

REPORT SUMMARY

EPRI
5443

SUBJECTS	Hazardous and toxic waste management / Transmission substation design and operation / Distribution substations	
TOPICS	PCB Chemical analysis Transformers	Capacitors PCDF-PCDD Insulating oil
AUDIENCE	Environmental managers / Distribution engineers	

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

Volumes 1-3

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

BACKGROUND	Partial oxidation of askarels—mixtures of polychlorinated biphenyls (PCB) and tri- and tetrachlorobenzenes—produces polychlorinated dibenzofurans (PCDF) and polychlorinated dibenzo- <i>p</i> -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.

- 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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**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**

**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 have relatively low levels 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).

CONTENTS

<u>Section</u>	<u>Page</u>
1 INTRODUCTION	1-1
2 EXPERIMENTAL	2-1
ACQUISITION OF IN-SERVICE SAMPLES	2-1
ANALYTICAL TECHNIQUES	2-2
SAMPLE PREPARATION AND SPIKING	2-2
ANALYTE ENRICHMENT	2-4
ANALYSIS	2-5
QUALITY ASSURANCE	2-5
RECOVERY OF INTERNAL STANDARDS	2-5
QUANTIFICATION	2-6
CALIBRATION CURVE	2-7
DETECTION LIMITS	2-8
BASELINE ANALYSES	2-8
IN-SERVICE ANALYSES	2-8
3 BASELINE ANALYSES	3-1
BACKGROUND RESEARCH	3-1
STANDARDS USED FOR SPIKING	3-2
RESULTS	3-4
Chemical Analyses	3-4
Baseline Recovery Data	3-4
Method Reliability	3-10
4 SUPPLEMENTAL ANALYSES	4-1
CROSS CHECK ANALYSES	4-1
ANALYSES FROM THE UNIVERSITY OF UMEA	4-1
5 ROUND ROBIN ANALYSES OF IN-SERVICE LIQUIDS	5-1
Accuracy Estimate	5-1
Comparison with Parallel Analyses	5-13
6 DISCUSSION	6-1

<u>Section</u>	<u>Page</u>
METHODS	6-1
IN-SERVICE LIQUID ANALYSES	6-2
SUMMARY	6-3
APPENDIX A	
IN-SERVICE LIQUID QUESTIONNAIRE	A-1
APPENDIX B	
ANALYTICAL CURVE DATA FOR THE CROSS CHECK ANALYSES	B-1
APPENDIX C	
LETTER REPORT FROM UMEA	C-1

783877

ILLUSTRATIONS

Figure

Page

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

4-2

TABLES

<u>Table</u>	<u>Page</u>
2.1 EQUIPMENT RECOMMENDED FOR SAMPLING FOR PCDF AND PCDD ANALYSES	2-2
2.2 SURVEY OF LIQUID SAMPLES AVAILABLE FOR THE IN-SERVICE TRANSFORMER LIQUIDS STUDY	2-3
3.1 BASELINE TEST LIQUIDS	3-1
3.2 CONCENTRATION OF PCDF/PCDD STANDARDS SPIKED INTO TRANSFORMER LIQUIDS	3-3
3.3 BATTELLE FURAN AND DIOXIN DATA FOR THE BASELINE ANALYSES STUDY	3-5
3.4 IITRI FURAN AND DIOXIN DATA FOR THE BASELINE ANALYSES STUDY	3-6
3.5 NYSDOH FURAN AND DIOXIN DATA FOR THE BASELINE ANALYSES STUDY	3-7
3.6 RADIAN FURAN AND DIOXIN DATA FOR THE BASELINE ANALYSES STUDY	3-8
3.7 ABSOLUTE RECOVERIES OF LABELLED STANDARDS IN THE BASELINE STUDY	3-9
3.8 FIVE LABORATORY RESULTS OF ANALYSIS OF AGED MINERAL OIL	3-11
5.1 CHLORINATED FURAN AND DIOXIN RESULTS - SAMPLE ISL-02-A	5-2
5.2 CHLORINATED FURAN AND DIOXIN RESULTS - SAMPLE ISL-03-A	5-3
5.3 CHLORINATED FURAN AND DIOXIN RESULTS - SAMPLE ISL-04-0	5-4
5.4 CHLORINATED FURAN AND DIOXIN RESULTS - SAMPLE ISL-08-A	5-5
5.5 CHLORINATED FURAN AND DIOXIN RESULTS - SAMPLE ISL-17-A	5-6
5.6 CHLORINATED FURAN AND DIOXIN RESULTS - SAMPLE ISL-23-0	5-7
5.7 CHLORINATED FURAN AND DIOXIN RESULTS - SAMPLE ISL-27	5-8
5.8 CHLORINATED FURAN AND DIOXIN RESULTS - SAMPLE EZ29-53-01	5-9
5.9 CHLORINATED FURAN AND DIOXIN RESULTS - SAMPLE E729-53-02	5-10
5.10 CHLORINATED FURAN AND DIOXIN RESULTS - SAMPLE EZ29-53-03	5-11
5.11 ACCURACY DETERMINATION USING SPIKED BASELINE LIQUID ANALYSES	5-12
5.12 MEAN FURAN RESULTS FOR SEVEN UTILITY DIELECTRIC FLUIDS	5-14

783879

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.

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 1242, 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; (1) 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 are 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 1984, the accuracy of PCDF analyses was hampered by a lack of accurate quantification standards. A major product of this

783883

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

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

783885

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.

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
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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

783887

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	12470/280 KVA	Mineral Oil	161	4,500	ISL-24-0	--
Arc Furnace 2	8	12470/280 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	248	?	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	--	3780 (1b)	ISL-07-A	--
Network Load Center 4	28	500 KVA	Aroclor 1260	--	3175 (1b)	ISL-08-A	41159-11-12
Network Load Center 5	20	750 KVA	Aroclor 1260	--	2650 (1b)	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 (1b)	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	Chlorestol	--	272	ISL-19-A	--
Network Load Center 17	20(Est.)	11.5 KVA	Inerteen	--	282	ISL-20-A	--
Network Load Center 18	10(Est.)	11.5 KVA	Inerteen	--	184	ISL-21-A	--
Network Load Center 19	20(Est.)	11.5 KVA	Chlorestol	--	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

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- $^{13}\text{C}_{12}$, 2,3,7,8-TCDF- $^{13}\text{C}_{12}$, 1,2,3,7,8-Penta-CDF- $^{13}\text{C}_{12}$, 1,2,3,4,7,8-Hexa-CDF- $^{13}\text{C}_{12}$, and Octa-CDD- $^{13}\text{C}_{12}$.

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- $^{13}\text{C}_{12}$. 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

783889

chromatographed through florisil columns to provide additional analyte enrichment. Each of the florisil columns was prepared using 5 g of activated florisil (60-100 mesh) which was slurry packed with hexane. The sample solutions were diluted with approximately 5 mL of hexane and transferred to the florisil columns. The columns were eluted with hexane, hexane/ethyl ether (94:6, v/v), and hexane/methylene chloride (25:75, v/v). The 25:75 hexane/methylene chloride fraction was collected and concentrated to approximately 20 µL. These solutions were stored at 0°C until they were analyzed.

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-¹³C₁₂ which was added following the column cleanup steps. Relative response factors were determined from triplicate analyses of a

standard mixture containing the labelled internal standards and the 1,2,3,4-TCDD-¹³C₁₂. The equation used to calculate the recoveries was:

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

Where:

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

QUANTIFICATION

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

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

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

Where:

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

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

783891

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

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

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

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

Where:

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

CALIBRATION CURVE

Calibration curves were generated for each of the native/isotopically labelled isomer pairs. The calibration standards were analyzed at least five times at each of four concentration levels between 0.04 and 2.5 parts-per-million (ppm). The 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:

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

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.

783893

GENP 011082

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

<u>Dielectric Fluid</u>	<u>Composition</u>
Aroclor 1016	Narrow boiling point fraction of Aroclor 1242.
Aroclor 1242	42% C1 (w/w)
Aroclor 1260	60% C1 (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))

GENP 011083

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/PCDD 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.

783895

TABLE 3.3

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

<u>Compound</u>	<u>Aroclor 1016</u>	<u>Aroclor 1242</u>	<u>Aroclor 1260</u>	<u>Tri and Tetra Chlorobenzene</u>	<u>Mineral Oil Run No. 1</u>	<u>Mineral Oil Run No. 2</u>
<u>Polychlorinated Dibenzofurans</u>						
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
<u>Polychlorinated Dibenzodioxins</u>						
Total TCDD	0	0	0	0	32	34
OCDD	NR	NR	NR	NR	NR	NR
<u>Specific Molecules and Unresolved Molecular Clusters</u>						
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-HxCDF	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.

TABLE 3.4

ITRI 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

TABLE 3.5

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

<u>Compound</u>	<u>Aroclor 1016</u>	<u>Aroclor 1242</u>	<u>Aroclor 1260</u>	<u>Tri and Tetra Chlorobenzene</u>	<u>Mineral Oil Aged</u>
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

TABLE 3.6

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

<u>Compound</u>	<u>Aroclor 1016</u>	<u>Aroclor 1242</u>	<u>Aroclor 1260</u>	<u>Tri and Tetra Chlorobenzene</u>	<u>Mineral Oil Aged</u>
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

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- $^{13}\text{C}_{12}$	100	93	95	95	97	116
1,2,3,7,8-PCDF- $^{12}\text{C}_{12}$	100	111	134	140	97	114
2,3,7,8-TCDD- $^{13}\text{C}_{12}$	100	67	86	86	101	118
OCDD- $^{13}\text{C}_{12}$	100	102	89	157	86	121
1,2,3,4,7,8-HxCDF- $^{13}\text{C}_{12}$	100	83	90	317	110	NA
1,2,3,4,6,7,8-HpCDF	100	57	45	1224*	68	NA

*Outliers

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 interferences 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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GENP 011091

3-11

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TABLE 3.8
FOUR-LABORATORY RESULTS OF ANALYSIS OF AGED MINERAL OIL (ng/g (w/w))

<u>Compound</u>	<u>Battelle</u>	<u>ITRI</u>	<u>NYSDOH</u>	<u>Radian</u>	<u>Group Mean</u>	<u>Native Spike Level</u>	<u>Confidence Interval (95%)</u>
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		

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.

GENP 011093

4-2

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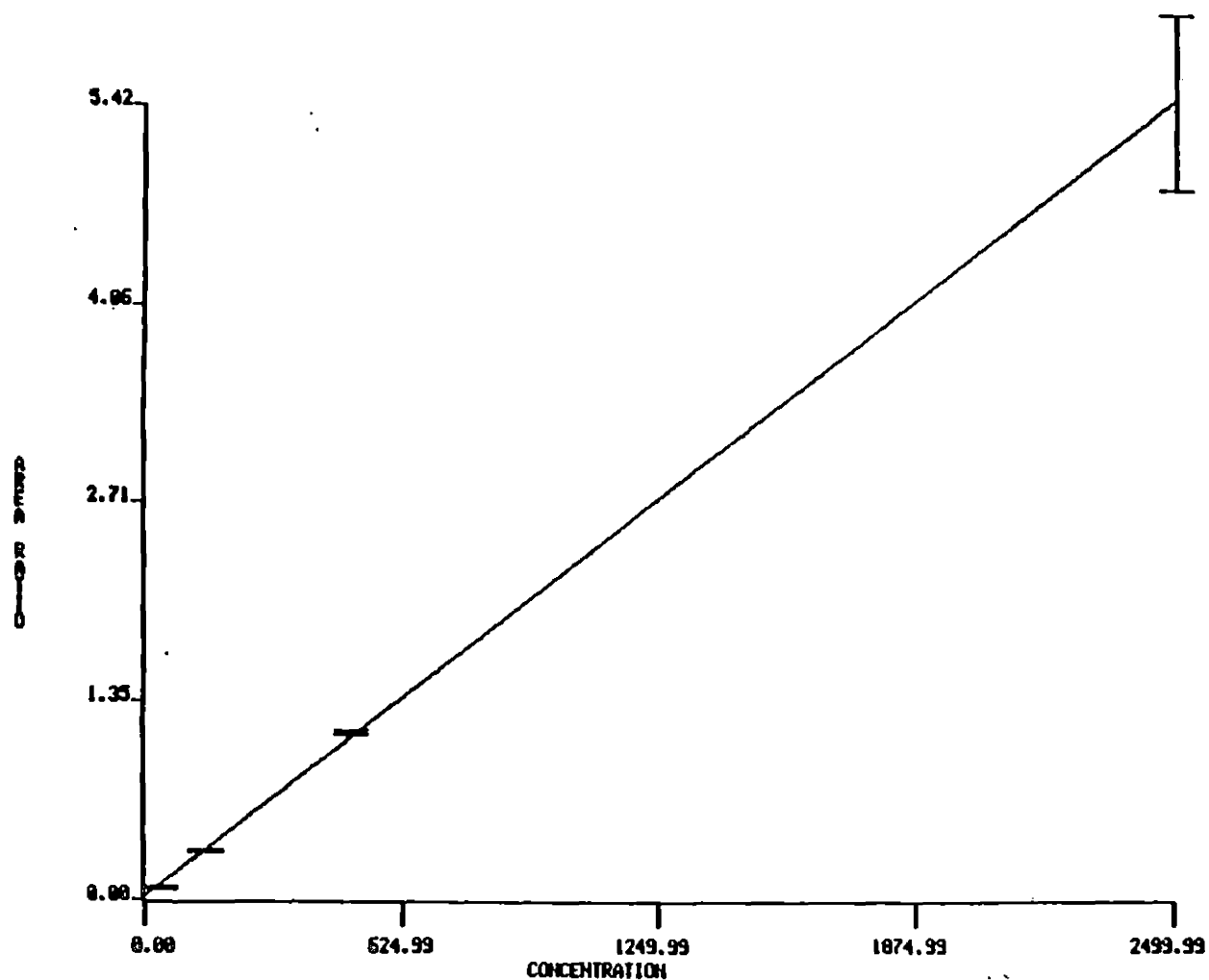


Figure 4-1. Calibration curve for 2,3,7,8-tetrachlorodibenzofuran over the range 40 pg to 2.5 ng

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 Table 5.1 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			Mean	Standard Deviation	Relative Standard Deviation
	Det 1	Det 2	Det 3			
<u>PCDF Congeners</u>						
Total TCDF	360	230	290	293	53	18%
Total P _n CDF	69	72	71	71	1	2%
Total H _x CDF	8,100	19,000	20,000	15,700	5,389	34%
Total H _p CDF	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%
<u>Furan Compounds</u>						
2,3,7,8-/2,3,4,8-TCDF	190	140	180	170	22	13%
2,3,4,7,8-P _n CDF	300	260	290	283	17	6%
1,2,3,7,8-/1,2,3,4,8-P _n CDF	69	72	71	71	1	2%
1,2,3,4,7,8-/1,2,3,4,7,9-H _x CDF	2,700	6,400	6,400	5,167	1,744	34%
1,2,3,6,7,8-H _x CDF	760	2,300	2,700	1,920	836	44%
2,3,4,6,7,8-H _x CDF	1,100	3,400	3,800	2,767	1,190	43%
1,2,3,4,6,7,8-H _p CDF	180	230	320	243	58	24%
1,2,3,4,7,8,9-H _p CDF	280	250	320	283	29	10%
<u>Dioxin Congeners</u>						
Total TCDD	NA	NA	NA	NA	NA	NA
OCDD	18	18	10	15	4	25%
<u>PCDD Compounds</u>						
2,3,7,8-TCDD	NA	NA	NA	NA	NA	NA

GENP 011095

TABLE 5.2

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

Congener	Determination			Mean	Standard Deviation	Relative Standard Deviation
	Det 1	Det 2	Det 3			
<u>PCDF Congeners</u>						
Total TCDF	170	110	40	170	53	50%
Total P _n CDF	2,300	2,100	720	1,707	702	41%
Total H _x CDF	52,000	11,000	9,700	24,233	19,641	81%
Total H _p CDF	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%
<u>Furan Compounds</u>						
2,3,7,8-/2,3,4,8-TCDF	31	30	40	34	4	13%
2,3,4,7,8-P _n CDF	130	130	110	123	9	8%
1,2,3,7,8-/1,2,3,4,8-P _n CDF	35	49	26	37	9	26%
1,2,3,4,7,8-/1,2,3,4,7,9-H _x CDF	29,000	6,100	5,100	13,400	11,038	82%
1,2,3,6,7,8-H _x CDF	6,000	1,100	1,200	2,767	2,287	83%
2,3,4,6,7,8-H _x CDF	1,800	240	210	750	743	99%
1,2,3,4,6,7,8-H _p CDF	1,100	4,500	3,100	2,900	1,395	48%
1,2,3,4,7,8,9-H _p CDF	1,200	2,600	2,600	2,133	660	31%
<u>Dioxin Congeners</u>						
Total TCDD	NA	NA	NA	NA	NA	NA
OCDD	18	12	NA	10	7	75%
<u>PCDD Compounds</u>						
2,3,7,8-TCDD	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			Mean	Standard Deviation	Relative Standard Deviation
	Det 1	Det 2	Det 3			
<u>PCDF Congeners</u>						
Total TCDF	NA	NA	NA	NA	NA	NA%
Total P _n CDF	NA	NA	NA	NA	NA	NA%
Total H _x CDF	NA	NA	NA	NA	NA	NA%
Total H _p CDF	NA	NA	NA	NA	NA	NA%
OCDF	NA	NA	NA	NA	NA	NA%
Total PCDF	NA	NA	NA	NA	NA	NA%
<u>Furan Compounds</u>						
2,3,7,8-/2,3,4,8-TCDF	NA	NA	NA	NA	NA	NA%
2,3,4,7,8-P _n CDF	NA	NA	NA	NA	NA	NA%
1,2,3,7,8-/1,2,3,4,8-P _n CDF	NA	NA	NA	NA	NA	NA%
1,2,3,4,7,8-/1,2,3,4,7,9-H _x CDF	NA	NA	NA	NA	NA	NA%
1,2,3,6,7,8-H _x CDF	NA	NA	NA	NA	NA	NA%
2,3,4,6,7,8-H _x CDF	NA	NA	NA	NA	NA	NA%
1,2,3,4,6,7,8-H _p CDF	NA	NA	NA	NA	NA	NA%
1,2,3,4,7,8,9-H _p CDF	NA	NA	NA	NA	NA	NA%
<u>Dioxin Congeners</u>						
Total TCDD	NA	NA	NA	NA	NA	NA%
OCDD	NA	13	11	8	6	71%
<u>PCDD Compounds</u>						
2,3,7,8-TCDD	NA	NA	NA	NA	NA	NA%

TABLE 5.4

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

Congener	Determination			Mean	Standard Deviation	Relative Standard Deviation
	Det 1	Det 2	Det 3			
<u>PCDF Congeners</u>						
Total TCDF	62	64	99	75	17	23%
Total P _n CDF	79	230	310	206	96	46%
Total H _x CDF	1,500	1,300	990	1,263	210	17%
Total H _p CDF	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%
<u>Furan Compounds</u>						
2,3,7,8-/2,3,4,8-TCDF	20	20	30	23	5	20%
2,3,4,7,8-P _n CDF	39	41	37	39	2	4%
1,2,3,7,8-/1,2,3,4,8-P _n CDF	22	25	34	27	5	19%
1,2,3,4,7,8-/1,2,3,4,7,9-H _x CDF	880	740	640	753	98	13%
1,2,3,6,7,8-H _x CDF	54	50	36	47	8	17%
2,3,4,6,7,8-H _x CDF	47	25	43	38	10	25%
1,2,3,4,6,7,8-H _p CDF	350	530	750	543	164	30%
1,2,3,4,7,8,9-H _p CDF	340	450	580	457	98	21%
<u>Dioxin Congeners</u>						
Total TCDD	NA	NA	NA	NA	NA	NA%
OCDD	NA	NA	NA	NA	NA	NA%
<u>PCDD Compounds</u>						
2,3,7,8-TCDD	NA	NA	NA	NA	NA	NA%

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GENP 011098

TABLE 5.5
CHLORINATED FURAN AND DIOXIN RESULTS (ppb (w/w), ng/g)
SAMPLE ISL-17-A

Congener	Determination			Mean	Standard Deviation	Relative Standard Deviation
	Det 1	Det 2	Det 3			
<u>PCDF Congeners</u>						
Total TCDF	970	580	610	720	177	25%
Total P _n CDF	11,000	6,700	6,500	8,067	2,076	26%
Total H _x CDF	14,000	36,000	16,000	22,000	9,933	45%
Total H _p CDF	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%
<u>Furan Compounds</u>						
2,3,7,8-/2,3,4,8-TCDF	400	380	350	377	21	5%
2,3,4,7,8-P _n CDF	2,300	2,400	1,800	2,167	262	12%
1,2,3,7,8-/1,2,3,4,8-P _n CDF	870	900	780	850	51	6%
1,2,3,4,7,8-/1,2,3,4,7,9-H _x CDF	4,700	7,200	4,100	5,333	1,342	25%
1,2,3,6,7,8-H _x CDF	1,800	3,200	2,300	2,433	579	24%
2,3,4,6,7,8-H _x CDF	620	6,800	930	2,783	2,832	102%
1,2,3,4,6,7,8-H _p CDF	920	560	1,300	927	302	33%
1,2,3,4,7,8,9-H _p CDF	740	860	990	863	102	12%
<u>Dioxin Congeners</u>						
Total TCDD	NA	NA	NA	NA	NA	NA%
OCDD	NA	18	NA	NA	8	141%
<u>PCDD Compounds</u>						
2,3,7,8-TCDD	NA	NA	NA	NA	NA	NA%

TABLE 5.6

CHLORINATED FURAN AND DIOXIN RESULTS (ppb (w/w), ng/g)
SAMPLE ISL-23-0

Congener	Determination			Mean	Standard Deviation	Relative Standard Deviation
	Det 1	Det 2	Det 3			
<u>PCDF Congeners</u>						
Total TCDF	NA	NA	NA	NA	NA	NA%
Total P _n CDF	NA	NA	NA	NA	NA	NA%
Total H _x CDF	NA	NA	NA	NA	NA	NA%
Total H _p CDF	NA	NA	NA	NA	NA	NA%
OCDF	NA	NA	NA	NA	NA	NA%
Total PCDF	NA	NA	NA	NA	NA	NA%
<u>Furan Compounds</u>						
2,3,7,8-/2,3,4,8-TCDF	NA	NA	NA	NA	NA	NA%
2,3,4,7,8-P _n CDF	NA	NA	NA	NA	NA	NA%
1,2,3,7,8-/1,2,3,4,8-P _n CDF	NA	NA	NA	NA	NA	NA%
1,2,3,4,7,8-/1,2,3,4,7,9-H _x CDF	NA	NA	NA	NA	NA	NA%
1,2,3,6,7,8-H _x CDF	NA	NA	NA	NA	NA	NA%
2,3,4,6,7,8-H _x CDF	NA	NA	NA	NA	NA	NA%
1,2,3,4,6,7,8-H _p CDF	NA	NA	NA	NA	NA	NA%
1,2,3,4,7,8,9-H _p CDF	NA	NA	NA	NA	NA	NA%
<u>Dioxin Congeners</u>						
Total TCDD	NA	NA	NA	NA	NA	NA%
OCDD	NA	12	NA	4	6	141%
<u>PCDD Compounds</u>						
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			Mean	Standard Deviation	Relative Standard Deviation
	Det 1	Det 2	Det 3			
<u>PCDF Congeners</u>						
Total TCDF	580	570	350	500	106	21%
Total P _n CDF	250	270	220	247	21	8%
Total H _x CDF	140	130	160	143	21	9%
Total H _p CDF	26	28	6	20	10	51%
OCDF	46	44	10	33	17	50%
Total PCDF	1,042	1,042	746	943	140	15%
<u>Furan Compounds</u>						
2,3,7,8-/2,3,4,8-TCDF	300	280	270	283	12	4%
2,3,4,7,8-P _n CDF	71	74	53	66	9	14%
1,2,3,7,8-/1,2,3,4,8-P _n CDF	580	570	350	500	106	21%
1,2,3,4,7,8-/1,2,3,4,7,9-H _x CDF	37	16	31	28	9	32%
1,2,3,6,7,8-H _x CDF	15	15	27	19	6	30%
2,3,4,6,7,8-H _x CDF	25	17	39	27	9	34%
1,2,3,4,6,7,8-H _p CDF	7	9	2	6	3	50%
1,2,3,4,7,8,9-H _p CDF	5	5	1	4	2	45%
<u>Dioxin Congeners</u>						
Total TCDD	NA	NA	NA	NA	NA	NA%
OCDD	NA	NA	NA	NA	NA	NA%
<u>PCDD Compounds</u>						
2,3,7,8-TCDD	NA	NA	NA	NA	NA	NA%

TABLE 5.8

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

Congener	Determination			Mean	Standard Deviation	Relative Standard Deviation
	Det 1	Det 2	Det 3			
<u>PCDF Congeners</u>						
Total TCDF	220	160	190	190	24	13%
Total P _n CDF	310	550	260	373	127	34%
Total H _x CDF	680	6,600	390	2,557	2,862	112%
Total H _p CDF	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%
<u>Furan Compounds</u>						
2,3,7,8-/2,3,4,8-TCDF	220	160	190	190	24	13%
2,3,4,7,8-P _n CDF	170	370	120	220	108	49%
1,2,3,7,8-/1,2,3,4,8-P _n CDF	140	170	140	150	14	9%
1,2,3,4,7,8-/1,2,3,4,7,9-H _x CDF	310	550	260	373	127	34%
1,2,3,6,7,8-H _x CDF	140	120	76	112	27	24%
2,3,4,6,7,8-H _x CDF	200	5,900	140	2,080	2,701	130%
1,2,3,4,6,7,8-H _p CDF	530	33	220	261	205	79%
1,2,3,4,7,8,9-H _p CDF	NA	NA	NA	NA	NA	NA%
<u>Dioxin Congeners</u>						
Total TCDD	19	19	23	20	2	9%
OCDD	NA	NA	1	NA	NA	141%
<u>PCDD Compounds</u>						
2,3,7,8-TCDD	19	19	23	20	2	9%

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GENP 011102

TABLE 5.9

CHLORINATED FURAN AND DIOXIN RESULTS (ppb (w/w), ng/g)
 SAMPLE E729-53-02 (Spiked Aroclor 1016)

Congener	Determination			Mean	Standard Deviation	Relative Standard Deviation
	Det 1	Det 2	Det 3			
<u>PCDF Congeners</u>						
Total TCDF	57	67	66	63	4	7%
Total P _n CDF	600	500	460	520	59	11%
Total H _x CDF	5,400	2,300	780	2,827	1,923	68%
Total H _p CDF	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%
<u>Furan Compounds</u>						
2,3,7,8-/2,3,4,8-TCDF	57	67	66	63	4	7%
2,3,4,7,8-P _n CDF	410	310	260	327	62	19%
1,2,3,7,8-/1,2,3,4,8-P _n CDF	180	180	190	183	5	3%
1,2,3,4,7,8-/1,2,3,4,7,9-H _x CDF	NA	NA	NA	NA	NA	NA%
1,2,3,6,7,8-H _x CDF	100	84	81	88	8	9%
2,3,4,6,7,8-H _x CDF	5,200	2,100	680	2,660	1,887	77%
1,2,3,4,6,7,8-H _p CDF	65	150	180	132	49	37%
1,2,3,4,7,8,9-H _p CDF	NA	NA	NA	NA	NA	NA%
<u>Dioxin Congeners</u>						
Total TCDD	46	46	44	45	1	2%
OCDD	NA	NA	NA	NA	NA	NA%
<u>PCDD Compounds</u>						
2,3,7,8-TCDD	46	46	45	46	NA	1%

TABLE 5.10

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

Congener	Determination			Mean	Standard Deviation	Relative Standard Deviation
	Det 1	Det 2	Det 3			
<u>PCDF Congeners</u>						
Total TCDF	1,400	1,700	970	1,357	300	22%
Total P _n CDF	1,100	1,300	1,200	1,200	82	7%
Total H _x CDF	20,000	4,700	11,000	11,900	6,279	53%
Total H _p CDF	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%
<u>Furan Compounds</u>						
2,3,7,8-/2,3,4,8-TCDF	1,200	1,300	880	1,127	179	16%
2,3,4,7,8-P _n CDF	590	410	800	627	194	31%
1,2,3,7,8-/1,2,3,4,8-P _n CDF	1,400	1,170	970	1,357	300	22%
1,2,3,4,7,8-/1,2,3,4,7,9-H _x CDF	1,900	1,800	1,600	1,767	125	7%
1,2,3,6,7,8-H _x CDF	1,200	93	780	691	456	66%
2,3,4,6,7,8-H _x CDF	10,000	770	6,500	5,757	3,805	66%
1,2,3,4,6,7,8-H _p CDF	55	850	49	318	376	118%
1,2,3,4,7,8,9-H _p CDF	300	360	180	280	75	27%
<u>Dioxin Congeners</u>						
Total TCDD	110	100	80	97	12	13%
OCDD	NA	12	NA	4	6	141%
<u>PCDD Compounds</u>						
2,3,7,8-TCDD	110	100	80	97	12	13%

783915

TABLE 5.11

ACCURACY DETERMINATION USING SPIKED BASELINE LIQUID ANALYSES

	Mineral Oil E729-53-01			Aroclor 106 E729-53-02			Corrected(2) Aroclor 1016 E729-53-02	Corrected Percent Difference
	Spike Level	Amount Found	Percent(1) Difference	Spike Level	Amount Found	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-TCDF	200	190	-5	53	63	19	63	19
1,2,3,7,8-/1,2,3,4,8-PnCDF	150	150	0	158	181	16	183	16
2,3,4,7,8-PnCDF	150	220	47	150	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.

GENP 011105

5-12

783916

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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GENP 011107

5-14

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TABLE 5.12
MEAN FURAN RESULTS FOR SEVEN UTILITY DIELECTRIC FLUIDS

<u>Sample Identifier</u>	<u>Network Transformer No. 1</u>	<u>Network Transformer No. 2</u>	<u>Network Transformer No. 3</u>	<u>Network Transformer No. 4</u>	<u>Arc Furnace Transformer</u>	<u>Precipi- tator Transformer</u>	<u>Capacitor</u>
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-04-0	ISL-23-0	ISL-17-A	ISL-27
Laboratory Code	17	12	11	16	15	14	13
<u>Battelle Furan Results</u>							
Total TCDF	293	17	53	0	0	177	106
Total PnCDF	71	96	702	0	0	2076	21
Total HxCDF	15700	1263	24233	0	0	22000	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
<u>Combined Furan Results (1)</u>							
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	6244	21830	14	18	188	21
Total PCDF	10914	9486	41071	154	34	23413	906
<u>Percent Difference in Furan Congener Results (2)</u>							
	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.

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 interferents 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 deviations 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,

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.

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

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

GENP 011111

Appendix A
IN-SERVICE LIQUID QUESTIONNAIRE

783923

GENP 011112

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

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: _____

783925

GENP 011114

DATA SHEET FOR EACH SAMPLE

Was Fluid Changed at Failure:

Any Record of Temperature Excursions:

Are Maintenance Records Available:

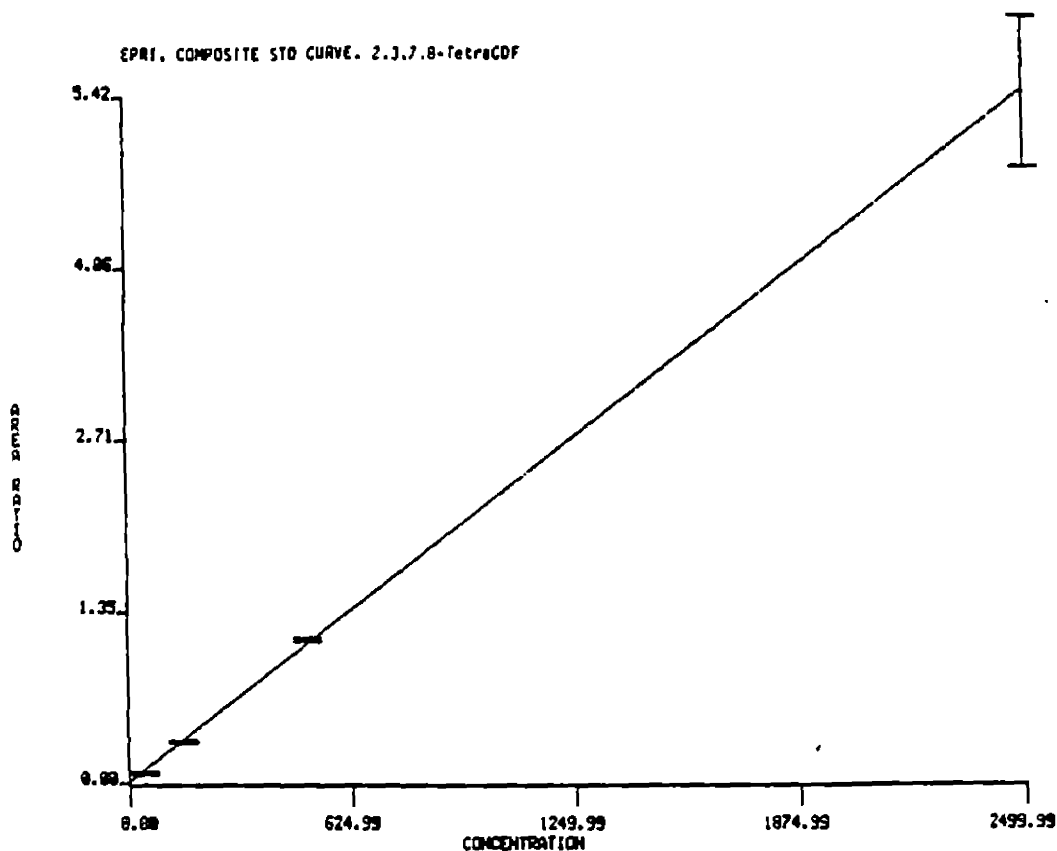
Any Other Pertinent Information About This Unit or the Sample Liquid:

Appendix B

ANALYTICAL CURVE DATA FOR THE CROSS CHECK ANALYSES

783927

GENP 011116



EPRI, COMPOSITE STD CURVE. 2.3.7.8-TetraCDF

X-VALUES	Y-VALUES				
37.9999	0.0794	0.0802	0.0764	0.0910	0.0848
149.9990	0.3249	0.3249	0.3394	0.3430	0.3441
499.9990	1.1474	1.1403	1.1407	1.1278	1.1334
2499.9900	5.8405	5.9640	5.7823	4.9650	4.4323
X-VALUE	Y-VALUE	STD DEV	RSD%	RES. E.	R. R. E.

DATA WITH RESPECT TO THE Y-VALUES

40.0001	0.0833	0.0033	4.46	0.0084	0.0050
150.0000	0.3364	0.0093	2.70	0.0144	0.0084
500.0000	1.1431	0.0117	1.01	0.0183	0.0104
2500.0000	5.4247	0.4013	11.08	0.9310	0.5443

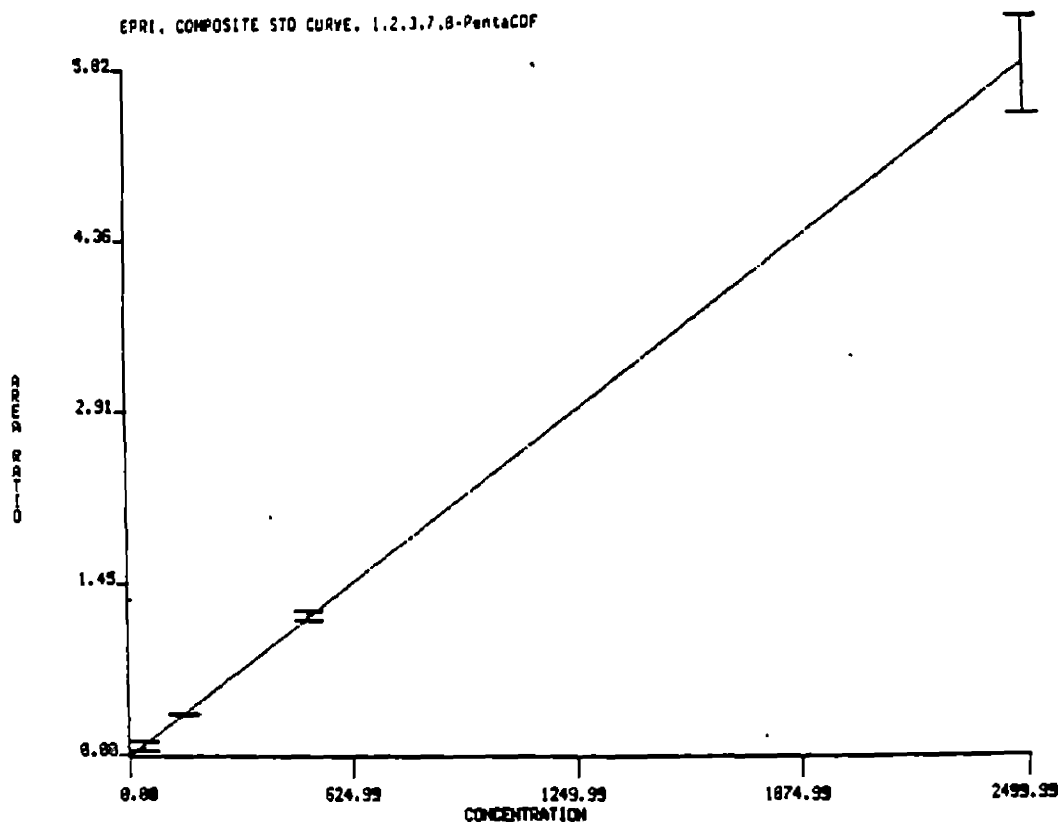
DATA WITH RESPECT TO THE REGRESSION LINE

40.0001	0.0833	0.0271	32.34	0.0427	0.0243
150.0000	0.3364	0.0133	3.93	0.0212	0.0122
500.0000	1.1431	0.0453	3.96	0.0719	0.0412
2500.0000	5.4247	0.4014	11.08	0.9311	0.5443

A SLOPE OF 0.00216 GIVES AN INTERCEPT OF 0.02048
 A SLOPE OF 442.02300 GIVES AN INTERCEPT OF -9.33863
 THE DATA HAS A CORRELATION COEFFICIENT OF 0.99993

GENP 011117

783928



EPRI, COMPOSITE STD CURVE, 1,2,3,7,8-PentaCDF

X-VALUES	Y-VALUES				
40.0000	0.0989	0.1021	0.0961	0.0929	0.0926
150.0000	0.3347	0.3332	0.3249	0.3321	0.3603
499.9999	1.2183	1.2171	1.2201	1.1449	1.1469
2499.9999	5.2080	5.2210	5.9900	5.5030	5.2400

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

DATA WITH RESPECT TO THE Y-VALUES

40.0000	0.0803	0.0396	49.19	0.0626	0.0337
150.0000	0.3441	0.0113	3.32	0.0182	0.0098
500.0000	1.1823	0.0398	3.35	0.0628	0.0339
2500.0000	5.8222	0.4165	7.15	0.6585	0.3546

DATA WITH RESPECT TO THE REGRESSION LINE

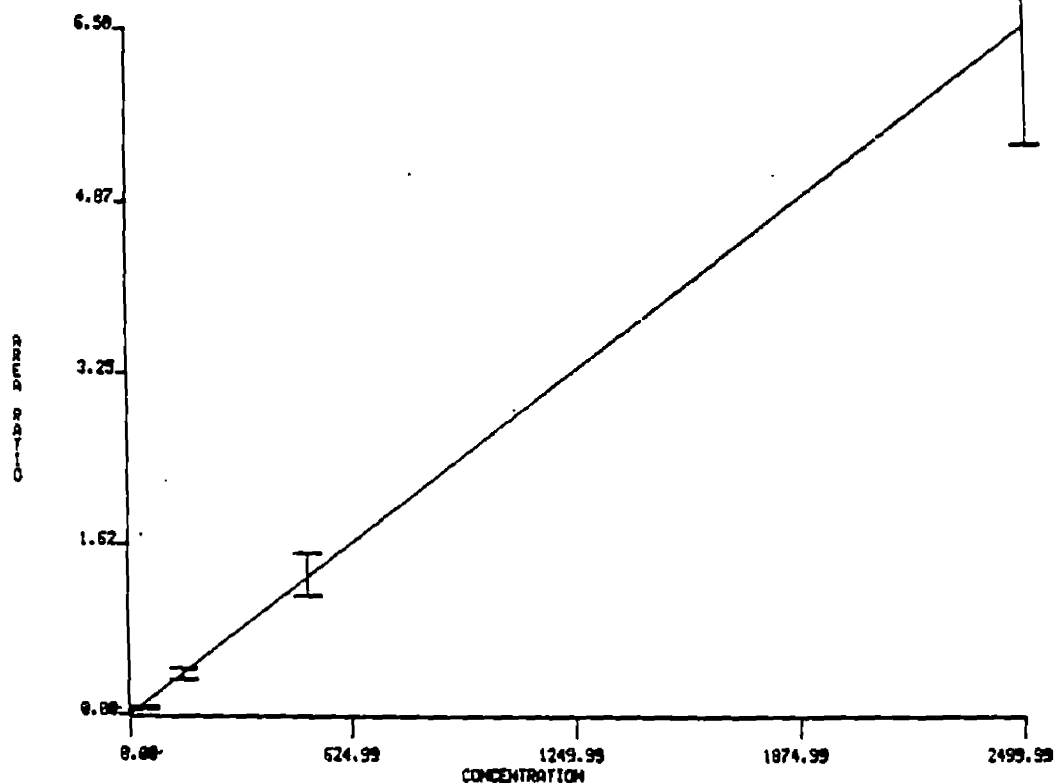
40.0000	0.0803	0.0413	51.31	0.0636	0.0333
150.0000	0.3441	0.0123	3.56	0.0196	0.0105
500.0000	1.1823	0.0446	3.76	0.0709	0.0380
2500.0000	5.8222	0.4165	7.15	0.6586	0.3546

A SLOPE OF 0.00233 GIVES AN INTERCEPT OF -0.00157
 A SLOPE OF 429.03700 GIVES AN INTERCEPT OF 0.67917
 THE DATA HAS A CORRELATION COEFFICIENT OF 0.99998

783929

GENP 011118

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



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

X-VALUES	Y-VALUES				
40.0000	0.0703	0.0743	0.0714	0.0893	0.0810
150.0000	0.4269	0.4403	0.4472	0.3384	0.3294
499.9990	1.9337	1.4388	1.4623	1.1233	1.1114
2499.9900	7.4235	7.4420	7.0960	9.1620	9.3965
X-VALUE	Y-VALUE	STD DEV	RSDX	RES. E.	R R. E.

DATA WITH RESPECT TO THE Y-VALUES

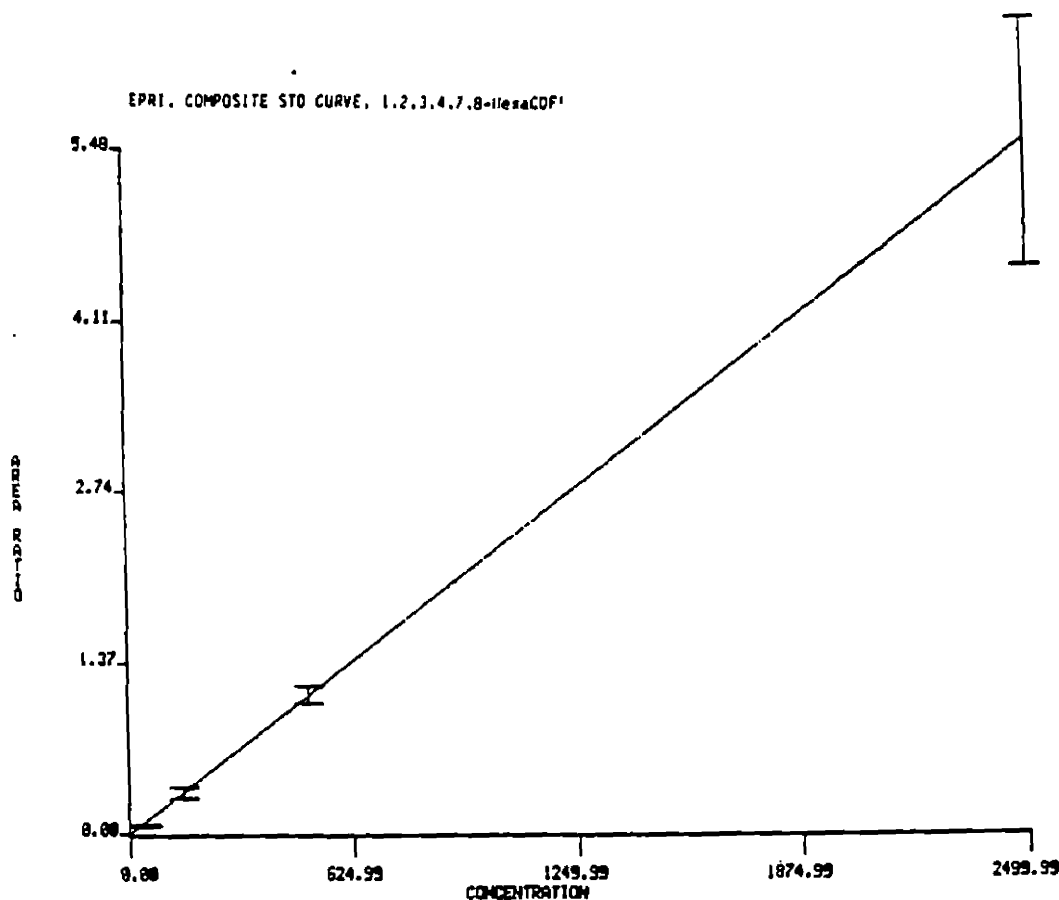
40.0000	0.0773	0.0080	10.33	0.0112	0.0039
150.0000	0.4009	0.0564	14.06	0.0797	0.0383
500.0000	1.3403	0.2030	19.03	0.2830	0.1370
2500.0000	6.5040	1.1296	17.36	1.3974	0.7678

DATA WITH RESPECT TO THE REGRESSION LINE

40.0000	0.0773	0.0369	47.63	0.0321	0.0251
150.0000	0.4009	0.0564	14.13	0.0801	0.0383
500.0000	1.3403	0.2030	19.29	0.2700	0.1394
2500.0000	6.5040	1.1296	17.36	1.3973	0.7679

A SLOPE OF 0.00260 GIVES AN INTERCEPT OF 0.00326
A SLOPE OF 384.30900 GIVES AN INTERCEPT OF -2.04203
THE DATA HAS A CORRELATION COEFFICIENT OF 0.99999

GENP 011119



EPRI. COMPOSITE STD CURVE, 1.2.3.4.7.8-HexaCOF¹

X-VALUES	Y-VALUES				
40.0000	0.0702	0.0777	0.0708	0.0844	0.0723
150.0000	0.3139	0.3101	0.3073	0.4198	0.3709
499.9999	1.1786	1.0725	1.2032	1.0597	1.0391
2499.9999	5.6335	5.7743	5.4700	4.6040	4.2120
X-VALUE	Y-VALUE	STD DEV	RSD%	RES. E.	R.R.E.

DATA WITH RESPECT TO THE Y-VALUES

40.0000	0.0764	0.0043	5.39	0.0102	0.0038
150.0000	0.3423	0.0447	13.04	0.0707	0.0403
500.0000	1.1145	0.0674	6.09	0.1048	0.0609
2500.0000	5.4872	0.9961	18.15	1.3750	0.8974

DATA WITH RESPECT TO THE REGRESSION LINE

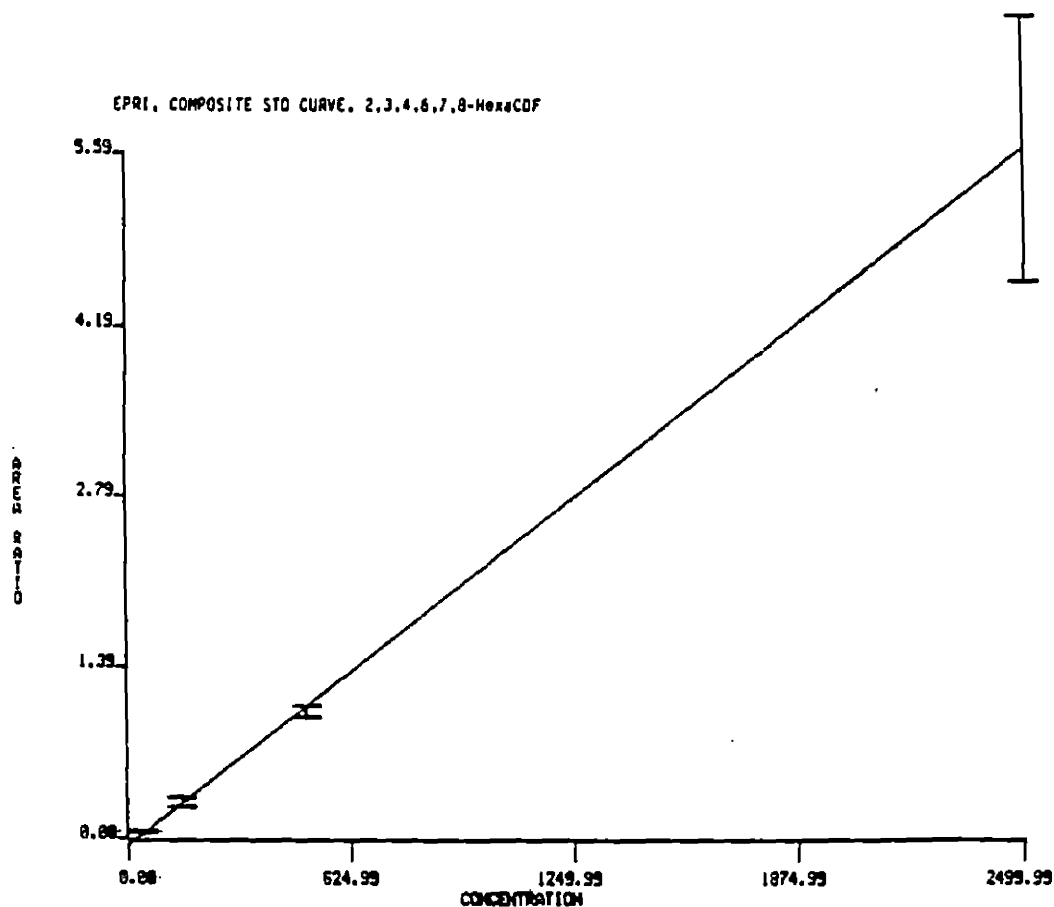
40.0000	0.0764	0.0199	25.94	0.0314	0.0179
150.0000	0.3423	0.0435	12.28	0.0720	0.0410
500.0000	1.1145	0.0688	6.17	0.1088	0.0620
2500.0000	5.4872	0.9961	18.15	1.3750	0.8974

A SLOPE OF 0.00219 GIVES AN INTERCEPT OF 0.00367
 A SLOPE OF 455.86400 GIVES AN INTERCEPT OF -2.38843
 THE DATA HAS A CORRELATION COEFFICIENT OF 0.99998

783931

GENP 011120

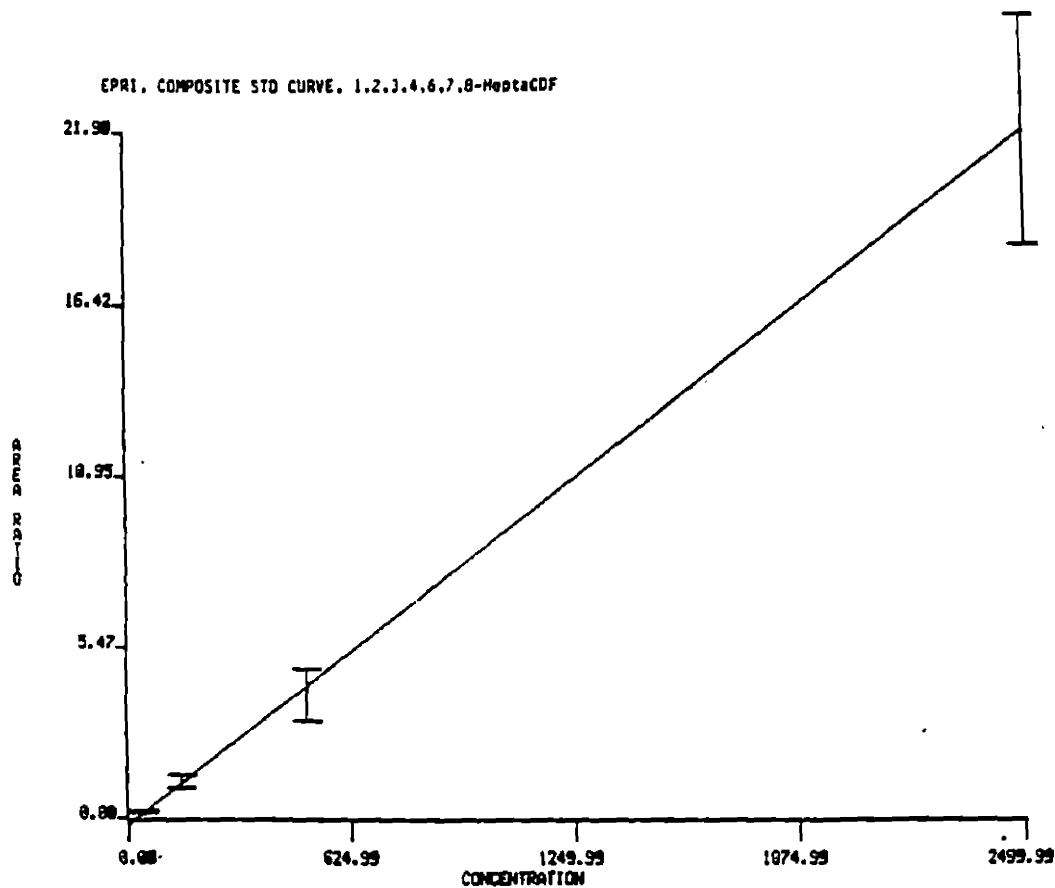
EPRI, COMPOSITE STD CURVE, 2,3,4,6,7,8-HexaCDF



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

X-VALUES	Y-VALUES				
40.0000	0.0398	0.0637	0.0373	0.0710	0.0715
150.0000	0.2834	0.2798	0.2854	0.2753	0.2984
499.9999	1.0389	1.0862	0.9732	1.0334	1.0598
2499.9999	5.4239	5.5679	5.3115	4.3340	7.3400
X-VALUE	Y-VALUE	STD DEV	RESID	RES. E.	R. R. E.
=====					
DATA WITH RESPECT TO THE Y-VALUES					
40.0000	0.0647	0.0063	9.93	0.0092	0.0032
150.0000	0.3046	0.0402	13.19	0.0349	0.0323
500.0000	1.0383	0.0419	4.03	0.0392	0.0339
2500.0000	5.3957	1.0892	19.46	1.3403	0.8798
DATA WITH RESPECT TO THE REGRESSION LINE					
40.0000	0.0647	0.0348	38.25	0.0350	0.0200
150.0000	0.3046	0.0429	14.06	0.0606	0.0347
500.0000	1.0383	0.0629	6.03	0.0889	0.0508
2500.0000	5.3957	1.0892	19.46	1.3406	0.8798
A SLOPE OF 0.00223 GIVES AN INTERCEPT OF -0.04686					
A SLOPE OF 443.63000 GIVES AN INTERCEPT OF 20.79230					
THE DATA HAS A CORRELATION COEFFICIENT OF 0.99993					

GENP 011121



EPRI, COMPOSITE STD CURVE, 1,2,3,4,6,7,8-HeptaCDF

X-VALUES	Y-VALUES				
40.0000	0.2673	0.2057	0.2483	0.2506	0.3065
150.0000	1.3476	1.1833	1.4126	0.8933	1.1430
499.9990	3.2079	4.2144	3.9303	4.0020	3.7310
2499.9900	23.2270	22.9794	24.0163	23.0300	21.7000
X-VALUE	Y-VALUE	STD DEV	RSDX	RES. E.	R. R. E.

DATA WITH RESPECT TO THE Y-VALUES

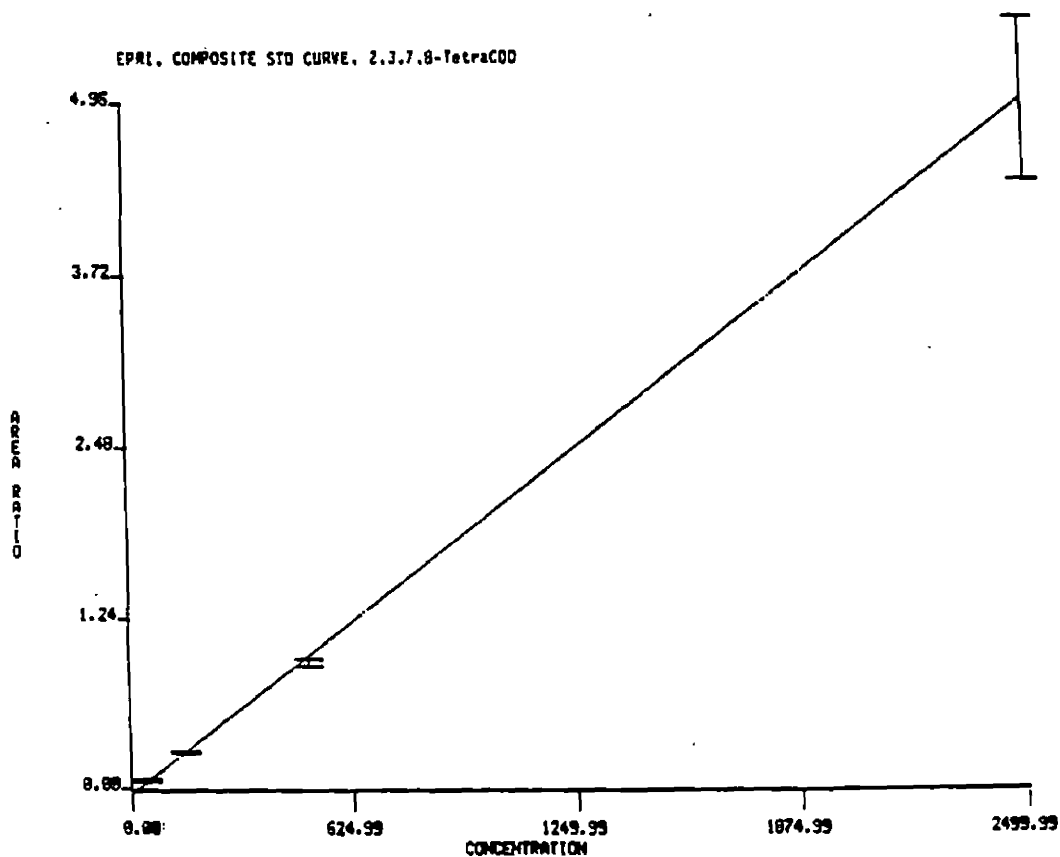
40.0000	0.2519	0.0340	13.46	0.0537	0.0079
150.0000	1.1927	0.1816	15.21	0.2871	0.0421
500.0000	3.9437	0.8478	21.49	1.3404	0.1965
2500.0000	21.9033	3.7442	17.09	5.9200	0.8676

DATA WITH RESPECT TO THE REGRESSION LINE

40.0000	0.2519	0.1359	53.80	0.2143	0.0314
150.0000	1.1927	0.2061	17.27	0.3258	0.0478
500.0000	3.9437	0.8913	22.60	1.4096	0.2066
2500.0000	21.9033	3.7443	17.09	5.9268	0.8677

A SLOPE OF 0.00883 GIVES AN INTERCEPT OF -0.22126.
 A SLOPE OF 113.20600 GIVES AN INTERCEPT OF 23.04810
 THE DATA HAS A CORRELATION COEFFICIENT OF 0.99983

783933



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

X-VALUES	Y-VALUES				
40.0000	0.0602	0.0605	0.0619	0.0763	0.0877
150.0000	0.2680	0.2833	0.2703	0.2758	0.2817
499.9990	0.9703	0.9534	0.9117	0.8976	0.9212
2499.9900	4.8330	4.8233	4.7193	4.9390	4.1390
X-VALUE	Y-VALUE	STD DEV	RSD%	RES. E.	R.R. E.

DATA WITH RESPECT TO THE Y-VALUES

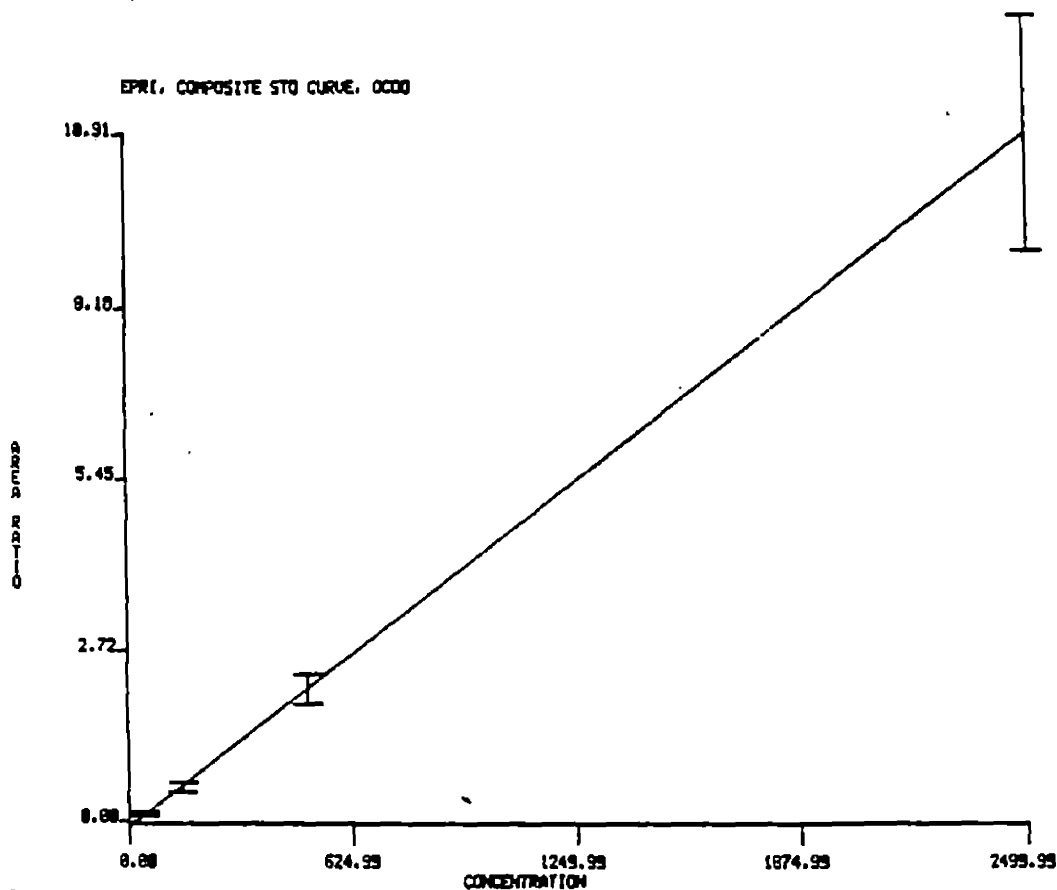
40.0000	0.0663	0.0066	9.87	0.0104	0.0067
150.0000	0.2760	0.0061	2.19	0.0096	0.0062
500.0000	0.9282	0.0278	2.98	0.0439	0.0282
2500.0000	4.9690	0.4066	12.20	0.9392	0.4149

DATA WITH RESPECT TO THE REGRESSION LINE

40.0000	0.0663	0.0233	39.10	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	0.4067	12.20	0.9392	0.4150

A SLOPE OF 0.00199 GIVES AN INTERCEPT OF -0.03408
 A SLOPE OF 500.32900 GIVES AN INTERCEPT OF 17.03620
 THE DATA HAS A CORRELATION COEFFICIENT OF 0.99992

GENP 011123



EPRI, COMPOSITE STD CURVE, OGDG

X-VALUES	Y-VALUES				
40.0000	0.0978	0.1027	0.1032	0.1333	0.1389
150.0000	0.3364	0.3040	0.3418	0.4943	0.3581
500.9990	2.2410	2.0311	2.1635	2.4200	2.1320
2499.9900	12.3693	12.5443	12.8469	9.9800	9.1020
X-VALUE	Y-VALUE	STD DEV	RESID	RES. E.	R.R.E.

DATA WITH RESPECT TO THE Y-VALUES

40.0000	0.1247	0.0248	21.44	0.0423	0.0124
150.0000	0.3544	0.0713	12.89	0.1127	0.0329
500.0000	2.1203	0.2292	10.80	0.3623	0.1037
2500.0000	10.9141	1.8884	17.30	2.9858	0.8709

DATA WITH RESPECT TO THE REGRESSION LINE

40.0000	0.1247	0.0394	31.34	0.0423	0.0182
150.0000	0.3544	0.0774	13.94	0.1224	0.0337
500.0000	2.1203	0.2292	10.80	0.3623	0.1037
2500.0000	10.9141	1.8884	17.30	2.9858	0.8709

A SLOPE OF 0.004377 GIVES AN INTERCEPT OF -0.07755
 A SLOPE OF 227.47100 GIVES AN INTERCEPT OF 17.84260
 THE DATA HAS A CORRELATION COEFFICIENT OF 0.99999

GENP 011124

Appendix C
LETTER REPORT FROM UMEA

GENP 011125

783936

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 liquids

Levels in inservice liquids:

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.

783937

LARS-OWE KJELLER
Umeå Universitet
901 87 UMEÅ Sweden

Umeå 85-06-18

EPRI-prodjekt 2028

Calibration curve, raw counts normalized for ¹³C-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

783938

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

783939

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 = amount 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.

783940

GENP 011129

LARS-OWE KJELLER
Umeå universitet
902 85 UMEÅ Sweden

Umeå 86-06-17

EPRI-project 2028

Levels of dioxins and dibenzofurans in inservice liquid (ng/g)^{1 2}

Att nr. 41159-11-	11	12	13	14	15	16	17
TCDF							
1168	<1.1	0.46	11	1.2	<0.04	<0.05	<0.34
1179/1178	5.4	2.0	5.0	8.9	<0.04	<0.05	<0.34
1147	4.0	1.4	110	6.1	<0.04	<0.05	3.0
1468	5.4	1.9	Int	23	<0.04	<0.05	3.0
1247/1167	8.5	2.1	Int	27	<0.04	<0.05	14
1148	2.3	2.2	2.5	4.8	<0.04	<0.05	5.4
1146/1248	85	11	130	170	<0.04	<0.05	75
1246/1217/1268/1478/1369	14	6.7	95	61	<0.04	<0.05	31
1214/2349	5.4	1.4	32	9.7	<0.04	<0.05	5.4
1238/1467/2468/1236	2.3	4.2	9.1	15	<0.04	<0.05	8.4
1149	<1.1	<0.14	<0.03	<0.32	<0.04	<0.05	<0.34
1278	9.9	8.4	29	110	<0.04	<0.05	56
1267/1279	4.0	2.5	7.6	16	<0.04	<0.05	13
1469	<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
2368	8.5	4.6	Int	41	<0.04	<0.05	16
2467	4.5	0.81	37	31	<0.04	<0.05	2.3
1219/2347	9.0	3.9	140	68	<0.04	<0.05	13
1269	<1.1	<0.14	<0.03	<0.32	<0.04	<0.05	<0.34
2378	18	14	8.8	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	8.8	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
REC ¹³ C-2378-TCDF	45%	50%	47%	54%	65%	67%	81%

TCDD No TCDD isomers detected. Detection limit 0.2 ng/g

REC ¹³ C-2378-TCDD	41%	48%	49%	50%	56%	44%	26%
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C-5

GENP 011130

783941



GENP 011131

783942

Alt nr. 41159-11-

11 12 13 14 15 16 17

PnCDD

13468	<1.1	2.5	2.0	33	<0.05	<0.06	<0.36
12468	27	5.6	7.0	200	<0.05	<0.06	30
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	15	360	<0.05	<0.06	58
23469/12347	150	14	15	340	<0.05	<0.06	60
13469	<1.1	<0.17	<0.04	<0.35	<0.05	<0.06	<0.36
12348/12370	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	0.98	110	<0.05	<0.06	18
12367	200	22	29	1200	<0.05	<0.06	130
12469/23469	<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	7.0	6.5	6.0	200	<0.05	<0.06	50
TOT PnCDD	2100	310	160	10000	ND	ND	1600

REC 13C-12378-PnCDD

558 478 528 578 738 638 868

PnCDD

No PnCDD isomers detected. Detection limit 0.2 ng/g

BaCDD

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	4.8	1500	<0.06	<0.07	490
124679	<1.7	11	0.35	150	<0.06	<0.07	15
123479/123478	5300	570	14	4200	<0.06	<0.07	1300
123678	530	47	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	10	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 BaCDD	9700	1000	31	12000	ND	ND	2600

REC 13C-123478-BaCDD

498 508 518 568 788 698 958

BaCDD

No BaCDD isomers detected. Detection limit 0.2 ng/g

Att nr. 41159-11-

HpCDF¹

	11	12	13	14	15	16	17
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	5400
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OCDD

12346789	<10	7.7	<0.73	<4.7	<1.2	8.5	<5.2
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REC ¹³C-OCDD

ND	45%	41%	69%	43%	41%	100%
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¹ All quantifications are made with the ¹²C-compounds in RADIANT calibration standards set.

² Correction for recovery is made.

³ Correction for recovery made with ¹³C-123478-HxCDF spike.

⁴ The values are not corrected for recovery.

783943

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

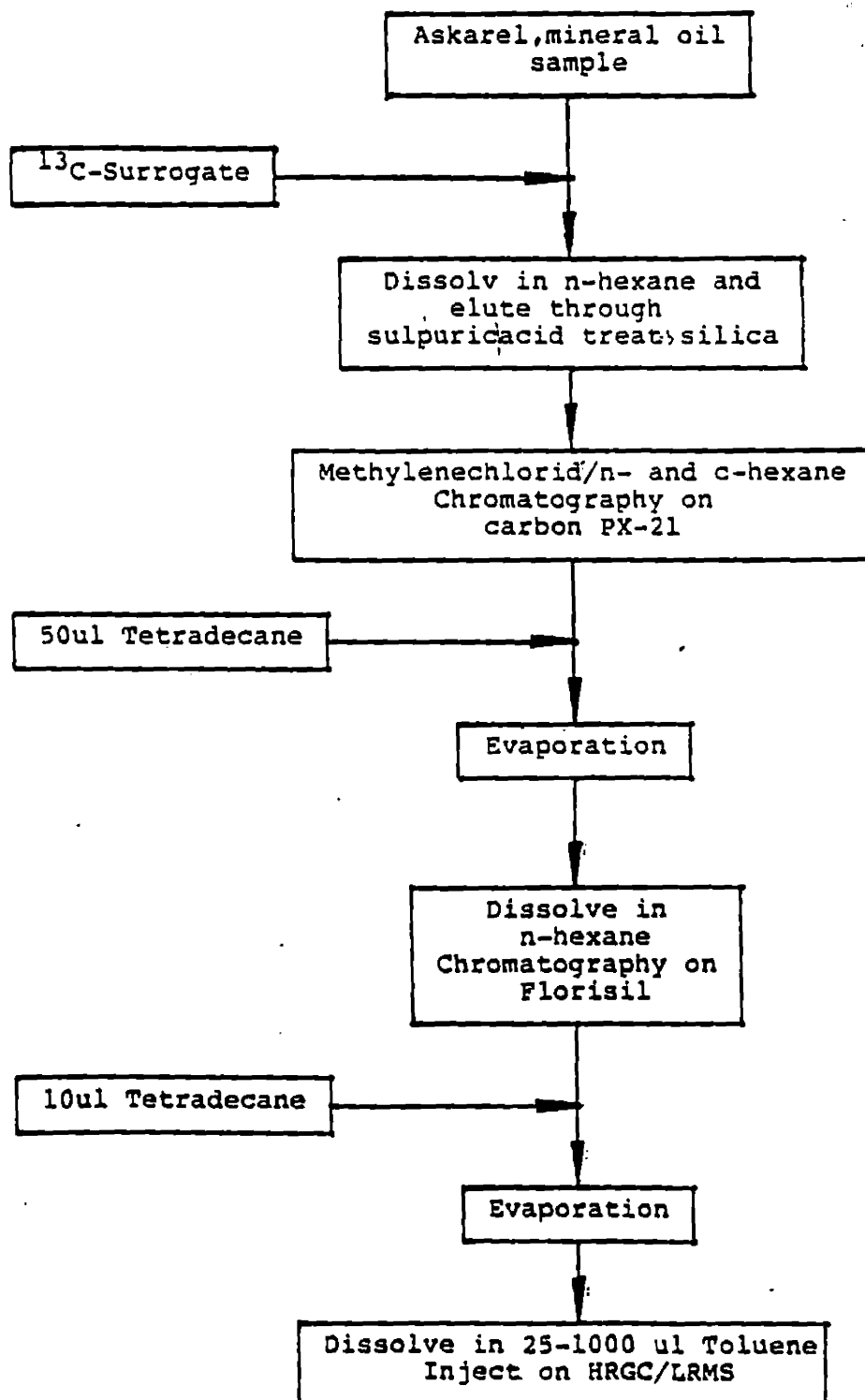
MS-Conditions

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

783944

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



783945

GENP 011134

LARS-OWE KJELLER
Umeå Universitet
901 87 UMEA Sweden

Umeå 86-06-18

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 ₁
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%

783946

The values are given in ng/g

ND = Not Detected.

ND¹ = Not detected due to interferens from the big
2,3,7,8-TCDF peak.

ND² = Not detected , no singnal for 13C-OCDDn.

GENP 011136