,2,3,7,8,9-HXCDF	.	.	.	.	.
		1,2,3,6,7,8-HXCDF	.	.	.	.	.
		2,3,4,6,7,8-HXCDF	.	.	.	.	.
		1,2,3,4,6,7,8-HPCDF	5.00	2.00	0.50	2.50	2.33

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TABLE B-1 (cont'd.)

Sample	Lab	Compound	Det 1	Det 2	Det 3	Mean	Std Dev
16	IITRI	TOTAL TCDF	.	.	.	.	.
		TOTAL PNCDF	358.00	87.00	215.00	210.00	136.00
		TOTAL HXCDF	819.00	191.00	381.00	387.00	214.00
		TOTAL HPCDF	114.00	33.00	62.00	89.70	41.00
		OCDF	37.00	37.00	37.00	37.00	0.00
		TOTAL TCDD	.	.	.	.	.
		OCDD	23.00	23.00	26.00	25.30	2.52
		2,3,7,8-TCDD	3.00	3.00	3.00	3.00	0.00
		2,3,7,8 - 2,3,4,8-TCDF	5.00	5.00	5.00	5.00	0.00
		1,2,3,7,8 - 1,2,3,4,8-PNCDF	72.00	19.00	40.00	43.70	26.70
		2,3,4,7,8-PNCDF	111.00	28.00	63.00	69.30	41.10
		1,2,3,4,7,8 - 1,2,3,4,7,9-HXCDF	243.00	68.00	144.00	131.00	88.20
		1,2,3,7,8,8-HXCDF	15.00	4.00	8.00	9.30	5.57
		1,2,3,6,7,8-HXCDF	87.00	21.00	46.00	51.30	33.30
		2,3,4,6,7,8-HXCDF	32.00	11.00	19.00	20.70	10.80
		1,2,3,4,8,7,8-HPCDF	43.00	12.00	23.00	27.00	14.40
17	IITRI	TOTAL TCDF	431.00	344.00	275.00	350.00	78.20
		TOTAL PNCDF	1221.00	987.00	810.00	872.00	218.00
		TOTAL HXCDF	2511.00	2800.00	1748.00	1021.00	283.00
		TOTAL HPCDF	1913.00	2273.00	1430.00	1672.00	423.00
		OCDF	6048.00	6548.00	5801.00	6232.00	147.00
		TOTAL TCDD	.	.	.	.	.
		OCDD	22.00	23.00	13.00	18.30	5.51
		2,3,7,1-TCDD	0.50	0.50	0.50	0.50	0.00
		2,3,7,8 - 2,3,4,8-TCDF	132.00	142.00	58.00	131.00	26.70
		1,2,3,7,8 - 1,2,3,4,8-PNCDF	320.00	382.00	237.00	383.00	42.20
		2,3,4,7,8-PNCDF	180.00	178.00	139.00	165.00	22.60
		1,2,3,4,7,8 - 1,2,3,4,7,8-HXCDF	1219.00	1131.00	820.00	1090.00	153.00
		1,2,3,7,8,8-HXCDF	.	.	.	.	.
		1,2,3,8,7,8-HXCDF	118.00	115.00	115.00	116.00	2.31
		2,3,4,6,7,8-HXCDF	74.00	81.00	53.00	70.00	13.50
		1,2,3,4,6,7,8-HPCDF	1095.00	1270.00	776.00	1047.00	250.00
1	BATTELLE	TOTAL TCDF	220.00	160.00	180.00	190.00	30.00
		TOTAL PNCDF	310.00	330.00	260.00	373.00	135.00
		TOTAL HXCDF	880.00	8600.00	300.00	2337.00	3505.00
		TOTAL HPCDF	330.00	33.00	220.00	281.00	251.00
		OCDF	.	.	.	.	.
		TOTAL TCDD	.	.	2.60	2.60	
		OCDD	.	.	0.76	0.76	
		2,3,7,8-TCDD	19.00	19.00	23.00	20.30	2.31
		2,3,7,8 - 2,3,4,8-TCDF	220.00	180.00	190.00	190.00	30.00
		1,2,3,7,8 - 1,2,3,4,8-PNCDF	140.00	170.00	140.00	130.00	17.30
		2,3,4,7,8-PNCDF	170.00	370.00	120.00	220.00	132.00
		1,2,3,4,7,8 - 1,2,3,4,7,9-HXCDF	310.00	320.00	150.00	260.00	95.40
		1,2,3,7,8,9-HXCDF	.	.	.	.	.
		2,3,4,8,7,8-HXCDF	200.00	2900.00	140.00	2080.00	3301.00
		1,2,3,4,8,7,8-HPCDF	530.00	33.00	220.00	261.00	251.00

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TABLE B-1 (cont'd.)

Sample	Lab	Compound	Det. 1	Det. 2	Det. 3	Mean	Std. Dev
2	BATTELLE	TOTAL TCDF	67.00	57.00	44.00	63.30	9.51
		TOTAL PnCDF	800.00	500.00	460.00	520.00	72.10
		TOTAL HxCDF	9800.00	2300.00	780.00	2827.00	2355.00
		TOTAL HpCDF	65.00	160.00	340.00	185.00	141.00
		OCDF					
		TOTAL TCDD	46.00	48.00	44.00	45.30	1.15
		OCDD					
		2,3,7,8-TCDD	45.00	48.00	44.00	45.30	1.15
		2,3,7,8 - 2,3,4,6-TCDF	61.00	61.00	60.00	63.30	5.51
		1,2,3,7,8 - 1,2,3,4,8-PnCDF	180.00	180.00	180.00	183.00	6.77
		2,3,4,7,8-PnCDF	810.00	610.00	260.00	527.00	76.48
		1,2,3,4,7,8 - 1,2,3,4,7,8-HxCDF					
		1,2,3,7,8,9-HxCDF					
		2,3,4,6,7,8-HxCDF	5200.60	2100.00	800.00	2800.00	2311.00
		1,2,3,4,6,7,8-HpCDF	86.00	180.00	340.00	102.00	141.00
3	BATTELLE	TOTAL TCDF	1400.00.	1700.00	870.00	1367.00	287.00
		TOTAL PnCDF	1100.00	1800.00	1200.00	1200.00	100.00
		TOTAL HxCDF	30000.00	6700.00	11000.00	11000.00	7000.00
		TOTAL HpCDF	1700.00	3000.00	860.00	1787.00	1172.00
		OCDF	9000.00	8000.00	2600.00	6197.00	1358.00
		TOTAL TCDD	110.00	100.00	90.00	95.70	15.30
		OCDD					
		2,3,7,8-TCDD	110.00	100.00	80.00	96.70	15.30
		2,3,7,8 - 2,3,4,6-TCDF	1700.00	1300.00	960.00	1187.00	210.00
		1,2,3,7,8 - 1 2,3,4,8-PnCDF	200.00	200.00	250.00	237.00	32.10
		2,3,4,7,8-PnCDF	500.00	616.00	600.00	637.00	237.00
		1,2,3,4,7,8 - 1,2,3,4,7,8-HxCDF	1000.00	1000.00	1000.00	1767.00	153.00
		1,2,3,7,8,9-HxCDF	1800.00	93.00	750.06	891.00	556.00
		2,3,4,6,7,8-HxCDF	10000.00	776.00	8500.00	3759.00	4640.00
		1,2,3,4,6,7,8-HpCDF	88.00	650.00	88.00	310.00	461.00
13	BATTELLE	TOTAL TCDF	170.00	130.00	49.00	107.00	65.10
		TOTAL PnCDF	2300.00	2100.00	720.00	1707.00	668.00
		TOTAL HxCDF	82000.00	11000.00	8700.00	34233.00	34053.00
		TOTAL HpCDF	5800.00	13000.00	11000.00	9267.00	4039.00
		OCDF	21960.00	28000.00	21000.00	24000.00	3494.00
		TOTAL TCDD					
		OCDD	10.00	12.00	0.00	10.00	8.17
		2,3,7,8-TCDD					
		2,3,7,8 - 2,3,4,8-TCDF	31.00	30.00	40.00	33.70	5.51
		1,2,3,7,8 - 1,2 3,4,6-PnCDF	30.00	48.00	26.00	34.70	11.90
		2,3,4,7,8-PnCDF	130.00	730.00	110.00	123.00	31.30
		1,2,3,4,7,8 - 1,2,3,4,7,8-HxCDF	28000.00	8100.00	5100.00	13400.00	13519.00
		2,3,4,7,8,9-HxCDF	1000.00	430.00	660.00	1030.00	860.00
		2,3,4,6,7,8-HxCDF	1600.00	260.00	210.00	750.00	909.00
		1,2,3,4,6,7,8-HpCDF	1300.00	4900.00	3100.00	2900.00	1709.00

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TABLE B-1 (cont'd.)

Sample	Lab	Compound	Det. 1	Det. 2	Det. 3	Mean	Std. Dev.
12	BATTELLE	TOTAL TCDF	62.00	64.00	89.00	75.00	20.40
		TOTAL PNCDF	70.00	250.00	310.00	206.00	117.00
		TOTAL HXCDF	1000.00	1500.00	980.00	1263.00	357.00
		TOTAL HPCDF	1500.00	2100.00	2700.00	2100.00	800.00
		OCDF	4000.00	4800.00	4800.00	4867.00	483.00
		TOTAL TCDD	.	.	.	.	
		OCDD	.	.	.	.	
		2,3,7,8-TCDD					
		2,3,7,8 + 2,3,4,6-TCDF	30.00	30.00	30.00	33.30	5.77
		1,2,3,7,8 + 1,2,3,4,8-PNCDF	82.00	31.00	94.00	77.00	6.24
		2,3,4,7,8-PNCDF	56.00	41.00	57.00	39.00	1.00
		1,2,3,4,7,8 + 1,2,3,6,7,8-HXCDF	660.00	740.00	840.00	753.00	131.00
		1,2,3,7,8,9-HXCDF	44.00	50.00	38.00	44.10	9.45
		2,3,4,6,7,8-HXCDF	47.00	25.00	43.00	38.30	11.70
		1,2,3,4,6,7,8-HPCDF	350.00	620.00	786.00	585.00	200.00
13	BATTELLE	TOTAL TCDF	840.00	870.00	388.00	500.00	130.00
		TOTAL PNCDF	220.00	170.00	220.00	267.00	23.20
		TOTAL HXCDF	140.00	330.00	160.00	145.00	11.30
		TOTAL HPCDF	22.00	58.00	0.00	10.00	12.40
		OCDF	46.00	44.00	30.00	33.30	20.20
		TOTAL TCDD	.	.	.	.	
		OCDD	.	.	.	.	
		2,3,7,8-TCDD					
		2,3,7,8 + 2,3,4,6-TCDF	300.00	280.00	220.60	267.00	41.60
		1,2,3,7,8 + 1,2,3,4,8-PNCDF	10.00	8.30	7.00	8.73	1.12
		2,3,4,7,8-PNCDF	71.00	74.00	53.00	66.00	11.40
		1,2,3,4,7,8 + 1,2,3,6,7,8-HXCDF	37.00	18.00	21.00	28.00	10.80
		1,2,3,7,8,9-HXCDF	16.00	13.00	27.00	18.00	6.93
		2,3,4,6,7,8-HXCDF	30.00	17.80	39.00	27.00	11.10
		1,2,3,4,6,7,8-HPCDF	7.10	5.50	1.00	6.60	2.33
14	BATTELLE	TOTAL TCDF	870.00	560.00	810.00	720.00	117.00
		TOTAL PNCDF	31000.00	8700.00	8500.00	8067.00	2548.00
		TOTAL HXCDF	14000.00	36000.00	10000.00	21000.00	12166.00
		TOTAL HPCDF	3100.00	7800.00	4100.00	3367.00	797.00
		OCDF	150.00	170.00	220.00	180.00	28.10
		TOTAL TCDD	.				
		OCDD	.	10.00	.	10.00	
		2,3,7,8-TCDD					
		2,3,7,8 + 2,3,4,6-TCDF	400.00	380.00	350.00	377.00	25.20
		1,2,3,7,8 + 1,2,3,4,8-PNCDF	870.00	800.00	780.00	830.00	62.40
		2,3,4,7,8-PNCDF	2300.00	5400.00	1600.00	3167.00	321.00
		1,2,3,4,7,8 + 1,2,3,6,7,8-HXCDF	4700.00	7200.00	4100.00	5333.00	1644.00
		1,2,3,7,8,9-HXCDF	1700.00	6800.00	2000.00	4367.00	2666.00
		2,3,4,6,7,8-HXCDF	620.00	9800.00	930.00	3783.00	5411.00
		1,2,3,4,6,7,8-HPCDF	920.00	500.00	1300.00	817.00	370.01

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TABLE B-1 (cont'd.)

Sample	Lab	Compound	Det. 1	Det. 2	Det. 3	Mean	Std. Dev.
16	BATTELLE	TOTAL TCDF	.	.	.	.	.
		TOTAL PNCDF	.	.	.	.	.
		TOTAL HXCDF	.	.	.	.	.
		TOTAL HPCDF	.	.	.	.	.
		OCDF	.	12.00	.	12.00	
		TOTAL TCDD	.	.	.	.	.
		OCDD	.	.	.	.	.
		2,3,7,8-TCDD	.	.	.	.	.
		2,3,7,8 + 2,3,4,8-TCDF	.	.	.	.	.
		1,2,3,7,8 + 1,2,3,4,8-PNCDF	.	.	.	.	.
		2,3,4,7,8-PNCDF	.	.	.	.	.
		1,2,3,4,7,8 + 1,2,3,4,7,8-HXCDF	.	.	.	.	.
		1,2,3,7,8,9-HXCDF	.	.	.	.	.
		2,3,4,6,7,8-HXCDF	.	.	.	.	.
		1,2,3,4,6,7,8-HPCDF	.	.	.	.	.
16	BATTELLE	TOTAL TCDF	.	.	.	.	.
		TOTAL PNCDF	.	.	.	.	.
		TOTAL HXCDF	.	.	.	.	.
		TOTAL HPCDF	.	.	.	.	.
		OCDF	.	.	.	.	.
		TOTAL TCDD	.	.	.	.	.
		OCDD	.	13.00	11.00	12.00	1.41
		2,3,7,8-TCDD	.	.	.	.	.
		2,3,7,8 + 2,3,4,8-TCDF	.	.	.	.	.
		1,2,3,7,8 + 1,2,3,4,8-PNCDF	.	.	.	.	.
		2,3,4,7,8-PNCDF	.	.	.	.	.
		1,2,3,4,7,8 + 1,2,3,4,7,8-HXCDF	.	.	.	.	.
		1,2,3,7,8,9-HXCDF	.	.	.	.	.
		2,3,4,6,7,8-HXCDF	.	.	.	.	.
		1,2,3,4,6,7,8-HPCDF	.	.	.	.	.
17	BATTELLE	TOTAL TCDF	960.00	830.00	780.00	523.00	93.10
		TOTAL PNCDF	870.00	830.00	670.00	867.00	84.30
		TOTAL HXCDF	6700.00	19000.00	20000.00	15700.00	6601.00
		TOTAL HPCDF	1400.00	1400.00	2000.00	1667.00	306.00
		OCDF	4300.00	4800.00	5100.00	4733.00	404.00
		TOTAL TCDD	.	.	.	.	.
		OCDD	10.00	10.00	10.00	15.30	4.62
		2,3,7,8-TCDD	.	.	.	.	.
		2,3,7,8 + 0,3,4,8-TCDF	190.00	140.00	160.00	170.00	25.50
		1,2,3,7,8 + 1,2,3,4,6-PNCDF	68.00	71.00	71.00	70.70	1.53
		0,2,4,7,8-PNCDF	300.00	280.00	280.00	282.00	20.00
		1,2,3,4,7,8 + 1,2,3,4,7,8-HXCDF	2700.00	6400.00	6000.00	5333.00	2294.00
		1,2,3,7,8,9-HXCDF	780.00	2200.00	2700.00	1893.00	1024.00
		2,3,4,6,7,8-HXCDF	1100.00	3400.00	3800.00	2767.00	1457.00
		1,2,3,4,6,7,8-HPCDF	180.00	230.00	320.00	243.00	70.00

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TABLE B-1 (cont'd.)

Sample	Lab	Compound	Det. 1	Det. 2	Det. 3	Mean	Std. Dev.
1	RADIAN EXT1	TOTAL TCDF	186.00	188.00	177.00	178.00	10.00
		TOTAL PNCDF	285.00	303.00	303.00	290.00	21.00
		TOTAL HXCDF	493.00	483.00	483.00	486.00	6.08
		TOTAL HPCDF	458.00	386.00	389.00	412.00	40.10
		OCDF	19.00	10.00	13.00	14.00	4.58
		TOTAL TCDD	24.00	23.00	25.00	24.70	0.58
		OCDD	10.00	10.00	10.00	10.00	0.00
		2,3,7,8-TCDD	24.00	25.00	25.00	24.70	0.58
		2,3,7,8 + 2,3,4,8-TCDF	168.69	188.00	177.00	178.00	10.00
		1,2,3,7,8 + 1,2,3,4,8-PNCDF	144.00	147.00	148.00	146.00	2.08
		2,3,4,7,8-PNCDF	131.00	156.00	152.00	144.00	13.00
		1,2,3,4,7,8 + 1,2,3,6,7,8-HXCDF	288.00	288.00	282.00	286.00	3.46
		1,2,3,7,8,9-HXCDF	5.00	3.00	3.00	3.00	0.00
		1,2,3,6,7,8-HXCDF	83.00	49.00	53.00	51.[illegible]	2.08
		2,3,4,6,7,8-HXCDF	178.00	186.00	170.00	172.00	7.78
		1,2,3,4,6,7,8-HPCDF	486.00	388.00	389.00	423.00	40.10
2	RADIAN EXT1	TOTAL TCDF	83.00	84.00	83.00	82.70	1.53
		TOTAL PNCDF	286.00	305.00	301.00	301.00	3.52
		TOTAL HXCDF	194.00	188.00	185.00	190.00	3.11
		TOTAL HPCDF	568.00	536.00	536.00	548.00	17.30
		OCDF	125.00	126.00	129.00	127.00	2.08
		TOTAL TCDD	52.00	49.00	51.00	50.70	1.53
		OCDD	10.00	10.00	10.00	10.00	0.00
		2,3,7,8-TCDD	52.00	49.00	51.00	50.70	1.53
		2,3,7,8 + 2,3,4,8-TCDF	83.00	84.00	83.00	82.76	1.53
		1,2,3,7,8 + 1,2,3,4,8-PNCDF	138.00	139.00	137.00	137.00	2.00
		2,3,4,7,8-PNCDF	143.00	144.00	144.00	144.00	0.58
		1,2,3,6,7,8 + 1,2,3,4,7,8-HXCDF	8.00	8.00	8.00	8.00	0.00
		1,2,3,7,8,9-HXCDF	3.00	3.00	3.00	3.00	0.00
		1,2,3,6,7,8-HXCDF	61.00	87.00	53.00	37.70	3.06
		2,3,4,6,7,8-HXCDF	133.00	133.00	133.00	133.00	0.58
		1,2,3,4,6,7,8-HPCDF	888.00	528.00	539.00	549.00	17.30
3	RADIAN EXT1	TOTAL TCDF	1583.00	1418.00	1431.00	1490.00	98.10
		TOTAL PNCDF	1606.00	1310.00	1328.00	1412.00	167.00
		TOTAL HXCDF	2348.00	2193.00	2306.00	2453.00	271.00
		TOTAL HPCDF	2492.00	2416.00	2383.00	2424.00	64.80
		OCDF	4029.00	3810.00	2801.00	3913.00	114.00
		TOTAL TCDD	100.00	100.00	97.00	99.00	1.73
		OCDD	10.00	10.00	10.00	10.00	0.00
		2,3,7,8-TCDD	100.00	100.00	97.00	98.00	1.53
		2,3,7,8 + 2,3,4,8-TCDF	3141.00	1187.00	5165.00	1336.00	12.20
		1,2,3,7,8 + 1,2,3,4,8-PNCDF	300.00	323.00	321.00	315.00	12.70
		2,3,4,7,8-PNCDF	285.00	282.00	278.00	280.00	2.08
		1,2,3,6,7,8 + 1,2,3,4,7,8-HXCDF	1142.00	1168.00	1174.00	1187.00	22.70
		1,2,3,7,8,9-HXCDF	31.00	34.00	33.00	32.70	1.53
		1,2,3,6,7,8-HXCDF	322.00	294.00	288.00	305.00	15.70
		2,3,4,6,7,8-HXCDF	317.00	324.00	323.00	321.00	3.51
		1,2,3,4,6,7,8-HPCDF	781.00	780.00	762.00	774.00	10.70

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TABLE B-1 (cont'd.)

Sample	Lab	Compound	Det. 1	Det. 2	Det. 3	Mean	Std. Dev
11	RADIAN EXT1	TOTAL TCDF	197.00	161.00	128.00	162.00	18.70
		TOTAL PNCDF	8206.00	2217.00	1870.00	2031.00	313.00
		TOTAL HXCDF	7143.00	7708.00	6977.00	6976.00	628.00
		TOTAL HPCDF	11821.00	11208.00	8000.00	10143.00	1956.00
		OCDF	28720.00	26358.00	22700.00	26059.00	2667.00
		TOTAL TCDD	3.00	3.00	3.00	3.00	0.00
		OCDD	10.00	10.00	10.00	10.00	0.00
		2,3,7,8-TCDD	3.00	3.00	3.00	3.00	0.00
		2,3,7,8 + 2,3,4,8-TCDF	36.00	26.00	32.00	30.00	3.46
		1,2,3,7,8 + 1,2,3,4,8-PNCDF	1619.00	998.00	1100.00	1007.00	104.00
		2,3,4,7,8-PNCDF	137.00	516.00	69.00	107.00	34.69
		1,2,3,4,7,8 + 1,2,3,4,7,8-HXCDF	6974.00	9348.00	6582.00	6927.00	383.00
		1,2,3,7,8,9-HXCDF	278.00	275.00	227.00	260.00	28.60
		1,2,3,6,7,8-HXCDF	334.00	231.00	394.00	320.00	32.30
		2,3,4,6,7,8-HXCDF	207.00	210.00	182.00	196.00	30.00
		1,2,3,4,6,7,8-HPCDF	4231.00	6810.00	3050.00	3937.00	873.00
12	RADIAN EXT1	TOTAL TCDF	72.00	80.00	83.00	87.00	6.76
		TOTAL PNCDF	331.00	348.00	285.00	512.00	42.13
		TOTAL HXCDF	887.00	1088.00	879.00	989.00	85.00
		TOTAL HPCDF	2368.00	2580.00	2008.00	2302.60	333.00
		OCDF	8116.00	7827.00	6328.00	8000.00	818.60
		TOTAL TCDD	3.00	3.00	5.00	3.00	0.00
		OCDD	10.00	10.00	10.00	10.00	0.00
		2,3,7,8-TCDD	3.00	3.00	3.00	3.00	0.00
		2,3,7,8 + 2,3,4,8-TCDF	26.00	30.00	30.00	28.70	3.06
		1,2,3,7,8 + 1,2,3,8,9-PNCDF	101.00	141.00	113.00	118.00	19.80
		2,3,4,7,8-PNCDF	38.00	42.00	27.00	36.00	7.94
		1,2,3,6,7,8 + 1,2,3,4,7,8-HXCDF	951.00	748.00	819.00	973.00	68.00
		1,2,3,7,8,9-HXCDF	37.00	34.00	58.00	36.70	2.52
		1,2,3,6,7,8-HXCDF	57.00	48.00	36.00	37.00	3.00
		2,3,4,6,7,8-HXCDF	23.00	26.00	18.00	23.00	5.00
		1,2,3,4,6,7,8-HPCDF	738.00	763.00	265.00	682.00	101.00
13	RADIAN EXT1	TOTAL TCDF	212.00	973.00	802.00	965.00	97.10
		TOTAL PNCDF	239.00	320.00	210.00	289.00	48.50
		TOTAL HXCDF	20.00	35.00	13.00	16.00	3.61
		TOTAL HPCDF	3.00	3.00	5.00	3.00	0.00
		OCDF	23.00	17.00	10.00	16.70	6.51
		TOTAL TCDD	3.00	3.00	3.00	3.00	0.00
		OCDD	10.00	10.00	10.00	10.00	0.00
		2,3,7,8-TCDD	3.00	3.00	3.00	3.00	0.00
		2,3,7,8 + 2,3,4,6-TCDF	227.00	277.00	251.00	238.00	25.00
		1,2,3,7,8 + 1,2,3,8,9-PNCDF	15.00	16.00	17.00	16.00	1.00
		2,3,4,7,8-PNCDF	60.00	98.00	53.00	55.70	8.33
		1,2,3,6,7,8 + 1,2,3,4,7,8-HXCDF	23.00	20.00	18.00	20.30	1.53
		1,2,3,7,8,9-HXCDF	3.00	3.00	3.00	3.00	1.15
		1,2,3,6,7,8-HXCDF	3.00	5.00	3.00	3.00	0.00
		2,3,4,6,7,8-HXCDF	3.00	3.00	3.00	3.00	0.00
		1,2,3,4,6,7,8-HPCDF	3.00	3.00	3.00	3.00	0.00

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TABLE B-1 (cont'd.)

Sample	Lab	Compound	Det. 1	Det. 2	Det. 3	Mean	Std Dev
14	RADIAN EXT1	TOTAL TCDF	818.60	988.00	835.00	880.00	92.50
		TOTAL PNCDF	13100.00	9083.00	7335.00	10139.00	3847.00
		TOTAL HXCDF	9438.00	11187.00	9846.00	9823.00	1376.00
		TOTAL HPCDF	3010.00	3384.00	1608.00	2001.00	384.00
		OCDF	200.00	184.00	193.00	192.00	8.61
		TOTAL TCDD	3.00	3.00	3.00	3.00	0.00
		OCDD	10.00	10.00	10.00	10.00	0.00
		2,3,7,8-TCDD	3.00	3.00	3.00	3.00	0.00
		2,3,7,8 + 3,3,4,8-TCDF	368.00	388.00	318.00	331.00	32.10
		1,2,3,7,8 + 1,2,3,4,8-PNCDF	1436.00	1422.00	1186.00	1410.00	222.00
		2,3,4,7,8-PNCDF	1800.00	1650.00	1204.00	1555.00	313.00
		1,2,3,4,7,8 + 1,2,3,6,7,8-HXCDF	6127.00	6688.00	3858.00	4211.00	420.00
		1,2,3,7,8,9-HXCDF	1166.00	1432.00	1107.00	1235.00	172.00
		1,2,3,4,7,8-HXCDF	612.00	612.00	788.00	841.00	81.70
		2,3,4,6,7,8-HXCDF	808.00	1008.00	871.00	947.00	106.00
		1,2,3,4,6,7,8-HPCDF	871.00	774.00	810.00	452.00	133.00
15	RADIAN EXT1	TOTAL TCDF	80.00	3.00	3.00	10.70	27.10
		TOTAL PNCDF	80.00	3.00	3.00	10.70	27.10
		TOTAL HXCDF	34.00	16.00	81.00	23.00	10.10
		TOTAL HPCDF	47.00	33.00	21.00	33.70	13.00
		OCDF	108.00	103.00	113.00	107.00	5.11
		TOTAL TCDD	3.00	3.00	3.00	3.00	0.00
		OCDD	10.00	10.00	10.00	10.00	0.00
		2,3,7,8-TCDD	3.00	3.00	3.00	3.00	0.00
		2,3,7,8 + 3,3,4,8-TCDF	80.00	3.00	3.00	8.67	8.67
		1,2,3,7,8 + 1,2,3,4,8-PNCDF	20.00	3.00	3.00	8.89	8.81
		2,3,4,7,8-PNCDF	80.00	3.00	3.00	8.67	8.67
		1,2,3,4,7,8 + 1,2,3,6,7,8-HXCDF	50.00	17.00	24.00	30.30	17.40
		1,2,3,7,8,9-HXCDF	20.00	3.00	3.00	8.67	8.67
		1,2,3,4,7,8-HXCDF	20.00	3.00	3.00	8.67	8.67
		2,3,4,6,7,8-HXCDF	20.00	3.00	3.00	8.67	8.67
		1,2,3,4,6,7,8-HPCDF	30.00	21.00	21.00	24.00	5.20
16	RADIAN EXT1	TOTAL TCDF	3.00	8.00	3.00	2.00	0.00
		TOTAL PNCDF	3.00	3.00	3.00	3.00	0.00
		TOTAL HXCDF	21.00	9.00	11.00	13.70	8.43
		TOTAL HPCDF	50.00	11.00	24.00	28.30	19.80
		OCDF	231.00	44.00	107.00	94.00	44.80
		TOTAL TCDD	3.00	3.00	1.00	3.00	0.00
		OCDD	10.00	10.00	10.00	10.00	0.00
		2,3,7,8-TCDD	3.00	3.00	3.00	3.00	0.00
		2,3,7,8 + 3,3,4,8-TCDF	3.00	3.00	3.00	3.00	0.00
		1,2,3,7,8 + 1,2,3,4,8-PNCDF	3.00	3.00	3.00	3.00	0.00
		2,3,4,7,8-PNCDF	3.00	3.00	3.00	3.00	0.00
		1,2,3,4,7,8 + 1,2,3,6,7,8-HXCDF	24.00	13.00	14.00	16.70	6.43
		1,2,3,7,8,9-HXCDF	3.00	3.00	3.00	3.00	0.00
		1,2,3,4,7,8-HXCDF	3.00	3.00	3.00	3.00	0.00
		2,3,4,6,7,8-HXCDF	3.00	3.00	3.00	3.00	0.00
		1,2,3,4,6,7,8-HPCDF	10.00	3.00	11.00	11.33	4.51

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TABLE B-1 (cont'd.)

Sample	Lab	Compound	Det. 1	Det. 2	Det. 3	Mean	Std. Dev.
17	RADIAN EXT1	TOTAL TCDF	438.00	000.00	337.00	801.00	86.60
		TOTAL PNCDF	1260.00	1308.00	1197.00	1328.00	181.00
		TOTAL HXCDF	8242.00	2482.00	3068.00	2291.00	207.00
		TOTAL HPCDF	2217.00	2346.00	1758.00	2126.00	322.00
		OCDF	4857.00	8402.00	4295.00	4691.00	888.00
		TOTAL TCDD	3.00	3.00	3.00	3.00	0.00
		OCDD	10.00	10.00	10.00	10.00	0.00
		2,3,7,8-TCDD	3.00	3.00	3.00	3.00	0.00
		2,3,7,8 + 2,3,4,6-TCDF	162.00	189.00	818.00	190.00	37.50
		1,2,3,7,8 + 1,2,3,4,6-PNCDF	300.00	366.00	307.00	323.00	37.40
		2,3,4,7,8-PNCDF	207.00	803.00	136.00	203.00	44.70
		1,2,3,4,7,8 + 1,2,3,4,7,9-HXCDF	1418.00	1047.00	1251.00	1697.00	143.00
		1,2,3,7,8,9-HXCDF	36.00	83.00	86.00	50.70	2.89
		1,2,3,6,7,8-HXCDF	93.00	87.00	83.00	87.30	4.51
		2,3,4,6,7,8-HXCDF	98.00	111.00	104.00	805.00	9.03
		1,2,3,4,6,7,8-HPCDF	1984.00	1163.00	837.00	1032.00	134.00
1	RADIAN EXT2	TOTAL TCDF	189.00	191.00	176.00	163.00	12.10
		TOTAL PNCDF	309.00	317.00	293.00	307.00	11.30
		TOTAL HXCDF	477.00	486.00	478.00	481.00	4.73
		TOTAL HPCDF	411.00	433.00	455.00	434.00	22.00
		OCDF	11.00	10.00	10.00	10.30	0.58
		TOTAL TCDD	35.00	28.00	34.00	85.00	1.00
		OCDD	10.00	20.00	10.00	38.00	0.00
		2,3,7,8-TCDD	28.00	28.00	24.00	25.00	1.00
		2,3,7,8 + 2,3,8,8-TCDF	186.00	161.00	176.00	165.00	12.30
		1,2,3,7,8 + 1,2,3,4,6-PNCDF	142.00	138.00	134.00	137.00	4.16
		2,3,4,7,8-PNCDF	167.00	181.00	181.00	183.00	3.46
		1,2,3,4,7,8 + 1,2,3,4,7,8-HXCDF	838.00	863.00	281.60	258.00	8.11
		1,2,3,7,0,8-HXCDF	3.00	3.00	3.00	3.00	0.00
		1,2,3,6,7,8-HXCDF	47.00	47.00	82.00	88.70	2.80
		8,3,4,6,7,2-HXCDF	174.00	178.00	170.00	177.00	2.89
		1,2,3,4,6,7,8-HPCDF	411.00	428.00	458.00	434.00	82.00
2	RADIAN EXT2	TOTAL TCDF	63.00	60.00	87.00	59.70	2.52
		TOTAL PNCDF	320.00	305.00	300.00	310.00	8.39
		TOTAL HXCDF	187.00	197.00	184.00	189.00	1.73
		TOTAL HPCDF	577.00	868.00	828.00	800.00	25.80
		OCDF	188.00	128.00	118.00	123.00	5.03
		TOTAL TCDD	30.00	32.00	80.00	30.70	1.15
		DCDD	10.00	10.00	10.00	10.00	0.00
		2,3,7,8-TCDD	50.00	52.00	80.00	50.70	1.15
		2,3,7,8 + 8,3,4,8-TCDF	82.00	80.00	37.00	39.70	2.52
		1,2,3,7,8 + 1,2,3,4,8-PNCDF	187.00	121.00	133.00	153.00	3.21
		2,3,4,7,8-PNCDF	163.00	154.00	154.00	157.00	5.20
		1,2,3,4,7,8 + 1,2,3,4,7,9-HXCDF	8.00	8.00	8.00	8.00	0.00
		1,2,3,7,8,8-HXCDF	3.00	3.00	3.00	3.00	0.00
		1,2,3,6,7,8-HXCDF	57.00	68.00	55.00	58.70	1.53
		2,3,4,6,7,8-HXCDF	140.00	139.00	136.00	139.00	0.58
		1,2,3,4,6,7,8-HPCDF	577.00	896.00	828.00	600.00	25.80

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TABLE B-1 (cont'd.)

Sample	Lab	Compound	Det. 1	Det. 2	Det. 3	Mean	Std Dev
3	RADIAN EXT2	TOTAL TCDF	1807.00	1536.00	1474.00	1472.00	83.50
		TOTAL PNCDF	2267.00	1368.00	1129.00	1265.00	135.00
		TOTAL HXCDF	1333.00	2400.00	2425.00	2052.00	822.00
		TOTAL HPCDF	2085.00	2253.00	2388.00	2248.00	147.00
		OCDF	3772.00	3608.00	3407.00	3602.00	321.00
		TOTAL TCDD	101.00	102.00	131.00	105.00	5.51
		OCDD	10.00	10.00	10.00	10.00	0.00
		2,3,7,8-TCDD	101.00	102.00	111.00	105.00	5.51
		2,3,7,8 + 2,3,4,8-TCDF	1150.00	1093.00	1068.00	1104.00	42.00
		1,2,3,7,8 + 1,2,3,4,8-PNCDF	309.00	307.00	275.00	230.00	20.20
		2,3,4,7,8-PNCDF	279.00	272.00	252.00	268.00	14.00
		1,2,3,4,7,8 + 1,2,3,4,7,8-HXCDF	1187.00	1185.00	1151.00	1168.00	23.90
		1,2,3,7,8,9-HXCDF	36.00	23.00	33.00	34.00	2.73
		1,2,3,6,7,8-HXCDF	274.00	200.00	329.00	293.00	27.30
		2,3,4,6,7,8-HXCDF	326.00	285.00	330.00	348.00	38.60
		1,2,3,4,6,7,8-HPCDF	751.00	787.00	838.00	781.00	62.70
11	RADIAN EXT2	TOTAL TCDF	583.00	179.00	146.00	188.00	20.30
		TOTAL PNCDF	2058.00	1896.00	2078.00	2043.00	41.10
		TOTAL HXCDF	7138.00	7188.00	6821.00	7083.00	126.00
		TOTAL HPCDF	11075.00	10980.00	11175.00	11080.00	92.60
		OCDF	10182.00	11283.00	9554.00	10340.00	874.00
		TOTAL TCDD	3.00	3.00	3.00	3.00	0.00
		OCDD	10.00	10.00	10.00	10.00	0.00
		2,3,7,8-TCDD	3.00	3.00	3.00	3.00	0.00
		2,3,7,8 + 2,3,4,8-TCDF	38.00	39.60	38.00	38.00	0.08
		1,2,3,7,8 + 1,2,3,4,8-PNCDF	5003.00	1000.00	1038.00	1014.00	21.10
		2,3,4,7,8-PNCDF	111.00	103.00	107.00	107.00	4.00
		1,2,3,4,7,8 + 1,2,3,6,7,8-HXCDF	6873.00	6720.00	6748.00	6780.00	80.50
		1,2,3,7,8,9-HXCDF	274.00	256.00	262.00	255.00	11.78
		1,2,3,6,7,8-HXCDF	283.00	890.00	297.00	310.00	64.50
		2,3,4,6,7,8-HXCDF	200.00	193.00	188.00	200.00	6.08
		1,2,3,4,6,7,8-HPCDF	4165.00	4171.00	4218.00	4185.00	29.00
13	RADIAN EXT2	TOTAL TCDF	103.00	97.00	99.00	88.70	3.08
		TOTAL PNCDF	271.00	266.00	280.00	272.00	7.09
		TOTAL HXCDF	855.00	846.00	936.00	879.00	49.90
		TOTAL HPCDF	2339.00	2236.00	2482.00	2332.00	123.00
		OCDF	5429.00	3238.00	5193.00	5283.00	128.00
		TOTAL TCDD	3.00	3.00	3.00	3.00	0.00
		OCDD	10.00	10.00	10.00	10.00	0.00
		2,3,7,8-TCDD	3.00	3.00	3.00	3.00	0.00
		2,3,7,8 + 2,3,4,8-TCDF	53.00	53.00	30.00	32.00	1.73
		1,2,3,7,8 + 1,2,3,4,8-PNCDF	98.00	102.00	105.00	101.00	4.16
		2,3,4,7,8-PNCDF	35.00	37.00	35.00	33.70	1.15
		1,2,3,4,7,8 + 1,2,3,6,7,8-HXCDF	528.00	530.00	534.00	531.00	3.06
		1,2,3,7,8,9-HXCDF	38.00	37.00	41.00	38.70	2.08
		1,2,3,6,7,8-HXCDF	44.00	45.00	41.00	44.70	3.51
		2,3,4,6,7,8-HXCDF	35.00	37.00	35.00	35.70	1.15
		1,2,3,4,6,7,8-HPCDF	872.00	834.00	708.00	871.00	37.00

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TABLE B-1 (Cont'd.)

Sample	Lab	Compound	Det. 1	Det. 2	Det. 3	Mean	Std. Dev.
10	RADIAN ENTS	TOTAL TCDF	702.00	827.00	843.00	804.00	82.70
		TOTAL PNCDF	337.00	298.00	323.00	319.00	20.80
		TOTAL HXCDF	53.00	48.00	44.00	51.30	4.65
		TOTAL HPCDF	17.00	16.00	17.00	16.70	0.58
		OCDF	27.00	25.00	29.00	26.30	1.15
		TOTAL TCDD	3.00	3.00	3.00	3.00	0.00
		OCDD	10.00	10.00	10.00	10.00	0.00
		2,3,7,8-TCDD	3.00	3.00	3.00	3.00	0.00
		2,3,7,8 + 2,3,4,8-TCDF	806.00	814.00	828.00	819.00	12.10
		1,2,3,7,8 + 1,2,3,4,8-PNCDF	16.00	14.00	18.00	13.30	1.10
		2,3,4,7,8-PNCDF	87.00	58.00	86.00	87.00	1.00
		1,2,3,6,7,8 + 1,2,3,4,7,8-HXCDF	88.00	24.00	85.00	84.70	0.58
		2,3,7,8,9-HXCDF	8.60	8.00	3.00	6.33	1.53
		1,2,3,8,7,8-HXCDF	8.00	6.00	6.00	5.67	0.38
		2,3,4,8,7,8-HXCDF	13.00	10.00	12.00	11.30	1.15
		1,2,3,4,8,7,8-HPCDF	7.00	8.00	8.00	7.87	0.58
14	RADIAN ENTS	TOTAL TCDF	843.00	851.00	901.00	865.00	30.10
		TOTAL PNCDF	8086.00	8361.00	8024.00	8079.00	275.00
		TOTAL HXCDF	9644.00	9961.00	9884.00	9563.00	581.00
		TOTAL HPCDF	2218.00	2273.00	1608.00	2032.00	370.00
		OCDF	176.00	186.00	218.00	193.00	22.10
		TOTAL TCDD	3.00	3.00	3.00	3.00	0.00
		OCDD	10.00	10.00	10.00	10.00	0.00
		2,3,7,8-TCDD	3.00	3.00	3.00	3.00	0.00
		2,3,7,8 + 2,3,4,8-TCDF	330.00	336.00	341.00	342.00	7.09
		1,2,3,7,8 + 1,2,3,4,8-PNCDF	1347.00	1337.00	877.00	1220.00	811.00
		2,3,4,7,8-PNCDF	1674.00	1838.00	1657.00	1834.00	81.10
		1,2,3,4,7,8 + 1,2,3,4,7,8-HXCDF	4432.00	4427.00	3281.00	4043.00	860.00
		1,2,3,7,8,8-HXCDF	1244.00	1248.00	743.00	1078.00	280.00
		1,2,3,8,7,8-HXCDF	488.00	714.00	478.00	753.00	110.00
		2,3,4,8,7,8-HXCDF	870.00	882.00	582.00	854.00	127.00
		1,2,3,4,8,7,8-HPCDF	738.00	738.00	342.00	600.00	130.00
15	RADIAN ENTS	TOTAL TCDF	3.00	3.00	3.00	3.00	0.00
		TOTAL PNCDF	3.00	3.00	3.00	3.00	0.00
		TOTAL HXCDF	10.00	17.00	10.00	10.30	0.58
		TOTAL HPCDF	36.00	34.00	27.00	31.70	4.04
		OCDF	56.00	59.00	56.00	57.70	1.53
		TOTAL TCDD	3.00	3.00	3.00	3.00	0.00
		OCDD	10.00	10.00	10.00	10.00	0.00
		2,3,7,8-TCDD	3.00	3.00	3.00	3.00	0.00
		2,3,7,8 + 2,3,4,8-TCDF	3.00	3.00	3.00	3.00	0.00
		1,2,3,7,8 + 1,2,3,4,8-PNCDF	3.00	3.00	3.00	3.00	0.00
		2,3,4,7,8-PNCDF	3.00	3.00	3.00	3.00	0.00
		1,2,3,4,7,8 + 1,2,3,4,7,8-HXCDF	13.00	14.00	13.00	13.30	0.58
		1,2,3,7,8,8-HXCDF	3.00	5.00	3.00	3.60	0.00
		1,2,3,8,7,8-HXCDF	3.00	3.00	3.00	3.00	0.00
		2,3,4,8,7,8-HXCDF	3.00	3.00	3.00	3.00	0.00
		1,2,3,4,8,7,8-HPCDF	14.00	13.00	18.00	15.00	1.00

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TABLE B-1 (cont'd.)

Sample	Lab	Compound	Det. 1	Det 2	Det 3	Mean	Std Dev
16	RADIAN EXT2	TOTAL TCDF	3.00	3.00	3.00	3.00	0.00
		TOTAL PNCDF	3.00	3.00	3.00	3.00	0.00
		TOTAL HXCDF	3.00	3.00	3.00	3.00	0.00
		TOTAL HPCDF	3.00	3.00	3.00	3.00	0.00
		OCDF	23.00	26.00	37.00	28.30	7.37
		TOTAL TCDD	3.00	3.00	3.00	3.00	0.00
		OCDD	11.00	13.00	12.00	12.00	1.00
		2,3,7,8-TCDD	3.00	3.00	3.00	3.00	0.00
		2,3,7,8 + 3,3,4,8-TCDF	3.00	3.00	3.00	3.00	0.00
		1,2,3,7,8 + 1,2,3,4,8-PNCDF	3.00	3.00	3.00	3.00	0.00
		2,3,4,7,8-PNCDF	3.00	3.00	3.00	3.00	0.00
		1,2,3,4,7,8 + 1,2,3,4,7,9-HXCDF	9.00	9.00	9.00	9.00	0.00
		1,2,3,7,8,9-HXCDF	3.00	3.00	3.00	3.00	0.00
		1,2,3,6,7,8-HXCDF	3.00	3.00	3.00	3.00	0.00
		2,3,4,6,7,8-HXCDF	3.00	3.00	3.00	3.00	0.00
		1,2,3,4,6,7,8-HPCDF	3.00	3.00	3.00	3.00	0.00
17	RADIAN EXT2	TOTAL TCDF	462.00	383.00	419.00	421.00	39.60
		TOTAL PNCDF	1333.00	1116.00	1098.00	1177.00	131.00
		TOTAL HXCDF	2336.00	2302.00	2319.00	2323.00	20.30
		TOTAL HPCDF	2411.00	2609.00	2880.00	2567.00	139.00
		OCDF	414.00	385.00	398.00	399.00	14.30
		TOTAL TCDD	3.00	3.00	3.00	3.00	0.00
		OCDD	10.00	10.00	10.00	10.00	0.00
		2,3,7,8-TCDD	3.00	3.00	3.00	3.00	0.00
		2,3,7,8 + 2,3,4,8-TCDF	284.00	184.00	144.00	171.00	11.00
		1,2,3,7,8 + 1,2,3,4,8-PNCDF	318.00	316.00	256.00	287.00	49.00
		2,3,4,7,8-PNCDF	204.00	198.00	201.00	197.00	9.64
		1,2,3,6,7,8 + 1,2,3,4,7,8-HXCDF	1384.00	1401.00	1397.00	1396.00	11.30
		1,2,3,7,8,9-HXCDF	88.00	99.00	87.00	87.30	1.33
		1,2,3,6,7,8-HXCDF	100.00	83.00	85.00	82.70	19.00
		2,3,4,6,7,8-HXCDF	110.00	107.00	120.00	108.00	1.73
		1,2,3,4,6,7,8-HPCDF	1389.00	1242.00	1383.00	1230.00	59.60
1	RADIAN EXT2	TOTAL TCDF	183.00	186.00	182.00	183.00	3.61
		TOTAL PNCDF	298.00	292.00	300.00	283.00	54.00
		TOTAL HXCDF	463.00	490.00	477.00	474.00	7.84
		TOTAL HPCDF	388.00	384.00	376.00	375.00	9.02
		OCDF	10.00	10.00	10.00	10.00	0.00
		TOTAL TCDD	24.00	22.00	23.00	23.00	1.00
		OCDD	10.00	10.00	10.00	10.00	0.00
		2,3,7,8-TCDD	24.00	22.00	23.00	23.00	1.00
		2,3,7,8 + 2,3,4,8-TCDF	188.00	188.00	182.00	185.00	3.21
		1,2,3,7,8 + 1,2,3,4,8-PNCDF	140.00	139.00	143.00	140.00	1.00
		8,3,4,7,8-PNCDF	160.00	153.00	159.00	157.00	3.21
		1,2,3,6,7,8 + 1,2,3,4,7,8-HXCDF	290.00	288.00	293.00	291.00	9.64
		1,2,3,7,8,9-HXCDF	3.00	3.00	3.00	3.00	0.00
		1,2,3,6,7,8-HXCDF	97.00	41.00	91.00	43.00	3.46
		2,3,4,6,7,8-HXCDF	170.00	170.00	170.00	172.00	2.31
		1,2,3,4,6,7,8-HPCDF	388.00	384.00	376.00	375.00	9.02

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TABLE B-1 (cont'd.)

Sample	Lab	Compound	Det. 1	Det. 2	Det. 3	Mean	Std. Dev.
2	RADIAN ENTS	TOTAL TCDF	80.00	60.00	81.00	80.30	8.88
		TOTAL PNCDF	306.00	500.00	306.00	304.06	3.48
		TOTAL HXCDF	201.00	1e1.00	190.00	191.00	8.39
		TOTAL HPCDF	581.00	498.00	519.00	527.00	33.00
		OCDF	125.00	123.00	136.00	128.00	7.00
		TOTAL TCDD	80.00	81.00	48.00	69.70	1.53
		OCDD	10.00	10.00	10.00	10.00	0.00
		2,3,7,8-TCDD	50.00	51.00	48.00	68.70	1.53
		2,3,7,8 + 2,3,4,8-TCDF	80.00	80.00	81.00	80.30	0.58
		1,2,3,7,8 + 1,2,3,4,8-PNCDF	160.00	154.00	157.00	158.00	1.53
		2,3,4,7,8-PNCDF	150.00	146.00	149.00	148.00	3.08
		1,2,3,4,7,8 + 1,2,3,4,7,8-HXCDF	8.00	8.00	8.00	8.00	0.00
		1,2,3,7,8,9-HXCDF	3.00	3.00	3.00	3.00	0.00
		1,3,3,8,7,8-HXCDF	84.00	33.00	81.00	80.00	4.58
		2,3,4,8,7,8-HXCDF	137.00	129.00	138.00	134.00	4.93
		1,2,3,4,8,7,8-HPCDF	661.00	606.00	616.00	626.00	33.00
3	RADIAN ENTS	TOTAL TCDF	1693.00	1676.00	1582.00	1373.00	20.80
		TOTAL PNCDF	1681.00	5311.00	5318.00	1283.00	87.90
		TOTAL HXCDF	3244.00	3171.00	3244.00	3220.00	42.10
		TOTAL HPCDF	2294.00	1976.00	2026.00	2065.80	148.00
		DCDF	4130.00	3966.00	4441.00	4189.00	228.00
		TOTAL TCDD	90.80	83.00	94.00	84.30	1.53
		OCDD	10.00	10.00	10.00	10.00	0.00
		2,3,7,8-TCDD	85.00	83.00	84.00	84.30	1.53
		2,3,7,8 + 2,3,4,8-TCDF	1156.00	1121.00	1171.00	1149.00	25.49
		1,2,3,7,8 + 1,2,3,4,8-PNCDF	333.00	331.00	311.00	335.00	12.20
		2,3,4,7,8-PNCDF	200.00	382.00	782.00	287.00	8.58
		1,2,3,4,7,8 + 1,2,3,4,7,8-HXCDF	1214.00	1164.00	1188.00	1181.00	35.26
		1,2,3,7,8,8-HXCDF	38.00	88.00	38.00	38.30	0.58
		1,2,3,8,7,8-HXCDF	292.00	304.00	289.00	290.00	6.00
		2,3,4,8,7,8-HXCDF	317.00	703.00	315.00	312.00	8.43
		1,2,3,4,8,7,8-HPCDF	786.00	704.00	728.00	740.00	42.00
51	RADIAN ENTS	TOTAL TCDF	158.00	173.00	176.00	169.00	10.49
		TOTAL PNCDF	2030.00	2087.00	2084.00	2084.00	3.51
		TOTAL HXCDF	7270.00	7041.00	7058.00	7123.00	131.00
		TOTAL HPCDF	11681.00	10345.00	10751.00	10859.00	548.00
		OCDF	28538.00	28448.00	28828.00	28138.00	1430.00
		TOTAL TCDD	3.00	3.00	3.00	3.00	0.00
		OCDD	10.00	10.00	10.00	10.00	0.00
		2,3,7,8-TCDD	3.00	3.00	3.00	3.00	0.00
		2,3,7,8 + 2,3,4,8-TCDF	38.00	40.00	40.00	38.30	1.15
		1,2,3,7,8 + 1,2,3,4,8-PNCDF	800.00	1014.00	1043.00	1018.00	22.80
		2,3,4,7,8-PNCDF	110.00	112.00	118.00	113.00	3.06
		1,2,3,4,7,8 + 1,2,3,4,7,8-HXCDF	8013.00	4882.00	4876.00	4816.00	83.80
		1,2,3,7,8,8-HXCDF	874.00	281.00	271.00	248.00	6.81
		1,2,3,8,7,8-HXCDF	310.00	303.00	303.00	305.00	4.04
		2,3,4,8,7,8-HXCDF	188.00	200.00	201.00	200.00	1.00
		1,2,3,4,8,7,8-HPCDF	4347.00	4013.00	4133.00	4172.00	167.00

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TABLE B-1 (cont'd.)

Sample	Lab	Compound	Det. 1	Det. 2	Det. 3	Mean	Std. Dev.
12	RADIAN EXT3	TOTAL TCDF	103.00	88.00	120.00	107.00	16.00
		TOTAL PNCDF	322.00	316.00	308.00	314.00	7.33
		TOTAL HXCDF	850.00	821.00	834.00	872.00	44.10
		TOTAL HPCDF	2244.00	1544.00	2134.00	2247.00	83.00
		OCDF	5764.00	5638.00	5494.00	5748.00	132.00
		TOTAL TCDD	3.00	3.00	3.00	3.00	0.00
		OCDD	10.00	10.00	10.00	10.00	0.00
		2,3,7,8-TCDD	3.00	3.00	3.00	3.00	0.00
		2,3,7,8 + 2,3,4,8-TCDF	32.00	31.00	41.00	34.70	5.51
		1,2,3,7,8 + 1,2,3,4,8-PNCDF	103.00	100.00	100.00	103.00	3.00
		2,3,4,7,8-PNCDF	37.00	40.00	41.00	39.30	2.08
		1,2,3,4,7,8 + 1,2,3,4,7,8-HXCDF	890.00	881.00	848.00	851.00	25.80
		1,2,3,7,8,8-HXCDF	37.00	36.00	37.00	37.30	0.58
		1,3,3,8,7,8-HXCDF	34.00	34.00	30.00	48.30	8.04
		2,3,8,8,7,8-HXCDF	37.00	41.00	36.00	28.70	2.08
		1,2,3,4,8,7,8-HPCDF	888.00	878.00	818.00	830.00	32.00
13	RADIAN EXT3	TOTAL TCDF	700.00	997.00	831.00	873.00	0.00
		TOTAL PNCDF	307.00	324.00	330.00	330.00	4.50
		TOTAL HXCDF	48.00	31.00	34.00	44.30	.1.80
		TOTAL HPCDF	3.00	3.00	10.00	5.33	4.04
		OCDF	88.00	26.00	28.00	27.30	1.15
		TOTAL TCDD	3.00	2.00	3.00	3.00	0.00
		OCDD	10.00	10.00	10.00	10.00	0.00
		2,3,7,8-TCDD	3.00	2.00	5.00	3.00	0.00
		2,3,7,8 + 2,3,4,8-TCDF	273.00	277.00	201.00	268.00	5.77
		1,2,3,7,8 + 1,2,3,4,8-PNCDF	20.00	20.00	20.00	20.00	0.00
		2,3,4,7,8-PNCDF	88.00	81.00	82.00	60.70	1.53
		1,2,3,4,7,8 + 1,2,3,4,7,8-HXCDF	23.00	24.00	27.00	24.70	2.08
		1,2,3,7,8,8-HXCDF	4.00	5.00	3.00	4.00	1.00
		1,2,3,8,7,8-HXCDF	4.00	3.00	3.00	3.33	0.58
		2,3,4,8,7,8-HXCDF	11.00	8.00	13.00	10.70	2.52
		1,2,3,4,8,7,8-HPCDF	2.00	3.00	10.00	5.33	4.04
14	RADIAN EXT3	TOTAL TCDF	818.00	870.00	804.00	888.00	18.40
		TOTAL PNCDF	8138.00	8232.00	8030.00	8134.00	133.00
		TOTAL HXCDF	8817.00	8903.00	8713.00	8812.00	94.10
		TOTAL HPCDF	2131.00	2138.00	2003.00	2110.00	40.80
		OCDF	187.00	194.00	280.00	218.00	36.70
		TOTAL TCDD	3.00	3.00	3.00	3.00	0.00
		OCDD	10.00	10.00	10.00	10.00	0.00
		2,3,7,8-TCDD	3.00	3.00	3.00	3.00	0.00
		2,3,7,8 + 2,3,4,8-TCDF	343.00	337.00	341.00	341.00	4.00
		1,2,3,7,8 + 1,2,3,4,8-PNCDF	852.00	856.00	1051.00	886.00	56.00
		2,3,8,7,8-PNCDF	1712.00	1758.00	1704.00	1728.00	33.00
		1,2,3,6,7,8 + 1,2,3,6,7,8-HXCDF	4305.00	4486.00	4200.00	4354.00	144.00
		1,2,3,7,8,8-HXCDF	1222.00	1218.00	1183.00	1211.00	15.10
		1,2,3,8,7,8-HXCDF	682.00	588.00	614.00	682.00	11.00
		2,3,4,6,7,8-HXCDF	976.00	972.00	940.00	883.00	19.70
		1,2,3,4,8,7,8-HPCDF	707.00	703.00	891.00	701.00	9.12

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TABLE B-1 (cont'd.)

Sample	Lab	Compound	Det. 1	Det. 2	Det. 3	Mean	Std Dev
15	RADIAN EXT3	TOTAL TCDF	8.00	3.00	8.00	3.00	9.00
		TOTAL PNCDF	3.00	3.00	3.00	3.00	0.00
		TOTAL HXCDF	89.00	20.00	18.00	22.00	5.28
		TOTAL HPCDF	66.00	51.00	85.00	50.30	5.03
		OCDF	82.00	100.00	100.00	97.30	4.82
		TOTAL TCDD	3.00	3.00	3.00	3.00	0.00
		OCDD	10.00	10.00	10.00	10.00	0.00
		2,3,7,8-TCDD	3.00	3.00	3.00	3.00	0.00
		2,3,7,8 + 2,3,4,8-TCDF	3.00	3.00	3.00	3.00	0.00
		1,2,3,7,8 + 1,2,3,4,8-PNCDF	3.00	3.00	3.00	3.00	0.00
		2,3,4,7,8-PNCDF	3.00	3.00	3.00	3.00	0.00
		1,2,3,4,7,8 + 1,2,3,4,7,9-HXCDF	21.00	18.00	21.00	20.70	0.43
		1,2,3,7,8,9-HXCDF	3.00	3.00	3.00	3.00	0.00
		1,2,3,6,7,8-HXCDF	3.00	3.00	3.00	3.00	0.00
		2,3,4,6,7,8-HXCDF	3.00	3.00	3.00	3.00	0.00
		1,2,3,4,6,7,8-HPCDF	22.00	24.00	27.00	24.30	2.32
16	RADIAN EXT3	TOTAL TCDF	3.00	7.00	3.00	4.33	2.31
		TOTAL PNCDF	3.00	3.00	3.00	3.00	0.00
		TOTAL HXCDF	6.00	3.00	3.00	4.67	1.89
		TOTAL HPCDF	3.00	3.00	3.00	3.00	0.00
		OCDF	10.00	10.00	10.00	10.00	0.00
		TOTAL TCDD	3.00	3.00	3.00	3.00	0.00
		OCDD	10.00	10.00	10.00	10.00	0.00
		2,3,7,8-TCDD	3.00	3.00	3.00	3.00	0.00
		2,3,7,8 + 2,3,4,8-TCDF	3.00	7.00	3.00	4.33	2.31
		1,2,3,7,8 + 1,2,3,4,8-PNCDF	3.00	3.00	3.00	3.00	0.00
		2,3,4,7,8-PNCDF	3.00	3.00	3.00	3.00	0.00
		1,2,3,4,7,8 + 1,2,3,4,7,9-HXCDF	11.00	8.00	8.00	9.00	1.73
		1,2,3,7,8,9-HXCDF	3.00	3.00	3.00	3.00	0.00
		1,2,3,6,7,8-HXCDF	3.00	3.00	3.00	3.00	0.00
		2,3,4,6,7,8-HXCDF	3.00	3.00	3.00	3.00	0.00
		1,2,3,4,6,7,8-HPCDF	3.00	3.00	2.00	3.00	0.00
17	RADIAN EXT3	TOTAL TCDF	312.00	312.00	318.00	314.00	3.21
		TOTAL PNCDF	1263.00	1119.00	1334.00	1139.00	110.00
		TOTAL HXCDF	3360.00	3374.00	3380.00	3365.00	8.08
		TOTAL HPCDF	3415.00	3362.00	3385.00	3360.00	28.00
		OCDF	4412.00	4334.00	4236.00	4334.00	59.70
		TOTAL TCDD	3.00	3.00	3.00	3.00	0.00
		OCDD	10.00	10.00	10.00	10.00	0.00
		2,3,7,8-TCDD	3.00	3.00	3.00	3.00	0.00
		2,3,7,8 + 2,3,4,8-TCDF	382.00	184.00	186.00	184.00	2.00
		1,2,3,7,8 + 1,2,3,4,8-PNCDF	313.00	313.00	338.00	322.00	14.50
		2,3,4,7,8-PNCDF	187.00	183.00	200.00	190.00	9.29
		1,2,3,4,7,8 + 1,2,3,4,7,9-HXCDF	1400.00	1432.00	1424.00	1421.00	13.30
		1,2,3,7,8,9-HXCDF	84.00	88.00	73.00	68.30	4.51
		1,2,3,6,7,8-HXCDF	70.00	73.00	83.00	85.30	5.03
		2,3,4,6,7,8-HXCDF	108.00	103.00	115.00	109.00	6.00
		1,2,3,4,6,7,8-HPCDF	1175.00	1163.00	1141.00	1192.00	17.90

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APPENDIX C

PROJECT SUMMARY

PROJECT SUMMARY

INTRODUCTION

During the past four years Electric Power Research Institute (EPRI) has sponsored a research program to evaluate methodology for the analysis of selected individual congeners of polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in dielectric fluids. This program included the synthesis of native and isotopically labeled PCDD and PCDF analytical standards (1). Analytical standards and spiked matrix samples were prepared by a contract laboratory and then distributed to four other participating laboratories as part of a round robin study. These samples were analyzed blind by five independent contract laboratories.

The study was conducted in two phases. Phase I involved the analysis of PCDF's and PCDD's in five spiked baseline samples; for example, Aroclor-1016, Aroclor-1242, Aroclor-1260, tri- and tetrachlorobenzene mixture, aged mineral oil, and four in-service dielectric fluids (1-4). Since validated analytical methods did not exist before this program was initiated, this phase of the program was necessary to assess any deficiencies and optimize the analytical methodology. Each participating laboratory used their best available in-house extraction and analysis techniques (1-4). After evaluating these results and implementing several improvements to the methodology, then Phase II was initiated.

Phase II was designed to provide quantitative data on PCDF and PCDD congeners in selected in-service dielectric fluids and to make a statistical interlaboratory comparison of the analytical methods. The specific aims were (1) to determine the accuracy of analysis by each participating laboratory for a selected list of PCDF's and PCDD's in spiked samples, (2) to determine the precision of analysis in each laboratory for PCDF's and PCDD's in spiked and in-service utility samples, (3) to perform an interlaboratory comparison and thus a comparison of methods employed for accuracy and precision, and finally (4) to measure the levels of PCDF's and PCDD's in a few selected in-service utility samples.

METHODS

Five independent laboratories participated in the interlaboratory study. Each laboratory was provided with aliquots of the three baseline and seven in-service utility samples (4). Also, native and isotopically labeled PCDD and PCDF analytical standards were prepared by one laboratory (4) and distributed to each participating laboratory. Subsequently, each laboratory employed their best

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available in-house extraction and analysis techniques (Table 1). Each laboratory added five carbon-13 labeled PCDD or PCDF congeners as internal standards to the sample. Some laboratories employed a liquid-liquid extraction step, either hexane/acetone or hexane/sulfuric acid/water, whereas others applied aliquots of the sample directly to a chromatographic column. All laboratories performed a purification step using open column chromatography (Table 1). For example, Lab-A used acid alumina, PX-21 carbon and neutral alumina chromatography, respectively, for purification; Lab-B used LH20, basic alumina and acidic alumina; and Lab-C used a combination of sulfuric acid silica/silica sodium hydroxide followed by basic alumina and florisil. Lab-D used a sandwich of acid silica, basic silica and silica followed by PX-21 carbon, acid silica/silica and then acidic alumina; Lab-E used sulfuric acid impregnated silica, PX-21 carbon and florisil. Various solvent evaporation techniques were also used. Specifically, Lab-A used heat and vacuum; Lab-B used rotary evaporation, while Labs-C and -D used nitrogen blowdown.

During extract analysis, Lab-A used both high and low resolution MS, in the electron impact mode. Lab-B, D and E used only low resolution mass spectrometry while Lab-C used exclusively high resolution mass spectrometry. All laboratories employed high resolution gas chromatography (HRGC), although different stationary phases and GC operating parameters were used.

Calibration curves were generated over the linear response range of each gas chromatograph/mass spectrometry system at five concentrations. All labs used the same initial stock calibration solution prepared by one laboratory containing eight native and five isotopically labeled PCDD's and PCDF's (1).

The samples analyzed in the round robin study are shown in Table 2. Two samples were spiked with a selected number of congeners at known concentrations into mineral oil and Aroclor 1016, respectively. A third sample, Aroclor 1260, was spiked at known levels with these same congeners but it also contained enoogenous PCDF's and PCDD's. Samples 11-17 (Table 2) were in-service utility samples that were selected to represent the various types of utility uses (5). In some cases the dielectric was Arochlor 1260, or mineral oil containing PCBs. Dielectric fluids from transformers, capacitors, or precipitators were selected. Some samples represented devices that had been in use for many years (Table 2).

A large database was produced in this study. An example of the measurements that were performed for dioxins and furans by Lab-B on sample No. 14 is shown in Table 3. All of the five participating laboratories reported either measurable values or limits of detection for each of these compounds in each of the ten samples. With the exception of one laboratory, each laboratory performed triplicate instrumental analysis on a single extract from each sample. The mean and standard deviation were calculated (Table 3). Lab-E reported only one

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TABLE 1. ANALYTICAL PROCEDURES EMPLOYED BY ROUND ROBIN LABS

Step	Lab-A	Lab-B	Lab-C
1. Add standards	+	+	+
2. Extraction	• Hex/acetone	-	• Hex/H_2SO_4; H_2O
3. Chromatography	• Acid alumina • PX-21 carbon • Neutral alumina	• LH-20 • Basic alumina • Acidic alumina	• Silica/H_2SO_4-silica/ NaOH-silica • Basic alumina (2Xs) • Florisil
4. Solvent evaporation	• Δ and vacuum	• Roto-evaporation	• N_2 blow-down
5. Analysis	• HRGC/LRMS (EI) • HRGC/HRMS (EI)	• HRGC/LRMS (EI)	• HRGC/HRMS (EI)

Step	Lab-D	Lab-E
1. Add standards	+	+
2. Extraction	-	-
3. Chromatography	• Acid silica/basic silica/silica • PX-21 carbon • Acid silica/silica • Acid alumina	• H_2SO_4-silica • PX-21 carbon • Florisil
4. Solvent evaporation	• N_2 blow-down	
5. Analysis	• HRGC/LRMS (EI)	• HRGC/LRMS (EI

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TABLE 2. SAMPLES ANALYZED IN ROUND ROBIN STUDY

Sample No.	Dielectric	Utility Appliance	Service Life (yr)
1	Spiked mineral oil	-	-
2	Spiked Aroclor 1016	-	-
3	Spiked Aroclor 1260	-	-
11	Aroclor 1260	Transformer (LCN)[a]	31
12	Aroclor 1260	Transformer (LCN)	28
13	?	Capacitor	?
14	?	Precipitator	27
15	Mineral oil (150 ppm PCB)	Transformer (Arc furnace)	8
16	Mineral oil (100 ppm PCB)	Transformer (LCN)	?
17	Aroclor 1260	Transformer (LCN)	20

[a]LCN = load circuit network.

TABLE 3. EXAMPLE OF MEASUREMENTS PERFORMED FOR DIOXINS/FURANS BY A LAB ON ONE SAMPLE (LAB B, SAMPLE 14)- PPB

Compound	Measurement 1	2	3	Mean	S.D.
2,3,7,8-TCDD	(0.5)[a]	(0.5)	(0.5)	(0.5)	(0.0)
Total TCDD	(0.5)	(0.5)	(0.5)	(0.5)	(0.0)
OCDD	8	13	5	8.7	4.0
2,3,7,8 + 2,3,4,8-TCDF	297	248	282	276	25
Total TCDF	970	617	576	721	217
1,2,3,7,8 + 1,2,3,4,8-PNCDF	1115	1039	1023	1059	452
2,3,4,7,8-PNCDF	1171	1504	1726	1694	96
Total PNCDF	9236	6589	6002	7276	1723
1,2,3,4,7,8 + 1,2,3,4,7,9-HXCDF	3802	3711	3775	3763	47
1,2,3,7,8,9-HXCDF	174	187	233	198	31
1,2,3,6,7,8-HXCDF	1195	1155	1137	1162	30
2,3,4,6,7,8-HXCDF	387	472	509	456	63
Total HXCDF	10,598	9918	10,666	10,394	414.0
1,2,3,4,6,7,8-HPCDF	728	905	884	839	97
Total HPCDF	1725	2196	2254	2058	290
OCDF	293	626	374	431	174

[a]( ) = Limit of detection.

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measurement on each sample extract. Lab-D, on the otherhand, extracted each sample three times and then performed three instrumental determinations on each of the extracts, thus producing nine measurements per sample.

RESULTS AND DISCUSSION

Accuracy of Measurement

The accuracy of measurement for specific selected congeners, for each laboratory and by sample matrix was examined. To gain insight into measurement accuracy, samples were spiked with known amounts of each congener and the percent accuracy of the mean of triplicate measurements was calculated and expressed as the mean divided by the spiked amount times one hundred.

Table 4 shows an example of these data for just one chemical, 2,3,7,8-TCDD. These statistical data were obtained for each compound measured. The percent accuracy for spiked samples for 2,3,7,8-TCDD by sample and laboratory is shown. Lab-D performed triplicate extraction/purification on each of the samples which also provided an estimate of precision for the entire analytical procedure. The mean value of the accuracy for 2,3,7,8-TCDD is given in Table 4 and the range for all determinations is shown in parenthesis. For these two samples the percent accuracy is in general very good. Lab-E only performed a single determination and experienced a lower percent accuracy than the other four laboratories.

Accuracy of analysis for 2,3,4,6,7,8-hexachlorodibenzofuran congener is shown in Table 5. The percent accuracy of measurement for this PCDF, by laboratory and sample is given in Table 5. The accuracy of determination was quite good for four of the five laboratories. Lab-C reported more variable recoveries with a range of 80-3371 in sample No. 1. Data such as these were obtained for each congener to determine the percent accuracy in two samples. With the exception noted above, acceptable accuracies were obtained.

A third sample also was spiked at known concentrations with these congeners, but there were endogenous levels present in the Aroclor 1260. Thus, the percent accuracy could not be calculated.

The median and range of percent accuracy across all the chemicals that were spiked into the two samples is summarized in Table 6. As indicated, the accuracy is reasonable in most cases with a few exceptions where the range was quite large. The determination of the hexa CDF congeners by Lab-C yielded this large overall variability.

Precision of Measurement

Similarly to accuracy, the precision of measurement by congener, laboratory and sample matrix was also investigated. The coefficients of variation for the determination of 1,2,3,7,8- plus 1,2,3,4,8-pentachlorodibenzofuran (not chromatographically resolved) by compound and laboratory are given in Table 7. In

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TABLE 4. PERCENT ACCURACY FOR SPIKED SAMPLES FOR 2,3,7,8-TCDD BY SAMPLE AND LABORATORY

Laboratory	Sample 1	Sample 2
A	75 (68-85)	91 (75-103)
B	83 (68-96)	101 (100-104)
C	81 (76-92)	85 (83-87)
D-1	99 (96-100)	96 (92-98)
D-2	100 (96-104)	96 (94-98)
D-3	92 (88-96)	94 (91-96)
E	56[a]	72[a]

[a]Single determination.

TABLE 5. PERCENT ACCURACY FOR SPIKED SAMPLES FOR 2,3,4,6,7,8-HXCDF BY SAMPLE AND LABORATORY

Laboratory	Sample 1	Sample 2
A	92 (86-97)	114 (106-123)
B	94 (93-96)	123 (119-129)
C	1189 (80-3371)	2015 (515-3939)
D-1	98 (97-101)	100 (100-101)
D-2	101 (99-102)	106 (105-106)
D-3	99 (97-99)	102 (98-104)
E	97[a]	83

[a]Single determination.

TABLE 6. MEDIAN AND RANGE OF PERCENT ACCURACY ACROSS ALL COMPOUNDS FOR SPIKED SAMPLES

Laboratory	Sample 1	Sample 2
A	88 (68-105)	107 (75-135)
B	96 (68-124)	112 (55-149)
C	94 (8-3371)	120 (12-3939)
D-1	99 (81-114)	101 (90-121)
D-2	101 (88-114)	105 (89-119)
D-3	94 (67-107)	99 (91-121)
E	103 (56-116)	114 (42-120)

TABLE 7. COEFFICIENTS OF VARIATION FOR 1,2,3,7,8 + 1,2,3,4,8-PNCDF BY COMPOUND AND LABORATORY

	Laboratory No.					
Sample	A	B	C	D-1	D-2	D-3
1	12.0	2.1	11.5	1.4	3.0	0.7
2	11.5	1.8	3.1	1.3	2.1	1.0
3	0.9	4.1	13.6	4.0	6.8	3.7
11	12.9	6.3	31.6	10.4	2.1	2.2
12	26.1	4.8	23.1	16.6	4.5	2.9
13	8.4	7.1	12.8	6.3	7.5	0.3
14	3.8	4.6	7.3	15.6	17.3	5.7
15	11.7	-	-	-	-	-
16	-	61.1	-	-	-	-
17	4.0	14.9	2.2	11.5	18.4	4..

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general across all the samples, the coefficients of variation (i.e., precision) were quite low. Lab-D performed triplicate extractions on each baseline and utility sample and then performed triplicate instrumental determinations on each extract. Good precision for both extraction and measurement were observed. Another example is shown in Table 8 for 1,2,3,4,6,7,8-heptachlorodibenzofuran by compound and laboratory. For this particular congener, a greater variability was observed amongst Labs-B and C.

The median and range of coefficients of variation across all compounds by laboratory and samples are given in Table 9. A small range in the coefficients of variation was observed except for Lab-C which had relatively poor precision.

Components Contributing to Variability

A more detailed statistical analysis was performed to determine the contribution of instrumental measurement, method extraction/purification, and sample type to the total variability of a reported value for a PCDD or PCDF congener. The variance components for a set of measurements made on 2,3,7,8-TCDD across all except two samples, samples 15 and 16 (most data were non-measurable values), are listed in Table 10. The total variance and the percentage of the total variance apportioned to either the sample or the instrumental measurement step are shown. The greatest variance is attributed to the sample type as compared to the instrumental measurement step. Lab-A, as compared to the other laboratories, exhibited a higher percentage of variability for the measurement step (14.6%). The remaining three laboratories exhibited the major variability (99+%) from the sample type.

Table 11 gives the variance components for 2,3,4,5,6,7,8-hexachlorodibenzofuran across all sample types analyzed. Again, the total variance and the percent of the total variance for each of the laboratories are given for the sample and the measurement step. Except for Lab-C, the predominant variance is associated with the sample type. For Lab-C, 30% of the variability in these results was associated with the instrumental measurement step.

The variance components by congener for Lab-D are depicted in Table 12. Lab-D performed triplicate extraction on the utility sample and triplicate instrumental determinations on each sample extract. Thus, it was possible to apportion the variability due to sample type, extraction, and measurement. The largest contribution to variation in the reported values was associated with the types of sample or sample matrix analyzed. Variability resulting from the extraction steps was smaller while an insignificant variation was attributed to the instrumental determination step.

The measured values between each lab were tested to determine whether they were significantly different from one to another. The Levene's test of

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TABLE 8. COEFFICIENTS OF VARIATION FOR 1,2,3,4,6,7,8-HPCDF BY COMPOUND AND LABORATORY

Sample	Laboratory No.					
	A	B	C	D-1	D-2	D-3
1	4.0	10.9	96.2	9.7	5.1	2.4
2	11.7	20.4	76.1	3.2	4.3	6.3
3	4.1	12.1	144.9	1.4	5.4	5.7
11	10.3	17.8	58.9	17.6	0.7	4.0
12	9.9	18.7	36.9	14.9	5.5	4.9
13	21.1	31.6	60.9	-	7.5	-
14	1.6	11.5	39.9	20.4	17.6	1.2
15	-	60.6	-	21.7	6.7	10.3
16	-	53.4	-	57.4	-	-
17	3.4	23.9	29.2	14.9	4.8	1.6

TABLE 9. MEDIAN AND RANGE OF COEFFICIENTS OF VARIATION ACROSS ALL COMPOUNDS BY LABORATORY AND SAMPLE

Laboratory	Sample							
	1	2	3	11	12	13	14	17
A	11.8 (4-16)	11.2 (3-40)	3.3 (1-5)	8.6 (1-47)	19.2 (2-59)	13.5 (3-13)	2.8 (1-5?)	4.3 (2-10)
B	4.2 (0-17)	2.2 (1-46)	4.6 (1-30)	14.1 (6-46)	6.6 (4-20)	17.6 (4-38)	12.6 (1-47)	10.2 (2-28)
C	41.5 (11-159)	13.9 (2-87)	29.8 (8-145)	49.9 (9-121)	23.8 (3-57)	31.2 (10-62)	30.5 (7-125)	22.2 (2-53)
D-1	4.9 (1-27)	2.4 (0-5)	2.7 (1-12)	13.6 (7-32)	12.2 (7-22)	11.1 (6-38)	12.4 (4-26)	11.8 (5-22)
D-2	4.0 (1-7)	2.7 (0.4)	3.4 (2-30)	2.1 (0-21)	6.5 (1-8)	7.5 (2-24)	14.6 (1-27)	4.9 (1-23)
D-3	2.4 (1-21)	3.1 (1-8)	2.2 (1-7)	2.5 (0-6)	4.9 (2-20)	8.2 (0-27)	3.8 (1-17)	2.1 (0.8)

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TABLE 10. VARIANCE COMPONENTS FOR 2,3,7,8-TCDD ACROSS ALL SAMPLES (1,2,3,11,12,13,14,17)

	Variance Components			% of Total	
Laboratory	Total	Sample	Measurement	Sample	Measurement
A	8.05	6.87	1.18	85.4	14.6
B	5.46	5.45	0.00	99.9	0.1
C	2.12	2.12	0.00	99.8	0.2
D-1	2.25	2.25	0.00	99.9+	0.0
D-2	2.30	2.30	0.00	99.9+	0.0
D-3	2.19	2.19	0.00	99.9+	0.0
E	7.52	-	-	-	-

TABLE 11. VARIANCE COMPONENTS FOR 2,3,4,6,7,8-HXCDF ACROSS ALL SAMPLES (1,2,3,11,12,13,14,17)

	Variance Components			% of Total	
Laboratory	Total	Sample	Measurement	Sample	Measurement
A	3.27	3.25	0.01	99.5	0.5
B	2.62	2.59	0.03	99.0	1.0
C	4.53	3.15	1.38	69.6	30.4
D-1	3.11	3.10	0.01	99.6	0.4
D-2	1.77	1.76	0.01	99.2	0.8
D-3	1.85	1.84	0.01	99.5	0.5
E	4.27	-	-	-	-

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TABLE 12. VARIANCE COMPONENTS BY COMPOUND FOR LAB-D

Compound	Variance Components				% of Total		
	Total	Sample	Extraction	Meas	Sample	Extraction	Meas
2,3,7,8-TCDD	2.25	2.25	0.00	0.00	99.9+	0.0	0.0
Total TCDD	2.25	2.25	0.00	0.00	99.9+	0.0	0.0
OCDD	0.00	0.00	0.00	0.00	99.9	0.0	0.0
2,3,7,8 + 2,3,4,6-TCDF	1.48	1.47	0.00	0.00	99.5	0.2	0.3
Total TCDF	1.40	1.38	0.01	0.01	98.9	0.6	0.5
1,2,3,7,8 + 1,2,3,4,8-PNCDF	1.84	1.82	0.01	0.01	99.2	0.4	0.4
2,3,4,7,8-PNCDF	1.31	1.30	0.00	0.01	98.9	0.0	1.1
Total PNCDF	1.62	1.61	0.00	0.01	99.2	0.0	0.8
1,2,3,4,7,8 + 1,2,3,6,7,9-HXCDF	5.80	5.80	0.00	0.00	99.9	0.0	0.1
1,2,3,7,8,9-HXCDF	4.73	4.71	0.01	0.01	98.5	0.2	0.3
1,2,3,5,7,8-HXCDF	2.25	2.16	0.08	0.01	96.1	3.4	0.5
2,3,4,6,7,8-HXCDF	2.25	2.16	0.06	0.01	96.1	3.4	0.5
Total HXCDF	3.66	3.58	0.05	0.01	98.3	1.3	0.4
1,2,3,4,6,7,8-HPCDF	3.82	3.67	0.02	0.03	98.7	0.5	0.7
Total HPCDF	5.13	5.00	0.09	0.03	97.6	1.8	0.6
OCDF	7.73	7.41	0.30	0.03	95.8	3.9	0.2

differences amongst the laboratories by compound across the samples was applied to the data (6). For available data, the F value for these measurements and the degrees of freedom were calculated and are shown in Table 13. In every case, the values reported by each of the laboratories were significantly different from one to another at the 95% confidence level for each of the congeners except 1,2,3,6,7,8-hexachlorodibenzofuran, which was significantly different at the 99% confidence level. This test indicates that each laboratory reported statistically different quantitative values for each of these congeners in these samples.

Prediction of Variability in Future Measurements

In practical terms, what would be the predicted range of values if the analyses were repeated by a laboratory using one of the methods previously employed. Shown in Table 14 are the approximate 95% prediction intervals for the laboratories if they were to repeat the analysis for each of these chemicals in the same utility samples. In other words if one of the five laboratories were to repeat the analysis for 2,3,7,8-TCDD in sample No. 1, the reported value would fall within a range of 15-30 ppb. If 20 determinations were made, one value would be outside of this range. For 2,3,7,8-TCDD a factor of two variation would be anticipated. In some cases, the variability for other congeners may be as much as 20-fold or more. This variability does not appear to correlate to the congener concentrations actually present in the samples. For example, even though, in samples 11-17 the amount of 2,3,7,8-TCDD is quite low and the variability may be as much as a factor of 20-30 as indicated here, the reported values for 1,2,3,7,8,9-hexachlorodibenzofuran could vary over the range of 1-8869. In samples 11-17, a large variability in levels for the individual isomers are predicted as well as for the total, for example, the total hexachlorodibenzofuran.

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TABLE 13. LEVENE'S TEST OF DIFFERENCES AMONG LABS BY COMPOUND ACROSS SAMPLES

Compound	F-Value	Degrees of Freedom
2,3,7,8-TCDD	14.96**	5
Total TCDD	17.82**	5
OCDD	12.81**	5
2,3,7,8 + 2,3,4,8-TCDF	6.60**	5
Total TCDF	8.89**	5
1,2,3,7,8 + 1,2,3,4,8-PNCDF	4.39**	5
2,3,4,7,8-PNCDF	9.76**	5
Total PNCDF	11.15**	5
1,2,3,4,7,8 + I,2,3,4,7,9-HXCDF	17.80**	5
1,2,3,7,8,9-HXCDF	16.10**	5
1,2,3,6,78-HXCDF	2.96*	4
2,3,4,6,7,8-HXCDF	36.93**	5
Total HXCDF	23.12**	5
1,2,3,4,6,7,8-HPCDF	22.80**	5
Total HPCDF	17.39**	5
OCDF	6.97**	5

*Significant at 0.01 level (99%).
**Significant at 0.05 level (95%).

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TABLE 14. APPROXIMATE 95 PERCENT PREDICTION INTERVALS
(PPB)

Compound	1	2	3	11	12	13	14	17
2,3,7,8-TCDD	15- 30	40- 60	63- 132	1- 25	1- 20	1- 13	1- 32	1- 11
OCDD	1- 59	1- 40	2- 32	7- 19	5- 30	1- 70	1- 43	5- 32
2,3,7,8 + 2,3,4,8-TCDF	144- 221	57- 67	977- 1355	24- 61	15- 81	90- 459	251- 459	119- 241
1,2,3,7,8 + 1,2,3,4,8-PNCDF	123- 168	138- 193	226- 425	41- 7913	27- 264	8- 30	742- 1577	74- 746
2,3,4,7,8-PNCDF	99- 248	90- 321	164- 618	84- 145	28- 59	46- 80	1324- 2389	106- 403
1,2,3,4,7,8 + 1,2,3,4,7,8-HXCDF	182- 347	1- 15	825- 1838	2138- 12,579	447- 809	13- 36	3144- 5860	486- 5023
1,2,3,7,8,9-HXCDF	1- 34	1- 25	2- 965	1- 8869	4- 167	1- 61	64- 7800	1- 6136
1,2,3,6,7-HXCDF	31- 72	45- 72	254- 412	218- 603	20- 97	20- 10	561- 1385	43- 131
2,3,4,6,7,8-HXCDF	40- 1041	24- 1912	55- 3975	26- 879	9- 68	1- 51	196- 2882	10- 2237
1,2,3,4,6,7,8-HPCDF	103- 1104	137- 1530	96- 3,258	580- 18,405	418- 976	1- 17	482- 1130	79- 5652
OCDF	2- 89	67- 208	2280- 6436	9641- 64,743	3822- 10,453	7- 75	96- 457	442- 24,465
Total TCDF	144- 222	57- 67	1046 2321	57- 362	37- 321	389- 1247	532 1389	248 729
Total PNCDF	206- 431	220- 517	1004- 1682	1125- 3079	143- 590	179- 442	5846- 13,471	562- 1,999
Total HXCDF	155- 1862	40- 2118	798- 10,654	3041- 21,535	726- 1320	11- 198	5857- 21,657	610- 13,977
Total HPCDF	103- 1105	137- 1532	819- 4341	1581- 41,116	1467- 3090	2- 52	1391- 3483	242- 11,063
Total TCDD	6- 60	40- 60	53- 132	1- 21	1- 14	1- 15	1- 20	1- 10

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