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EPRI EL/EA-5443
Volume 2
Project 2028-6
Final Report
March 1988



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

Volume 2:
Formation of PCDF and PCDD in Askarel and Contaminated Mineral Oil Equipment

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MONS 218436

REPORT SUMMARY

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

TOPICS: PCB; Capacitors; Chemical analysis; PCDF-PCDD; Transformers; 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.

PROJECTS

RP2028-7, RP2028-6, 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 2
Research Project 2028-6

Final Report, March 1988

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ABSTRACT

A study was conducted by five independent laboratories to evaluate methods for the measurement of trace levels of polychlorinated dibenzofurans (PCDFs) and polychlorinated dibenzo-p-dioxins (PCDDs) in utility dielectric liquids. Each laboratory evaluated a different analytical method. The method evaluated by Battelle involved spiking with labelled internal standards, analyte enrichment by column chromatography, and analysis by high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS).

Baseline analyses of five dielectric fluids were conducted by each laboratory as an initial test of their methods. The variability of results between the five methods was within expectations, and the five methods were deemed suitable for round robin evaluation.

In the round robin evaluation, the five methods were used to analyze 10 liquid samples, including seven utility dielectric fluids. The liquid samples were spiked with native PCDD/PCDF to estimate accuracy. The Battelle results were generally within 70 percent of the spike value except for HxCDF which exhibited a strong positive bias. This result was considered an outlier. The Battelle results were consistently lower than the average results obtained for the five laboratories. Overall, the methods proved to be both rugged and reliable when used with labelled quantification and recovery standards.

The in-service liquids used in this study were found to hava relatively low lavels of PCDDs and trace amounts of PCDF. Liquids from transformers with more than 25 years of service had higher PCDF levels than liquids from newer transformers. Liquids from utility appliances exposed to thermal and electrical stresses did not have elevated PCDD or PCDF levels. PCDF levels increased as the Aroclor number (and relative amount of chlorination) increased.

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The authors are grateful for the technical assistance provided by Battelle scientists who developed the methods, and performed the analyses reported in this document. Sample preparation was coordinated by Joe Hatchel, data computation was conducted by Susan Watson, and mass spectral analyses were performed by Dan Aichele, Charles Sueper, and Michael Zimmerman.

We would also like to thank our colleagues who contributed the parallel analyses to this interlaboratory collaborative study. They are Dr. Sydney Gordon (Illinois Institute of Technology Research Institute), Drs. George Eadon and David Hilker (New York State Department of Health), Ms. Maureen Kilpatrick (Radian Corporation), Dr. Edo Pellizzari (Research Triangle Institute), and Dr. Christoffer Rappe (University of Umea).

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SUMMARY

SYNOPSIS

This report describes a study to develop reliable methods for the chemical analysis of polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) in utility dielectric liquids. Prior to this study a great deal of data was available on levels of PCDD and PCDF in utility fluids; but since the methods used to obtain this data had never been rigorously challenged in a statistically valid study, the reliability of the existing data bases was suspect. Current analytical methods are affected by high levels of polychlorinated biphenyl (PCB). Since PCB is an interferent in most methods proposed for the analysis of PCDD/PCDF, and many existing utility test appliances contain PCB as the major dielectric fluid or as a contaminant of other fluids (due to residual PCB), investigation of reliable analytical methods was warranted.

Five independent laboratories participated in this program. Each laboratory employed a different analytical procedure to measure trace levels of PCDF and PCDD in dielectric liquids. The method used by Battelle involved spiking with labelled internal standards, analyte enrichment by multiple column chromatography, and analysis by high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS).

BASELINE ANALYSES

The first phase of this study, baseline analyses, involved comparing methods for analyzing difficult matrices; e.g., Aroclor. Baseline analyses of five dielectric fluids were conducted by each laboratory as an initial test of their methods. The variability of results among the five methods was within expected levels. The five analytical procedures proved to be rugged and reliable when used with isotopically labelled, quantification and recovery standards. Use of labelled standards is especially important in the Askarel and mineral oil matrices since the high organic burden found in these materials requires secondary partitioning to remove interfering PCB and background hydrocarbons.

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The relative average deviation is the absolute difference between individual results and the mean (or true value), divided by the number of determinations. For samples such as Aroclor I242, Aroclor 1016, and mineral oil, the average deviation for baseline samples was often less than 50 percent. This result was found in individual laboratory replicate analyses and in grouped data from different laboratories. All five methods were deemed suitable for use in the second phase of the program.

ROUND ROBIN STATISTICAL ANALYSIS

The second phase of the study involved a more severe test, a round robin statistical evaluation that employed field samples collected from in-service utility applications. In the round robin evaluation, the five independent laboratories used different methods to analyze 10 liquid samples, including seven utility dielectric fluids. The in-service dielectric liquid samples were collected from four Askarel-filled network transformers, one arc furnace transformer, one electrostatic precipitator (ESP) transformer, and one capacitor.

The Battelle results were generally within 70 percent of the spike value except for hexachlorodibenzofurans, which exhibited a strong positive bias. This result was considered an outlier. The Battelle results were consistently lower than the average of results obtained for data from all five laboratories.

All samples of the in-service liquids tested had relatively low amounts of PCDD. This result supports the hypothesis that dioxins are not a major constituent of Askarel and PCB-containing fluids. Except for the mineral oils, trace amounts of polychlorinated dibenzofurans were found in all of the Aroclor samples tested. The mineral oil samples had extremely low amounts, if any, of PCDF. Even the in-service liquid from Transformer 4, a network distribution transformer that was involved in a high-energy excursion, had minimal amounts of PCDD and PCDF. Transformer 4 had visible carbon, and major signs of scorching on the case and in the area of the electrodes.

The Askarel transformers with more than 25 years of service tended to have higher levels of PCDF than the appliances put into service for a shorter time. It is possible that manufacturing controls improved as the production of Askarel matured in the 1960s such that Askarel was produced with lower levels of PCDF in the as-delivered fluids.

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Two utility appliances were selected by the EPRI Technical Advisory Committee for special attention: an Askarel-filled ESP transformer and an oil-filled arc furnace transformer. These two samples were the "worst case" for testing service stress on the dielectric fluids. The arc furnace had essentially no PCDF or PCDD, and the PCDF levels in the ESP transformer appeared to be dictated by the age of the unit (27 years of service) and the fluid composition (Aroclor 1260). This extended period of stress did not appear to elevate the PCDF levels above typical Aroclor 1260 levels.

One capacitor was tested in the in-service liquid screening program. It was found to have relatively low levels of PCDF compared to the other Askarel-filled units.

CONCLUSIONS

The in-service liquids used in this study were found to have minimal levels of PCDD and only trace amounts of PCDF. Liquids from transformers with more than 25 years of service had higher PCDF levels than liquids from newer transformers. Liquids from utility appliances exposed to thermal and electrical stresses did not show elevated PCDD or PCDF levels, indicating that high-energy events (electrical and thermal excursions) do not appear to generate PCDD or PCDF in utility electrical appliances that employ PCB. PCDF levels increased as the Aroclor number (and relative amount of chlorination) increased.

This study was successful in developing a set of methodologies that reliably determine trace levels of PCDF and PCDD in a very difficult matrix -- chlorinated organic oil. The development of commercially available reference standards, and the statistical validation of reference methods that can be used to analyze utility fluids was a major contribution to the quality and defensibility of data. The method verification program showed that a range of instrumentation can be successfully used to measure trace levels of PCDF and PCDD in utility fluids. In general, the methods employing low-resolution mass spectrometry (LRMS) require additional column chromatography to isolate PCDF/PCDD-enriched fractions for final HRGC/LRMS analysis. The precision of blind, spiked samples was superior to that expected by experienced analysts who had previously performed these analyses. The availability of labelled quantification standards helped improve method performance and lowered data scatter.

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Section 1

INTRODUCTION

The Electric Power Research Institute initiated this program to investigate the chemistry and analysis of polychlorinated dibenzofurans (PCDF) and polychlorinated dibenzo-p-dioxins (PCDD) as they relate to the utility use of Askarel, a dielectric liquid which contains polychlorinated biphenyl (PCB), frequently diluted with tri/tetra chlorinated benzene. Askarel is sometimes contaminated with traces of PCDF/PCDD. The program had three goals; (I) to develop reliable, well characterized analytical methods to measure PCDF/PCDD, (2) to measure PCDF/PCDD levels in typical dielectric liquids used in utility operations, and (3) to investigate possible PCDF/PCDD production in unusual transformer events such as high energy arcing.

This report describes analytical methodology and results of chemical analyses conducted by Battelle Columbus Division in support of EPRI Research Project 2028-6, "Formation of PCDD and PCDF in Askarel and Contaminated Mineral Oil Equipment". Chemical laboratories of four additional organizations conducted parallel measurements during this program: the Illinois Institute of Technology Research Institute, the New York State Department of Health, Radian Corporation, and the University of UMEA (Sweden). The data presented in this report were replicated by these four laboratories and separate reports ere available from each of the study participants. Combined data from the replicate analyses conducted by the five collaborating laboratories (including Battelle), are presented in a summary report prepared by the Research Triangle Institute. The summary report examines pooled data and gives a rigorous statistical analysis, including variability and reliability of analytical results reported by laboratories routinely conducting PCDF/PCDD analyses in Askarel, mineral oil, and related sample matrices.

Reliable analytical methods are especially difficult to develop for Askarel since PCB constitutes the major interference in most PCDF/PCDD analytical methods. In Askarel, the normal PCB concentration is 60-70 percent by weight. Thus, Askarel presents perhaps the most difficult matrix for these analyses. Parts-per-billion (ppb) levels of PCDF, and even lower concentrations of PCDD must be measured. When this program was initiated in early I984, the accuracy of PCDF analyses was hampered by a lack of accurate quantification standards. A major product of this

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study was the synthesis of a series of ^{13}C-labelled PCDF standards that allowed use of sensitive isotope dilution techniques to measure PCDF. Quantification and recovery measurements based on labelled standards permit the chemist to measure accurate mass spectral response ratios for naturally occurring PCDF (and PCDD) compared to the response factors of labelled standards spiked into the sample matrix.

The method development phase involved testing methods proposed by the five participating laboratories: Battelle, the Illinois Institute of Technology, Research Institute (IITRI), the New York State Department of Health (NYS), Radian Corporation, and the University of Umea. These five methods were challenged by analyzing PCDF/PCDD in baseline liquids, a series of five typical sample matrices: Aroclor 1260, Aroclor 1242, Aroclor 1016, chlorobenzene, and mineral oil containing approximately 50 ppm of Aroclor 1260. The baseline Askarel liquids contained native PCDF/PCDD, and the mineral oil was spiked with labelled PCDF.

The presence of PCDF/PCDD in typical utility liquids was investigated by measuring characteristic compounds and congener groups in samples provided by EPRI member utilities. A report was generated by the General Electric Company which outlined the main types and distribution of PCB containing liquids (1). A repository was established at Battelle where samples of transformer oils provided by several EPRI members were stored. A questionnaire was developed, and a data base was accumulated on the repository samples. Seven of these liquids were selected by the EPRI Technical Advisory Committee. The seven samples, along with three control liquids, were analyzed by the participating laboratories. The seven "in-service" liquids selected for analysis represented either high energy operation, or utility applications that typify PCB usage. The data collected in the in-service liquid study were analyzed by chemists and statisticians at the Research Triangle Institute (RTI). A separate report will be generated by RTI that summarizes the results of all five laboratories. In summary, the independent methods worked well, indicating that good results can be expected when appropriate quality control procedures are applied.

Arcing experiments were conducted by General Electric. Transformer test units were fabricated out of the normal materials of transformer construction. These test units were exposed to high electric energy such as might be expected in catastrophic transformer failure. In the engineering tests, final PCDF/PCDD levels were either the same or lowered from initial levels, indicating that short term

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electrical discharges are not a primary source of production for PCDF/PCDD in transformer liquids.

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Section 2

EXPERIMENTAL

ACQUISITION OF IN-SERVICE SAMPLES

The selection of in-service dielectric fluids for this study was coordinated by the EPRI Technical Advisory Committee with the assistance of Dr. Thomas Rouse of the General Electric Company. It was important to select a series of in-service liquids that represented a range of utility applications. In the early planning for this program, Dr. Rouse prepared a criteria document that discussed the distribution of Askarel among different types of electrical devices, the relative chemical stresses expected from these devices in normal usage, the dispersion of Askarels, heating processes in transformers, and situations that represent the worst case for Askarel usage. He estimated that the United States has 140,000 Askarel-filled transformers in service, 30 million oil-filled transformers, and 5-10 million power capacitors. The oil-filled transformers constitute a large number; however, only about 50,000 are considered PCB-containing (>500 ppm (w/w)), and another approximately 1 million are PCB-contaminated (50-500 ppm). Since PCDF and PCDD are minor constituents of PCB, PCB-containing and PCB-contaminated transformers are expected to contain very low concentrations of PCDF/PCDD (perhaps not measurable). Dr. Rouse published an EPRI report (1) in which he recommended establishing a repository of 30-40 in-service samples that would be reviewed by the technical advisory group to select a final set of in-service liquids for exhaustive testing by the methods developed in this program.

The samples recommended by Dr. Rouse for inclusion in the final test group are given in Table 2-1.

In order to acquire suitable samples for this study, several participating utility representatives were asked to survey their records on available samples, searching for dielectric materials that met the criteria established by Dr. Rouse. To prescreen the available samples, a questionnaire was developed and a data base of questionnaire information maintained. A copy of the questionnaire is given in Appendix A.

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TABLE 2.1

EQUIPMENT RECOMMENDED FOR SAMPLING FOR
PCDF AND PCDD ANALYSES

ASKAREL-FILLED	
Load Center/Network Transformers	8-10
Rectifier Transformers	1-2
Precipitator Transformers	2
Capacitors	4
OIL-FILLED WITH PCB	
Load Center/Network Transformers	4

After gathering completed questionnaires on a large number of candidate fluids, a repository was established, that contained the samples listed in Table 2.1. As shown in Table 2.2, suitable dielectric liquids were collected from each of the categories of interest. A final selection was made using information in the repository data base, and the materials listed in the last column of Table 2.2 were selected for inclusion in the in-service testing program.

ANALYTICAL TECHNIQUES

The following method description gives the procedures that were used by Battelle to analyze all Askarel and mineral oil samples in this program. The samples preparation procedures, the spiking protocols, the instrumental conditions, and the equations used to calculate final results are given here. The oil samples (five "baseline" samples) were spiked with labelled internal standards prior to distribution to the participating laboratories. The sample preparation and spiking procedures for the baseline liquids are given in a separate report in this series prepared by Radian Corporation (Austin, TX).

SAMPLE PREPARATION AND SPIKING

The seven in-service liquids were diluted to a concentration of approximately 2 µg/mL with hexane prior to spiking with internal standards. Aliquots of each liquid were weighed by difference into 100 mL volumetric flasks which were then filled to the mark with Distilled-in-Glass hexane. The flasks were placed on a

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TABLE 2.2

SURVEY OF LIQUID SAMPLES AVAILABLE FOR THE IN-SERVICE TRANSFORMER LIQUIDS STUDY

Utility Appliance	Service Life (Years)	Rating	Dielectric	PCB (ppm)	Volume (Gal.)	Field Code	Laboratory Code
CAPACITORS							
Capacitor 1	?	7200 KVAR	?	--	?	ISL-28	--
Capacitor 2	?	7200 KVAR	?	--	?	ISL-27	41159-11-13
Capacitor 3	?	?	Aroclor 1242	--	?	ISL-01-A	--
TRANSFORMERS							
Arc Furnace 1	8	12470/200 KVA	Mineral Oil	161	4,500	ISL-24-0	--
Arc Furnace 2	8	12470/200 KVA	Mineral Oil	150	4,500	ISL-23-0	41159-11-15
CIRCUIT BREAKER							
Circuit Breaker	30(Est.)	34.5 KV	Mineral Oil	403	360	ISL-29-0	--
LOAD CENTER NETWORK TRANSFORMERS							
Network Load Center 1	?	450 KVA	Mineral Oil	240	?	ISL-05-0	--
Network Load Center 2	30(Est.)	1500 KVA	Aroclor 1242	--	500	ISL-06-A	--
Network Load Center 3	21	1000 KVA	Inerteen	--	3700 (lb)	ISL-07-A	--
Network Load Center 4	20	500 KVA	Aroclor 1260	--	3175 (lb)	ISL-08-A	41159-11-12
Network Load Center 5	20	750 KVA	Aroclor 1260	--	2650 (lb)	ISL-02-A	41159 11-17
Network Load Center 6	19	500 KVA	Aroclor 1260	--	?	ISL-09-A	--
Network Load Center 7	20	750 KVA	Aroclor 1260	--	240	ISL-10-A	--
Network Load Center 8	19	500 KVA	Aroclor 1260	--	3200 (lb)	ISL-11-A	--
Network Load Center 9	31	500 KVA	Aroclor 1260	--	?	ISL-03-A	41159-11-11
Network Load Center 10	30(Est.)	243 KVA	Pyranol	--	195	ISL-12-A	--
Network Load Center 11	30(Est.)	559 KVA	Pyranol	--	370	ISL-13-A	--
Network Load Center 12	20(Est.)	313 KVA	?	--	195	ISL-14	--
Network Load Center 13	15(Est.)	339 KVA	Pyranol	--	360	ISL-15-A	--
Network Load Center 14	10(Est.)	126 KVA	Pyranol	--	490	ISL-16-A	--
Network Load Center 15	20(Est.)	11 KVA	Inerteen	--	235	ISL-18-A	--
Network Load Center 16	20(Est.)	11 KVA	Chlorextol	--	272	ISL-19-A	--
Network Load Center 17	20(Est.)	11.5 KVA	Inerteen	--	207	ISL-20-A	--
Network Load Center 18	10(Est.)	11.5 KVA	Inerteen	--	104	ISL-21-A	--
Network Load Center 19	20(Est.)	11.5 KVA	Chlorextol	--	277	ISL-22-A	--
Network Load Center 20	?	?	Mineral Oil	100	200	ISL-04-0	41159-11-16
PRECIPITATORS							
Precipitator 1	20(Est.)	440/53.5 KVA	?	--	94	ISL-26	--
Precipitator 2	20(Est.)	440/53.5 KVA	?	--	94	ISL-25	--
Precipitator 3	27	440/53.5 KVA	?	--	143	ISL-17-A	41159-11-14

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mechanical shaker and mixed overnight. After approximately 12 hours of mixing, the flasks were removed from the shaker and spiked with the five isotopically labelled internal standards. The internal standards were: 2,3,7,8-TCDD-$^{13}C_{12}$, 2,3,7,8-TCDF-$^{13}C_{12}$, 1,2,3,7,8-Penta-CDF-$^{13}C_{12}$, 1,2,3,4,7,8-Hexa-CDF-$^{13}C_{12}$, and Octa-CDD-$^{13}C_{12}$.

ANALYTE ENRICHMENT

One-milliliter aliquots (containing ~250 mg of the original fluid) of each sample were 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 purpose of these columns was to remove acidic and basic compounds from the solutions as well as materials that were easily oxidized. The silica gel support provided a large surface area for contact with the sample solutions thus improving the cleanup efficiency. The PCDD/PCDF isomers were eluted from the columns using 70 mL of hexane and the entire eluents, 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 columns 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.

Several of the sample solutions were still too contaminated with interferences to be analyzed. These solutions (41159-11-12,13,14,17 and E729-53-02,03) were

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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 $0^{o}C$ until they were analyzed.

ANALYSIS

The sample solutions were analyzed 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/ M, 10 percent valley definition). All HRGC/HRMS data were acquired by multiple-ion-detection (MID) using a VG Model 2035 Data System.

QUALITY ASSURANCE

The operation of the HRGC/HRMS was evaluated each day by analyzing standard mixtures of selected PCDD/PCDF compounds. These were used to define the chromatographic elution windows, the compound resolution of the chromatographic column, and to verify the quantitative accuracy of the analyses. The mass focus accuracy of the MID unit was evaluated at least every four hours by observing selected ion masses from perfluorokerosene (PFK) which was introduced continually into the ion source as a reference compound. Mass focus stability was assured by using a reference PFK "lock mass" to correct for any mass focus drift.

Native spike and laboratory method blank samples were also processed during the extraction and cleanup of the samples. The native spike samples were used to evaluate the accuracy of the quantification while the laboratory method blank sample was used to demonstrate freedom from laboratory contamination.

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

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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:

$$\text{Recovery (\%)} = \frac{Ais \times Qrs \times 100}{Ars \times Qis \times Rf}$$

Where:

Ais = Sum of integrated areas for internal standard;
Qrs = Quantity of recovery standard in ng;
Qis = Quantity of internal standard in ng;
Ars = Sum of integrated areas for recovery standard; and
Rf = 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:

$$\text{Quantity/Sample (ng/g)} = \frac{Ac \times Qis}{Ais \times Rf \times W}$$

Where:

Quantity = Total quantity in ng of target isomer or congener class
Ac = Sum of integrated areas for the target isomer or congener class
Qis = Quantity of internal standard in ng
Ais = Total integrated areas for the internal standard
Rf = 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

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average ratio of 0.76. By checking the isotope ratio of these peaks separately, they would be eliminated from the class total.

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

1. Simultaneous responses at buth 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 an isotopically labelled analog was available included the additional criterion that they eluted within 2 seconds of the internal standard.

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

$$\text{LOD/g (ng)} = \frac{Hc \times Qis \times 2.5}{His \times Rf \times W}$$

Where:

LOD = Single isomer limits of detection for a congener class in ng;
Hc = Height of congener class isomer;
Qis = Quantity of internal standard in ng;
His = Peak height of internal standard;
Rf = 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 response 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:

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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-$^{13}C_{12}$

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 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.

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Section 3

BASELINE ANALYSES

This section describes the baseline analyses performed by all five laboratories participating in this study. The baseline analyses were designed as a rigorous blind analysis of authentic Aroclor and mineral oil samples. If the proposed analytical methods performed well in the baseline tests, the additional steps of method validation, and screening of in-service utility fluids could be performed with confidence in the reported results. Consequently, the baseline analyses were critical to the success of this program.

BACKGROUND RESEARCH

Before the baseline analyses could be performed, five test liquids were obtained by Radian Corporation and a combination of native and labelled (^{13}C) PCDF/PCDD were spiked into the test liquids to ensure a rugged test of the proposed analytical techniques. The test liquids selected for the baseline study are listed in Table 3.1.

TABLE 3.1

BASELINE TEST LIQUIDS

Dielectric Fluid	Composition
Aroclor 1016	Narrow boiling point fraction of Aroclor 1242.
Aroclor 1242	42% Cl (w/w)
Aroclor 1260	60% Cl (w/w)
Chlorobenzenes	-Synthetic Mixture 1,2,4-Trichlorobenzene (51.2% (w/w)) 1,2,3-Trichlorobenzene (13.4% (w/w)) 1,2,4,5-Tetrachlorobenzene (2.6% (w/w)) 1,2,3,4-Tetrachlorobenzene (28.4% (w/w)) Pentachlorobenzene (4.4% (w/w))
Aged Mineral Oil	-Spiked Aroclor 1260 (500 ppm (w/w)) Tri/Tetrachlorobenzene Mix Listed Above (500 ppm (w/w))

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These five liquids are a good challenge set of utility dielectric fluids since they represent the major Aroclor types found in utility operations along with a synthetic mineral oil spiked with 500 ppm (w/w) Aroclor 1260 and tri/tetrachlorobenzenes. These five test liquids were selected to contain the major interferents and contamination problems that an analyst would face in handling any utility dielectric liquid.

STANDARDS USED FOR SPIKING

To challenge the five independent analytical methods proposed by the participating laboratories, a series of PCDF and PCDD standards were obtained. Since it is advantageous to have at least one calibration standard for each congener class, several compounds, both native and isotopically labelled PCDF, were synthesized for this program. The labelled compounds were used by most participants as quantification and recovery standards. The labelled PCDF/PCDD standards, in this case all labelled standards incorporating isotopically enriched carbon-13, were added to the sample before laboratory extractions and isolation of the PCDF/PCDD. Having an isotopically labelled standard characteristic of each congener class maximizes the accuracy of the final determinations. Since the labelled standard corrects for any losses during sample preparation, the labelled standard should be similar to the congener class being analyzed. In the ideal case, the analyst will select a labelled standard for every analyte. Since only a few such standards are available, one labelled standard may be used to quantify an entire chlorination number envelope. The standards and spike levels used in the baseline study are given in Table 3.2.

The choice of standards in this program was governed by several considerations. PCDD levels are typically very low in PCB-containing liquids. Also contaminated mineral oil contains Aroclors at $\leq$500 ppm. The expected PCDF levels in Aroclors would be a few millionths by weight of the Aroclor content. Very low PCDF levels and less PCDD would be expected in the aged mineral oil sample tested. The expected low concentrations of native PCDF/PCDD permitted use of native PCDF/PCDD standards in the mineral oil sample. Very little interference would occur from native PCDF/PCDD in the mineral oil. The "Special PCDF/PCDD Mix" provided by Dr. Christoffer Rappe (U. of Umea, Sweden) was only used to spike the mineral oil samples since all of the standards in his mixture were native furans.

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TABLE 3.2

CONCENTRATION OF PCDF/PCDD STANDARDS SPIKED
INTO TRANSFORMER LIQUIDS(ppb(w/w))

Compound	(1) Spike Level Radian Mix	(2) Spike Level Rappe Mix	Mineral Oil Spike (1+2)
Total TCDD			
OCDD-$^{13}C_{12}$	100		100
1,3,4-TrCDF		116	116
2,3,7,8-TCDD-$^{13}C_{12}$	100		100
2,3,7,8-TCDD	0-100		UNK (4)
2,3,7,8-TCDF-$^{13}C_{12}$ (3)	100		100
2,3,7,8-TCDF	0-150		UNK (4)
2,3,4,8-TCDF	0-150		UNK (4)
2,3,4,7,8-PnCDF		100	100
1,2,3,7,8-PnCDF-$^{13}C_{12}$ (3)	100		100
1,2,3,7,8-PnCDF (3)	0-150		UNK (4)
1,2,3,4,8-PnCDF		100	100
1,2,3,4,7,8-HxCDF (3)	0-150	100	UNK (4)
1,2,3,4,6,7,8-HpCDF (3)	0-150		UNK (4)
Aroclor 1260		510	510
T/TCB		530	530

(1) Standards obtained for this program. The spiking levels are shown for the "Baseline" experiments.
(2) These are standards provided by Professor Christoffer Rappe (U. of Umea, Sweden).
(3) Standards synthesized for this program by Radian Corporation (Austin, TX).
(4) UNK - Unknown. These standards were spiked blind and the statistical performance of blind data will be treated in another volume in this series.

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RESULTS

Chemical Analyses

The results of chemical analyses performed by Battelle on the baseline samples are given in Table 3.3. All results are given as parts-per-billion by weight in the original oil (ng/g).

These data are interesting because they show the expected trends in the Aroclor PCDF/PCDD concentrations. PCDD are not found at the detection limit of the high resolution mass spectrometer used for this analysis, approximately 10 ppb (w/w) in the mineral oil samples. Trace levels of PCDF are observed with the concentrations increasing as the level of chlorination increases in the supporting Aroclor. The PCDF levels increase as the Aroclor number (and relative amount of chlorination increase), Aroclor 1260 >Aroclor 1242 >Aroclor 1016. Even though Aroclor 1016 is similar in composition to Aroclor 1242, the wider distribution of PCB congener groups in Aroclor 1242 would produce higher quantities of the high chlorination number PCB, 6-10 chlorine atoms per molecule, which are believed to be the precursors of PCDF when HCl elimination is the route for PCDF formation.

An increase in PCDF concentrations is shown in Table 3.3 as the total high chlorine PCB concentration increases. Total PCDF levels increase from 280 ppb for Aroclor 1016, to 1,710 ppb for Aroclor 1242, to 10.4 ppm for Aroclor 1260. Data for three of the participating laboratories are given in Tables 3.4 through 3.6. These data show the same trends observed in the Battelle data. The measured levels of spiked PCDF/PCDF were also similar among the reporting laboratories.

Baseline Recovery Data

The recovery of labelled standards is used to determine how much of the native PCDF/PCDD present in the sample is lost during the sample preparation steps of candidate methods. Since the internal quantification standard corrects for method losses, the reported value should be accurate within the measured precision of the method; however, excessive loss of analytes during sample preparation will have a profound affect on both method sensitivity, and precision. Recoveries for six labelled PCDF/PCDD standards spiked into the baseline samples are given in Table 3.7.

These data are interesting because they show the outliers that can affect individual data points.

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TABLE 3.3

BATTELLE FURAN AND DIOXIN DATA FOR THE BASELINE ANALYSES STUDY (ppb (w/w))

Compound	Aroclor 1016	Aroclor 1242	Aroclor 1260	Tri and Tetra Chlorobenzene	Mineral Oil Run No. 1	Mineral Oil Run No. 2
Polychlorinated Dibenzofurans						
Total TCDF	0	990	640	0	119	115
Total PnCDF	5	400	2100	2	270	228
Total HxCDF	190	84	3100	82	278	246
Total HpCDF	85	184	2100	100	128	113
OCDF	NR*	52	2500	NR	152	157
Total PCDF	280	1710	10440	184	947	859
Polychlorinated Dibenzodioxins						
Total TCDD	0	0	0	0	32	34
OCDD	NR	NR	NR	NR	NR	NR
Specific Molecules and Unresolved Molecular Clusters						
2,3,7,8-TCDD	0	0	0	0	32	34
2,3,7,8-/2,3,4,8-TCDF	0	84	150	0	119	115
1,2,3,7,8-/1,2,3,4,8-PnCDF	0	54	480	0	170	143
2,3,4,7,8-PnCDF	0	0	0	0	98	95
1,2,3,4,7,8-HxDF	190	84	1700	82	246	262
1,2,3,7,8,9-HxCDF	NR	NR	NR	NR	NR	NR
2,3,4,6,7,8-HxCDF	NR	NR	NR	NR	NR	NR
1,2,3,4,6,7,8-HpCDF	85	147	680	100	113	120

* NR=Not Reported.

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TABLE 3.4

IITRI FURAN AND DIOXIN DATA FOR THE BASELINE ANALYSES STUDY (ppb (w/w))

Compound	Aroclor 1016	Aroclor 1242	Aroclor 1260	Tri and Tetra Chlorobenzene	Mineral Oil Aged
Total TCDF	30	866	612	0	70
Total PnCDF	42	353	1037	0	165
Total HxCDF	92	105	1433	103	207
Total HpCDF	81	109	1985	98	40
OCDF	20	127	4154	0	393
Total TCDD	0	0	0	0	42
OCDD	0	0	1	1	0
2,3,7,8-TCDD	0	0	0	0	42
2,3,7,8-/2,3,4,8-TCDF	8	227	193	0	70
1,2,3,7,8-/1,2,3,4,8-PnCDF	11	42	231	0	112
2,3,4,7,8-PnCDF	0	51	88	0	52
1,2,3,4,7,8-HxCDF	76	63	601	103	206
1,2,3,7,8,9-HxCDF	0	0	0	0	0
2,3,4,6,7,8-HxCDF	0	0	0	0	0
1,2,3,4,6,7,8-HpCDF	58	77	684	98	68

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TABLE 3.5

NYSDOH FURAN AND DIOXIN DATA FOR THE BASELINE ANALYSES STUDY (ppb (w/w))

Compound	Aroclor 1016	Aroclor 1242	Aroclor 1260	Tri and Tetra Chlorobenzene	Mineral Oil Aged
Total TCDF	1	1900	940	3	95
Total PnCDF	7	584	996	13	0
Total HxCDF	350	140	5500	1000	1100
Total HpCDF	92	130	2430	91	0
OCDF	0	2300	NA	0	0
Total TCDD	0	0	0	0	42
OCDD	0	0	0	0	0
2,3,7,8-TCDD	0	0	7	0	43
2,3,7,8-/2,3,4,8-TCDF	0	150	190	0	34
1,2,3,7,8-/1,2,3,4,8-PnCDF	0	1000	220	1	140
2,3,4,7,8-PnCDF	0	0	0	0	0
1,2,3,4,7,8-HxCDF	0	0	0	0	0
1,2,3,7,8,9-HxCDF	0	0	0	0	0
2,3,4,6,7,8-HxCDF	0	0	0	0	0
1,2,3,4,6,7,8-HpCDF	0	0	0	0	0

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TABLE 3.6

RADIAN FURAN AND DIOXIN DATA FOR THE BASELINE ANALYSES STUDY (ppb (w/w))

Compound	Aroclor 1016	Aroclor 1242	Aroclor 1260	Tri and Tetra Chlorobenzene	Mineral Oil Aged
Total TCDF	0	0	0	0	125
Total PnCDF	0	0	477	0	226
Total HxCDF	97	60	872	161	178
Total HpCDF	80	46	807	170	36
OCDF	0	24	1786	0	126
Total TCDD	0	0	0	0	0
OCDD	0	0	0	386	0
2,3,7,8-TCDD	0	0	0	0	0
2,3,7,8-/2,3,4,8-TCDF	0	0	0	0	125
1,2,3,7,8-/1,2,3,4,8-PnCDF	0	0	477	0	159
2,3,4,7,8-PnCDF	0	0	0	0	66
1,2,3,4,7,8-HxCDF	97	60	872	161	177
1,2,3,7,8,9-HxCDF	0	0	0	0	0
2,3,4,6,7,8-HxCDF	0	0	0	0	0
1,2,3,4,6,7,8-HpCDF	80	46	807	170	36

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TABLE 3.7

ABSOLUTE RECOVERIES OF LABELLED STANDARDS
IN THE BASELINE STUDY (UNIVERSITY OF UMEA)

	Spike Level (ppb)	Aroclor 1016	Aroclor 1242	Aroclor 1260	Chloro-benzenes	Mineral Oil
2,3,7,8-TCDF-$^{13}C_{12}$	100	93	95	95	97	116
1,2,3,7,8-PCDF-$^{12}C_{12}$	100	111	134	140	97	114
2,3,7,8-TCDD-$^{13}C_{12}$	100	67	86	86	101	118
OCDD-$^{13}C_{12}$	100	102	89	157	86	121
1,2,3,4,7,8-HxCDF-$^{13}C_{12}$	100	83	90	317	110	NA
1,2,3,4,6,7,8-HpCDF	100	57	45	1224*	68	NA

*Outliers

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One effect is evident in these data, the recoveries from chlorobenzene and mineral oil appear to be superior to recoveries from Aroclors. The Aroclors contain the major interferents in the analysis of PCDF and PCDD. It appears that there may be matrix dependent difficulties in the analytical preparation of complex samples.

Method Reliability

The baseline data are grouped to show the relative performance of the four laboratories reported here. A compilation of data for aged mineral oil, baseline sample results is given in Table 3.8.

Method reliability is compared by computing the Student's-t variability for four independent determinations around the mean value, the known spiked amount of standard PCDF/PCDD.

In the four determinations shown the Student's-t variability of the mean varies from 20 to 167 percent. This is the degree of expected scatter in a group of four PCDD/PCDF determinations conducted by independent laboratories using the Student's-t distribution to approximate variance at the 95 percent confidence level.

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TABLE 3.8

FOUR-LABORATORY RESULTS OF ANALYSIS OF AGED MINERAL OIL (ng/g (w/w))

Compound	Battelle	ITTRI	NYSDOH	Radian	Group Mean	Native Spike Level	Confidence Interval (95%)
Total TCDF	115	70	95	125	101		
Total PnCDF	228	165	0	226	155	200	109%
Total HxCDF	246	207	1100	178	433		
Total HpCDF	113	40	0	36	47		
OCDF	157	393	0	126	169	160	167%
Total TCDD	34	42	42	0	30		
2,3,7,8-TCDD	34	42	43	0	30		
2,3,7,8-/2,3,4,8-TCDF	115	70	34	125	86		
1,2,3,7,8-/1,2,3,4,8-PnCDF	143	112	140	159	139	100	20%
2,3,4,7,8-PnCDF	95	52	0	66	53	100	41%
1,2,3,4,7,8-HxCDF	262	206	0	177	161		
1,2,3,4,6,7,8-HpCDF	120	68	0	36	56		

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Section 4

SUPPLEMENTAL ANALYSES

CROSS CHECK ANALYSES

To validate the analytical curve for each method proposed by the participating laboratories, a series of calibration runs were performed to establish the variability, linear dynamic range, and the limit of detection for each instrument. The calibration range is different from the method range. The validation of the calibration curve range only deals with standard solutions eluted through a tuned gas chromatograph or mass spectrometer (GC/MS) system. The quantities used to develop the calibration curve were 40 pg, 150 pg, 500 pg, and 2.5 ng. Each concentration level was analyzed with five replicates. The analytes used for the calibration curve validation were 2,3,7,8-TCDD, OCDD, 2,3,7,8-TCDF, 1,2,3,7,8-PCDF, 2,3,4,7,8-PCDF, 1,2,3,4,7,8-HxCDF, 2,3,4,6,7,8-HxCDF, and 1,2,3,4,5,7,8-HpCDF.

An illustration of the type of calibration plot generated in this study is given in Figure 1, which shows the standard curve for 2,3,7,8-TCDF.

The complete set of calibration curve plots, along with statistical parameters describing calibration precision are given in Appendix B. The standard deviation and the relative standard deviation at each point show the variability of response which increases at higher concentrations. The calibration curves were linear over the range of concentrations measured.

ANALYSES FROM THE UNIVERSITY OF UMEA

Under a subcontract to Battelle, the University of Umea participated in the baseline and round robin analyses. A letter report of the data from Umea is included as Appendix C.

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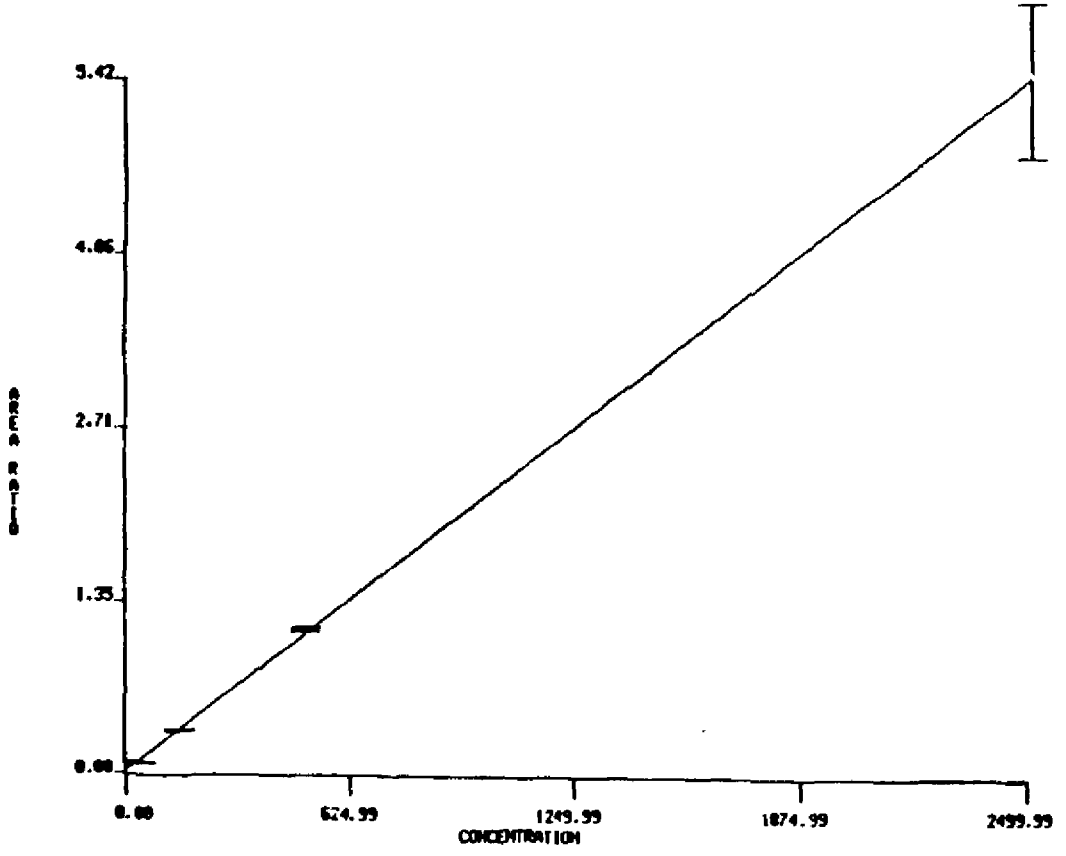

Figure 4-1. Calibration curve for 2,3,7,8-tetrachlorodibenzofuran over the range 40 pg to 2.5 ng

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Section 5

ROUND ROBIN ANALYSES OF IN-SERVICE LIQUIDS

The main thrust of this study was to evaluate a series of congeners and individual molecular species in typical in-service utility transformer and capacitor liquids. Ten (10) liquid samples, including the seven utility dielectric fluids, were analyzed for PCDD/PCDF using the methods developed in this program. All five participating laboratories contributed independent data sets, which will be statistically analyzed by an independent contractor, the Research Triangle Institute. The results of the Battelle analyses are given in Tabla 5.I to 5.10.

Accuracy Estimate

The in-service analyses were designed with a quality control check on accuracy of reported PCDD/PCDF concentrations. The "Baseline" liquids included with actual utility operating fluids were spiked with known amounts of several PCDD/PCDF standards. These known spike concentrations allowed an estimate of accuracy using the mean of three determinations performed by each participating laboratory compared with the "true" or spiked concentration. The "Baseline" analyses revealed that the aged mineral oil sample and the Aroclor 1016 had minimal concentrations of the PCDD/PCDF standards present as contaminants. Thus, native PCDD/PCDF were suitable spike materials.

The Battelle results for in-service liquids are presented in Table 5.11 for the mineral oil and Aroclor 1016 samples. Table 5.11 gives the spike levels and compares the percent difference in spiked levels with measured levels of PCDD/PCDF.

The Battelle results are generally within ±70 percent of the spike value except for one notable exception. HxCDF exhibited a strong positive bias. Most of the elevated HxCDF levels were 2,3,4,6,7,8-HxCDF. The HxCDF measured levels were 438 percent higher than the HxCDF spike levels in mineral oil, and 1325 percent higher in Aroclor 1016, even after subtraction of the native HxCDF found in the earlier baseline investigations. These HxCDF data are deemed to be outliers.

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TABLE 5.1

CHLORINATED FURAN AND DIOXIN RESULTS (ppb (w/w), ng/g)
SAMPLE ISL-02-A

Congener	Determination Det 1	Det 2	Det 3	Mean	Standard Deviation	Relative Standard Deviation
PCDF Congeners						
Total TCDF	360	230	290	293	53	18%
Total P_nCDF	69	72	71	71	1	2%
Total H_xCDF	8,100	19,000	20,000	15,700	5,389	34%
Total H_pCDF	1,600	1,400	2,000	1,667	249	15%
OCDF	4,300	4,800	5,100	4,733	330	7%
Total PCDF	14,429	25,502	27,461	22,464	5,738	26%
Furan Compounds						
2,3,7,8-/2,3,4,8-TCDF	190	140	180	170	22	13%
2,3,4,7,8-P_nCDF	300	260	290	283	17	6%
1,2,3,7,8-/1,2,3,4,8-P_nCDF	69	72	71	71	1	2%
1,2,3,4,7,8-/1,2,3,4,7,9-H_xCDF	2,700	6,400	6,400	5,167	1,744	34%
1,2,3,6,7,8-H_xCDF	760	2,300	2,700	1,920	836	44%
2,3,4,6,7,8-H_xCDF	1,100	3,400	3,800	2,767	1,190	43%
1,2,3,4,6,7,8-H_pCDF	180	230	320	243	58	24%
1,2,3,4,7,8,9-H_pCDF	280	250	320	283	29	10%
Dioxin Congeners						
Total TCDD	NA	NA	NA	NA	NA	NA
OCDD	18	18	10	15	4	25%
PCDD Compounds						
2,3,7,8-TCDD	NA	NA	NA	NA	NA	NA

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TABLE 5.2

CHLORINATED FURAN AND DIOXIN RESULTS (ppb (w/w), ng/g)
SAMPLE ISL-03-A

Congener	Determination Det 1	Det 2	Det 3	Mean	Standard Deviation	Relative Standard Deviation
PCDF Congeners						
Total TCDF	170	110	40	170	53	50%
Total P_nCDF	2,300	2,100	720	1,707	702	41%
Total H_xCOF	52,000	11,000	9,700	24,233	19,641	81%
Total H_pCDF	3,800	13,000	11,000	9,267	3,951	43%
OCDF	22,000	28,000	22,000	24,000	2,828	12%
Total PCDF	80,270	54,210	43,460	59,313	15,455	26%
Furan Compounds						
2,3,7,8-/2,3,4,8-TCOF	31	30	40	34	4	13%
2,3,4,7,8-P_nCDF	130	130	110	123	9	8%
1,2,3,7,8-/1,2,3,4,8-P_nCOF	35	49	26	37	9	26%
1,2,3,4,7,8-/1,2,3,4,7,9-H_xCDF	29,000	6,100	5,100	13,400	11,038	82%
1,2,3,6,7,8-H_xCDF	6,000	1,100	1,200	2,767	2,287	83%
2,3,4,6,7,8-H_xCDF	1,800	240	210	750	743	99%
1,2,3,4,6,7,8-H_pCDF	1,100	4,500	3,100	2,900	1,395	48%
1,2,3,4,7,8,9-H_pCDF	1,200	2,600	2,6DD	2,133	660	31%
Dioxin Congeners						
Total TCDO	NA	NA	NA	NA	NA	NA
OCDD	18	12	NA	10	7	75%
PCDD Compounds						
2,3,7,8-TCOD	NA	NA	NA	NA	NA	NA

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TABLE 5.3

CHLORINATED FURAN AND DIOXIN RESULTS (ppb (w/w), ng/g)
SAMPLE ISL-04-0

Congener	Determination Det 1	Det 2	Det 3	Mean	Standard Deviation	Relative Standard Deviation
PCDF Congeners						
Total TCDF	NA	NA	NA	NA	NA	NA%
Total P_nCDF	NA	NA	NA	NA	NA	NA%
Total H_xCDF	NA	NA	NA	NA	NA	NA%
Total H_pCDF	NA	NA	NA	NA	NA	NA%
OCDF	NA	NA	NA	NA	NA	NA%
Total PCDF	NA	NA	NA	NA	NA	NA%
Furan Compounds						
2,3,7,8-/2,3,4,8-TCDF	NA	NA	NA	NA	NA	NA%
2,3,4,7,8-P_nCDF	NA	NA	NA	NA	NA	NA%
1,2,3,7,8-/1,2,3,4,8-P_nCDF	NA	NA	NA	NA	NA	NA%
1,2,3,4,7,8-/1,2,3,4,7,9-H_xCDF	NA	NA	NA	NA	NA	NA%
1,2,3,6,7,8-H_xCDF	NA	NA	NA	NA	NA	NA%
2,3,4,6,7,8-H_xCDF	NA	NA	NA	NA	NA	NA%
1,2,3,4,6,7,8-H_pCOF	NA	NA	NA	NA	NA	NA%
1,2,3,4,7,8,9-H_pCDF	NA	NA	NA	NA	NA	NA%
Dioxin Congeners						
Total TCDD	NA	NA	NA	NA	NA	NA%
OCDO	NA	13	11	8	6	71%
PCDD Compounds						
2,3,7,8-TCDD	NA	NA	NA	NA	NA	NA%

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TABLE 5.4

CHLORINATED FURAN AND DIOXIN RESULTS (ppb (w/w), ng/g)
SAMPLE ISL-08-A

Congener	Determination Det 1	Det 2	Det 3	Mean	Standard Deviation	Relative Standard Deviation
PCDF Congeners						
Total TCDF	62	64	99	75	17	23%
Total P_nCDF	79	230	310	206	96	46%
Total H_xCDF	1,500	1,300	990	1,263	210	17%
Total H_pCDF	1,500	2,100	2,700	2,100	490	23%
OCDF	4,000	4,800	4,900	4,567	403	9%
Total PCDF	7,141	8,494	8,999	8,211	784	10%
Furan Compounds						
2,3,7,8-/2,3,4,8-TCDF	20	20	30	23	5	20%
2,3,4,7,8-P_nCDF	39	41	37	39	2	4%
1,2,3,7,8-/1,2,3,4,8-P_nCOF	22	25	34	27	5	19%
1,2,3,4,7,8-/1,2,3,4,7,9-H_xCDF	880	740	640	753	98	13%
1,2,3,6,7,8-H_xCDF	54	50	36	47	8	17%
2,3,4,6,7,8-H_xCDF	47	25	43	38	10	25%
1,2,3,4,6,7,8-H_pCDF	350	530	750	543	164	30%
1,2,3,4,7,8,9-H_pCDF	340	450	580	457	98	21%
Dioxin Congeners						
Total TCDO	NA	NA	NA	NA	NA	NA%
OCDD	NA	NA	NA	NA	NA	NA%
PCOD Compounds						
2,3,7,8-TCDD	NA	NA	NA	NA	NA	NA%

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TABLE 5.5

CHLORINATED FURAN AND DIOXIN RESULTS (ppb (w/w), ng/g)
SAMPLE ISL-17-A

Congener	Determination Det 1	Det 2	Det 3	Mean	Standard Deviation	Relative Standard Deviation
PCDF Congeners						
Total TCDF	970	580	610	720	177	25%
Total P_nCDF	11,000	6,700	6,500	8,067	2,076	26%
Total H_xCDF	14,000	36,000	16,000	22,000	9,933	45%
Total H_pCDF	3,100	2,800	4,200	3,367	602	18%
OCDF	150	170	220	180	29	16%
Total PCDF	29,220	46,250	27,530	34,333	8,455	25%
Furan Compounds						
2,3,7,8-/2,3,4,8-TCDF	400	380	350	377	21	5%
2,3,4,7,8-P_nCDF	2,300	2,400	1,800	2,167	262	12%
1,2,3,7,8-/1,2,3,4,8-P_nCDF	870	900	780	850	51	6%
1,2,3,4,7,8-/1,2,3,4,7,9-H_xCDF	4,700	7,200	4,100	5,333	1,342	25%
1,2,3,6,7,8-H_xCDF	1,800	3,200	2,300	2,433	579	24%
2,3,4,6,7,8-H_xCDF	620	6,800	930	2,783	2,832	102%
1,2,3,4,6,7,8-H_pCDF	920	560	1,300	927	302	33%
1,2,3,4,7,8,9-H_pCDF	740	860	990	863	102	12%
Dioxin Congeners						
Total TCDD	NA	NA	NA	NA	NA	NA%
OCDD	NA	18	NA	NA	8	141%
PCDD Compounds						
2,3,7,8-TCDD	NA	NA	NA	NA	NA	NA%

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TABLE 5.6

CHLORINATED FURAN AND DIOXIN RESULTS (ppb (w/w), ng/g)
SAMPLE ISL-23-O

Congener	Determination Det 1	Det 2	Det 3	Mean	Standard Deviation	Relative Standard Deviation
PCDF Congeners						
Total TCDF	NA	NA	NA	NA	NA	NA%
Total P_nCDF	NA	NA	NA	NA	NA	NA%
Total H_xCDF	NA	NA	NA	NA	NA	NA%
Total H_pCDF	NA	NA	NA	NA	NA	NA%
DCDF	NA	NA	NA	NA	NA	NA%
Total PCDF	NA	NA	NA	NA	NA	NA%
Furan Compounds						
2,3,7,8-/2,3,4,8-TCDF	NA	NA	NA	NA	NA	NA%
2,3,4,7,8-P_nCDF	NA	NA	NA	NA	NA	NA%
1,2,3,7,8-/1,2,3,4,8-P_nCDF	NA	NA	NA	NA	NA	NA%
1,2,3,4,7,8-/1,2,3,4,7,9-H_xCDF	NA	NA	NA	NA	NA	NA%
1,2,3,6,7,8-H_xCDF	NA	NA	NA	NA	NA	NA%
2,3,4,6,7,8-H_xCDF	NA	NA	NA	NA	NA	NA%
1,2,3,4,6,7,8-H_pCDF	NA	NA	NA	NA	NA	NA%
1,2,3,4,7,8,9-H_pCDF	NA	NA	NA	NA	NA	NA%
Dioxin Congeners						
Total TCDD	NA	NA	NA	NA	NA	NA%
OCDD	NA	12	NA	4	6	141%
PCDD Compounds						
2,3,7,8-TCDD	NA	NA	NA	NA	NA	NA%

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TABLE 5.7

CHLORINATED FURAN AND DIOXIN RESULTS (ppb (w/w), ng/g)
SAMPLE ISL-27

Congener	Determination Det 1	Det 2	Det 3	Mean	Standard Deviation	Relative Standard Deviation
PCDF Congeners						
Total TCDF	580	570	350	500	106	21%
Total P_nCDF	250	270	220	247	21	8%
Total H_xCDF	140	130	160	143	21	9%
Total H_pCDF	26	28	6	20	10	51%
OCDF	46	44	10	33	17	50%
Total PCDF	1,042	1,042	746	943	140	15%
Furan Compounds						
2,3,7,8-/2,3,4,8-TCDF	300	280	270	283	12	4%
2,3,4,7,8-P_nCDF	71	74	53	66	9	14%
1,2,3,7,8-/1,2,3,4,8-P_nCDF	580	570	350	500	106	21%
1,2,3,4,7,8-/1,2,3,4,7,9-H_xCDF	37	16	31	28	9	32%
1,2,3,6,7,8-H_xCDF	15	15	27	19	6	30%
2,3,4,6,7,8-H_xCDF	25	17	39	27	9	34%
1,2,3,4,6,7,8-H_pCDF	7	9	2	6	3	50%
1,2,3,4,7,8,9-H_pCDF	5	5	1	4	2	45%
Dioxin Congeners						
Total TCOD	NA	NA	NA	NA	NA	NA%
OCDD	NA	NA	NA	NA	NA	NA%
PCDD Compounds						
2,3,7,8-TCDD	NA	NA	NA	NA	NA	NA%

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TABLE 5.8

CHLORINATED FURAN AND DIOXIN RESULTS (ppb (w/w), ng/g)
SAMPLE EZ29-53-01 (Spiked Mineral Oil)

Congener	Determination Det 1	Det 2	Det 3	Mean	Standard Deviation	Relative Standard Deviation
PCDF Congeners						
Total TCDF	220	160	190	190	24	13%
Total P_nCDF	310	550	260	373	127	34%
Total H_xCDF	680	6,600	390	2,557	2,862	112%
Total H_pCDF	530	33	220	261	205	79%
OCDF	NA	NA	3	1	1	141%
Total PCDF	1,740	7,343	1,063	3,382	2,815	83%
Furan Compounds						
2,3,7,8-/2,3,4,8-TCDF	220	160	190	190	24	13%
2,3,4,7,8-P_nCDF	170	370	120	220	108	49%
1,2,3,7,8-/1,2,3,4,8-P_nCDF	140	170	140	150	14	9%
1,2,3,4,7,8-/1,2,3,4,7,9-H_xCOF	310	550	260	373	127	34%
1,2,3,6,7,8-H_xCDF	140	120	76	112	27	24%
2,3,4,6,7,8-H_xCDF	200	5,900	140	2,080	2,701	130%
1,2,3,4,6,7,8-H_pCDF	530	33	220	261	205	79%
1,2,3,4,7,8,9-H_pCDF	NA	NA	NA	NA	NA	NA%
Dioxin Congeners						
Total TCDD	19	19	23	20	2	9%
OCDD	NA	NA	1	NA	NA	141%
PCDD Compounds						
2,3,7,8-TCDD	19	19	23	20	2	9%

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TABLE 5.9

CHLORINATED FURAN AND DIOXIN RESULTS (ppb (w/w), ng/g)
SAMPLE E729-53-D2 (Spiked Aroclor 1D16)

Congener	Determination Det 1	Det 2	Det 3	Mean	Standard Deviation	Relative Standard Deviation
PCDF Congeners						
Total TCDF	57	67	66	63	4	7%
Total P_nCDF	600	500	460	520	59	11%
Total H_xCDF	5,400	2,300	780	2,827	1,923	68%
Total H_pCDF	65	150	340	185	115	62%
OCDF	110	120	120	117	5	4
Total PCDF	6,232	3,137	1,766	3,712	1,868	50%
Furan Compounds						
2,3,7,8-/2,3,4,8-TCDF	57	67	66	63	4	7%
2,3,4,7,8-P_nCDF	410	310	260	327	62	19%
1,2,3,7,8-/1,2,3,4,8-P_nCOF	180	180	190	183	5	3%
1,2,3,4,7,8-/1,2,3,4,7,9-H_xCDF	NA	NA	NA	NA	NA	NA%
1,2,3,6,7,8-H_xCOF	100	84	81	88	8	9%
2,3,4,6,7,8-H_xCDF	5,200	2,100	680	2,660	1,887	77%
1,2,3,4,6,7,8-H_pCDF	65	150	180	132	49	37%
1,2,3,4,7,8,9-H_pCDF	NA	NA	NA	NA	NA	NA%
Dioxin Congeners						
Total TCDD	46	46	44	45	1	2%
OCDO	NA	NA	NA	NA	NA	NA%
PCDD Comoounds						
2,3,7,8-TCDD	46	46	45	46	NA	1%

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TABLE 5.10

CHLORINATED FURAN AND DIOXIN RESULTS (ppb (w/w), ng/g)
SAMPLE EZ29-53-03 (Spiked Aroclor 1260)

Congener	Determination Det 1	Det 2	Det 3	Mean	Standard Deviation	Relative Standard Deviation
PCDF Congeners						
Total TCDF	1,400	1,700	970	1,357	300	22%
Total P_nCDF	1,100	1,300	1,200	1,200	82	7%
Total H_xCDF	20,000	4,700	11,000	11,900	6,279	53%
Total H_pCDF	1,700	3,000	660	1,787	957	54%
OCDF	5,000	4,900	2,600	4,167	1,109	27%
Total PCDF	29,200	15,600	16,430	20,410	6,225	30%
Furan Compounds						
2,3,7,8-/2,3,4,8-TCDF	1,200	1,300	880	1,127	179	16%
2,3,4,7,8-P_nCDF	590	410	800	627	194	31%
1,2,3,7,8-/1,2,3,4,8-P_nCDF	1,400	1,170	970	1,357	300	22%
1,2,3,4,7,8-/1,2,3,4,7,9-H_xCDF	1,900	1,800	1,600	1,767	125	7%
1,2,3,6,7,8-H_xCDF	1,200	93	780	691	456	66%
2,3,4,6,7,8-H_xCDF	10,000	770	6,500	5,757	3,805	66%
1,2,3,4,6,7,8-H_pCDF	55	850	49	318	376	118%
1,2,3,4,7,8,9-H_pCDF	300	360	180	280	75	27%
Dioxin Congeners						
Total TCDD	110	100	80	97	12	13%
OCDD	NA	12	NA	4	6	141%
PCDO Compounds						
2,3,7,8-TCDD	110	100	80	97	12	13%

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TABLE 5.11

ACCURACY DETERMINATION USING SPIKED BASELINE LIQUID ANALYSES

	Mineral Oil E729-53-01			Aroclor 106 E729-53-02			Corrected(2)	Corrected
	Spike Level	Amount Found	Percent(1) Difference	Spike Level	Amount Found	Percent Difference	Aroclor 1016 E729-53-02	Percent Difference
Total TCDF	200	190	-5	53	63	19	63	19
Total PnCDF	300	373	24	316	520	65	515	63
Total HxCDF	475	2557	438	185	2827	1428	2637	1325
Total HpCDF	400	261	-35	526	185		100	-81
OCDF	0	1		132	117		117	-11
Total PCDF	1375	3382	146	1212	3712	206	3432	183
Total TCDD	25	2	-92	53	45	-15	45	-15
OCDD	0	0		0	0		0	
2,3,7,8-TCDD	25	2	-92	53	46	-13	46	-13
2,3,7,8-/2,3,4,8-FCDF	200	190	-5	53	63	19	63	19
1,2,3,7,8-/1,2,3,4,8-PnCDF	150	150	0	158	183	16	183	16
2,3,4,7,8-PnCDF	150	220	47	158	327	107	327	107
1,2,3,4,7,8-/ 1,2,3,4,7,9-HxCDF	250	373	49	0	0	--	-190	--
1,2,3,6,7,8-HxCDF	50	0	-100	53	88	66	88	66
2,3,4,6,7,8-HxCDF	175	2080	1089	132	2660	1915	2660	1915
1,2,3,4,6,7,8-HpCDF	400	261	-35	526	132	-75	132	-75
1,2,3,4,7,8,9-HpCDF	--	0	--	--	0	--	-85	--

(1) Percent Difference = 100 (Measured Value - True Spike)/True Spike

(2) Corrected by subtracting the Aroclor 1016 "Baseline" PCDD/PCDF concentrations from the measured values.

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Comparison with Parallel Analyses

The Battelle results are compared with the results reported by the other four laboratories participating in this program in Table 5.12. The data presented in this table for the other laboratories are taken from a draft statistical report (2) presented by Edo Pellizari (Research Triangle Institute, Research Triangle Park, N.C.) at a meeting of the five participating laboratories held in Washington, D.C. on November 19, 1986.

The Battelle results averaged over three replicate determinations are presented in Table 5.12 where the average reported values by the five collaborating laboratories conducting parallel analyses are also given.

The two sets of data compare favorably; except for hexachlorinated furans, the Battelle results are consistently lower overall than the data contributed by other laboratories. The general trends in the data such as very low values for PCDD/PCDF in mineral oil samples was apparent in all the reported data. The 30-year-old network transformer containing Askarel (Sample Number 3 in Table 5.12) had the highest reported PCDF level of all the in-service samples tested, approximately 32 ppm (w/w) using the average of all reported determinations.

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TABLE 5.12

MEAN FURAN RESULTS FOR SEVEN UTILITY DIELECTRIC FLUIDS

	Network Transformer No. 1	Network Transformer No. 2	Network Transformer No. 3	Network Transformer No. 4	Arc Furnace Transformer	Precipitator Transformer	Capacitor
Sample Identifier							
Fluid	Askarel	Askarel	Askarel	Mineral Oil	Mineral Oil	Askarel	Askarel
Years Service	20	28	30	UNK	UNK	27	UNK
Field Code	ISL-02-A	ISL-08 A	ISL-03 A	ISL-04 O	ISL-23-O	ISL-17-A	ISL-27
Laboratory Code	17	12	11	16	15	14	13
Battelle Furan Results							
Total TCDF	293	17	53	0	0	177	106
Total PnCDF	71	96	702	0	0	2076	21
Total HxCDF	15700	1263	24733	0	0	77000	143
Total HpCDF	249	490	3951	0	0	602	10
OCDF	330	403	2828	0	0	29	17
Total PCDF	16643	2269	31767	0	0	24884	297
Combined Furan Results (1)							
Total TCDF	415	128	158	1	1	782	586
Total PnCDF	991	279	1672	45	4	7746	221
Total HxCDF	4886	1012	10824	80	2	12931	67
Total HpCDF	1277	1822	6587	15	8	1767	12
OCDF	3346	6744	21830	14	18	188	21
Total PCDF	10914	9486	41071	154	34	23413	906
Percent Difference in Furan Congener Results (2)							
	52%	-76%	-23%	(3)	(3)	6%	67%

(1) Combined Mean = Average reported values from the five participating laboratories.
(2) Percent Difference = (Combined Mean - Battelle Value)/Combined Mean X 100%
(3) Zero value division not possible.

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Section 6

DISCUSSION

This study produced a great amount of insight into the variability of analytical methods applied to trace analysis in a complex dielectric fluid matrix. PCB constitute the principal class of interferants for modern mass spectrometric methods when used to analyze polychlorinated aromatic species such PCDF and PCDD. Several conclusions can be drawn concerning performance of the methodology and the accurate screening of in-service dielectric fluids.

METHODS

The analytical procedures proved to be both rugged and reliable when used with labelled quantification and recovery standards. The quantification standards are used to calculate errors from extraction and sorbent partitioning losses. This is especially important in the Askarel and mineral oil matrix since the high organic burden found with this matrix requires secondary partitioning to remove interfering PCB and the background hydrocarbons from mineral oil.

Random outliers were observed in this study. One example was the elevated levels of hexachlorodibenzofuran found in the in-service analyses. This kind of acute error can arise from a mistake in the gravimetric preparation and dilution of the labelled recovery standard. Another possible cause for this random error is selective partitioning losses during sample clean up. Observing this type of spurious result indicates that the methods should be used with enough quality control checks to "flag" this type of error during the analysis. Using a second labeled internal standard to quantify the mass recovery of the quantification standards would identify this problem if it is related to quantification standard losses.

The observed data variability in this program was smaller than the participants had anticipated before the program began. In this very difficult matrix, a chlorinated oil, most analysts would predict a variability of one to two orders of magnitude (10x to 100x scatter around the true value). In most cases, the relative standard devia-tions were found to be less than 100 percent. The relative average deviation is the absolute difference between individual results and the mean (or true value), divided by the number of determinations. For samples such as the Aroclor 1242,

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Aroclor 1016, and mineral oil, the average deviation was most often less than 50 percent. This result was seen in individual laboratory replicate analyses and in grouped data from different laboratories.

IN-SERVICE LIQUID ANALYSES

The in-service liquids tested in this program were found to have relatively low amounts of PCDD in all samples tested. This result supports the hypothesis held by many chemists who have investigated Askarel and PCB-containing fluids that dioxins are not a major constituent of these mixtures. Except for the mineral oils, polychlorinated dibenzofurans, however, were found in trace amounts in all of the samples tested. The mineral oil samples were found to have extremely low amounts of PCDD/PCDF if any were found at all. Even the in-service liquid from Transformer 4, a network distribution transformer that was involved in a high energy excursion, was found to have minimal amounts of PCDD and PCDF. Transformer 4 had visible carbon, and major signs of scorching on the case and the area of the electrodes.

The Askarel transformers with more than 25 years of service tended to have higher levels of PCDF than the appliances put into service for a shorter time. It is possible that manufacturing controls improved as the production of Askarel matured in the 1960s such that Askarel was produced with lower levels of PCDF in the as-delivered fluids. It would be interesting to obtain replacement Askarel with a known lot number which matched a sample with extended service life. Analyzing samples of an unused Askarel and comparing the PCDF levels in a sample subjected to heavy load and environmental stress for an extended period would challenge the theory that utility operation contributed to elevated PCDF levels in Askarel fluids used in transformer and capacitor applications.

Two utility appliances were selected by the EPRI Technical Advisory Committee for special attention. An Askarel-filled electrostatic precipitator (ESP) transformer, and an oil-filled arc furnace transformer. Both of these applications involve extended thermal and electrical excursions during daily operation. These two samples were the "worst case" for testing service stress on the dielectric fluids. The arc furnace had essentially no PCDF or PCDD, and the PCDF levels in the ESP transformer appeared to be dictated by the age of the unit (27 years of service) and the fluid composition (Aroclor 1260). This extended period of stress did not appear to elevate the PCDF levels above typical Aroclor 1260 contamination levels.

One capacitor was tested in the in-service liquid screening program. It was found to have relatively low levels of PCDF compared to the other Askarel-filled units.

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The observed distribution of PCDF seemed to follow a trend of higher concentrations of PCDF arising with the highest degree of chlorination Aroclor. The Aroclor 1260 with 60 percent chlorine by weight tended to have higher levels of PCDF in every comparable sample than Aroclor 1242, or Aroclor 1016, both of which have approximately 42 percent chlorine in the base Aroclor.

A second effect was observed in these data, the relative concentrations of PCDF congeners in any sample tends to favor the analogs with higher chlorination as the chlorination number of the underlying Aroclor increases. For instance the proportion of hexa, hepta, and octachlorodibenzofurans are higher in Aroclor 1260 than Aroclor 1242. If PCDF are formed by direct internal condensation with the addition of oxygen, HCl elimination can occur. This reaction would preferentially produce higher levels of chlorination in the product PCDF when high degrees of chlorination occur in the reactant PCB.

SUMMARY

This study was successful in developing a set of methodologies that reliably determine trace levels of PCDF and PCDD in a very difficult matrix -- chlorinated organic oil. The development of commercially available reference standards and the statistical validation of reference methods that can be used to analyze utility fluid was a major contribution to the quality and defensibility of data in this field. The method verification program showed that a range of instrumentation can be successfully used to measure trace levels of PCDF and PCDD in utility fluids. In general, the methods employing low resolution mass spectrometry require additional column chromatography to isolate PCDF/PCDD-enriched fraction for final gas chromatography. The precision of blind spiked samples was superior to the variance expected by experienced analysts who had previously performed this analysis. The availability of labelled quantification standards helped improve method performance and lower data scatter.

Although the in-service liquids tested in this program were a very limited set, there were interesting findings about the type and distribution of polychlorinated dioxin and furan species in the systems tested. Dioxin levels were very low, or not measurable in the liquids analyzed. The mineral-oil-filled equipment had levels that were found only at the quantification limits of the methods employed. Aroclor 1260 appears to have higher levels of PCDF with enrichment of the higher chlorine-number analogs, when compared to Aroclor 1242, 1016, or Aroclors with fewer chlorine atoms per molecule than 1260. This data base can not support the

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premise that the age of Askarel transformers tends to favor higher PCDF levels in older transformers since only four units were investigated.

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Appendix A

IN-SERVICE LIQUID QUESTIONNAIRE

GENERAL INFORMATION QUESTIONNAIRE

EPRI IN SERVICE LIQUIDS STUDY (RP 2028)

Respondant: _____

Samples provided	Number Shipped
Askarel	
Load Center/Network Transformers	_____
Rectifier Transformer	_____
Precipitator Transformer	_____
Capacitor	_____
Oil Filled	
Load Center/Network Transformer	_____

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DATA SHEET FOR EACH SAMPLE

EPRI IN SERVICE LIQUIDS STUDY (RP 2028)

General Information

Voltage Rating: _____

Liquid Volume: _____

Manufacturer and Year: _____

PCB/Askarel Manufacturer: (if available)

_____

_____

PCB/Askarel Type:

_____

_____

PCB Levels: (for oil filled, if known)

_____

_____

Additional Equipment Identification: (name plate data)

_____

_____

Equipment Maintenance History

Length of Actual Service: _____

Major Maintenance:

_____

_____

Recorded Failure in Service:

_____

_____

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DATA SHEET FOR EACH SAMPLE

Was Fluid Changed at Failure:

Any Record of Temperature Excursions:

Are Maintenance Records Available:

Any Other Pertinent Information About This Unit or the Sample Liquid:

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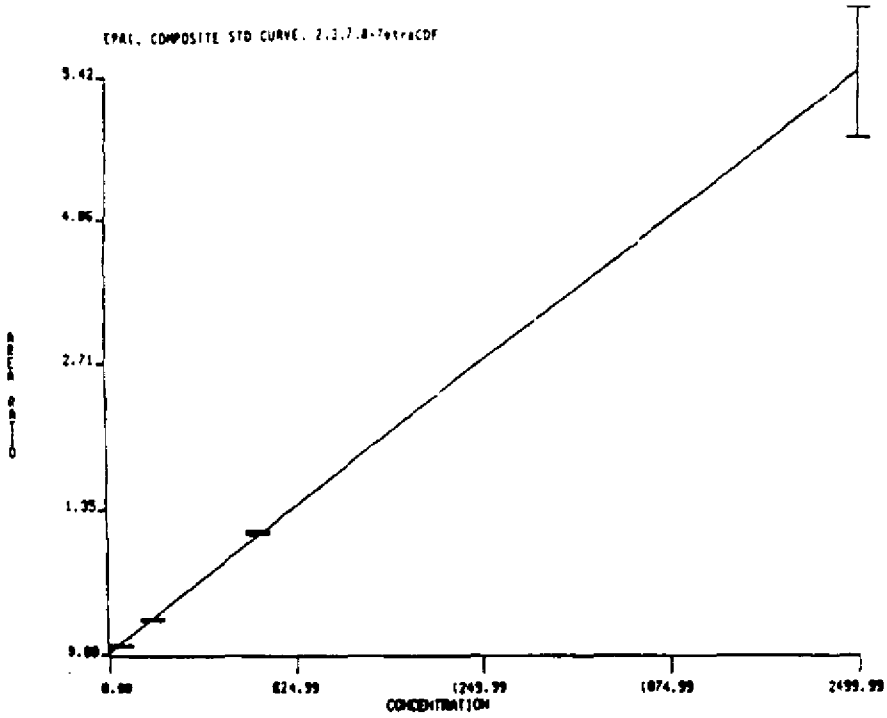
Appendix B

ANALYTICAL CURVE DATA FOR THE CROSS CHECK ANALYSES



EPRI, COMPOSITE STD CURVE, 2.1.7.8-TetraCDF

X-VALUES	Y-VALUES				
39.9999	0.0794	0.0802	0.0766	0.0910	0.0868
149.9990	0.3249	0.3249	0.3396	0.3430	0.3441
499.9990	1.1476	1.1605	1.1407	1.1278	1.1336
2499.9900	9.8405	9.9660	9.7829	4.9650	4.4329

X-VALUE	Y-VALUE	STD DEV	RSDX	RES E	R R E
40.0001	0.0833	0.0039	4.66	0.0086	0.0030
150.0000	0.3366	0.0093	2.70	0.0146	0.0084
900.0000	1.1431	0.0117	1.01	0.0189	0.0106
2900.0000	9.4247	0.4019	11.08	0.9910	0.9445

DATA WITH RESPECT TO THE REGRESSION LINE

40.0001	0.0833	0.0271	32.36	0.0487	0.0245
150.0000	0.3364	0.0139	3.99	0.0218	0.0122
900.0000	1.1431	0.0499	3.96	0.0719	0.0412
2900.0000	9.4247	0.4016	11.08	0.9911	0.9449

A SLOPE OF 0.00316 GIVES AN INTERCEPT OF 0.02068
A SLOPE OF 442.08300 GIVES AN INTERCEPT OF -0.93869
THE DATA HAS A CORRELATION COEFFICIENT OF 0.99993

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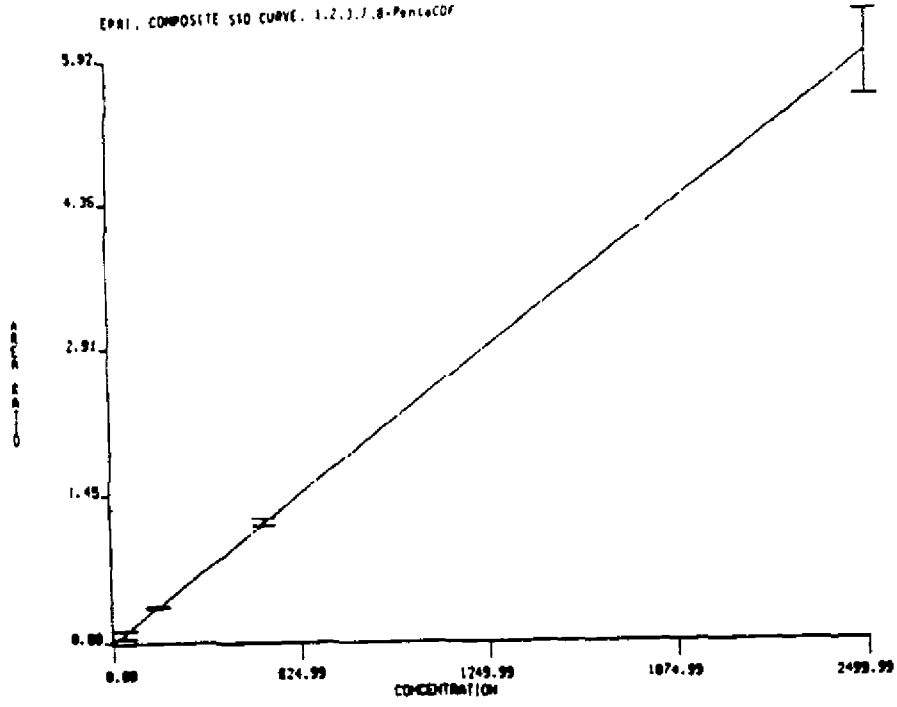
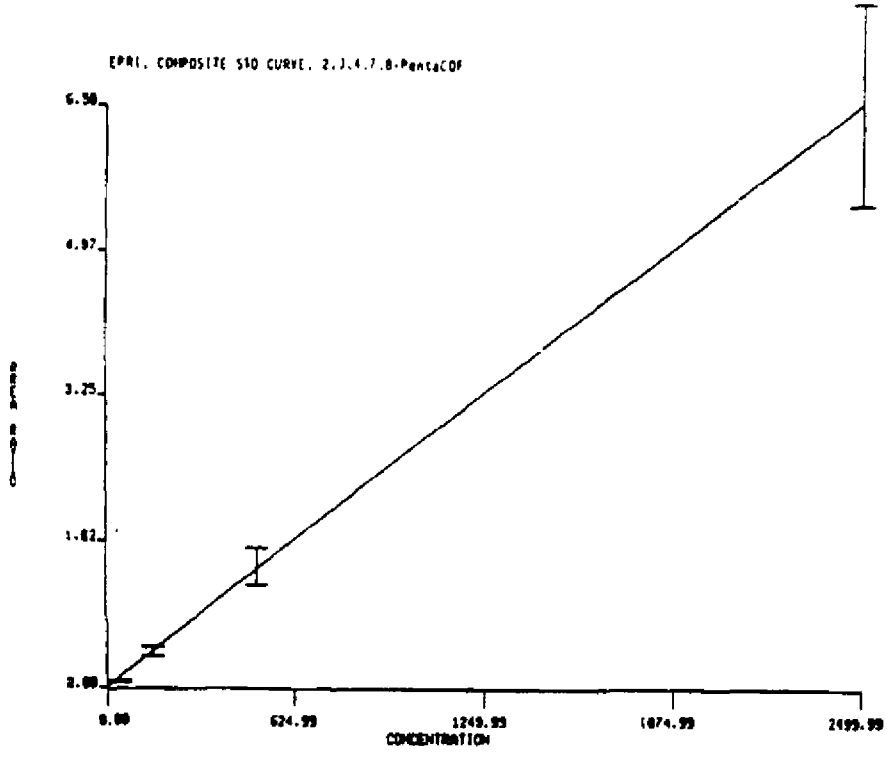


EPRI, COMPOSITE STD CURVE, 1.2.3.7.9-PentaCDF

X-VALUES	Y-VALUES				
40 0000	0 0989	0 1021	0 0961	0 0929	0 0926
190 0000	0 3547	0 3532	0 3249	0 3921	0 3603
400 0000	1 2183	1 2171	1 2201	1 1449	1 1469
2499 9900	4 2080	4 3210	9 9500	5 9030	5 2400

X-VALUE	Y-VALUE	STD DEV	RSDX	RES E	A R E
DATA WITH RESPECT TO THE Y-VALUES					
40 0000	0 0805	0 0396	49 19	0 0624	0 0337
190 0000	0 3441	0 0119	3 32	0 0188	0 0098
900 0000	1 1823	0 0398	3 39	0 0628	0 0339
2500 0000	9 8222	0 4169	7 15	0 6989	0 3946
DATA WITH RESPECT TO THE REGRESSION LINE					
40 0000	0 0803	0 0415	51 51	0 0636	0 0353
190 0000	0 3441	0 0183	3 56	0 0194	0 0109
900 0000	1 1823	0 0446	3 76	0 0703	0 0380
2500 0000	9 8222	0 4169	7 15	0 6586	0 3946

A SLOPE OF 0 00292 GIVES AN INTERCEPT OF -0 00197
A SLOPE OF 489 03700 GIVES AN INTERCEPT OF 0 67917
THE DATA HAS A CORRELATION COEFFICIENT OF 0 99998

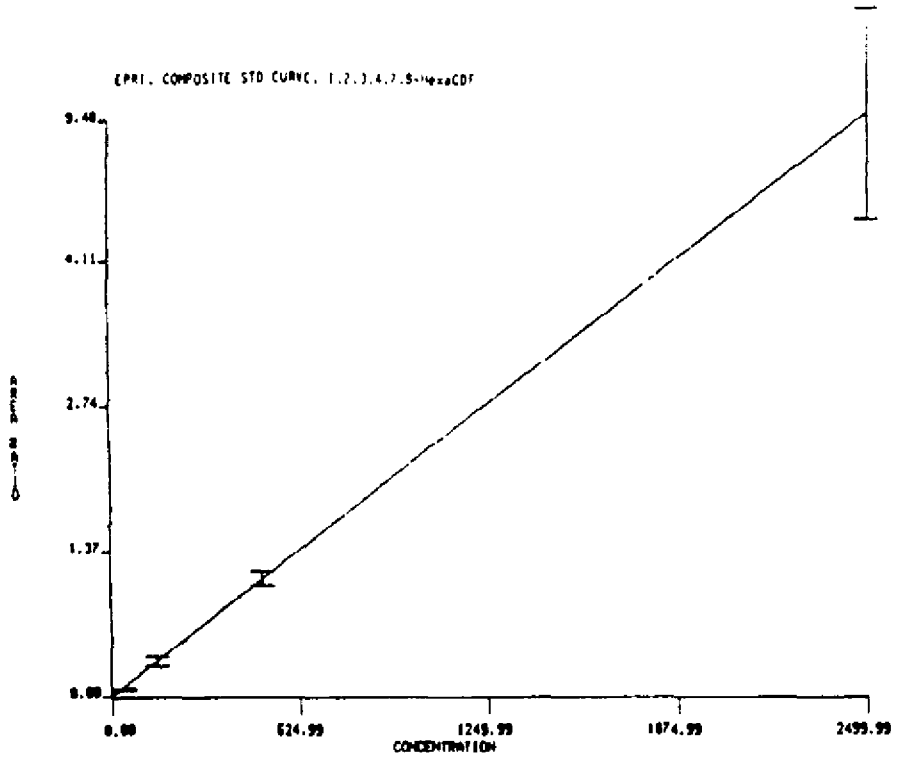


EPRI. COMPOSITE STD CURVE. 2.3.4.7.8-PentaCDF

X-VALUES	Y-VALUES				
40.0000	0.0703	0.0703	0.0714	0.0899	0.0810
150.0000	0.4369	0.4409	0.4478	0.3384	0.3394
499.9900	1.9297	1.4388	1.4623	1.1333	1.1114
2499.9900	7.4829	7.4420	7.0960	9.1680	9.3969

X-VALUE	Y-VALUE	STD DEV	RED1	RES E	A A E
DATA WITH RESPECT TO THE Y-VALUES					
40.0000	0.0773	0.0000	10.33	0.0113	0.0035
150.0000	0.4008	0.0364	14.06	0.0797	0.0383
500.0000	1.9403	0.2019	13.03	0.2890	0.1370
2500.0000	6.9040	1.1296	17.36	1.9974	0.7478
DATA WITH RESPECT TO THE REGRESSION LINE					
40.0000	0.0773	0.0369	47.43	0.0981	0.0291
150.0000	0.4003	0.0366	14.13	0.0801	0.0385
500.0000	1.9403	0.2930	11.89	0.2900	0.1394
2500.0000	6.9040	1.1296	17.36	1.9978	0.7479

A SLOPE OF 0.002680 GIVES AN INTERCEPT OF 0.00536
A SLOPE OF 384.30900 GIVES AN INTERCEPT OF -2.06203
THE DATA HAS A CORRELATION COEFFICIENT OF 0.99999

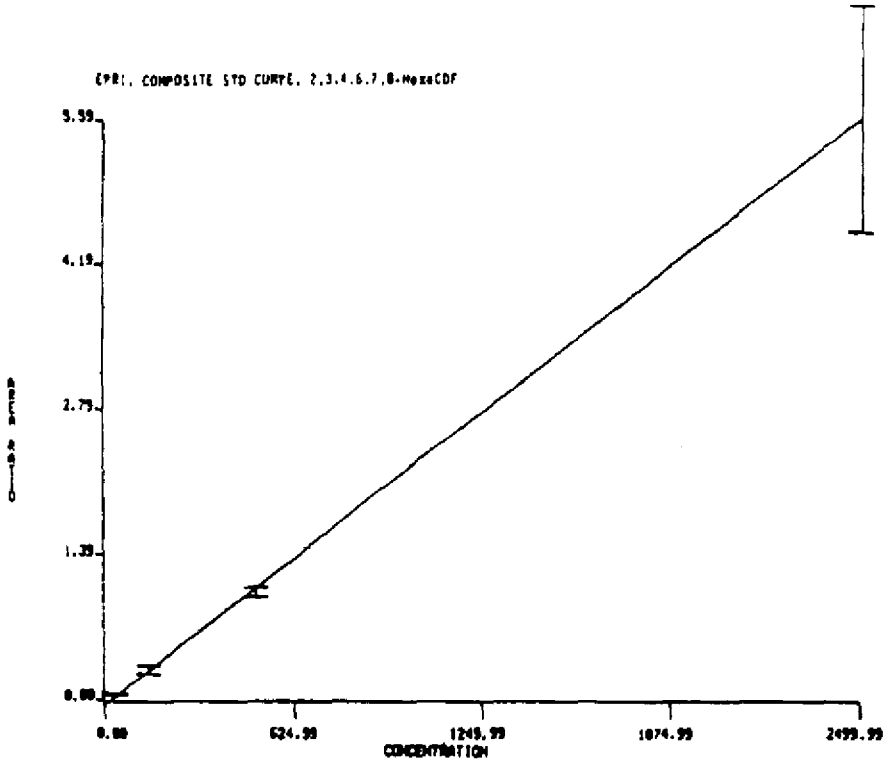


EPRI. COMPOSITE STD CURVE, 1,2,3,4,7,8-HexaCDF

X-VALUES	Y-VALUES				
40 0000	0 0702	0 0777	0 0708	0 0864	0 0723
150 0000	0 3139	0 3101	0 3073	0 4198	0 3709
499 9990	1 1784	1 0729	1 2032	1 0307	1 0391
2499 9900	9 6333	9 7769	9 4700	4 6040	4 3120

X-VALUE	Y-VALUE	STD DEV	RSDI	REG E.	A B E
DATA WITH RESPECT TO THE Y-VALUES					
40 0000	0 0764	0 0069	8 39	0 0102	0 0038
150 0000	0 3429	0 0447	13 04	0 0707	0 0403
500 0000	1 1149	0 0474	4 09	0 1048	0 0409
2500 0000	9 4872	0 9961	10 19	1 9730	0 8974
DATA WITH RESPECT TO THE REGRESSION LINE					
40 0000	0 0764	0 0199	23 94	0 0314	0 0179
150 0000	0 3429	0 0439	13 28	0 0720	0 0410
500 0000	1 1149	0 0488	4 17	0 1088	0 0420
2500 0000	9 4872	0 9961	10 19	1 9730	0 8974

A SLOPE OF 0 00219 GIVES AN INTERCEPT OF 0 00947
A SLOPE OF 499 84600 GIVES AN INTERCEPT OF -2 38869
THE DATA HAS A CORRELATION COEFFICIENT OF 0 99998



EPRI. COMPOSITE STD CURVE. 2,3,4,6,7,8-HexaCDF

X-VALUES	Y-VALUES				
40.0000	0.0990	0.0637	0.0973	0.0710	0.0719
150.0000	0.2836	0.2798	0.2854	0.2793	0.2986
499.9990	1.0389	1.0868	0.9732	1.0334	1.0598
2499.9900	9.4283	9.3678	9.3119	4.3340	7.3400

X-VALUE	Y-VALUE	STD DEV	RSD%	RES S.	R R E

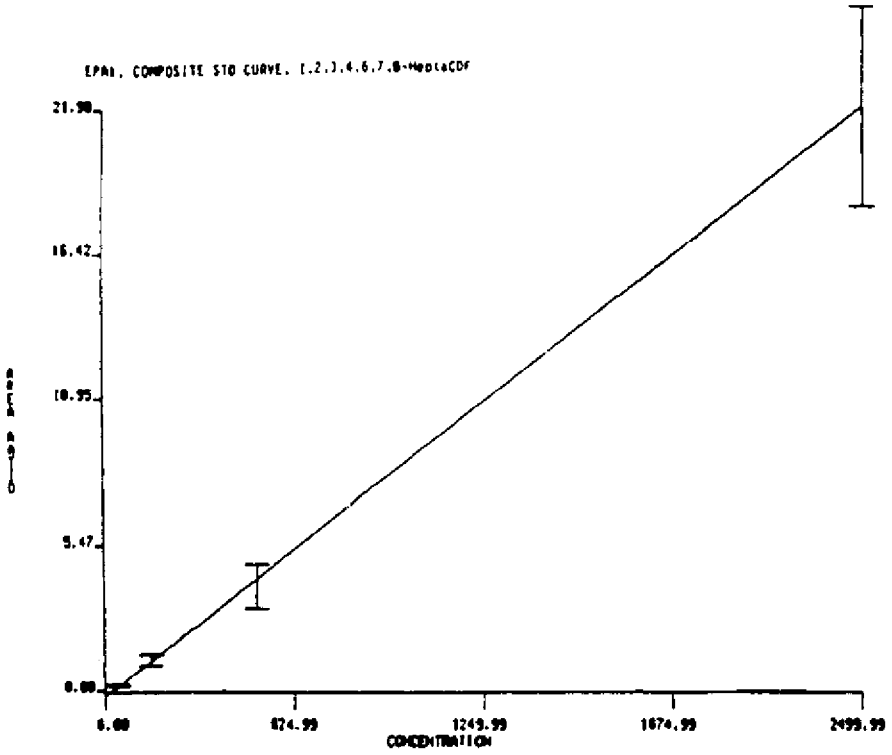
DATA WITH RESPECT TO THE Y-VALUES

40.0000	0.0647	0.0069	9.99	0.0098	0.0032
150.0000	0.3046	0.0402	13.19	0.0369	0.0329
500.0000	1.0383	0.0419	4.03	0.0393	0.0339
2500.0000	9.3937	1.0892	19.46	1.9403	0.8798

DATA WITH RESPECT TO THE REGRESSION LINE

40.0000	0.0647	0.0248	38.29	0.0380	0.0200
150.0000	0.3046	0.0429	14.06	0.0606	0.0247
500.0000	1.0383	0.0629	6.05	0.0889	0.0508
2500.0000	9.3937	1.0892	19.46	1.9404	0.8798

A SLOPE OF 0.00229 GIVES AN INTERCEPT OF -0.04686
A SLOPE OF 443.63000 GIVES AN INTERCEPT OF 20.79250
THE DATA HAS A CORRELATION COEFFICIENT OF 0.99993



EPA, COMPOSITE STD CURVE, 1,2,3,4,6,7,8-HpCDF

X-VALUES	Y-VALUES				
40 0000	0 2673	0 2097	0 2483	0 2906	0 3069
150 0000	1 2476	1 1899	1 4126	0 8939	1 1430
600 0000	3 2079	4 2144	3 9309	4 0030	3 7310
2400 0000	23 3270	22 9794	26 0169	23 0500	21 7000

X-VALUE	Y-VALUE	STD DEV	RSDI	REG. E	R.A.E.
DATA WITH RESPECT TO THE Y-VALUES					
40 0000	0 2919	0 0240	13 46	0 0837	0 0079
150 0000	1 1927	0 1016	19 21	0 2871	0 0681
600 0000	3 9437	0 8478	21 49	1 3404	0 1969
2400 0000	21 9035	3 7442	17 09	5 9200	0 8676
DATA WITH RESPECT TO THE REGRESSION LINE					
40 0000	0 2919	0 1239	93 80	0 2143	0 0314
150 0000	1 1927	0 2061	17 27	0 3238	0 0478
600 0000	3 9437	0 8919	22 60	1 4096	0 2066
2400 0000	21 9038	3 7449	17 09	5 9209	0 8677

A SLOPE OF 0 00883 GIVES AN INTERCEPT OF -0 22126
A SLOPE OF 113 20600 GIVES AN INTERCEPT OF 29 04810
THE DATA HAS A CORRELATION COEFFICIENT OF 0 99989

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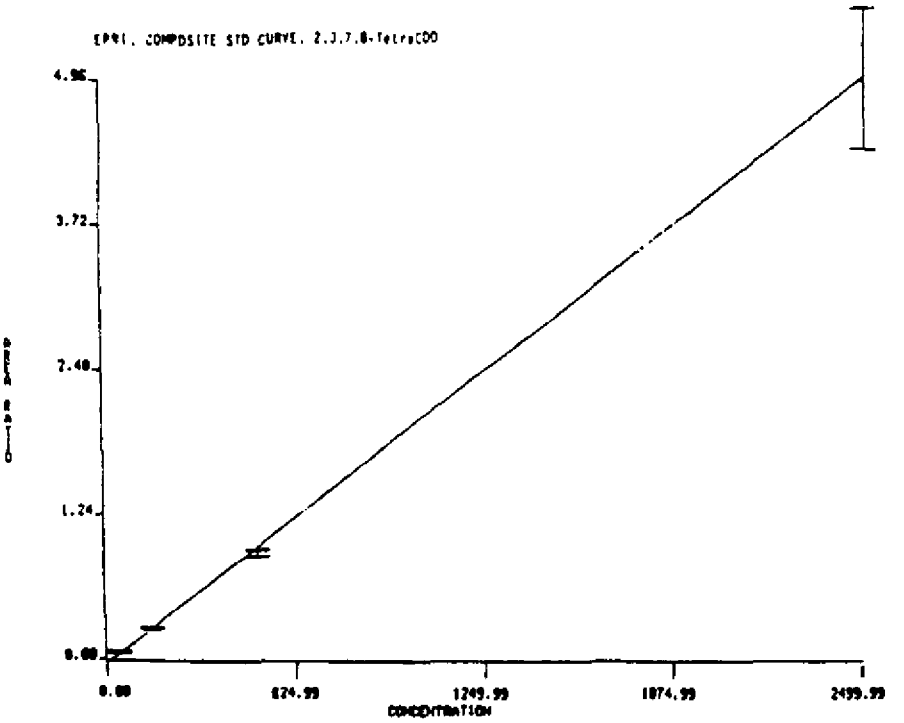


EPRI. COMPOSITE STD CURVE. 2,3,7,8-TetraCDD

X-VALUES	Y-VALUES				
40.0000	0.0602	0.0608	0.0619	0.0769	0.0677
150.0000	0.2600	0.2833	0.2703	0.2738	0.2817
499.9900	0.9703	0.9934	0.9117	0.8976	0.9218
2499.9900	4.8330	4.8233	4.7199	4.9390	4.1390

X-VALUE	Y-VALUE	STD DEV	RSDX	RES. E	R R E

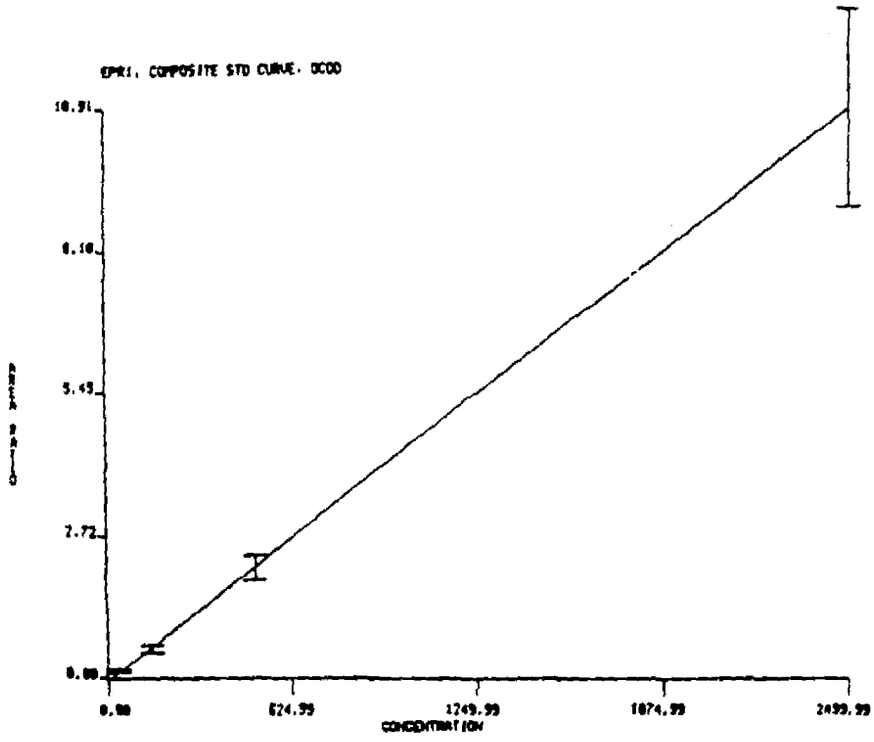
DATA WITH RESPECT TO THE Y-VALUES

40.0000	0.0663	0.0066	9.87	0.0104	0.0067
150.0000	0.2760	0.0061	2.19	0.0096	0.0062
500.0000	0.9288	0.0270	2.90	0.0439	0.0282
2500.0000	4.9690	0.6064	12.20	0.9892	0.6169

DATA WITH RESPECT TO THE REGRESSION LINE

40.0000	0.0663	0.0233	35.10	0.0368	0.0236
150.0000	0.2760	0.0128	4.62	0.0202	0.0130
500.0000	0.9282	0.0493	5.30	0.0779	0.0499
2500.0000	4.9690	0.6067	12.20	0.9892	0.6130

A SLOPE OF 0.00199 GIVES AN INTERCEPT OF -0.03408
A SLOPE OF 500.33900 GIVES AN INTERCEPT OF 17.09620
THE DATA HAS A CORRELATION COEFFICIENT OF 0.99993



EPRI, COMPOSITE STD CURVE, DCDD

X-VALUES	Y-VALUES				
40.0000	0.0978	0.1027	0.1088	0.1933	0.1989
190.0000	0.9364	0.9040	0.9418	0.4943	0.9981
499.9990	2.8410	2.0311	2.1639	2.4200	2.1320
8499.9900	10.3698	12.9448	12.8468	9.9800	9.1020

X-VALUE	Y-VALUE	STD DEV	RSDI	REG. E	R & E
40.0000	0.1847	0.0268	21.44	0.0423	0.0124
190.0000	0.9364	0.0713	12.89	0.1187	0.0329
500.0000	2.1208	0.2292	10.90	0.3623	0.1097
2500.0000	10.9161	1.8864	17.30	2.9898	0.8709

DATA WITH RESPECT TO THE REGRESSION LINE

40.0000	0.1847	0.0394	21.34	0.0423	0.0182
190.0000	0.9364	0.0774	13.96	0.1224	0.0357
500.0000	2.1209	0.0892	10.80	0.3623	0.1097
2500.0000	10.9161	1.9884	17.30	2.9898	0.8709

A SLOPE OF 0.00439 GIVES AN INTERCEPT OF -0.07755
A SLOPE OF 887.47100 GIVES AN INTERCEPT OF 17.44240
THE DATA HAS A CORRELATION COEFFICIENT OF 0.99999

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Appendix C

LETTER REPORT FROM UMEA

Umeå Universitet
901 87 Umeå

86-06-23

Analys results EPRI-pro jekt 2028

Formation of PCDD and PCDF in askarel and contaminated mineral oil equipment.

Contents.

Normalized raw counts for regression lines.

Levels in baseline liqids

Levels in inservice liqids:
TCDF/TCDDs
PnCDF/PnCDDs and HxCDF/HxCDDs
HpCDF/HpCDDs and OCDF/OCDDs

GC/MS Conditions.

Clean-up

By
Lars-Owe Kjeller
Umeå Universitet
901 87 umeå

Sweden.

MONS 218506

LARS-OWE KJELLER
Umeå Universitet
901 87 UMEÅ Sweden

Umeå 85-06-18

EPRI-prodjekt 2028

Calibration curve, raw counts normalized for ^{13}C-internalstandard.

Concentration injected pg	10	10	10
2.3.7.8-TCDF	9.5	12.4	10.8
2.3.7.8-TCDD	3.4	7.9	7.0
1.2.3.7.8-PnCDF	6.0	9.5	8.1
2.3.4.7.8-PnCDF	4.9	8.5	7.5
1.2.3.4.7.8-HxCDF	3.9	7.8	7.3
2.3.4.6.7.8-HxCDF	1.7	4.6	4.5
1.2.3.4.6.7.8-HpCDF	1.4	3.9	3.8
OCDF	ND	ND	ND

Concentration injected pg	40	40	40
2.3.7.8-TCDF	38.5	42.3	42.6
2.3.7.8-TCDD	18.0	27.6	27.8
1.2.3.7.8-PnCDF	24.8	35.0	37.8
2.3.4.7.8-PnCDF	17.8	29.0	29.0
1.2.3.4.7.8-HxCDF	19.1	27.3	27.3
2.3.4.6.7.8-HxCDF	8.8	18.2	18.2
1.2.3.4.6.7.8-HpCDF	5.8	13.0	13.0
OCDF	0.9	2.0	1.5

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Concentration injected pg	150	150	150
2.3.7.8-TCDF	160.9	155.1	160.1
2.3.7.8-TCDD	100.1	94.2	105.7
1.2.3.7.8-PnCDF	133.4	124.5	137.9
2.3.4.7.8-PnCDF	100.7	98.2	118.1
1.2.3.4.7.8-HxCDF	105.3	82.2	103.3
2.3.4.6.7.8-HxCDF	51.7	43.1	68.9
1.2.3.4.6.7.8-HpCDF	39.3	33.7	53.4
OCDF	5.6	2.1	6.7

Concentration injected pg	500	500	500
2.3.7.8-TCDF	545.3	570.0	550.9
2.3.7.8-TCDD	370.9	371.0	359.9
1.2.3.7.8-PnCDF	470.0	471.0	467.7
2.3.4.7.8-PnCDF	403.5	401.0	402.1
1.2.3.4.7.8-HxCDF	339.8	338.0	341.9
2.3.4.6.7.8-HxCDF	214.3	203.0	216.2
1.2.3.4.6.7.8-HpCDF	182.4	177.0	181.9
OCDF	23.5	17.0	17.4

Concentration injected pg	2500	2500	2500
2.3.7.8-TCDF	2791.7	2769.4	2767.9
2.3.7.8-TCDD	1925.0	1806.1	1924.3
1.2.3.7.8-PnCDF	2412.8	2384.7	2413.1
2.3.4.7.8-PnCDF	2012.5	1979.0	2061.7
1.2.3.4.7.8-HxCDF	1780.1	1760.3	1793.3
2.3.4.6.7.8-HxCDF	1118.9	1145.8	1100.5
1.2.3.4.6.7.8-HpCDF	973.4	889.8	952.1
OCDF	166.4	125.8	169.1

Concentration injected pg	7500	7500	7500
2.3.7.8-TCDF	8731.9	8593.7	9037.3
2.3.7.8-TCDD	5966.9	5480.0	5735.6
1.2.3.7.8-PnCDF	7401.8	7264.2	6989.2
2.3.4.7.8-PnCDF	6219.0	5897.8	5980.2
1.2.3.4.7.8-HxCDF	5565.6	5502.2	5494.7
2.3.4.6.7.8-HxCDF	3532.6	3577.6	3638.1
1.2.3.4.6.7.8-HpCDF	3067.2	2790.8	2768.4
OCDF	513.6	419.3	433.1

Characterization for the regression line $y = a*x + b$
y = amont of Dioxin/furans. x = normalized counts.

	a	b	Residual standard deviation.
2.3.7.8-TCDF	0.853	29.89	135.7
2.3.7.8-TCDD	1.306	18.28	117.5
1.2.3.7.8-PnCDF	1.037	9.24	77.5
2.3.4.7.8-PnCDF	1.240	6.76	76.1
1.2.3.4.7.8-HxCDF	1.357	24.50	38.0
2.3.4.6.7.8-HxCDF	0.487	-21.26	34.1
1.2.3.4.6.7.8-HpCDF	2.595	31.83	159.6
OCDF[1]	0.061	-4.44	22.6

[1] 10 pg conc. not included.

MONS 218509

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EPRI-prodject 2028

Level of dioxins and dibenzofurans in inservice liquid [ng/g][1 2]

Act nr. 41159-11-	11	12	13	14	15	16	17
TCDF							
1368	<1.1	0.46	11	1.2	<0.04	<0.05	<0.34
1379/1378	5.4	2.0	5.0	0.9	<0.04	<0.05	<0.34
1347	4.0	1.4	130	6.1	<0.04	<0.05	3.0
3460	5.4	1.9	Int	23	<0.04	<0.05	3.0
1247/1367	0.5	2.1	Int	27	<0.04	<0.05	14
1340	2.3	2.2	2.5	4.0	<4.04	<0.05	5.4
1346/1248	45	11	130	170	<0.04	<0.05	75
1246/3237/1260/1470/1369	14	6.7	95	61	<0.04	<0.05	31
1234/2349	5.4	1.4	32	9.7	<0.04	<0.05	5.4
1230/1467/2360/1236	2.3	4.2	9.1	15	<0.04	<0.05	0.4
3349	<1.1	<0.14	<0.03	<0.32	<0.04	<0.05	<0.34
1278	9.9	0.4	29	110	<0.04	<0.05	56
3267/1279	4.0	2.5	7.6	16	<0.04	<0.05	13
3469	<1.1	<0.14	<0.03	<0.32	<0.04	<0.05	<0.34
1249	<1.1	<0.14	<0.03	<0.32	<0.04	<0.05	<0.34
2360	0.5	4.6	Int	41	<0.04	<0.05	16
2467	4.5	0.01	37	31	<0.04	<0.05	2.1
1239/2347	9.0	3.9	140	60	<0.04	<0.05	13
1269	<1.1	<0.14	<0.03	<0.32	<0.04	<0.05	<0.34
2378	10	14	0.0	170	<0.04	<0.05	120
2348	20	7.0	86	120	<0.04	<0.05	40
2346	<1.1	<0.14	<0.03	<0.32	<0.04	<0.05	<0.34
2367	24	9.5	0.0	77	<0.04	<0.05	64
3467	<1.1	<0.14	<0.03	<0.32	<0.04	<0.05	<0.34
1289	<1.1	<0.14	<0.03	<0.32	<0.04	<0.05	<0.34
TOT TCDF	240	86	740	960	ND	ND	470
RMC ^{13}C-2378-TCDF	45%	50%	47%	54%	65%	67%	81%
TCDD	No TCDD isomers detected. Detection limit 0.2 ng/g						
RMC ^{13}C-2378-TCDD	41%	48%	49%	50%	56%	44%	26%

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MONS 218510

Act ar. 41159-11-	11	12	13	14	15	16	17
PnCDF							
13460	<1.1	2.5	2.0	33	<0.05	<0.06	<0.36
12460	27	5.6	7.0	200	<0.05	<0.06	10
23479	<1.1	1.9	3.0	65	<0.05	<0.06	<0.36
13478	<1.1	<0.17	<0.04	<0.35	<0.05	<0.06	<0.36
13479/12368	23	24	<0.04	490	<0.05	<0.06	54
12478	300	57	Int	2500	<0.05	<0.06	280
12479/13467	<1.1	3.1	2.0	81	<0.05	<0.06	16
12467	76	11	35	360	<0.05	<0.06	50
23469/12147	150	34	35	344	<0.05	<0.06	60
13469	<1.1	<0.17	<0.04	<0.35	<0.05	<0.06	<0.36
12348/12378	1100	100	13	1000	<0.05	<0.06	320
12346	35	4.3	1.5	<0.35	<0.05	<0.06	6.0
12379	<1.1	4.3	0.90	110	<0.05	<0.06	18
12367	200	22	29	1200	<0.05	<0.06	130
12469/23489	<1.1	<0.17	<0.04	49	<0.05	<0.06	<0.36
13489	<1.1	<0.17	<0.04	49	<0.05	<0.06	<0.36
12369	<1.1	<0.17	<0.04	<0.35	<0.05	<0.06	2.0
23468	<1.1	1.9	3.5	66	<0.05	<0.06	10
12349	<1.1	<0.17	<0.04	<0.35	<0.05	<0.06	<0.36
12489	21	4.3	21	1300.	<0.05	<0.06	4.0
23478	110	37	40	1900	<0.05	<0.06	560
12389	<1.1	<0.17	1.5	81	<0.05	<0.06	<0.36
23467	2.0	6.5	6.0	200	<0.05	<0.06	50
TOT PnCDF	2140	310	160	10000	ND	ND	1600
RRC ^{13}C-1237/8-PnCDF	55%	47%	52%	57%	73%	63%	86%
PnCDD	No PnCDD isomers detected. Detection limit 0.2 ng/g						
HxCDF							
123468	410	23	0.35	100	<0.06	<0.07	110
124678/134679	490	43	0.86	380	<0.06	<0.07	72
134678	800	86	4.4	1500	<0.06	<0.07	490
124679	<1.7	11	0.35	160	<0.06	<0.07	15
123479/123478	5300	570	14	4200	<0.06	<0.07	1300
123678	530	87	2.3	1000	<0.06	<0.07	83
124689	310	93	2.5	1100	<0.06	<0.07	68
123467	1100	70	1.6	460	<0.06	<0.07	230
123679	30	30	1.6	130	<0.06	<0.07	15
123469/123689	190	18	<0.05	670	<0.06	<0.07	52
123789	100	17	0.19	230	<0.10	<0.12	36
123489	330	34	1.5	1400	<0.10	<0.12	49
234678	120	18	0.75	470	<0.10	<0.12	73
TOT HxCDF	9700	1000	31	12000	ND	ND	2600.
RRC ^{13}C-1234/8-HxCDF	49%	50%	51%	56%	74%	69%	95%
HxCDD	No HxCDD isomers detected. Detection limit 0.2 ng/g						

C-6

MONS 218511

Att nr. 41159-11-	11	12	13	14	15	16	17
HpCDF[3]							
1234678	150	1000	1.7	880	<0.06	<0.07	22
1234679	16	40	<0.07	170	<0.06	<0.07	1.8
1234689	150	1000	1.2	610	<0.06	<0.07	15
1234789	80	460	0.27	470	<0.06	<0.07	3.8
TOT HpCDF	400	2500	3.2	2100	ND	ND	43
HpCDD	No HpCDD isomers detected. Detection limit 0.5 ng/g						
OCDF							
12346789	20000[4]	10000	5.4	100	<3.3	<3.8	54D0
OCDD							
12346789	<10	7.7	<0.73	<4.7	<1.2	8.5	<5.2
REC ^{13}C-OCDD	ND	45%	41%	69%	43%	41%	100%

[1] All quantifications are made with the ^{12}C-compunds in RADIAN calibration standards set.

[2] Corection for recovery is made.

[3] Corection for recovery made with ^{13}C-123478-HxCDF spike.

[4] The values ar not corected for recovery.

MONS 218512

High Resolution Gas Chromatography and Mass Spectrometry Conditions

Column

SUPELCO SP-2330, Fused Silica

Length	60	m
Diameter	0.25	mm
Film Thickness	0.20	um

GC-Conditions

HP 5890 with Helium as carrier gas

Column pressure	40 psi
Temperatur program:	100°C for 2 min splittless, to 180°C with 20°C/min, to 250°C with 3°C/min, hold at 250°C for 30 min.
Injections volym	1-3 ul

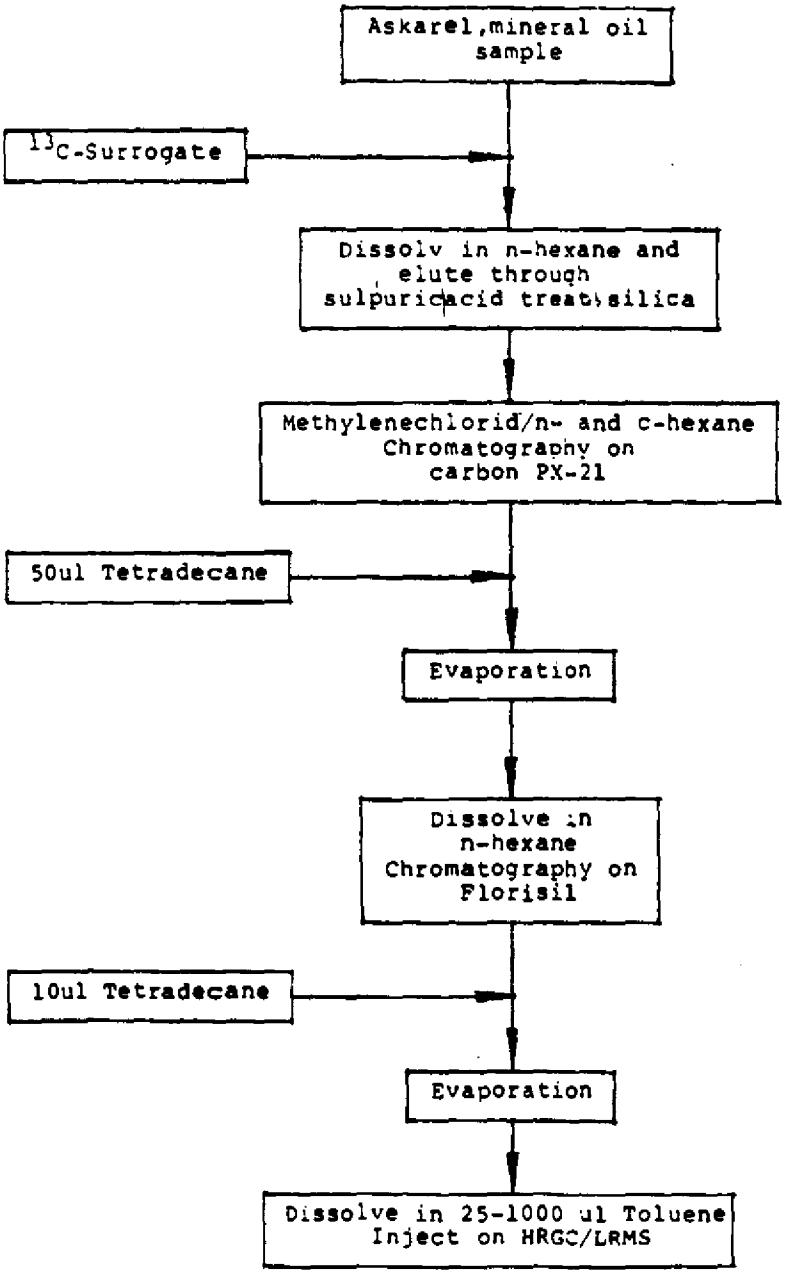
MS-Conditions

Instrument: VG 12-250 Low Resolution Quadrupole in EI mode

Electrone Energi	37	eV
Source Potential	9	V
Repeller Voltage	9	V
Amplifier Gain	Low sens SIR	
Multiplier voltage	2000	V
Tuning Calibrant	PFK	
Source Temp.	200	°C
Transfer Line Temp.	250	°C

MONS 218513

Clean-up technique for the determination of PCDF in askarel and miniral oil



MONS 218514

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EPRI-prodject 2028

Levels of dioxins and dibensofurans in baseline liquids

Att nr. E729-53-	01	02	03
2.3.7.8-TCDF	89	62	1300
2,3,4,8-TCDF	100	<0.8	ND[1]
Tot. TCDF's	190	62	2900
REC ^{13}C-2378-TCDF	60%	60%	67%
2.3.7.8-TCDD	14	38	92
Tot. TCDD's	14	38	92
REC ^{13}C-2378-TCDD	67%	58%	62%
1.2.3.4.8-/ 1.2.3.7.8-PnCDF	160	190	400
2.3.4.7.8-PnCDF	160	180	370
Tot. PnCDF's	320	370	1800
REC ^{13}C-12378-PnCDF	59%	63%	58%
1.2.3.7.8-PnCDD	<1.5	<1.3	<1.6
Tot. PnCDD's	ND	ND	ND
1.2.3.4.7.9-/ 1.2.3.4.7.8-HxCDF	290	<1.1	1400
1.2.3.6.7.8-HxCDF	31	40	370
1.2.3.7.8.9-HxCDF	<2.1	<1.1	<1.8
2.3.4.6.7.8-HxCDF	170	110	350
Tot. HxCDF's	490	150	2800
REC ^{13}C-123478-HxCDF	59%	66%	69%
1.2.3.4.7.8-HxCDD	<2.7	<2.2	<2.4
1.2.3.6.7.8-HxCDD	<2.7	<2.2	<2.4
1.2.3.7.8.9-HxCDD	<2.7	<2.2	<2.4
Tot. HxCDD's	ND	ND	ND
1,2,3,4,6,7,8-HpCDF	450	630	1000
Tot. HpCDF's	450	630	2300
Tot. HpCDD's	ND	ND	ND
OCDF	ND[2]	56	3800
OCDD	ND[2]	<10	<8.1
REC ^{13}C-OCDD	ND[2]	76%	110%

MONS 218515

The values are given in ng/g

ND = Not Detected.

ND^1 = Not detected due to interferens from the big 2,3,7,8-TCDF peak.

ND^2 = Not detected , no singnal for 13C-OCDDn.

MONS 218516



MONS 218517