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GREAT LAKES INTEGRATED ATMOSPHERIC DEPOSITION NETWORK (IADN)

QUALITY ASSURANCE REPORT 1990 -1992

Karen Harlin, Leon Olszewski,
Donald Gatz and Clyde Sweet

December 1993
(revised, November 1994)

Illinois State Water Survey
2204 Griffith Drive
Champaign, Illinois 61820

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INTEGRATED ATMOSPHERIC DEPOSITION NETWORK (IADN)

QUALITY ASSURANCE REPORT
1990-1992

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Table of Contents

List of Figures

List of Tables

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1.0 Executive Summary

1.1 Introduction

The Integrated Atmospheric Deposition Network (IADN) is a joint monitoring program between the United States and Canada. The program's objectives are to determine the status, change, and trends of toxic organics in the Great Lakes. The intent of the network is to measure and evaluate the concentration of toxic pollutants in the atmosphere and their deposition (particles, vapor, and precipitation) at a regional level of detail. The network provides continuous monitoring programs with sampling and analysis year-round. The Illinois State Water Survey (ISWS) provides research support to IADN for sample collection, sample analysis, method development, data management, data interpretation, data transfer to other researchers and agencies, and quality assurance. The ISWS measures meteorological and chemical parameters as described in the Quality Assurance Project Plan (QAPjP) (Gatz et al., 1992). The ISWS is responsible for three U.S. monitoring stations on the Great Lakes and has participated in a comparative sampling program at one Canadian station:

- Eagle Harbor, MI, on Lake Superior
- Sturgeon Point, near Evans Center, NY, on Lake Erie
- Sleeping Bear Dunes National Lakeshore, near Empire, MI, on Lake Michigan
- Point Petre, Canada, on Lake Ontario (Canadian station)

A companion report (Gatz et al., 1994) covers the actual chemical and meteorological data for the project.

1.2 Quality Assurance Program and Optimization

Binational Quality Assurance (QA) procedures and policies for the IADN have been developed and ISWS QA plans implemented. Quality assurance objectives and activities were defined in three documents: 1) Quality Assurance Program Plan (QAPP); 2) Quality Assurance Project Plan (QAPjP); and 3) Standard Operating Procedures (SOPs). These policies have been reviewed and revised periodically to accommodate changes in techniques and goals as the program evolved.

An interim Quality Assurance Program Plan (QAPP) (Brice and Hoffman, 1993) was developed in the spring of 1992. This plan is a comprehensive program-wide binational quality assurance plan. It outlines the elements of the IADN program and delineates the QA activities that are essential to produce data of sufficient quality to meet the program goals. It contains information of a general nature regarding all parties involved in the IADN. The plan was reviewed and revised during 1992-1993. A binational meeting was held in November 1993, after which all final revisions were made to the document. This document was signed by the participants on May 19, 1994, and was distributed to the ISWS in November 1994.

The Quality Assurance Project Plan (QAPjP) "Measurement of Toxic Atmospheric Deposition to the Great Lakes" (Gatz et al., 1992) was initiated in December, 1991. This plan was revised, approved, and distributed in March 1993. The plan details ISWS responsibilities for the IADN project.

ISWS laboratory and sampling Standard Operating Procedures (SOPs) were initiated in 1991. They were revised and redistributed periodically throughout the reporting period. Currently, laboratory SOPs are described in three manuals: 1) "Analysis of PCBs and Pesticides in Air and Precipitation Samples, Instrumental Analysis and Data Reduction" (Basu, et al., 1993); 2) "Analysis of PCBs, Pesticides, and PAHs in Air and Precipitation Samples, IADN Project, Sample Preparation Procedure" (Willett and Basu, 1993); 3) "Analysis of Air and Precipitation Samples by Gas

Chromatography-Mass Spectroscopy (GC-MS), Instrumental Analysis and Data Reduction" (Harlin and Peters, 1994). Sampling SOPs were distributed to all site operators and individual training took place at the start of sampling. Revised sampling SOPs were given to site operators at the IADN Operators Training Workshop held in Champaign, IL, November 1993. A third revision was distributed in December 1993 (Sweet, 1993).

Sampling and analytical protocols were modified and improved as the project evolved. Significant protocol changes are shown below:

Sampling modifications:

February, 1992	trapping agent for organics in precipitation samples changed from Empore® disks to XAD-2 resin
May, 1992	organic vapor trapping adsorbent changed from polyurethane foam (PUF) to XAD-2 resin

Laboratory modifications:

April, 1991	analytes alpha- and gamma-hexachlorocyclohexane, and dieldrin added
January, 1992	analytes p,p' DDD; p,p' DDE; p,p' DDT; and hexachlorobenzene added

Analysis of quartz fiber filter blanks showed high background levels for some analytes and their use was discontinued in December 1991. Measurements of organics in particulate matter were not adversely affected since the total suspended solids (TSP)/ total organic carbon (TOO filter samples (collected on glass fiber filters) were used for this purpose. Beginning March 1992, glass fiber filters were preconditioned at 450°C before use to avoid potential contaminants.

Special stability studies were conducted to evaluate the effects of sample storage prior to analysis. Some field samples were stored at -20°C for up to 12 months before the ISWS lab began analyses. In late 1992, sample stability measurements were initiated using paired (collocated) samples to determine the effects of sample storage at -20°C before extraction. One of the paired samples was extracted within the storage time specified in the QAPjP (1-2 months for organics). The "twin" sample was stored for six months or one year before extraction. Results from the six-month stability evaluation have been completed. Preliminary results indicated no analyte losses occurred after six months of storage at -20°C. Results from the one-year stability will be available in future reports.

Special studies were also conducted to determine the effect of field storage conditions on sample integrity since up to two weeks could elapse before samples are received from field sites. Paired (collocated) samples collected at Champaign, IL, were used to determine stability of the samples under field storage conditions. One of the paired samples was frozen immediately after collection. The "twin" sample was stored at room temperature for up to two weeks. Results revealed no significant differences in analyte concentrations between the room temperature (25°C) and freezer (-20°C) storage conditions.

Analytical methods were improved during the course of the study. Modifications included: 1) increasing or decreasing the laboratory matrix spiking levels to match concentrations observed in the site samples more closely; 2) increasing the number of quality control samples processed with each set of samples extracted; 3) documenting instrument linearity and detection limits for the gas chromatographic methods for all analytes; 4) analyzing reference standards (from a separate source) as instrument calibration checks; and 5) improving chromatographic resolution for

p,p' DDE was identified as a positive interference for PCB congener 77).

1.3 Data Quality Assessment

The QAPjP (Gatz et al., 1992) defines the measurement quality objectives (MQOs) established for this monitoring project. The MQOs are directed toward the attributes of precision, accuracy, completeness, and detectability of the analytes selected. Results of the ISWS efforts to meet the acceptance criteria for the established MQOs are compiled and published in periodic QA reports.

1.3.1 Detectability

The minimum detection limit (MDL) is the lowest analyte concentration that an analytical method can reliably detect. The MDL was defined as the mean analyte concentration plus three standard deviations of data obtained from lab matrix blanks. MDLs could not be calculated using this method since many lab matrix blanks yielded no detectable values for a number of analytes. An alternate method of determining the MDL requires spiking each sampling matrix with low-level standards and processing them through the entire analytical method. This work is now in progress.

A low-level calibration standard was used to calculate an instrument detection limit (IDL). The IDL is determined from a data set comprised of three separate chromatographic runs (7-10 samples per run) of a low-level standard. The IDL is defined as defined as three standard deviations of this data set. IDLs were calculated for all analytes and are listed in Table 4.1. For this reporting period an MDL was estimated by dividing the IDL by the average volume of sample obtained for each matrix and was expressed as the lowest detectable concentration (pg/m^3 or ng/L) in a typical sample (Table 4.1).

The limit of detection (LOD) was defined as the lowest analyte concentration that can be reliably detected. LODs are affected by the uncertainty introduced during sampling, handling, preparation, extraction, and analysis. The LOD was determined for all IADN target organic analytes using field blanks for each matrix sampled. All field blanks and site samples were handled in an identical manner. The LODs were defined as the mean analyte concentration plus three standard deviations, based on the matrix specific field blanks. Matrix specific LODs were computed for all IADN analytes. LODs are listed in Table 4.2.

1.3.2 Precision

Precision is a measure of mutual agreement among multiple measurements of the same property, usually under prescribed similar conditions. Several types of samples were collected to determine precision at various measurement phases.

Overall precision (sampling and laboratory) was evaluated with collocated field duplicates from identical samplers located at IADN master stations. The sampling precision MQO was based on the relative percent difference (RPD) from these paired samplers. The RPD acceptance limits were $\leq$ 50% for values greater than five times the LOD and $\leq$ 100% for values less than five times the LOD. The RPDs for all paired samples were compiled for each analyte for vapor cartridge (PUF and

XAD-2), filter (GFF), and precipitation (Empore and XAD-2). The data are listed in Table 4.3. A summary of paired sample RPD results for all analytes follows:

Relative percent difference MQO results:

Matrix	Number failing the MQO	Number passing the MQO	Total number	Percent acceptable
all matrices	243	2444	2687	91.0
precipitation-Empore	33	76	109	69.7
precipitation-XAD-2	35	249	284	87.7
vapor cartridge-PUF	127	1324	1451	91.3
vapor cartridge-XAD-2	36	570	606	94.1
filter-GFF	12	225	237	94.9

Of the matrices investigated, the precipitation-Empore collocated samples resulted in the lowest percent acceptable values. This matrix was replaced with wet XAD-2 in February 1992. RPDs with wet XAD-2 resulted in improved precision.

Laboratory precision was determined by the use of laboratory surrogate spikes (LSS) and laboratory matrix spikes (LMS). The MQO acceptance criterion for LSS and LMS precision was within two standard deviations of the data sets. Laboratory surrogate spikes are influenced by interferents originating from the matrices or from the samples, and are not indicative exclusively of laboratory precision. Analysis of split samples may be a better indicator of laboratory precision independent of sampling effects. Analysis of split sample results will be presented in future QA reports.

Three laboratory surrogate spikes were added to each sample extracted in the laboratory. Control charts (Figures 4.0-4.2) and statistical analysis from 458 surrogate spikes were compiled for the three surrogates (PCB congeners 14, 65, and 166). The RSD for the surrogate standards was 31, 21, and 20% for PCB 14, 65, and 166, respectively, from the 458 samples. The mean recovery ± 2 SD obtained for each surrogate was :

PCB	Mean (%)	Range (±2 SD)
14	95	36-154%
65	78	45-111 %
166	90	53-127%

PCB 14 surrogate resulted in a significantly higher SD than that observed for PCB 65 or PCB 166. Early eluting PCB congeners were more subject to interferences from extraneous peaks during chromatographic analysis. This sporadic interference is reflected in the precision statistics for PCB 14 surrogate spike and in the LOD value for PCB 5 + 8 , which elutes just before PCB 14 in the chromatogram (see Table 4.2). PCB 14 surrogate spike does not reflect the overall precision of the majority of the data. Other surrogates which may be better indicators of overall precision are undergoing method development and may be implemented for future reports (deuterated PAHs and pesticides).

A laboratory matrix spike was prepared and processed with each set of samples extracted. A representative matrix (filter, dry cartridge material, or wet XAD-2) was spiked with all analytes and processed identically to the site samples. Individual analyte recovery results are listed in Table 4.4.

Control charts for individual analytes are presented in Appendix A. The average recoveries for all analytes within the three target groups were:

	PCBs	Pesticides	PAHs
average recovery (%)	94.07	95.61	79.46
average std. dev. (%)	22.46	21.50	13.89

1.3.3 Accuracy

Accuracy is the level of agreement between an observed value and the "true" value of an analyte present in air or precipitation samples. Laboratory accuracy was evaluated with laboratory surrogate spikes (LSS), laboratory matrix spikes (LMS), interlaboratory comparison studies, and confirmation/reanalysis of selected samples performed at a separate laboratory.

Interlaboratory comparison studies for IADN participants were initiated in 1992 to provide an initial assessment of between-laboratory variability for the analysis of analytes in precipitation, ambient air, or both. The studies were sponsored by the Canada-Ontario Agreement (COA) Air Toxics Workgroup. The ISWS completed Phase I of these studies in 1992. Phase I required the determination of trace levels of metals, PCBs, pesticides, and PAHs in ampouled standards for direct instrument analysis. Phase II was initiated in July 1993, and was completed in December 1993. Phase II required the analysis of the same analytes as Phase I; however, two ampoules were standards for direct instrument analysis and two ampoules required a clean-up step before analysis. Results from the Phase I interlaboratory study are presented in Appendix B.

Laboratory surrogate spikes (LSS) were prepared by the addition of three surrogate standards (PCB congeners 14, 65, and 166) to every sample processed. The surrogate standard recovery was used to track the recovery of the analytes of interest in the individual site samples; and was used to assess overall laboratory accuracy. The MQO acceptance criterion for the average recovery of the three spiked surrogate standards was 50-130% and 98% of the 458 samples met this acceptance criterion. Additionally, 2/3 of the three surrogates must yield ≥ 50% and ≤130% recovery, and 99% of the samples met this acceptance criterion. Control charts of lab surrogate spikes are presented in Figures 4.0-4.2. The mean percent recoveries ± 1 SD computed for 458 samples processed through the reporting period were:

PCB	Mean recovery ± 1 SD
14	95 ± 29.5%
65	78 ± 16.5%
166	90 ± 18.5%

Individual analyte recovery was determined from the laboratory matrix spikes (LMS). These data were used to assess analyte specific laboratory accuracy. Recovery data for 56 individual analytes are listed on Table 4.4. Analyte specific control charts allow for monitoring the effects of method variables over time. Control charts are presented in Appendix A. Different symbols were used for each matrix on the control chart plots in Appendix A to allow for monitoring matrix specific differences. Matrix specific recovery data will be available in future QA reports. The MQO acceptance criterion required mean recoveries of 50-130% for all LMS samples. These set points were selected as the upper and lower control lines on the individual analyte control charts in Appendix A.

Confirmation or reanalysis of selected samples was performed by the Illinois Department of Energy and Natural Resources Hazardous Materials Laboratory, Champaign, IL. Gas chromatography-mass spectroscopy (GC-MS) was used on selected samples to: 1) confirm that target analytes were

present, and 2) confirm that the analytes were present at the reported levels. Analysis by a second laboratory provided needed analytical confirmation when outlying data points were found. A positive interference was suspected for some samples yielding abnormally high results. In some instances, a positive interference was identified. The results of this analysis are being compiled and will be available in subsequent reports.

1.3.4 Representativeness

Representativeness expresses the degree to which data accurately and precisely represent characteristics of a population, parameter, variations at a sampling point, a process condition, or an environmental condition. Representativeness for this project was a measure of the parameter variation at a sampling point and was evaluated by collecting random duplicate samples. The precision data from the collocated samples presented in section 4.2.1 and on Table 4.3 reflect the representativeness of the sampling system.

Sampling sites were selected to be free from local sources of contamination and to represent regional background concentrations of the target compounds. Comparison of data within and between sampling sites could, therefore, yield information useful for evaluation of representativeness criteria for this project. Data for the sampling sites are available in the 1990-1992 data report (Gatz et al. 1994). Descriptions of the sampling locations are presented in section 4.4 of this report.

The sampling, handling, and analysis protocols selected were consistent with those used by other U.S. and Canadian researchers whenever practical. This allows the comparison of data generated by this project with data from previous studies and from Canadian researchers.

Site samples were analyzed in their entirety; therefore, subsampling and sample homogeneity were not a concern for this reporting period.

1.3.5 Completeness

Completeness is the measure of the numbers of samples obtained compared to the numbers that were expected to be obtained under normal conditions. The completeness goal was 90% for sampling and 95% for laboratory data reported for each sample collected. Based on sampling frequencies, and allowing for sample compositing (monthly filter composites), the target number of samples/year/site (not including collocated duplicates) was 25/year for vapor cartridges, 12/year for particulate filters, and 13/year for precipitation. Sample results from the four sites through December 1992 yielded the following completeness statistics:

Matrix	Target # samples	Actual # samples	Percent completeness (sampling and laboratory)
Vapor Cartridge	158	175	111
Particulate Filter	76	75	99
Precipitation	77	82	106

Initial start-up at all sites required sampling at increased frequencies. This resulted in completeness levels over 100%.

1.3.6 Comparability

Comparability expresses the confidence level with which data sets can be compared. The data should be comparable within and between sites.

Within-site data comparability was assured by maintaining the same procedures throughout the duration of the project as much as was reasonable. When a procedure or an analysis was modified or changed, a comparison was made to verify that the data were identical, more precise, or more accurate than those previously obtained. Quality assurance and quality control samples allowed for laboratory and sampling performance to be monitored over the duration of the project.

Between-site comparability was assured by using sampling and analysis methods based on procedures employed by previous atmospheric deposition projects within the Great Lakes basin (Sweet et al., 1993). Data representativeness and comparability were also assured by using sampling, handling, and analysis protocols similar to those used by other U.S. and Canadian researchers when practical.

The Canadian sampling station at Point Petre was used for comparison studies by ISWS and Canadian researchers. Samples collected at this site allowed for comparison of methods and sampling protocols between groups. Since the first data reports from US and Canadian researchers are now being developed, comparability determinations from this site will be included in future QA reports.

Participation in interlaboratory studies also provide comparability data for analytical methods employed by different researchers within the IADN. Data from the Phase I interlaboratory study are presented in Appendix B.

1.4 Quality Assurance and Quality Control Samples

Quality assurance (QA) and quality control (QC) samples were incorporated into the sampling and laboratory procedures. The following QA/QC samples were included with each sample set whenever possible:

Site sample set:
One field blank (FB) per month per station for each matrix type
One pair of collocated field duplicate (CFD) samples per month from each master station for each matrix type

Laboratory sample set:
One matrix field blank (FB)
One set of collocated field duplicate (CFD) samples
One matrix/laboratory blank (LB)
One laboratory matrix spike (LMS) for each matrix prepared

Additional QA/QC performance checks ran with each set of samples processed included: 1) instrument calibration checks, 2) analysis of LSS, and 3) multiple internal calibration standards.

Internal QA procedures included: 1) analysis of interlaboratory performance check samples, 2) parallel analysis of old and new calibration and spiking standards before use of new solutions, 3) instrument linearity checks, and 4) documentation and identification of coelution interferences whenever possible.

Detailed laboratory records were maintained for: 1) sampling conditions, 2) sample handling, 3) instrument maintenance and calibration, 4) standard and reagent preparation, and 5) sample preparation.

Method development work included initial investigations with deuterated PAH surrogate standards. Additionally, work to improve recovery or eliminate interferences for target organics in individual matrices was continued. Results will be detailed in future reports.

2.0 Introduction

2.1 Purpose

This report presents the quality control and quality assurance data associated with the first data report for the U.S. sampling stations in the Integrated Atmospheric Deposition Network (IADN). The sampling period covered by these reports is October 1990 through December 1992.

2.2 Background

The Integrated Atmospheric Deposition Network (IADN) is the result of a joint effort between the United States and Canada to measure atmospheric deposition of toxic materials to the Great Lakes. The program was mandated by Annex 15 (Airborne Toxic Substances) of the Great Lakes Water Quality Agreement (GLWQA) between the United States and Canada. The GLWQA was originally signed in 1972 and amended in 1978 and again in 1987, when Annex 15 was added. The network also fulfills the requirements of the U.S. Clean Air Act Amendments (CAAA) of 1990, which called for a Great Lakes atmospheric deposition network.

The plan for development of the new network was approved in 1990 (Canada/U.S. Coordinating Committee on Annex 15, 1990). Measurements of the following toxic chemicals were to begin during Phase I (1991 and 1992):

- Total polychlorinated biphenyls (PCBs) and major congeners
- Alpha and gamma isomers of hexachlorocyclohexane (HCH)
- Polyaromatic hydrocarbons (PAHs), with benzo(a)pyrene (BaP) as the goal
- Lead

Toxicants to be monitored as a second priority included chlorinated pesticides such as DDT and its metabolites, chlordanes, trans-nonachlor, heptachlor epoxide, methoxychlor, dieldrin, hexachlorobenzene (HCB), endrin, arsenic, selenium, cadmium, and mercury.

The plan called for installation of one master (research grade) sampling station on each of the Great Lakes by the end of 1992. This schedule was advanced one year by the 1990 CAAA, which required one sampling site on each lake by the end of 1991. The plan also called for two or more satellite (routine) sites on each of the Great Lakes plus one or more background stations. Plans for installation of satellite sites have not yet been implemented.

The master stations operate two or more of the primary network samplers to provide the sampling replication necessary to determine sampling and analytical precision. They typically provide enough space and electric power to accommodate additional research. The satellite stations are expected to include single samplers of the same types used at the master stations. The samplers, sampling procedures, and sampler calibration are described in the data report (Gatz et al., 1994).

All sampling and analytical operations were governed by the Quality Assurance Project Plan (QAPjP) (Gatz et al., 1992). Laboratory and sampling standard operating procedures were detailed in four manuals (Willett and Basu, 1993, Basu et al., 1993, Harlin and Peters, 1994, Sweet, 1993).

2.3 Scope

The network's objectives are to determine the status, change, and trends of atmospheric concentrations and deposition of toxic organic compounds in the Great Lakes area. The intent of the network is to measure and evaluate the concentration and deposition of toxic pollutants in the

atmosphere (particles, vapor, and precipitation) at a regional level of detail. The network provides continuous monitoring programs with sampling and analysis year-round.

The Illinois State Water Survey (ISWS) provides research support to IADN for sample collection, sample analysis, method development, data management, data interpretation, data transfer to other researchers and agencies, and quality assurance. The ISWS is responsible for three U.S. monitoring stations on the Great Lakes (master stations) and participated in a comparative sampling program at one Canadian station. Figure 2.0 shows the locations of all IADN sampling sites. The stations included in this report are:

- Eagle Harbor, MI, on Lake Superior
- Sturgeon Point, near Evans Center, NY, on Lake Erie
- Sleeping Bear Dunes National Lakeshore, near Empire, MI, on Lake Michigan
- Point Petre, Canada, on Lake Ontario (Canadian station)

This report contains the quality control/quality assurance data associated with the organic chemical measurements from the sites shown above. Chemical analyses for the trace metals in airborne particles were carried out at the U.S. EPA's AREAL at Research Triangle Park, NC, and are not covered in this report. The sampling data were reported in the Great Lakes Integrated Atmospheric Deposition Network (IADN) Data Report 1990-1992 (Gatz et al., 1994). This report covers the sampling period from October 1990 through December 1992. None of the sites, however, were operational during this entire period. Results are included for the period during which each site was operational and for which analyses were completed through the end of May 1993. Organic compounds monitored included total PCBs and 33 selected congener peaks (representing 46 PCB congeners), 7 pesticides and pesticide metabolites, and 15 PAHs. The PCB congeners selected for this report account for about 90 percent of the total mass of PCBs in most samples. The total PCB levels reported represent the sum of the amounts of all detectable PCB congeners included in the assay (about 90 congeners). Table 2.0 lists the specific parameters included in the data report.

Figure 2.0
IADN Site Locations

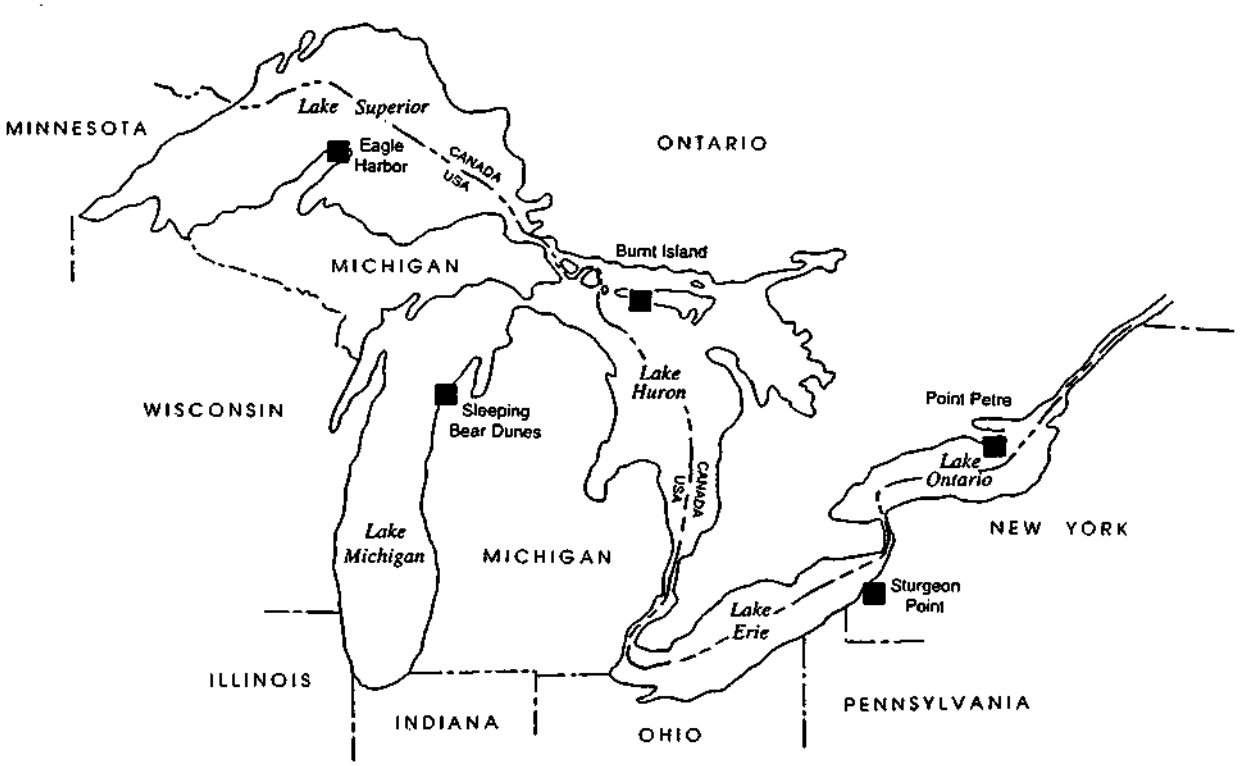

Table 2.0
Parameters Measured

Organic toxicants

PCBs
Total
5 + 8
6
16 + 32
17
18
21
22
28 + 31
33
37 + 42
41 + 64 + 71
43
44
47 + 48
49
52
53
56 + 60
66
70 + 76
74
81
84 + 92
87
95
99
101
105 + 132 + 153
110
118
119
138 + 163
149

PAHs:
acenaphthylene
acenaphthene
fluorene
phenanthrene
anthracene
fluoranthene
pyrene
benzo(a)anthracene
chrysene
benzo(b)fluoranthene
benzo(k)fluoranthene
benzo(a)pyrene
Indenod 23cd)pyrene
dibenzo(ah)anthracene
benzo(ghi)perylene

Pesticides
alpha-hexachlorocyclohexane
gamma-hexachlorocyclohexane
dieldrin
p,p' DDT
p,p' DDD
p,p' DDE
hexachlorobenzene

Trace metals
vanadium
chromium
manganese
nickel
copper
zinc
arsenic
selenium
cadmium
lead

Other
total suspended particles
total organic carbon

Meteorological parameters
temperature
precipitation
wind speed
wind direction

3.0 Quality Assurance Program

3.1 Documentation of Procedures

Binational Quality Assurance (QA) procedures and policies for the IADN have been developed and ISWS QA plans implemented. QA objectives and activities were defined in three documents: 1) Quality Assurance Program Plan (QAPP); 2) Quality Assurance Project Plan (QAPjP); and 3) Standard Operating Procedures (SOPs). These policies have been reviewed and revised periodically to accommodate changes in techniques and goals that occurred as the IADN program evolved. Archives have been maintained for outdated versions of QA plans and SOPs.

3.1.1 Quality Assurance Program Plan

An interim QAPP (Brice and Hoffman, 1993) was developed in the spring of 1992. The plan is a comprehensive program-wide binational quality assurance plan. It outlines the elements of the IADN program and delineates the QA activities that are essential in order to produce data of sufficient quality to meet the program goals. It contains information of a general nature regarding all parties involved in the IADN. The plan was reviewed and revised during 1992-1993. All final revisions were made to the document after a binational meeting in November 1993. This document was signed by the participants on May 19, 1994 and was distributed to the ISWS in November 1994.

3.1.2 Quality Assurance Project Plan

The QAPjP, "Measurement of Toxic Atmospheric Deposition to the Great Lakes" (Gatz et al., 1992), was initiated in December 1991. It was revised, approved, and distributed in March 1993. The plan details ISWS responsibilities associated with the IADN project and defines the QA objectives and activities specific to the ISWS.

3.1.3 Standard Operating Procedures

The first laboratory SOP manual, "Analysis of PCBs, Pesticides, and PAHs in Air and Precipitation Samples" (Willlett and Basu, 1992), was distributed in June 1992. This manual primarily described sample preparation procedures and included a section on instrumental analysis. In December 1992, instrumental analysis procedures (gas chromatographic analysis) were expanded into a separate SOP manual, "Analysis of PCBs and Pesticides in Air and Precipitation Samples" (Basu et al., 1992). This manual expanded upon and was limited to gas chromatographic analysis procedures. It was revised again in December 1993 as "Analysis of PCBs and Pesticides in Air and Precipitation Samples, Instrument Analysis and Data Reduction (Basu et al., 1993). In April 1993 a separate sample preparation procedure manual, "Analysis of PCBs, Pesticides, and PAHs in Air and Precipitation Samples, Sample Preparation Procedure" (Willett and Basu, 1993), was distributed. This manual expanded and revised sample preparation procedures and omitted instrumental analysis procedures. An SOP manual for PAH analysis, "Analysis of Air and Precipitation Samples by Gas Chromatography-Mass Spectroscopy (GC-MS), Instrumental Analysis and Data Reduction" (Harlin and Peters, 1994) was finalized in January 1994. Sampling SOPs were given to all site operators during individual training at the start of the sampling program at each site. Revised sampling SOPs were distributed to all site operators at the IADN Operators Training Workshop held in Champaign, IL in November 1993. A third revision was distributed in December 1993 (Sweet 1993).

4.0 Data Quality Assessment

The ISWS QAPjP (Gatz et al., 1992) defines the measurement quality objectives (MQOs) established for this project. The MQOs are directed toward the attributes of precision, accuracy, completeness, and detectability of the selected analytes. Results of the ISWS efforts to meet the acceptance criteria for the established MQOs will be compiled and published in periodic QA reports. This report presents the results of the QA/QC efforts for this project and covers the period associated with the Great Lakes Integrated Atmospheric Deposition Network (IADN) Data Report 1990-1992 (Gatz et al., 1994). Table 4.0 lists the MQOs for this project.

4.1 Detectability

4.1.1 Method Detection Limit and Instrument Detection Limit

The method detection limit (MDL) is the lowest analyte concentration that an analytical method can reliably detect. The MDL was defined as the average analyte concentrations plus three standard deviations (SD) of the data obtained from laboratory matrix blank (LB) results. The LB is prepared from the same matrix used for sampling, and is used to calculate the MDL and to identify matrix or laboratory contamination. MDLs could not be calculated using this method because many lab matrix blanks yielded no detectable values for a number of analytes. An alternate method of determining the MDL requires spiking each sampling matrix with low-level standards and processing them through the entire analytical method. This is now in progress. A low-level calibration standard was used to calculate an instrument detection limit (IDL), which is determined from a data set comprised of three separate chromatographic runs (7-10 samples per run) of a low-level standard. The IDL is defined as three standard deviations of this data set. IDLs were calculated for all analytes and are listed in Table 4.1. The MDL was estimated by dividing the IDL by the average volume of sample obtained for each matrix and expressed as the lowest detectable concentration (pg/m^3 or ng/L) in a typical sample (Table 4.1).

Lab blank (LB) data are presented in Table 4.5. The amount of each matrix used for the LBs were as follows:

Polyurethane Foam (PUF) Cartridge:	one 8 centimeter (cm) diameter cylindrical plug, 10 cm length (same as samples)
XAD-2 resin cartridge:	10-15 grams (g) XAD-2 (-1/3 actual sample size)
XAD-2 resin column (precipitation):	8 g XAD-2 (same as samples)
Particulate filter (glass fiber):	1 filter (samples and FB are monthly composites, 2-3 filters)

4.1.2 Limit of Detection

The limit of detection (LOD) is the lowest analyte concentration that can be reliably detected. LODs are affected by the uncertainty introduced during sampling, handling, preparation, extraction, and analysis. LODs were calculated using matrix specific field blanks. For this project all field blanks (FB) and site samples were handled, transported, and treated in an identical manner. For air-vapor FBs a representative sampling cartridge containing the adsorbent used (PUF or XAD-2) was placed inside a sampler at the sampling site for seven days. The sample collection procedure was followed, except that the pump was not turned on. A seven-day period was selected because this was the maximum time that cartridges were retained in a sampler at a site location. Particulate matter FBs were collected by placing a representative filter inside the sampler for seven days with no air drawn through it, as described for air-vapor. Precipitation FBs were collected by treating a sampling column and a routine sample collection column in an identical manner, except that the

column was not opened. The FB columns were allowed to remain in the collector for four weeks (interval used for precipitation collection). The FBs were used to identify system contamination. The LODs were reported as the amount of analyte detected in a representative amount of matrix used for sample collection. For this reporting interval the matrices were prepared as follows:

PUF vapor cartridge:	8 x 10 cm PUF plug in a glass cartridge
XAD-2 resin vapor cartridge:	~ 40 g dry XAD-2 in a stainless steel cartridge
XAD-2 resin column (precipitation):	~ 8 g of XAD-2 slurry packed with water to yield a 10 cm column in a 30 x 2 cm glass column
Particulate filter:	a composite of two or three glass fiber filters (each filter 20.3 x 25.4 cm)

A matrix specific LOD was calculated for each IADN target organic analyte using the FB data, which were sorted by matrix type. LODs were then calculated as the average mass plus three SD and reported as ng/matrix. Volume corrected LODs were calculated by dividing the ng/matrix values by the average sampling volumes. The volumes used for volume corrected LODs were: 815 cubic meters (m^3) for vapor cartridges, 2450 m^3 for particulate filters (representing a composite of three filters), and 10 L for precipitation. The units were ng/m^3 for vapor and particulate and ng/L for precipitation. The LOD is the maximum probable contribution of the blank to the sample. LOD values are presented in Table 4.2. Samples were not blank corrected in the data report; however, the LOD and the estimated MDL were reported for each analyte and each matrix.

During this reporting period, one vapor cartridge FB sample (Sturgeon Point, sample code: TBCFB920526) resulted in a high PCB blank value, but pesticide and PAH values did not appear to be affected. Due to a limited number of FB values for this matrix, the LODs were calculated with and without this value. The XAD-2 vapor LOD for total PCBs was reduced by 46% when the outlying data point was removed. The corrected LOD was used for the IADN data report and for LOD criteria in the sampling precision statistics (section 4.2.1). The PCB levels in this FB were greater than those obtained from site vapor samples and were deemed outliers by the Dixon method with a 95% confidence level (Taylor, 1988). Efforts to target contamination sources will continue. LOD values in Table 4.2 list the XAD-2 cartridge matrix results with and without the Sturgeon Point outlying data point.

The LOD for the quartz fiber filter (QFF) matrix is not included on Table 4.2. QFFs were used for particle sampling at the Eagle Harbor site only from November 1990 to November 1991. Analysis of QFF blanks resulted in high background levels for some analytes; therefore, their use was discontinued. LB and FB data using quartz filters are presented in Appendix D to detail the background contamination levels expected with this matrix.

4.2 Precision

Precision is a measure of mutual agreement among multiple measurements of the same property, usually under prescribed similar conditions. Several types of samples were collected to determine precision at various measurement phases.

4.2.1 Overall Precision

Overall precision (sampling and laboratory) was evaluated with collocated field duplicate samples obtained at IADN master stations. Two identical high-volume organics samplers and two MIC precipitation samplers were installed at three U.S. Master Stations (Eagle Harbor on Lake Superior, Sturgeon Point on Lake Erie, and Sleeping Bear Dunes on Lake Michigan). Samples were collected

simultaneously at these locations. Data from the paired samplers were combined and evaluated by the following criteria for inclusion into the data set:

1. Analyte values for both Sampler #1 and Sampler #2 must be greater than the LOD. Note: for precipitation-Empore samples the XAD-2 precipitation LOD was used; for XAD-2 cartridge samples, the corrected LOD with the outlying data point removed was used; for PAHs in the XAD-2 vapor cartridge, zero was used (see the discussion below).
2. Both Sampler #1 and Sampler #2 were deemed to have provided valid samples.
3. The volume sampled from Sampler #1 and Sampler #2 agreed within ± 15%

The MQOs for the sampling precision were based on the relative percent difference (RPD) from the paired samples that met the criteria described above. The RPD was defined as:

$$RPD = \frac{|C_1 - C_2|}{(C_1 + C_2) / 2} \times 100$$

where: C_1 and C_2 are duplicate observed values. The absolute difference was used. The RPD MQO acceptance criteria were:

RPD ≤ 50% for values greater than five times the LOD
and RPD ≤ 100% for values less than five times the LOD.

The RPDs for all paired samples were compiled for individual analytes for vapor cartridge (PUF and XAD-2), filter (GFF), and precipitation (Empore and XAD-2). The data are listed in Table 4.3. No LOD correction was made for PAH measurements from the XAD-2 vapor cartridge. Only one XAD-2 FB had been assayed for PAHs before compiling the data; therefore, no LOD statistics were available for this matrix (zero was used). Since the acceptance criteria are based on the LOD, all paired samples for PAHs were placed into the tighter acceptance criterion (>5 LOD = <50% RPD). Once an LOD for this matrix is established, the number of unacceptable values may decrease. A summary of paired sample RPD results for all analytes follows:

Paired Sample MQO results

Matrix	Number failing the MQO	Number passing the MQO	Total number	Percent acceptable
all matrices	243	2444	2687	91.0
precipitation-Empore	33	76	109	69.7
precipitation-XAD-2	35	249	284	87.7
vapor cartridge-PUF	127	1324	1451	91.3
vapor cartridge-XAD-2	36	570	606	94.1
filter-GFF	12	225	237	94.9

The precipitation-Empore collocated samples resulted in the lowest percent acceptable values of the matrices investigated. This matrix was replaced with wet XAD-2 in February 1992. RPDs with wet XAD-2 showed improved precision.

The RSD for the paired differences was also calculated for each matrix and each analyte. The data are shown in Table 4.3.

The RSD was defined as:

$$\textit{Relative Standard Deviation} = \frac{S_j}{\overline{C}}$$

where

$$S_j = \left[\frac{\Sigma\, d_i^2 - \frac{(\Sigma\, d_i)^2}{n}}{n-1}\right]^{1/2}$$

and

$$\overline{C} = \sum_{i=1}^{n} \frac{\left(\frac{C_1 \pm C_2}{2}\right)_i}{n}$$

where d_i is the difference for each pair of duplicate samples and n is the number of paired samples.

4.2.2 Laboratory Precision

Laboratory precision was evaluated from results of laboratory surrogate spikes (LSS) and laboratory matrix spikes (LMS). The MQO acceptance criterion for LSS and LMS precision was within two standard deviations of the data sets. LSS are influenced by interferents originating from the matrices or from the samples and are not indicative exclusively of laboratory precision. Analysis of split samples may be a better indicator of laboratory precision independent of sample effects. Split samples have been analyzed; however, the data are not available for this report. Analysis of split sample results will be presented in future QA reports.

4.2.2.1 Laboratory Surrogate Spikes

Three LSS (PCB congeners 14, 65 and 166) were added to every sample extracted in the laboratory and can be used to monitor the integrity of the results reported for each individual sample. Statistical analysis from 458 samples were compiled for the three surrogates and are presented below.

PCB	mean recovery (%)	SD (%)	2 SD range (%)	RSD (%)
14	95.0	±29.5	36-154	31
65	78.2	±16.5	45-111	21
166	90.3	±18.5	53-127	20

PCB 14 surrogate resulted in a significantly higher SD than that observed for PCB 65 and PCB 166. Early eluting PCB congeners were more subject to interference from extraneous peaks during chromatographic analysis. This sporadic interference is reflected in the precision statistics for PCB 14 surrogate spike and in the LOD value for PCB 5 + 8, which elutes just before PCB 14 in the chromatogram (see Table 4.2). Surrogate spike PCB 14 is not representative of the precision obtained for the majority of the data. Other surrogates which may be better indicators of overall precision are undergoing method development and may be implemented for future reports (deuterated PAHs and pesticides).

4.2.2.2 Laboratory Matrix Spikes

A LMS was prepared and processed with each set of samples extracted. A representative matrix (filter, dry cartridge material, or wet XAD-2) was spiked with all analytes and processed identically to the site samples. Individual analyte recovery results are listed in Table 4.4. Control charts for individual analytes are presented in Appendix A. The average recoveries for all analytes within the three target groups were:

	PCBs	Pesticides	PAHs
average recovery (%)	94.17	95.61	79.46
average SD. (%)	22.46	21.50	13.89

Compounds for which the 2 SD value was > ±50% included: PCBs 16 + 32, 21, 99, 119, 81, a-HCH, g-HCH, dieldrin, p,p' DDT, p,p' DDD, pyrene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(123cd)pyrene, dibenzo(ah)anthracene, and benzo(ghi)perylene. Two changes in procedures occurred during this reporting period which would affect the precision results: 1) adjustments to the target level spiked, and 2) improved chromatographic resolution. The pesticide and PAH target levels were adjusted to more closely resemble those found from site samples. Of the eighteen compounds listed above, thirteen are pesticides and PAHs that were directly affected by these changes. Precision should improve once target spike levels become consistent. The PCB LMS remained consistent throughout the reporting period; therefore, the data in Table 4.4 do reflect the expected precision for congener specific and total PCBs. Chromatographic resolution was improved for all analytes to avoid interferences from unresolved compounds. This change should result in improved laboratory precision for all analytes.

4.3 Accuracy

Accuracy is the level of agreement between an observed value and the "true" value of an analyte present in air or precipitation samples. Sampling and laboratory accuracy were both evaluated as described below.

4.3.1 Sampling Accuracy

Sampling accuracy for air samples was established by performing quarterly flow checks of the sample flow rate. An orifice calibrator was used to measure the flow rates.

Matrix break-through was determined from previous work (Sweet et al., 1993). Two vapor trap cartridges were installed in series on the same air sampler. More than 90% of the measured analytes were recovered from the front cartridge. Sampling volumes were kept below the levels used in break-through experiments to maximize trapping efficiency.

Sample break-through experiments for precipitation columns samples were made by collecting samples at a site in Chicago, where analyte levels are high enough for accurate measurements. Both the column and effluent precipitation that has passed through the column were analyzed. More than 90% of the analytes were retained on the column.

Site FBs also served as monitors of sampling accuracy by indicating positive contaminants that could bias the data reported.

4.3.2 Laboratory Accuracy

Laboratory accuracy was evaluated with laboratory surrogate spikes (LSS), laboratory matrix spikes (LMS), laboratory matrix blanks (LB), interlaboratory comparison studies, and confirmation or reanalysis of selected samples at an independent laboratory.

4.3.2.1 Interlaboratory Comparison Studies

Interlaboratory comparison studies for IADN participants were initiated in 1992 to provide an initial assessment of between-laboratory variability for the analysis of analytes in precipitation, ambient air, or both. The studies were sponsored by the Canada-Ontario Agreement (COA) Air Toxics Workgroup, and conducted as a joint project between the Atmospheric Environment Service (AES) of Environment Canada and the Quality Management Unit (QMU), Laboratory Services Branch (LSB) of the Ontario Ministry of Environment and Energy (MOEE).

The ISWS completed Phase I of these studies in 1992 which required the determination of trace levels of PCB Isomers (Study 92-1), PAHs (Study 92-2), organochlorine pesticides (Study 92-3) and trace metals (Study 92-4) in ampouled standards by direct instrument analysis. Phase II was initiated in July 1993, and was completed in December 1993. Phase II required the determination of the same analytes as Phase I; however, two ampoules were standards for direct instrument analysis and two ampoules required a clean-up step before analysis. Results of the Phase I Interlaboratory study are presented in Appendix B.

Some difficulties were encountered when comparing ISWS laboratory results with the target organic values. For all organics investigated (PCBs, pesticides, and PAHs), the test samples contained analytes not included in ISWS procedures and for which gas chromatographic retention data were unknown. There was a high probability that some of these analytes coeluted with compounds routinely reported. If coelution was present, falsely elevated results would be reported for the analytes affected. In order to evaluate these effects, it is recommended that future studies provide a qualitative standard of analytes not included in an individual laboratory's routine procedures.

For the PCB study, six laboratories received four blind ampouled standards containing 75 PCB isomers (Study 92-1). The results of the study demonstrated interlaboratory means and medians that appeared to agree with the target levels of PCB congeners for isomers that had three or more chlorine atoms. However, between-laboratory variability was frequently > 20%. This level may be unacceptable for the IADN database. Mono and di-chlorinated biphenyl analysis resulted in more problems than the other isomers. Differences in standards, coeluting interferents, or losses in the injector were deemed the probable causes. It was recommended by the study coordinator (Sylvia Cussion) that a common reference standard would reduce the variability between labs. Results reported for synthetic mixes of congener specific PCBs can be affected by the calibration method used by the laboratory. Congener specific standards can be prepared by mixing individual PCB congeners or by mixing Aroclor solutions. Coeluting PCB congener results will be the most affected, for example, PCB congeners 5 and 8 coelute. ISWS uses an Aroclor® mixture of 1232 +

1248 + 1262 (Mullin, 1985) as the calibration standard. Instrument calibration is based on the total amount that congeners 5 + 8 contribute to the mixed standard (the individual contribution of the two congeners is unknown). If the test solution contained only PCB 5 or PCB 8, the amount reported could be biased high or low. The error would be dependent upon the percent contribution each peak made to the total amount used for calibration. It is recommended that the method of calibration for PCBs be detailed by the participating laboratories for future comparisons.

Six laboratories participated in the study of polyaromatic hydrocarbons (PAHs) (study 92-2). Each lab assayed four blind ampouled standards containing 20 different PAHs. The results indicated a low bias relative to the target values for many of the parameters for all but one lab and the study coordinator recommended the use of a common reference standard. Co-elution contributed to between-laboratory variability and may have been an important source of between-laboratory bias.

Six laboratories also participated in the organochlorine pesticide study (92-3). Each lab received four blind ampouled standards containing 18 different pesticides. The results indicated that the participants agreed within 20% of the target values for most analytes. The within-laboratory performance tended to be consistent across the concentration range, although some erratic results were reported. Between-participant bias may be as high as 30-40%, and the use of a common reference standard was also recommended.

The ISWS participated in the trace metals portion of the study in both Phase I and Phase II. The Phase I metals results (Study 92-4) are included in Appendix B for reference only; they do not reflect laboratory accuracy for the metals data associated with the IADN project. The ISWS lab did not perform metals analysis of the IADN samples during this period. Participation in the Phase I trace metals program was for use in evaluating future use of this laboratory only. Trace metal results for the reporting period covered in this report were performed by a separate contractor.

4.3.2.2 Laboratory Surrogate Spikes

Laboratory surrogate spikes (LSS) were prepared by the addition of three surrogate standards (PCB congeners 14, 65 and 166) to every sample processed. The surrogate standard recovery was used to track the recovery of the analytes of interest in the individual sites samples, and was used to assess overall laboratory accuracy. The MQO acceptance criterion for the average recovery of the three spiked surrogate standards was 50-130%, and 98% of the 458 samples met this acceptance criterion. An additional requirement was that 2/3 of the three surrogates must yield $\geq 50\%$ and $\leq 130\%$ recovery, and 99% of the samples met these acceptance criteria. Control charts of lab surrogate spikes are presented in Figures 4.0-4.2. The control charts show the outlying values for each individual surrogate spike. The mean percent recoveries ± one standard deviation computed for 458 samples processed through the reporting period were:

PCB 14: 95 ± 29.5%
PCB 65: 78 ± 16.5%
PCB 166: 90 ± 18.5%

A detailed breakdown of the three surrogate results is presented below:

Total number of samples: 458
Number of samples with average recovery ≥ 50% and ≤130% recovery: 449 (98%)
Number of samples with 2/3 of surrogate spikes ≥ 50% and ≤130% recovery: 451 (98.5%)
Number of samples with 3/3 of surrogate spikes ≥ 50% and ≤130% recovery: 404 (88.2%)
Number of samples with PCB 14 >50% and ≤130% recovery: 436 (95.2%)
Number of samples with PCB 65 >50% and ≤130% recovery: 431 (94.1%)
Number of samples with PCB 166 >50% and ≤130% recovery: 446 (97.4%)

4.3.2.3 Laboratory Matrix Spikes

Individual analyte recovery was determined from the laboratory matrix spikes (LMS). These data were used to assess analyte specific laboratory accuracy. Recovery data for 56 individual analytes are listed in Table 4.4. Analyte-specific control charts allow for monitoring the effects of method variables over time. Control charts for the LMS are presented in Appendix A. Different symbols were used for each matrix on the control chart plots in Appendix A to allow for monitoring matrix-specific differences. Matrix-specific LMS recovery will be available in future QA reports. The MQO acceptance criterion required mean recoveries of 50-130% for all LMS samples and 70% of the individual analytes. These set points were selected as the upper and lower control lines on the individual analyte control charts in Appendix A.

4.3.2.4 Laboratory and Field Matrix Blanks

Matrix-specific field blanks (FB) were used to assess site or matrix interferences, which would yield false positive results or otherwise bias the data. A summary of the matrix-specific FB data is shown in Table 4.2. The MQO acceptance criteria for FBs require each analyte to be <LOD. Since the LODs were only recently computed, the evaluation of FB data meeting the acceptance criteria will be provided with future data reports.

Matrix-specific laboratory blanks (LB) can also be used to assess laboratory method or matrix interferences that would yield false positive results or otherwise bias the data. The LB data are shown in Table 4.5. The MQO acceptance criteria for LBs require each analyte to be <MDL or <IDL when no MDL is available. Since the IDLs were recently computed, the evaluation of LB data will be provided with future data reports.

Analysis of quartz fiber filter (QFF) blanks (both LB and FB) resulted in high background levels for some analytes and their use was discontinued. Particulate results at the Eagle Harbor site only where QFF were used were not adversely affected since the total suspended particulate (TSP)/total organic carbon (TOC) glass fiber filter samples (GFF) were used for organic analyses during this sampling period. Only GFF were used for all other sites. Sampling protocols were modified in early 1992 to precondition the GFFs at 450°C to eliminate potential contaminants. Summary data for QFF FBs and LBs are presented in Appendix D for reference use only. The data were not used for calculation of LODs or other QA/QC parameters.

4.3.2.5 Analysis by a Separate Laboratory

Confirmation or reanalysis of selected samples was performed by the Illinois Department of Energy and Natural Resources Hazardous Materials Laboratory (HML), Champaign, IL. Gas chromatography-mass spectroscopy (GC-MS) was used on selected samples to 1) confirm that target analytes were present, and 2) to confirm that the analytes were present at the reported levels. Analysis by a separate laboratory provided for analytical confirmation when outlying data points were found. A

positive interference was suspected for some samples yielding abnormally high results. In some instances, a positive interference was identified. The results of these analyses are being compiled and will be reported in subsequent reports.

4.4 **Representativeness**

Representativeness expresses the degree to which data accurately and precisely represent characteristics of a population, parameter, variations at a sampling point, a process condition, or an environmental condition. Sampling sites were selected on or near the Lakeshore so as to be free from local sources of contamination and representative of regional background concentrations of the target compounds. Comparison of data within and between sampling sites could, therefore, yield information useful for evaluation of representativeness criteria for this project. A brief description of the U.S. IADN sampling sites follows:

The **Eagle Harbor** IADN site is located at a Michigan Department of Natural Resources (DNR) boat launching facility about 100 meters (m) from Lake Superior, one kilometer (km) east of the town of Eagle Harbor, MI, on the Keweenaw peninsula. There are trees between the lake and the site and a few boat storage buildings near the site on DNR property. The nearest residence is about 300 m to the east. The site is served by an unpaved county road. The surrounding area is mostly wooded with a few summer cabins and it receives moderate use during the tourist season (June-August) and very light use during the rest of the year. The only pollution sources within 40 km are private residences, small commercial establishments, and two-lane state highways with light traffic. The nearest urban area is Houghton-Hancock about 50 km to the southwest. Sources of atmospheric deposition there include an airport, shipping activities, power plants, copper recycling, and some mining-related industry, as well as typical urban sources. This site is also a GLAD network site.

The **Sturgeon Point** IADN site is located at the Erie Company Water Authority's Sturgeon Point intake plant near Evans Center, NY. It is about 25 km southwest of Buffalo in an open field about 100 m from Lake Erie. Access is by a paved plant road used only by plant employees. The surrounding area contains a mix of residential, agricultural, and commercial development with no sources other than the intake plant closer than 1 km to the site. Major pollution sources within 40 km include a large power plant about 20 km southwest at Dunkirk, NY, the NY throughway 10 km to the south, and numerous steel and chemical industry sources about 20 km to the northeast in Lakawanna, NY. In addition, the city of Buffalo, NY, has many urban and industrial sources. This site is also a GLAD network site.

The **Sleeping Bear** IADN site is located about 5 km south of Empire, MI, and 1 km west of Michigan route 22, just south of Esch Road. It is on property that is part of Sleeping Bear Dunes National Lakeshore operated by the National Park Service. The site is an open grassy field on a secondary dune about 100 m above and 1 km east of Lake Michigan. The surrounding area contains wooded areas, agriculture (small fruits), and some summer cottages. It receives moderate use during the tourist season (May-October) and light use at other times. There are residences and farms about 0.5 km from the site. The closest urban area is Traverse City, MI about 50 km to the east. Traverse City has very little industry but has the usual mix of urban sources. This site is also a GLAD network site.

Representativeness for this project was also a measure of the parameter variation at a sampling point and was evaluated by collecting random duplicate samples. The precision data from the collocated samples presented in section 4.2.1 and on Table 4.3 reflect the representativeness of the sampling system. A review of the site results in the data report provides information for comparisons between sampling sites. The data require a detailed review to make decisions

concerning sampling frequency and the number of sites required to achieve representative data. The site data are presented in Tables 8-11 in the IADN data report (Gatz et al., 1994).

The sampling, handling and analysis protocols were selected to be consistent with those used by other U.S. and Canadian researchers whenever practical. This allowed for the comparison of ISWS data generated in this project with data from previous studies and from Canadian researchers.

Site samples were analyzed in their entirety; therefore, subsampling and sample homogeneity were not a concern for this phase of the project.

4.5 Completeness

Completeness is the measure of the number of samples obtained compared to the number expected to be obtained under normal conditions. The completeness MQO acceptance criteria was 90% for sampling and 95% for laboratory data reported for each sample collected. Based on site sampling frequencies and allowing for sample compositing (monthly filter composites), the target number of samples/year/site not including collocated duplicate samples was: 25 for vapor cartridges; 12 for particulate filters; and 13 for precipitation. Sample results from the four sites through December, 1992 yielded the following completeness statistics:

All Sites

	Target # of samples	*Actual # of samples*	*Percent completeness (sampling and laboratory)*
Vapor cartridge	158	175	111
Particulate filter	76	75	99
Precipitation	77	82	106

Point Petre

	Target # of samples	*Actual # of samples*	*Percent completeness (sampling and laboratory)*
Vapor cartridge	48	55	115
Particulate filter	23	19	83
Precipitation	24	26	110

Eagle Harbor

	Target # of samples	*Actual # of samples*	*Percent completeness (sampling and laboratory)*
Vapor cartridge	53	60	113
Particulate filter	25	30	120
Precipitation	27	29	107

Sturgeon Point

	Target # of samples	*Actual # of samples*	*Percent completeness (sampling and laboratory)*
Vapor cartridge	28	29	103
Particulate filter	14	13	93
Precipitation	13	13	100

Sleeping Bear

	Target # of samples	*Actual # of samples*	*Percent completeness (sampling and laboratory)*
Vapor cartridge	26	28	108
Particulate filter	13	12	92
Precipitation	12	13	108

Initial start-up at all sites required sampling at increased frequencies. This resulted in completeness levels over 100%.

4.6 Comparability

Comparability expresses the confidence level with which data sets can be compared. The data should be comparable within and between sites.

4.6.1 Comparability within Sites

Within site data comparability was assured by maintaining the same procedures throughout the duration of the project within reason. When a procedure or a laboratory method was modified or changed, a comparison was made to verify that the data were identical, more precise or more accurate than those previously obtained. Changes to SOPs required a discussion of the change and its impact on the study. QA and QC samples allowed for the laboratory and sampling performance to be monitored over the duration of the project.

4.6.2 Comparability between Sites

Between site comparability was assured by using sampling and analysis methods based on procedures employed with previous atmospheric deposition projects within the Great Lakes basin (Sweet et al., 1993). Data representativeness and comparability were also assured by using sampling, handling, and analysis protocols as similar to those used by other U.S. and Canadian researchers as practical.

The Canadian station at Point Petre served as a site for sampling equipment from both the ISWS and Canadian researchers. Samples collected at this site allowed for the comparison of methods and sampling protocols between groups. Since the first data reports are now being generated by IADN participants, insufficient data are currently available for comparability determinations from this site. Comparability data from the Point Petre site will be reported in future QA reports.

Participation in the binational interlaboratory studies also provided comparability data for sample preparation and analytical methods employed by different researchers within the IADN.

Figure 4.0 Surrogate recovery control chart for PCB congener 14

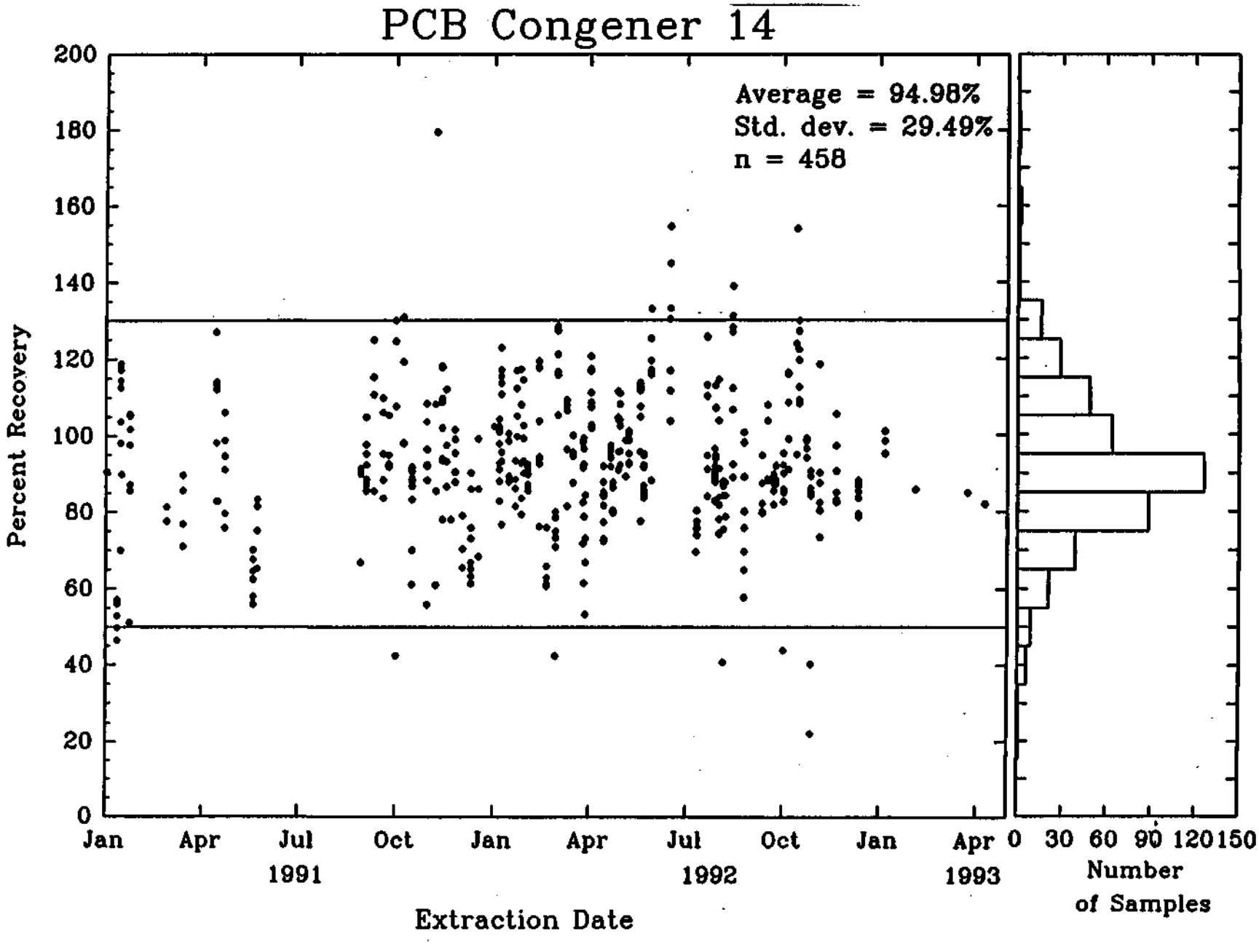

Figure 4.1 Surrogate recovery control chart for PCB congener 65

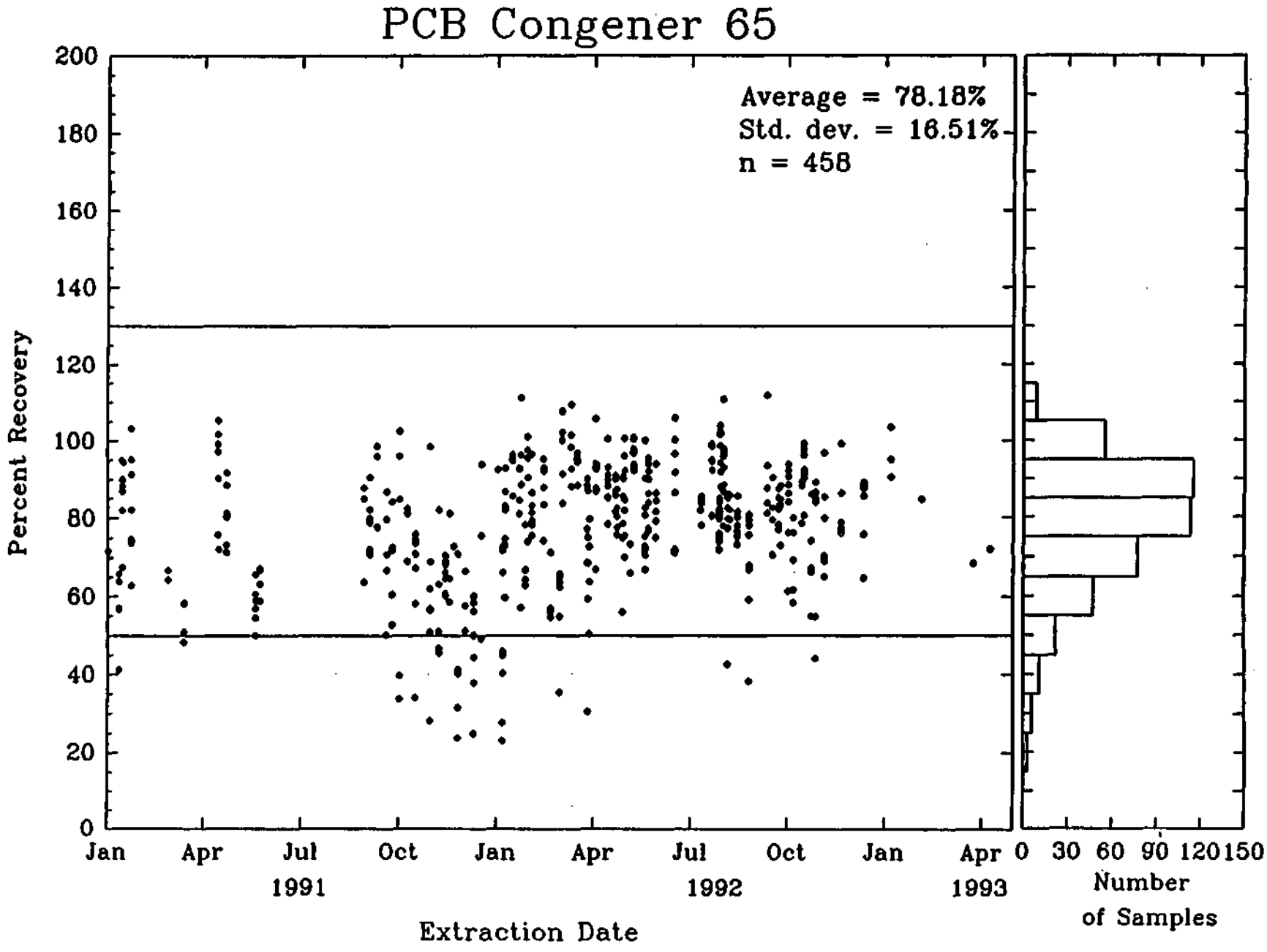

Figure 4.2 Surrogate recovery control chart for PCB congener 166

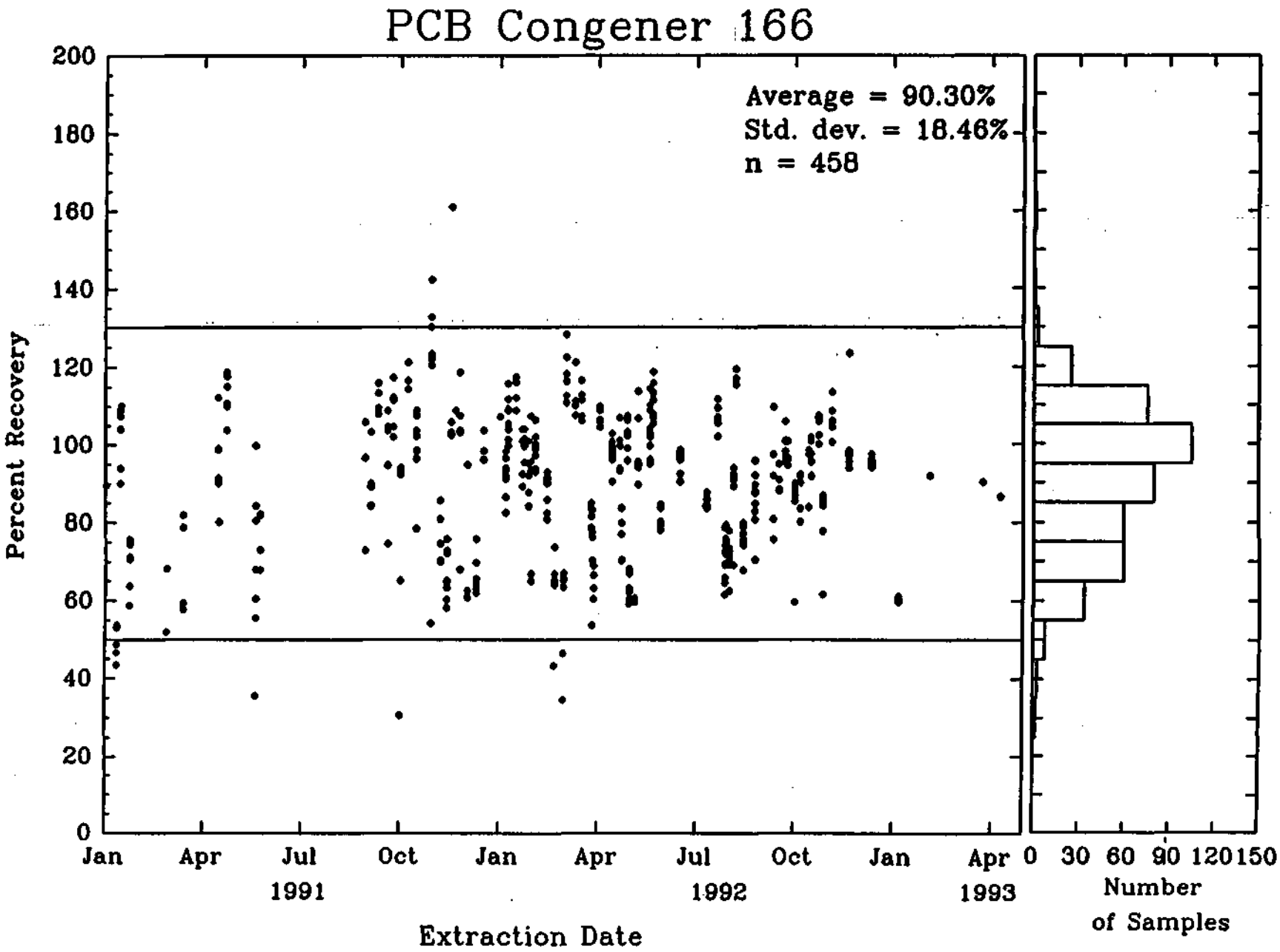

Table 4.0
Measurement Quality Objectives

Parameter	Sample Type	Frequency	Acceptance Criteria
PCB			
Precision	CFD	1/sampling set/Master site	RPD[a] = ± 100% <5 x LOD < ±50%
	LSS	1/sample processed	<2SD of target
	LMS	1/laboratory set	<2SD
Accuracy	FB	1/month/site/matrix	<LOD (LOD = mean + 3 σ FB)
	LSS	1/sample	50 - 130 % recovery
	LMS	1/laboratory set	50 - 130 % recovery
	GC/MS Confirmation	variable as needed	Confirm target analytes
	Interlab. comparisons	variable as available	To be determined
Completeness	Field samples	na	>90%
	Laboratory samples	na	>95%
LOD	Field samples	updated 1/yr	as total ng collected on matrix: individ. congener = 0.05 - 50 ng; total = 10-50 ng (varies with matrix)
MDL	LB/LMS	min 1/yr	3σ
Organochlorine Pesticides			
Precision	CFD	1/sampling set/Master site	RPD = ± 100% <5 x LOD < ±50%
	LSS	1/sample processed	<2SD
	LMS	1/laboratory set	<2SD
Accuracy	FB	1/month/site/matrix	<LOD <(LOD = mean +3 σ FB)
	LSS	1/sample	50 - 130 % recovery
	LMS	1/laboratory set	50 - 130 % recovery
	GC/MS confirmation	variable as needed	Confirm target analytes
	Interlab. comparisons	variable as available	To be determined
Completeness	Field samples	na	>90%
	Laboratory samples	na	>95%
LOD	Field samples	updated 1/yr	0.1-25 ng for individual analyte collected on matrix (varies with matrix)
MDL	LB/LMS	min 1/yr	3σ
PAHs			
Precision	CFD	1/sampling set/Master site	RPD =± 100% <5 x LOD < ±50%
	LSS	1/sample processed	<2SD
	LMS	1/laboratory set	<2SD
Accuracy	FB	1/month/site/matrix	<LOD (LOD = mean + 3 σ FB)
	LSS	1/sample	50 - 130 % recovery
	LMS	1/laboratory set	50 - 130 % recovery
	Interlab. comparisons	variable as available	To be determined
Completeness	Field samples	na	>90%
	Laboratory samples	na	>95%
LOD	Field samples	updated 1/yr	(2-50 ng) for individual analyte collected on matrix (varies with matrix)
MDL	LB/LMS	min 1/yr	3σ
Wind Speed	factory calibration	Annually	
Precision			±5% (1-100 mph)
Accuracy			±5% (1-100 mph)
Completeness			95%
Wind Direction	compass reading	Annually	
Precision			±5°
Accuracy			±10°
Completeness			95%

Table 4.1
Instrument Detection Limit (IDL)
and Estimated Method Detection Limit (MDL)

Major PCB congeners	*IDL (pg)*[1]	*Est. MDL*[2] *vapor (pg/m3)*	*Est. MDL*[3] *particulate* (pg/m^3)	*Est. MDL*[4] *precipitation (ng/L)*	# *chlorine atoms*
Total PCBs	1.532	1.88	0.63	0.153	
6	0.054	0.07	0.02	0.005	***2***
17	0.026	0.03	0.01	0.003	3
18	0.023	0.03	0.01	0.003	3
21	NA	NA	NA	NA	3
22	0.102	0.13	0.04	0.010	3
33	0.030	0.04	0.01	0.003	3
43	0.045	0.05	0.02	0.004	4
44	0.241	0.30	0.10	0.024	4
49	0.054	0.07	0.02	0.005	4
52	0.034	0.04	0.01	0.003	4
53	0.017	0.02	0.01	0.002	4
66	0.049	0.06	0.02	0.005	4
74	0.048	0.06	0.02	0.005	4
81	0.031	0.04	0.01	0.003	4
87	0.048	0.06	0.02	0.005	5
95	0.017	0.02	0.01	0.002	5
99	0.032	0.04	0.01	0.003	5
101	0.024	0.03	0.01	0.002	5
110	0.022	0.03	0.01	0.002	5
118	0.070	0.09	0.03	0.007	5
119	NA	NA	NA	NA	5
149	0.055	0.07	0.02	0.006	6
5 + 8	0.171	0.21	0.07	0.017	2,2
16 + 32	0.035	0.04	0.01	0.004	3,3
28 + 31	0.124	0.15	0.05	0.012	3,3
37 + 42	0.036	0.04	0.01	0.004	3,4
47 + 48	0.030	0.04	0.01	0.003	4,4
56 + 60	0.077	0.09	0.03	0.008	4,4
70 + 76	0.063	0.08	0.03	0.006	4,4
84 + 92	0.042	0.05	0.02	0.004	5,5
138 + 163	0.065	0.08	0.03	0.006	6,6
41 +71 +64	0.083	0.10	0.03	0.008	4,4,4
105 + 132 + 153	0.113	0.14	0.05	0.011	5,6,6

[1] IDL = pg amount of analyte detected by the instrument (based on 1 ul injected); also equivalent to ng analyte found per sample

[2] est MDL (vapor) = IDL/815 m^3 * 1000

[3] est. MDL (particulate) = IDL/2450 m^3 * 1000

[4] est. MDL (precipitation) = IDL/10 L

Table 4.1 (concluded)

Polycyclic Aromatic Hydrocarbons	***IDL (pg)***	***Est. MDL vapor (pg/my)***	***Est. MDL particulate (pg/m3)***	***Est. MDL precipitation (ng/L)***	***# fused rings***
Acenaphthene	7.8	9.5	3.17	0.78	3
Acenaphthylene	7.0	8.6	2.85	0.70	3
Anthracene	10.8	13.2	4.39	1.08	3
Benzo(a)anthracene	7.4	9.1	3.03	0.74	4
Benzo(b)fluoranthene	6.7	8.2	2.74	0.67	5
Benzo(k)fluoranthene	10.0	12.3	4.09	1.00	5
Benzo(ghi)perylene	9.3	11.4	3.79	0.93	6
Benzo(a)pyrene	13.0	16.0	5.33	1.30	5
Chrysene	6.6	8.1	2.71	0.66	4
Dibenzo(ah)anthracene	13.3	16.3	5.43	1.33	5
Fluoranthene	8.6	10.6	3.53	0.86	4
Fluorene	7.3	8.9	2.96	0.73	3
Indeno(123,cd)pyrene	9.5	11.7	3.89	0.95	6
Phenanthrene	4.7	5.8	1.92	0.47	3
Pyrene	6.7	8.2	2.74	0.67	4
Pesticides					
p,p'-DDD	0.099	0.12	0.04	0.010	
p,p'-DDE	0.054	0.07	0.02	0.005	
p,p'-DDT	0.631	0.77	0.26	0.063	
Dieldrin	0.060	0.07	0.02	0.060	
Hexachlorobenzene	0.076	0.09	0.03	0.008	
a-HCH	0.169	0.21	0.07	0.017	
y-HCH	0.039	0.05	0.02	0.004	

Table 4.2 Limit of Detection (LOD) and Field Blank Statistics

All Cartridges (PUF & XAD)									
Analyte	*LOD (ng/matrix)*	*LOD (pg/m^3)*	*Std Dev (ng/matrix)*	*N*	*Non zero*	*Average (ng/matrix)*	*Median (ng/matrix)*	*Minimum (ng/matrix)*	*Maximum (ng/matrix)*
PCBs:									
5+8	12.3659	15.1729	3.5288	44	38	1.7794	0.781	0	22.311
6	0.7251	0.8897	0.2121	44	17	0.0886	0	0	1.213
16+32	2.7906	3.4240	0.8306	44	21	0.2985	0	0	5.038
17	2.4817	3.0450	0.714	44	36	0.3397	0.175	0	4.341
18	3.6028	4.4206	1.0461	44	35	0.4642	0.177	0	6.335
21	0.5906	0.7247	0.1856	44	3	0.0336	0	0	1.206
22	2.5422	3.1193	0.7645	44	13	0.2484	0	0	4.562
28+31	8.5987	10.5506	2.4973	44	31	1.1066	0.365	0	14.822
33	5.2543	6.4470	1.5379	44	29	0.6403	0.179	0	7.797
37+42	1.283	1.5742	0.3778	44	18	0.1494	0	0	2.243
41+71+64	2.0732	2.5438	0.6002	44	29	0.2725	0.078	0	3.093
43	0.2179	0.2674	0.0668	44	6	0.0173	0	0	0.378
44	2.9982	3.6788	0.8513	44	29	0.4441	0.188	0	4.826
47+48	2.4427	2.9972	0.7224	44	21	0.2753	0	0	3.998
49	1.5933	1.9550	0.4588	44	32	0.2168	0.0873	0	2.648
52	3.0422	3.7328	0.8862	44	37	0.3835	0.126	0	5.308
53	0.4142	0.5082	0.1256	44	10	0.0373	0	0	0.787
56+60	0.9441	1.1584	0.2725	44	23	0.1266	0.0445	0	1.686
66	1.3134	1.6115	0.3889	44	19	0.1465	0	0	2.428
70+76	2.2603	2.7734	0.6511	44	26	0.307	0.116	0	3.95
74	0.7061	0.8664	0.2076	44	18	0.0831	0	0	1.286
81	0.2299	0.2821	0.0547	44	33	0.0658	0.0692	0	0.279
84+92	1.3967	1.7137	0.4041	44	26	0.1844	0.0665	0	2.426
87	0.7897	0.9690	0.2242	44	22	0.1169	0	0	1.339
95	2.5615	3.1429	0.7442	44	34	0.3288	0.123	0	4.593
99	0.4987	0.6119	0.1417	44	26	0.0734	0.0379	0	0.857
101	1.6962	2.0812	0.4881	44	34	0.2316	0.115	0	3.04
105+132+153	1.5927	1.9542	0.44	44	32	0.2725	0.143	0	2.559
110	1.2891	1.5817	0.3596	44	37	0.2102	0.103	0	2.108
118	0.6096	0.7480	0.169	44	20	0.1024	0	0	0.863
119	0.1289	0.1582	0.0399	44	5	0.009	0	0	0.242
138+163	0.7391	0.9069	0.2019	44	25	0.1333	0.0561	0	1.063
149	1.3679	1.6784	0.3783	44	28	0.2329	0.104	0	1.675
TOTAL PCBs	76.3228	93.6476	21.5487	44	44	11.6765	5.4037	0.7728	132.7396

Table 4.2 Limit of Detection (LOD) and Field Blank Statistics (continued)

All Cartridges (PUF & XAD) continued									
Analyte	*LOD (ng/matrix)*	*LOD (pg/m^3)*	*Std Dev (ng/matrix)*	*N*	*Non zero*	*Average (ng/matrix)*	*Median (ng/matrix)*	*Minimum (ng/matrix)*	*Maximum (ng/matrix)*
PESTICIDES:									
p,p' DDD	1.2011	1.4737	0.3748	49	4	0.0765	0	0	2.378
p,p' DDE	0.8319	1.0207	0.2233	44	25	0.1617	0.09	0	1.05
p,p' DDT	2.5058	3.0746	0.7651	49	6	0.2105	0	0	4.51
DIELDRIN	1.9537	2.3972	0.5571	49	18	0.2824	0	0	2.44
HCB	1.5634	1.9183	0.3941	44	31	0.3808	0.29	0	1.383
a-HCH	3.4958	4.2893	1.0255	49	17	0.4193	0	0	5.7256
g-HCH	1.3415	1.6460	0.3955	49	14	0.1548	0	0	1.713
PAHs:									
ACENAPHTHENE	7.3	8.9571	2.1	38	8	0.8	0	0	8.7
ACENAPHTHYLENE	7.0	8.5890	2.0	38	8	0.8	0	0	9.0
ANTHRACENE	0	0	0	38	0	0	0	0	0
BENZO(a)ANTHRACENE	10.3	12.6380	2.9	38	8	1.3	0	0	9.2
BENZO(b)FLUORANTHENE	16.6	20.3681	4.8	38	7	2.0	0	0	18.8
BENZO(k)FLUORANTHENE	19.3	23.6810	5.6	38	6	2.2	0	0	20.7
BENZO(ghi)PERYLENE	13.1	16.0736	4.0	38	4	1.1	0	0	22.4
BENZO(a)PYRENE	11.5	14.1104	3.5	38	3	0.9	0	0	16.1
CHRYSENE	11.1	13.6196	3.2	38	8	1.4	0	0	10.1
DIBENZO(ah)ANTHRACENE	5.3	6.5031	1.7	38	1	0.2	0	0	10.3
FLUORANTHENE	21.3	26.1350	5.5	38	21	4.7	1.1	0	18.1
FLUORENE	21.8	26.7485	5.6	38	29	4.8	2.9	0	25.9
INDENO(123,cd)PYRENE	5.8	7.1166	1.8	38	2	0.3	0	0	10.2
PHENANTHRENE	79.8	97.9141	22.0	38	35	13.7	8.8	0	138.6
PYRENE	21.1	25.8896	5.7	38	17	3.8	0	0	26.8

Table 4.2 Limit of Detection (LOD) and Field Blank Statistics (continued)

All Cartridges (PUF & XAD)----outlier removed (TBCFB920526)									
Analyte	*LOD (ng/matrix)*	*LOD (pg/m^3)*	*Std Dev (ng/matrix)*	*N*	*Non zero*	*Average (ng/matrix)*	*Median (ng/matrix)*	*Minimum (ng/matrix)*	*Maximum (ng/matrix)*
PCBs:									
5+8	5.7932	7.1082	1.497	43	37	1.3019	0.781	0	6.94
6	0.4246	0.5210	0.1207	43	16	0.0624	0	0	0.551
16+32	1.3368	1.6402	0.3828	43	20	0.1883	0	0	2.045
17	1.2983	1.5930	0.3505	43	35	0.2466	0.175	0	1.872
18	1.8618	2.2844	0.5113	43	34	0.3277	0.177	0	2.829
21	0.5979	0.7336	0.1878	43	3	0.0343	0	0	1.206
22	1.2493	1.5329	0.367	43	12	0.1481	0	0	1.882
28+31	4.6954	5.7612	1.3025	43	30	0.7877	0.365	0	6.972
33	3.6848	4.5212	1.0702	43	28	0.4739	0.179	0	6.325
37+42	0.6772	0.8309	0.1921	43	17	0.1007	0	0	0.874
41+71+64	1.4461	1.7744	0.413	43	28	0.2069	0.078	0	2.306
43	0.1185	0.1454	0.0365	43	5	0.009	0	0	0.215
44	1.8823	2.3096	0.5133	43	28	0.3422	0.188	0	2.577
47+48	2.2596	2.7725	0.6752	43	20	0.234	0	0	3.998
49	0.9438	1.1580	0.2611	43	31	0.1603	0.0873	0	1.432
52	1.6096	1.9750	0.4468	43	36	0.269	0.126	0	2.518
53	0.159	0.1951	0.0463	43	9	0.0199	0	0	0.188
56+60	0.4629	0.5680	0.1241	43	22	0.0903	0.0445	0	0.471
66	0.5691	0.6983	0.1585	43	18	0.0934	0	0	0.638
70+76	1.1862	1.4555	0.3213	43	25	0.2222	0.116	0	1.196
74	0.325	0.3988	0.0899	43	17	0.0551	0	0	0.367
81	0.2294	0.2815	0.0549	43	32	0.0647	0.0692	0	0.279
84+92	0.7466	0.9161	0.2048	43	25	0.1322	0.0665	0	0.913
87	0.4469	0.5483	0.1194	43	21	0.0884	0	0	0.53
95	1.2419	1.5238	0.3374	43	33	0.2296	0.123	0	1.631
99	0.2731	0.3351	0.0726	43	25	0.0551	0.0379	0	0.286
101	0.8196	1.0056	0.2177	43	33	0.1663	0.115	0	1.048
105+132+153	1.0015	1.2288	0.2607	43	31	0.2193	0.143	0	1.009
110	0.7857	0.9640	0.2065	43	36	0.1661	0.103	0	0.995
118	0.4504	0.5526	0.1218	43	19	0.0847	0	0	0.421
119	0.1197	0.1469	0.0376	43	4	0.0069	0	0	0.242
138+163	0.5383	0.6605	0.1421	43	24	0.1117	0.0561	0	0.595
149	1.1229	1.3778	0.3078	43	27	0.1994	0.104	0	1.53
TOTAL PCBs	40.3377	49.4941	10.4922	43	43	8.8611	5.4037	0.7728	52.3568

Table 4.2 Limit of Detection (LOD) and Field Blank Statistics (continued)

All Cartridges (PUF & XAD) --with outlier removed (continued)									
Analyte	*LOD (ng/matrix)*	*LOD (pg/m^3)*	*3Std Dev (ng/matrix)*	*N*	*Non zero*	*Average (ng/matrix)*	*Median (ng/matrix)*	*Minimum (ng/matrix)*	*Maximum (ng/matrix)*
PESTICIDES:									
p,p' DDD	1.2143	1.4899	0.3787	48	4	0.0781	0	0	2.378
p,p' DDE	0.8394	1.0299	0.2246	43	25	0.1655	0.119	0	1.05
p,p' DDT	2.3203	2.8470	0.7168	48	5	0.1698	0	0	4.51
DIELDRIN	1.6248	1.9936	0.4624	48	17	0.2375	0	0	2.31
HCB	1.5729	1.9299	0.3943	43	31	0.3897	0.308	0	1.383
a-HCH	2.321	2.8479	0.6707	48	16	0.3087	0	0	2.7575
g-HCH	1.3566	1.6632	0.3991	48	14	0.158	0	0	1.713
PAHs:									
ACENAPHTHENE	5.8	7.1166	1.7	37	7	0.6	0	0	7.5
ACENAPHTHYLENE	7.1	8.7117	2.1	37	8	0.8	0	0	9.0
ANTHRACENE	0	0	0	37	0	0	0	0	0
BENZO(a)ANTHRACENE	10.4	12.7607	3.0	37	8	1.3	0	0	9.2
BENZO(b)FLUORANTHENE	16.8	20.6135	4.8	37	7	2.1	0	0	18.8
BENZO(k)FLUORANTHENE	19.5	23.9264	5.7	37	6	2.3	0	0	20.7
BENZO(ghi)PERYLENE	13.3	16.3190	4.0	37	4	1.1	0	0	22.4
BENZO(a)PYRENE	11.6	14.2331	3.5	37	3	0.9	0	0	16.1
CHRYSENE	11.3	13.8650	3.2	37	8	1.5	0	0	10.1
DIBENZO(ah)ANTHRACENE	5.4	6.6258	1.7	37	1	0.2	0	0	10.3
FLUORANTHENE	19.7	24.1718	5.0	37	20	4.4	1.1	0	15.8
FLUORENE	17.8	21.5951	4.4	37	28	4.2	2.9	0	15.9
INDENO(123,cd)PYRENE	5.9	7.2393	1.8	37	2	0.3	0	0	10.2
PHENANTHRENE	29.8	36.5644	6.4	37	34	10.4	8.8	0	31.7
PYRENE	20.7	25.3988	5.6	37	16	3.6	0	0	26.8

Table 4.2 Limit of Detection (LOD) and Field Blank Statistics (continued)

All PUF Cartridges									
Analyte	*LOD (ng/matrix)*	*LOD (pg/m^3)*	*Std Dev (ng/matrix)*	*N*	*Non zero*	*Average (ng/matrix)*	*Median (ng/matrix)*	*Minimum (ng/matrix)*	*Maximum (ng/matrix)*
PCBs:									
5+8	3.2258	3.9580	0.7827	34	28	0.8775	0.632	0	2.446
6	0.2178	0.2672	0.0629	34	8	0.029	0	0	0.258
16+32	0.6495	0.7969	0.1822	34	14	0.1027	0	0	0.792
17	0.5688	0.6979	0.1414	34	26	0.1446	0.101	0	0.55
18	0.7683	0.9427	0.1961	34	25	0.18	0.108	0	0.69
21	0.6782	0.8321	0.2115	34	3	0.0435	0	0	1.206
22	0.4165	0.5110	0.1221	34	6	0.05	0	0	0.444
28+31	1.8436	2.2621	0.4868	34	21	0.3832	0.178	0	1.639
33	1.0256	1.2584	0.276	34	19	0.1974	0.0555	0	1.044
37+42	0.5634	0.6913	0.1663	34	9	0.0643	0	0	0.874
41+71+64	0.4898	0.6010	0.1293	34	21	0.1017	0.0653	0	0.5
43	0	0	0	34	0	0	0	0	0
44	1.0333	1.2679	0.2807	34	19	0.191	0.0514	0	1.153
47+48	2.4802	3.0432	0.748	34	14	0.236	0	0	3.998
49	0.3314	0.4066	0.0847	34	22	0.077	0.0513	0	0.347
52	0.507	0.6221	0.1271	34	27	0.1255	0.0984	0	0.531
53	0.0918	0.1126	0.0277	34	4	0.0085	0	0	0.137
56+60	0.3061	0.3756	0.0835	34	14	0.0554	0	0	0.277
66	0.2739	0.3361	0.0777	34	10	0.0407	0	0	0.286
70+76	0.5576	0.6842	0.1502	34	16	0.1068	0	0	0.477
74	0.2279	0.2796	0.0656	34	9	0.031	0	0	0.219
81	0.1852	0.2272	0.0435	34	23	0.0545	0.065	0	0.147
84+92	0.4816	0.5909	0.1352	34	16	0.0759	0	0	0.692
87	0.2799	0.3434	0.0759	34	13	0.0522	0	0	0.265
95	0.4614	0.5661	0.1161	34	24	0.1129	0.0835	0	0.372
99	0.2558	0.3139	0.0701	34	17	0.0455	0	0	0.286
101	0.3464	0.4250	0.0849	34	24	0.0915	0.081	0	0.327
105+132+153	0.7578	0.9298	0.1986	34	24	0.1617	0.11	0	0.86
110	0.6603	0.8102	0.1803	34	27	0.1192	0.0742	0	0.995
118	0.3109	0.3815	0.0875	34	10	0.0483	0	0	0.307
119	0.1334	0.1637	0.0421	34	1	0.0071	0	0	0.242
138+163	0.4303	0.5280	0.1159	34	16	0.0823	0	0	0.39
149	1.1384	1.3968	0.324	34	18	0.1661	0.0259	0	1.53
TOTAL PCBs	24.1052	29.5769	6.0182	34	34	6.0505	4.1038	0.7728	33.7603

Table 4.2 Limit of Detection (LOD) and Field Blank Statistics (continued)

All PUF Cartridges (continued)									
Analyte	*LOD (ng/matrix)*	*LOD (pg/m^3)*	*Std Dev (ng/matrix)*	*N*	*Non zero*	*Average (ng/matrix)*	*Median (ng/matrix)*	*Minimum (ng/matrix)*	*Maximum (ng/matrix)*
PESTICIDES:									
p,p' DDD	1.2765	1.5663	0.402	36	2	0.0703	0	0	2.378
p,p' DDE	0.8923	1.0948	0.2415	34	19	0.1676	0.09	0	1.05
p,p' DDT	1.1684	1.4336	0.3567	36	3	0.098	0	0	1.745
DIELDRIN	0.9848	1.2083	0.2855	36	10	0.1282	0	0	1.11
HCB	1.6555	2.0313	0.4188	34	24	0.399	0.308	0	1.383
a-HCH	1.5764	1.9342	0.4811	36	7	0.133	0	0	2.7575
g-HCH	1.3279	1.6293	0.3959	36	7	0.14	0	0	1.713
PAHs:									
ACENAPHTHENE	5.8	7.1166	1.7	37	7	0.6	0	0	7.5
ACENAPHTHYLENE	7.1	8.7117	2.1	37	8	0.8	0	0	9.0
ANTHRACENE	0	0	0	37	0	0	0	0	0
BENZO(a)ANTHRACENE	10.4	12.7607	3.0	37	8	1.3	0	0	9.2
BENZO(b)FLUORANTHENE	16.8	20.6135	4.8	37	7	2.1	0	0	18.8
BENZO(k)FLUORANTHENE	19.5	23.9264	5.7	37	6	2.3	0	0	20.7
BENZO(ghi)PERYLENE	13.3	16.3190	4.0	37	4	1.1	0	0	22.4
BENZO(a)PYRENE	11.6	14.2331	3.5	37	3	0.9	0	0	16.1
CHRYSENE	11.3	13.865	3.2	37	8	1.5	0	0	10.1
DIBENZO(ah)ANTHRACENE	5.4	6.6258	1.7	37	1	0.2	0	0	10.3
FLUORANTHENE	19.7	24.1718	5.0	37	20	4.4	1.1	0	15.8
FLUORENE	17.6	21.5951	4.4	37	28	4.2	2.9	0	15.9
INDENO(123,cd)PYRENE	5.9	7.2393	1.8	37	2	0.3	0	0	10.2
PHENANTHRENE	29.8	36.5644	6.4	37	34	10.4	8.8	0	31.7
PYRENE	20.7	25.3988	5.6	37	16	3.6	0	0	26.8

Table 4.2 Limit of Detection (LOD) and Field Blank Statistics (continued)

All XAD-2 Cartridges									
Analyte	*LOD (ng/matrix)*	*LOD (pg/m^3)*	*Std Dev (ng/matrix)*	*N*	*Non zero*	*Average (ng/matrix)*	*Median (ng/matrix)*	*Minimum (ng/matrix)*	*Maximum (ng/matrix)*
PCBs:									
5+8	25.4475	31.2239	6.8672	10	10	4.8458	2.159	0.566	22.311
6	1.4617	1.7935	0.3901	10	9	0.2913	0.104	0	1.213
16+32	5.9306	7.2768	1.6554	10	7	0.9643	0.387	0	5.038
17	5.0976	6.2547	1.3648	10	10	1.0031	0.415	0.142	4.341
18	7.4563	9.1488	2.0085	10	10	1.4306	0.581	0.177	6.335
21	0	0	0	10	0	0	0	0	0
22	5.42	6.6503	1.499	10	7	0.923	0.359	0	4.562
28+31	17.5583	21.5439	4.6639	10	10	3.5665	1.432	0.579	14.822
33	10.8137	13.2683	2.8891	10	10	2.1463	0.649	0.268	7.797
37+42	2.5548	3.1347	0.7053	10	9	0.4386	0.157	0	2.243
41+71+64	4.2263	5.1856	1.1243	10	8	0.8532	0.34	0	3.093
43	0.4744	0.5821	0.1326	10	6	0.0765	0.0141	0	0.378
44	5.8207	7.1420	1.5054	10	10	1.3044	0.51	0.334	4.826
47+48	2.4575	3.0153	0.6827	10	7	0.4092	0.128	0	2.052
49	3.207	3.9350	0.8382	10	10	0.6922	0.291	0.135	2.648
52	6.2636	7.6854	1.6675	10	10	1.261	0.486	0.238	5.308
53	0.8914	1.0937	0.252	10	6	0.1352	0.0524	0	0.787
56+60	1.9105	2.3442	0.514	10	9	0.3685	0.213	0	1.686
66	2.7397	3.3616	0.7445	10	9	0.5062	0.267	0	2.428
70+76	4.499	5.5202	1.1704	10	10	0.9877	0.402	0.236	3.95
74	1.4472	1.7757	0.3956	10	9	0.2604	0.114	0	1.286
81	0.3301	0.4050	0.0753	10	10	0.1041	0.0782	0.0306	0.279
84+92	2.7935	3.4276	0.7468	10	10	0.5531	0.203	0.112	2.426
87	1.5401	1.8897	0.401	10	9	0.3369	0.194	0	1.339
95	5.2623	6.4568	1.3998	10	10	1.0628	0.421	0.279	4.593
99	0.9647	1.1837	0.2655	10	9	0.1681	0.0744	0	0.857
101	3.4662	4.2530	0.9193	10	10	0.7081	0.302	0.195	3.04
105+132+153	3.0151	3.6995	0.7886	10	8	0.6491	0.425	0	2.559
110	2.3918	2.9347	0.624	10	10	0.5196	0.234	0.135	2.108
118	1.0451	1.2823	0.2529	10	10	0.2864	0.209	0.0743	0.863
119	0.1195	0.1466	0.0345	10	4	0.0157	0	0	0.103
138+163	1.3032	1.5990	0.3321	10	9	0.3068	0.154	0	1.063
149	1.9442	2.3855	0.4946	10	10	0.4603	0.255	0.138	1.675
TOTAL PCBs	153.8134	188.7281	41.0027	10	10	30.805	12.4902	5.87	132.7396

Table 4.2 Limit of Detection (LOD) and Field Blank Statistics (continued)

All XAD-2 Cartridges (continued)									
Analyte	*LOD (ng/matrix)*	*LOD (pg/m^3)*	*Std Dev (ng/matrix)*	*N*	*Non zero*	*Average (ng/matrix)*	*Median (ng/matrix)*	*Minimum (ng/matrix)*	*Maximum (ng/matrix)*
PESTICIDES:									
p,p' DDD	1.0397	1.2757	0.3153	13	2	0.0935	0	0	1.096
p,p' DDE	0.6395	0.7847	0.1659	10	6	0.1416	0.0829	0	0.46
p,p' DDT	4.6993	5.7660	1.3924	13	3	0.522	0	0	4.51
DIELDRIN	3.3518	4.1126	0.8808	13	8	0.7093	0.445	0	2.44
HCB	1.2976	1.5921	0.3262	10	7	0.319	0.26	0	0.85
a-HCH	6.186	7.5902	1.6579	13	10	1.2121	0.465	0	5.7256
g-HCH	1.4681	1.8013	0.4241	13	7	0.1957	0.0477	0	1.48
PAHs:									
ACENAPHTHENE				1	1	8.7	8.7	8.7	8.7
ACENAPHTHYLENE				1	0	0	0	0	0
ANTHRACENE				1	0	0	0	0	0
BENZO(a)ANTHRACENE				1	0	0	0	0	0
BENZO(b)FLUORANTHENE				1	0	0	0	0	0
BENZO(k)FLUORANTHENE				1	0	0	0	0	0
BENZO(ghi)PERYLENE				1	0	0	0	0	0
BENZO(a)PYRENE				1	0	0	0	0	0
CHRYSENE				1	0	0	0	0	0
DIBENZO(ah)ANTHRACENE				1	0	0	0	0	0
FLUORANTHENE				1	1	18.1	18.1	18.1	18.1
FLUORENE				1	1	15.9	25.9	25.9	25.9
INDENO(123,cd)PYRENE				1	0	0	0	0	0
PHENANTHRENE				1	1	138.6	138.6	138.6	138.6
PYRENE				1	1	11.1	11.1	11.1	11.1

Table 4.2 Limit of Detection (LOD) and Field Blank Statistics (continued)

XAD-2 Cartridge with outlier removed (TBCFB 920526)									
Analyte	*LOD (ng/matrix)*	*LOD (pg/m^3)*	*Std Dev (ng/matrix)*	*N*	*Non zero*	*Average (ng/matrix)*	*Median (ng/matrix)*	*Minimum (ng/matrix)*	*Maximum (ng/matrix)*
PCBs:									
5+8	10.2876	12.6228	2.4607	9	9	2.9052	2.159	0.566	6.94
6	0.7937	0.9739	0.2016	9	8	0.1889	0.104	0	0.551
16+32	2.6928	3.3040	0.727	9	6	0.5116	0.387	0	2.045
17	2.4838	3.0476	0.6172	9	9	0.6322	0.415	0.142	1.872
18	3.6304	4.4545	0.9149	9	9	0.8856	0.581	0.177	2.829
21	0	0	0	9	0	0	0	0	0
22	2.6194	3.2140	0.7002	9	6	0.5186	0.359	0	1.882
28+31	9.0123	11.0580	2.2321	9	9	2.3158	1.432	0.579	6.972
33	7.8956	9.6879	2.1257	9	9	1.5184	0.649	0.268	6.325
37+42	0.9613	1.1795	0.241	9	8	0.2382	0.157	0	0.752
41+71+64	3.0344	3.7232	0.81	9	7	0.6043	0.34	0	2.306
43	0.2723	0.3341	0.0764	9	5	0.043	0.0141	0	0.215
44	3.3201	4.0737	0.8023	9	9	0.9131	0.51	0.334	2.577
47+48	1.2187	1.4953	0.3306	9	6	0.2267	0.128	0	0.925
49	1.8256	2.2400	0.4502	9	9	0.4748	0.291	0.135	1.432
52	3.1512	3.8665	0.7799	9	9	0.8113	0.486	0.238	2.518
53	0.2951	0.3621	0.0774	9	5	0.0628	0.0524	0	0.188
56+60	0.7393	0.9071	0.1724	9	8	0.2221	0.213	0	0.471
66	0.9918	1.2169	0.233	9	8	0.2926	0.267	0	0.638
70+76	1.9638	2.4096	0.435	9	9	0.6585	0.402	0.236	1.196
74	0.5006	0.6142	0.118	9	8	0.1465	0.114	0	0.367
81	0.3443	0.4225	0.0803	9	9	0.1033	0.0782	0.0306	0.279
84+92	1.2308	1.5102	0.2952	9	9	0.345	0.203	0.112	0.913
87	0.7122	0.8739	0.1622	9	8	0.2255	0.194	0	0.53
95	2.2717	2.7874	0.5337	9	9	0.6705	0.421	0.279	1.631
99	0.3274	0.4017	0.0785	9	8	0.0916	0.0744	0	0.232
101	1.4581	1.7891	0.3363	9	9	0.449	0.302	0.195	1.048
105+132+153	1.5536	1.9063	0.3722	9	7	0.4368	0.425	0	1.009
110	1.0101	1.2394	0.2223	9	9	0.3431	0.234	0.135	0.806
118	0.6561	0.8050	0.1446	9	9	0.2223	0.209	0.0743	0.421
119	0.0455	0.0558	0.0131	9	3	0.006	0	0	0.0375
138+163	0.7944	0.9747	0.1905	9	8	0.2227	0.154	0	0.595
149	0.9835	1.2067	0.2194	9	9	0.3253	0.255	0.138	0.784
TOTAL PCBs	70.6978	86.7458	17.0729	9	9	19.479	12.4902	5.87	52.3568

Table 4.2 Limit of Detection (LOD) and Field Blank Statistics (continued)

XAD-2 Cartridge with outlier removed (continued)									
Analyte	*LOD (ng/matrix)*	*LOD (pg/m^3)*	*Std Dev (ng/matrix)*	*N*	*Non zero*	*Average (ng/matrix)*	*Median (ng/matrix)*	*Minimum (ng/matrix)*	*Maximum (ng/matrix)*
PESTICIDES:									
p,p' DDD	1.0887	1.3358	0.3291	12	2	0.1013	0	0	1.096
p,p' DDE	0.6615	0.8117	0.168	9	6	0.1574	0.126	0	0.46
p,p' DDT	4.4567	5.4683	1.357	12	2	0.3855	0	0	4.51
DIELDRIN	2.7503	3.3746	0.7283	12	7	0.5651	0.393	0	2.31
HCB	1.3279	1.6293	0.3245	9	7	0.3544	0.29	0	0.85
a-HCH	3.5709	4.3815	0.9116	12	9	0.836	0.3199	0	2.1471
g-HCH	1.5316	1.8793	0.4398	12	7	0.212	0.0477	0	1.48
PAHs:									
ACENAPHTHENE				0					
ACENAPHTHYLENE				0					
ANTHRACENE				0					
BENZO(a)ANTHRACENE				0					
BENZO(b)FLUORANTHENE				0					
BENZO(k)FLUORANTHENE				0					
BENZO(ghi)PERYLENE				0					
BENZO(a)PYRENE				0					
CHRYSENE				0					
DIBENZO(ah)ANTHRACENE				0					
FLUORANTHENE				0					
FLUORENE				0					
INDENO(123,cd)PYRENE				0					
PHENANTHRENE				0					
PYRENE				0					

Table 4.2 Limit of Detection (LOD) and Field Blank Statistics (continued)

Precipitation-XAD-2									
Analyte	*LOD (ng/matrix)*	*LOD (ng/L)*	*Std Dev (ng/matrix)*	*N*	*Non zero*	*Average (ng/matrix)*	*Median (ng/matrix)*	*Minimum (ng/matrix)*	*Maximum (ng/matrix)*
PCBs:									
5+8	0.6203	0.0620	0.1748	27	13	0.0959	0	0	0.77
6	0.1749	0.0175	0.0517	27	6	0.0196	0	0	0.239
16+32	0.4584	0.0458	0.1364	27	14	0.0492	0.0127	0	0.702
17	0.1704	0.0170	0.0481	27	14	0.026	0.0141	0	0.227
18	0.1932	0.0193	0.0506	27	20	0.0413	0.0319	0	0.234
21	0.043	0.0043	0.0133	27	2	0.0029	0	0	0.0675
22	0.9443	0.0944	0.2873	27	7	0.0824	0	0	1.337
28+31	0.7299	0.0730	0.2072	27	10	0.1081	0	0	0.758
33	0.6101	0.0610	0.1628	27	24	0.1216	0.0819	0	0.813
37+42	0.2253	0.0225	0.0622	27	12	0.0386	0	0	0.244
41+71+64	0.2213	0.0221	0.0578	27	17	0.0476	0.033	0	0.246
43	0	0	0	27	0	0	0	0	0
44	0.4136	0.0414	0.1129	27	14	0.0749	0.0277	0	0.383
47+48	0.1411	0.0141	0.044	27	2	0.0091	0	0	0.224
49	0.2303	0.0230	0.0615	27	18	0.0457	0.0223	0	0.211
52	0.3162	0.0316	0.0814	27	24	0.0718	0.0526	0	0.315
53	0.0208	0.0021	0.0065	27	1	0.0012	0	0	0.0333
56+60	0.5233	0.0523	0.148	27	16	0.0792	0.0333	0	0.616
66	0.3442	0.0344	0.1017	27	6	0.0389	0	0	0.452
70+76	0.6008	0.0601	0.1634	27	21	0.1105	0.065	0	0.709
74	0.1634	0.0163	0.0483	27	8	0.0184	0	0	0.23
81	0.1654	0.0165	0.0326	27	24	0.0675	0.0667	0	0.13
84+92	0.4703	0.0470	0.1279	27	19	0.0864	0.0421	0	0.46
87	0.3534	0.0353	0.1054	27	4	0.037	0	0	0.378
95	0.5133	0.0513	0.1427	27	18	0.0852	0.037	0	0.553
99	0.1447	0.0145	0.0417	27	13	0.0194	0	0	0.208
101	0.4529	0.0453	0.1225	27	23	0.0853	0.0468	0	0.513
105+132+153	1.6711	0.1671	0.4998	27	16	0.1717	0.0359	0	2.316
110	0.6617	0.0662	0.1802	27	22	0.121	0.0554	0	0.671
118	0.2794	0.0279	0.0745	27	14	0.0557	0.0354	0	0.242
119	0.1845	0.0185	0.0559	27	3	0.0168	0	0	0.258
138+163	0.6726	0.0673	0.1943	27	16	0.0895	0.024	0	0.798
149	0.2904	0.0290	0.0786	27	14	0.0544	0.0323	0	0.27
TOTAL PCBs	13.3612	1.3361	3.5663	27	27	2.6622	1.7013	0.3998	16.5069

Table 4.2 Limit of Detection (LOD) and Field Blank Statistics (continued)

Precipitation-XAD-2 (continued)									
Analyte	*LOD (ng/matrix)*	*LOD (ng/L)*	*3Std Dev (ng/matrix)*	*N*	*Non zero*	*Average (ng/matrix)*	*Median (ng/matrix)*	*Minimum (ng/matrix)*	*Maximum (ng/matrix)*
PESTICIDES:									
p,p' DDD	0.0297	0.0030	0.0093	30	1	0.0016	0	0	0.0504
p,p' DDE	0.5857	0.0586	0.1737	27	12	0.0646	0	0	0.873
p,p' DDT	0.0697	0.0070	0.0214	30	2	0.0055	0	0	0.0858
DIELDRIN	1.2603	0.1260	0.3589	30	20	0.1833	0.156	0	1.97
HCB	0.8087	0.0809	0.2417	27	13	0.0833	0	0	1.207
a-HCH	3.8244	0.3824	1.1823	30	8	0.2772	0	0	6.3192
g-HCH	2.2678	0.2268	0.6842	30	12	0.215	0	0	3.21
PAHs:									
ACENAPHTHENE	3.4	0.3400	1.0	12	1	0.2	0	0	3.5
ACENAPHTHYLENE	0	0	0	12	0	0	0	0	0
ANTHRACENE	10.8	1.0800	3.3	12	1	0.9	0	0	11.0
BENZO(a)ANTHRACENE	2.3	0.2300	0.6	12	2	0.2	0	0	1.8
BENZO(b)FLUORANTHENE	22.0	2.2	6.5	12	2	2.4	0	0	21.0
BENZO(k)FLUORANTHENE	0	0	0	12	0	0	0	0	0
BENZO(ghi)PERYLENE	7.8	0.7800	2.4	12	1	0.6	0	0	7.9
BENZO(a)PYRENE	25.5	2.5500	7.6	12	2	2.6	0	0	25.0
CHRYSENE	3.2	0.3200	0.9	12	1	0.2	0	0	3.3
DIBENZO(ah)ANTHRACENE	10.2	1.0200	3.1	12	1	0.8	0	0	10.3
FLUORANTHENE	34.2	3.4200	9.3	12	5	6.1	0	0	28.4
FLUORENE	16.7	1.6700	4.7	12	4	2.6	0	0	13.8
INDENO(123,cd)PYRENE	10.1	1.0100	3.0	12	1	0.8	0	0	10.2
PHENANTHRENE	49.7	4.9700	13.6	12	9	8.8	4.	0	47.4
PYRENE	29.5	2.9500	8.1	12	4	4.9	0	0	20

Table 4.2 Limit of Detection (LOD) and Field Blank Statistics (continued)

Filter-Glass Fiber									
Analyte	*LOD (ng/matrix)*	*LOD (pg/m^3)*	*Std Dev (ng/matrix)*	*N*	*Non zero*	*Average (ng/matrix)*	*Median (ng/matrix)*	*Minimum (ng/matrix)*	*Maximum (ng/matrix)*
PCBs:									
5+8	0.243	0.0992	0.0658	10	4	0.0456	0	0	0.167
6	0.0523	0.0213	0.0158	10	1	0.0047	0	0	0.0476
16+32	0.1418	0.0579	0.0386	10	4	0.0258	0	0	0.0952
17	0.1006	0.0411	0.0222	10	8	0.0338	0.0361	0	0.0601
18	0.1823	0.0744	0.0478	10	7	0.0386	0.0236	0	0.153
21	0	0	0	10	0	0	0	0	0
22	0.196	0.0800	0.0494	10	6	0.0475	0.0448	0	0.124
28+31	0.7098	0.2897	0.1829	10	6	0.1611	0.122	0	0.511
33	0.28	0.1143	0.0533	10	10	0.1201	0.12	0.0326	0.186
37+42	0.1233	0.0503	0.0351	10	3	0.0178	0	0	0.1
41+71+64	0.6952	0.2838	0.1912	10	7	0.1214	0.082	0	0.617
43	0.275	0.1122	0.0833	10	1	0.025	0	0	0.25
44	0.3636	0.1484	0.1007	10	4	0.0615	0	0	0.23
47+48	0.1489	0.0608	0.0416	10	4	0.0241	0	0	0.109
49	0.1419	0.0579	0.0307	10	9	0.0496	0.0616	0	0.0849
52	0.1834	0.0749	0.045	10	7	0.0482	0.0427	0	0.112
53	0.4385	0.1790	0.1313	10	3	0.0444	0	0	0.398
56+60	0.3487	0.1423	0.0871	10	8	0.0873	0.0592	0	0.257
66	0.1163	0.0475	0.0338	10	2	0.0147	0	0	0.0902
70+76	1.5609	0.6371	0.4444	10	7	0.2275	0.0598	0	1.4
74	0.1029	0.0420	0.0278	10	4	0.0194	0	0	0.0702
81	0.172	0.0702	0.0325	10	9	0.0743	0.0749	0	0.114
84+92	0.3115	0.1271	0.0811	10	7	0.0681	0.0469	0	0.232
87	0.3875	0.1582	0.1093	10	3	0.0595	0	0	0.293
95	0.2926	0.1194	0.0762	10	8	0.0639	0.049	0	0.247
99	0.1474	0.0602	0.0395	10	5	0.0287	0	0	0.102
101	0.4202	0.1715	0.1032	10	10	0.1105	0.0564	0.0202	0.315
105+132+153	0.6886	0.2811	0.1915	10	5	0.114	0	0	0.523
110	0.676	0.2759	0.1798	10	8	0.1365	0.0691	0	0.557
118	0.9252	0.3776	0.25	10	5	0.175	0	0	0.654
119	0	0	0	10	0	0	0	0	0
138+163	0.7872	0.3213	0.2031	10	8	0.1777	0.113	0	0.551
149	0.9479	0.3869	0.2536	10	8	0.1868	0.0772	0	0.783
TOTAL PCBs	21.286	8.6882	5.4535	10	10	4.9253	2.382	0.7023	17.6937

Table 4.2 Limit of Detection (LOD) and Field Blank Statistics (continued)

Filter-Glass Fiber (continued)									
Analyte	**LOD (ng/matrix)**	**LOD (pg/m^3)**	**Std Dev (ng/matrix)**	**N**	**Non zero**	**Average (ng/matrix)**	**Median (ng/matrix)**	**Minimum (ng/matrix)**	**Maximum (ng/matrix)**
PESTICIDES:									
p,p' DDD	4.9203	2.0083	1.4963	11	2	0.4313	0	0	4.733
p,p' DDE	0.2396	0.0978	0.0627	10	5	0.0514	0	0	0.144
p,p' DDT	0.9706	0.3962	0.2787	11	4	0.1344	0	0	0.885
DIELDRIN	5.8871	2.4029	1.7004	11	3	0.7858	0	0	5.116
HCB	0.1451	0.0592	0.038	10	5	0.0309	0	0	0.0877
a-HCH	0.6447	0.2631	0.1786	11	4	0.1089	0	0	0.488
g-HCH	0.2919	0.1191	0.0865	11	2	0.0323	0	0	0.268
PAHs:									
ACENAPHTHENE	0	0	0	6	0	0	0	0	0
ACENAPHTHYLENE	0	0	0	6	0	0	0	0	0
ANTHRACENE	0	0	0	6	0	0	0	0	0
BENZO(a)ANTHRACENE	11.4	4.6531	3.2	6	2	1.5	0	0	7.4
BENZO(b)FLUORANTHENE	23.1	9.4286	6.6	6	2	3.3	0	0	14.9
BENZO(k)FLUORANTHENE	22.0	8.9796	6.2	6	2	3.4	0	0	13.4
BENZO(ghi)PERYLENE	18.1	7.3878	5.3	6	2	2.1	0	0	12.0
BENZO(a)PYRENE	0	0	0	6	0	0	0	0	0
CHRYSENE	17.0	6.9388	4.3	6	5	3.9	2.3	0	11.1
DIBENZO(ah)ANTHRACENE	0	0	0	6	0	0	0	0	0
FLUORANTHENE	37.3	15.2245	8.8	6	5	10.7	12.0	0	19.3
FLUORENE	11.4	4.6531	3.3	6	1	1.2	0	0	7.5
INDENO(123,cd)PYRENE	44.8	18.2857	12.6	6	3	6.8	0	0	28.1
PHENANTHRENE	43.7	17.8367	11.6	6	5	8.7	4.5	0	28.7
PYRENE	81.5	33.2653	22.2	6	5	14.9	9.6	0	54.6

Table 4.3
Sampling Precision

XAD-2 Cartridge:

Analyte	(1)	RSD	(2)	(3)	(4)	(5)
5+8	15	0.5311	11	0	4	1
6	14	0.5013	9	0	5	1
16+32	8	0.3478	6	0	2	1
17	15	0.48	11	0	4	1
18	15	0.3677	11	0	4	1
21	1		0	0	1	1
22	14	0.2962	13	0	1	0
28+31	14	0.3691	12	0	2	1
33	8	0.1486	8	0	0	0
37+42	15	0.2341	13	0	2	0
41+71+64	9	0.1833	8	0	1	0
43	8	0.4382	8	0	0	0
44	15	0.62	12	0	3	1
47+48	13	0.2572	12	0	1	0
49	15	0.2326	13	0	2	0
52	15	0.2143	13	0	2	0
53	10	0.252	2	0	8	1
56+60	15	0.2159	11	0	4	0
66	16	0.3795	10	0	6	1
70+76	15	0.1982	13	0	2	0
74	16	0.3876	13	0	3	1
81	2	0.1241	2	0	0	0
84+92	15	0.2299	11	0	4	0
87	15	0.2687	12	0	3	0
95	15	0.1651	11	0	4	0
99	16	0.2053	8	0	8	1
101	15	0.1907	11	0	4	0
105+132+153	11	0.2863	10	0	1	0
110	15	0.4558	9	0	6	2
118	12	0.3407	11	0	1	0
119	11	0.7424	4	0	7	2
138+163	14	0.3713	12	0	2	1
149	14	0.2020	12	0	2	0
Total PCBs	15	0.2007	11	0	4	0

Table 4.3 (continued)
Sampling Precision

XAD-2 Cartridge (continued)

Analyte	(1)	RSD	(2)	(3)	(4)	(5)
p,p' DDD	9	0.4394	3	0	6	0
p,p' DDE	16	0.2007	2	0	14	1
P,P' DDT	9	0.5090	6	0	3	1
DIELDRIN	19	0.2686	7	0	12	2
HCB	16	0.1413	0	0	16	1
a-HCH	20	0.2868	0	0	20	2
g-HCH	20	0.1213	1	0	19	1
ACENAPHTHENE	7	0.9352	0	0	7	2
ACENAPHTHYLENE	7	0.4273	0	0	7	2
ANTHRACENE	7	0.2146	0	0	7	0
BENZO(a)ANTHRACENE	3	0.4197	0	0	3	1
BENZO(b)FLUORANTHENE	2	0.1400	0	0	2	1
BENZO(k)FLUORANTHENE	1		0	0	1	0
BENZO(ghi)PERYLENE	0		0	0	0	0
BENZO(a)PYRENE	0		0	0	0	0
CHRYSENE	6	0.3596	0	0	6	0
DIBENZO(ah)ANTHRACENE	0		0		0	0
FLUORANTHENE	7	0.1252	0	0	7	1
FLUORENE	7	0.244	0	0	7	2
INDENO(123,cd)PYRENE	0		0	0	0	0
PHENANTHRENE	7	0.1976	0	0	7	1
PYRENE	7	0.4156	0	0	7	1

(1): Number of pairs where both sampler results were > LOD
RSD: Relative standard deviation (see report text for definition)
(2): Number of pairs where the mean result for the two samplers was < 5LOD
(3): Number of pairs where the mean result for the two samplers was <5LOD and the RPD was > 100%
(4): Number of pairs where the mean result for the two samplers was ≥ 5LOD
(5): Number of pairs where the mean result for the two samplers was ≥ 5LOD and the RPD was > 50%

The volumes of the two samplers must agree within 15% to be used for precision calculations.
Sampler results were compared with LOD before volume correction.
Sampler differences were computed after volume correction.
Units used in calculations: picogram/m3
Maximum number of pairs found: 20

Table 4.3 (continued)
Sampling Precision

PUF Cartridge:

Analyte	(1)	RSD	(2)	(3)	(4)	(5)
5+8	38	0.6018	15	0	23	4
6	29	0.6535	8	0	21	6
16+32	25	0.5373	10	0	15	4
17	36	0.5116	10	0	26	5
18	37	0.5054	8	0	29	6
21	2	0.0427	2	0	0	0
22	27	0.6047	8	0	19	6
28+31	38	0.4882	16	0	22	5
33	29	0.5077	14	0	15	3
37+42	24	0.3805	17	0	7	1
41+71+64	30	0.5303	16	1	14	4
43	12	0.4446	0	0	12	3
44	30	0.5145	16	1	14	4
47+48	7	0.2279	7	0	0	0
49	38	0.4241	16	0	22	4
52	39	0.4093	10	0	29	5
53	12	0.6564	2	0	10	3
56+60	38	0.4749	16	1	22	5
66	35	0.3403	9	0	26	3
70+76	37	0.3448	23	0	14	1
74	34	0.5808	20	1	14	2
81	6	0.3725	6	0	0	0
84+92	33	0.3152	18	0	15	1
87	31	0.3024	21	0	10	1
95	33	0.3242	14	0	19	1
99	28	0.6457	16	0	12	3
101	37	0.2819	15	0	22	1
105+132+153	21	0.4511	15	0	6	1
110	33	0.3128	24	0	9	1
118	27	0.5969	18	0	9	2
119	5	0.4084	5	0	0	0
138+163	30	0.3529	23	0	7	2
149	16	0.273	15	0	1	0
Total PCBs	37	0.384	22	0	15	3

Table 4.3 (continued)
Sampling Precision

PUF Cartridge (continued)

Analyte	(1)	RSD	(2)	(3)	(4)	(5)
p,p' DDD	9	0.3096	4	0	5	0
P,P' DDE	28	0.4361	13	0	15	2
P,P' DDT	20	1.5581	14	0	6	2
DIELDRIN	33	0.4103	3	0	30	6
HCB	28	0.1749	0	0	28	0
a-HCH	41	0.3773	0	0	41	4
g-HCH	41	0.5471	2	0	39	4
ACENAPHTHENE	35	0.3654	35	1	0	0
ACENAPHTHYLENE	29	0.5567	29	0	0	0
ANTHRACENE	39	0.5522	0	0	39	6
BENZO(a)ANTHRACENE	12	0.8589	12	1	0	0
BENZO(b)FLUORANTHENE	6	0.0193	6	0	0	0
BENZO(k)FLUORANTHENE	1		1	0	0	0
BENZO(ghi)PERYLENE	1		1	0	0	0
BENZO(a)PYRENE	4	0.6114	4	0	0	0
CHRYSENE	28	0.6718	28	1	0	0
DIBENZO(ah)ANTHRACENE	0		0	0	0	0
FLUORANTHENE	40	0.3353	40	2	0	0
FLUORENE	41	0.3006	41	2	0	0
INDENO(123,cd)PYRENE	2	0.5052	2	0	0	0
PHENANTHRENE	41	0.3587	41	2	0	0
PYRENE	38	0.4953	38	0	0	0

(1): Number of pairs where both sampler results were > LOD
RSD: Relative standard deviation (see report text for definition)
(2): Number of pairs where the mean result for the two samplers was < 5LOD
(3): Number of pairs where the mean result for the two samplers was <5LOD and the RPD was > 100%
(4): Number of pairs where the mean result for the two samplers was ≥ 5LOD
(5): Number of pairs where the mean result for the two samplers was ≥ 5LOD and the RPD was > 50%

The volumes of the two samplers must agree within 15% to be used for precision calculations.
Sampler results were compared with LOD before volume correction.
Sampler differences were computed after volume correction.
Units used in calculations: picogram/m3
Maximum number of pairs found: 41

Table 4.3 (continued)
Sampling Precision

Glass Fiber Filter

Analyte	(1)	RSD	(2)	(3)	(4)	(5)
5+8	8	0.601	8	0	0	0
6	1		1	0	0	0
16+32	5	0.9144	5	1	0	0
17	9	0.3246	8	0	1	0
18	4	0.0793	4	0	0	0
21	0		0	0	0	0
22	0		0	0	0	0
28+31	7	0.3665	7	0	0	0
33	9	0.5776	9	0	0	0
37+42	1		1	0	0	0
41+71+64	0		0	0	0	0
43	0		0	0	0	0
44	3	0.6327	3	0	0	0
47+48	0		0	0	0	0
49	4	0.4517	4	0	0	0
52	5	0.568	5	0	0	0
53	0		0	0	0	0
56+60	1		1	0	0	0
66	3	0.1777	3	0	0	0
70+76	0		0	0	0	0
74	2	0.6053	2	0	0	0
81	0		0	0	0	0
84+92	3	0.2234	3	0	0	0
87	0		0	0	0	0
95	2	0.0104	2	0	0	0
99	2	0.1664	2	0	0	0
101	0		0	0	0	0
105+132+153	4	0.4859	4	0	0	0
110	0		0	0	0	0
118	0		0	0	0	0
119	0		0	0	0	0
138+163	1		1	0	0	0
149	0		0	0	0	0
Total PCBs	0		0	0	0	0

Table 4.3 (continued)
Sampling Precision

Glass Fiber Filter (continued)

Analyte	(1)	RSD	(2)	(3)	(4)	(5)
p,p' DDD	0		0	0	0	0
p,p' DDE	7	0.4499	6	0	1	0
p,p' DDT	10	2.2136	6	0	4	1
DIELDRIN	3	0.6278	3	1	0	0
HCB	5	1.7853	4	0	1	1
a-HCH	6	0.713	5	0	1	1
g-HCH	8	0.5375	7	0	1	0
ACENAPHTHENE	2	1.4771	0	0	2	1
ACENAPHTHYLENE	5	0.2286	0	0	5	0
ANTHRACENE	9	0.3682	0	0	9	1
BENZO(a)ANTHRACENE	10	0.334	10	1	0	0
BENZO(b)FLUORANTHENE	10	0.2216	10	0	0	0
BENZO(k)FLUORANTHENE	10	0.2598	10	0	0	0
BENZO(ghi)PERYLENE	10	0.2859	10	0	0	0
BENZO(a)PYRENE	10	0.3094	0	0	10	2
CHRYSENE	10	0.2513	10	1	0	0
DIBENZO(ah)ANTHRACENE	10	0.5302	0	0	10	1
FLUORANTHENE	9	0.3322	9	0	0	0
FLUORENE	5	0.1794	5	0	0	0
INDENO(123,cd)PYRENE	9	0.3454	9	0	0	0
PHENANTHRENE	7	0.3151	7	0	0	0
PYRENE	8	0.3329	8	0	0	0

(1): Number of pairs where both sampler results were > LOD
RSD: Relative standard deviation (see report text for definition)
(2): Number of pairs where the mean result for the two samplers was < 5LOD
(3): Number of pairs where the mean result for the two samplers was <5LOD and the RPD was > 100%
(4): Number of pairs where the mean result for the two samplers was ≥5LOD
(5): Number of pairs where the mean result for the two samplers was ≥5LOD and the RPD was > 50%

The volumes of the two samplers must agree within 15% to be used for precision calculations.
Sampler results were compared with LOD before volume correction.
Sampler differences were computed after volume correction.
Units used in calculations: picogram/m3
Maximum number of pairs found: 14

Table 4.3 (continued)
Sampling Precision

Precipitation XAD-2:

Analyte	(1)	RSD	(2)	(3)	(4)	(5)
5+8	7	0.4858	5	2	2	0
6	1		1	0	0	0
16+32	2	0.3322	2	0	0	0
17	4	0.7222	3	0	1	1
18	6	1.0261	5	0	1	1
21	0		0	0	0	0
22	0		0	0	0	0
28+31	2	0.1732	2	0	0	0
33	3	0.1017	3	0	0	0
37+42	1		1	0	0	0
41+71+64	3	0.9945	3	0	0	0
43	0		0	0	0	0
44	1		1	0	0	0
47+48	0		0	0	0	0
49	1		1	0	0	0
52	1		1	0	0	0
53	1		1	1	0	0
56+60	1		1	0	0	0
66	2	0.0804	2	0	0	0
70+76	2	0.4456	2	0	0	0
74	3	0.4262	3	0	0	0
81	0		0	0	0	0
84+92	2	0.0115	2	0	0	0
87	0		0	0	0	0
95	0		0	0	0	0
99	3	0.9255	3	0	0	0
101	0		0	0	0	0
105+132+153	0		0	0	0	0
110	2	0.1952	2	0	0	0
118	3	0.1703	3	0	0	0
119	0		0	0	0	0
138+163	2	0.1723	2	0	0	0
149	0		0	0	0	0
Total PCBs	3	0.5788	3	0	0	0

Table 4.3 (continued)
Sampling Precision

Precipitation XAD-2 (continued)

Analyte	(1)	RSD	(2)	(3)	(4)	(5)
p,p' DDD	6	1.1581	1	0	5	4
P,P' DDE	8	0.3137	7	0	1	0
p,p' DDT	13	0.6538	0	0	13	7
DIELDRIN	19	0.3969	6	0	13	2
HCB	0		0	0	0	0
a-HCH	16	0.8237	7	1	9	7
g-HCH	13	1.2158	6	1	7	2
ACENAPHTHENE	5	0.3668	5	0	0	0
ACENAPHTHYLENE	12	0.37	0	0	12	3
ANTHRACENE	5	0.1305	5	0	0	0
BENZO(a)ANTHRACENE	13	0.3445	13	0	0	0
BENZO(b)FLUORANTHENE	11	0.2265	11	0	0	0
BENZO(k)FLUORANTHENE	13	0.3467	0	0	13	3
BENZO(ghi)PERYLENE	13	0.2992	13	0	0	0
BENZO(a)PYRENE	7	0.2217	7	0	0	0
CHRYSENE	13	0.2825	13	0	0	0
DIBENZO(ah)ANTHRACENE	10	0.0955	10	0	0	0
FLUORANTHENE	12	0.2301	12	0	0	0
FLUORENE	7	0.2531	7	0	0	0
INDENO(123,cd)PYRENE	13	0.2857	13	0	0	0
PHENANTHRENE	9	0.2817	9	0	0	0
PYRENE	10	0.2823	10	0	0	0

(1): Number of pairs where both sampler results were > LOD
RSD: Relative standard deviation (see report text for definition)
(2): Number of pairs where the mean result for the two samplers was < 5LOD
(3): Number of pairs where the mean result for the two samplers was <5LOD and the RPD was > 100%
(4): Number of pairs where the mean result for the two samplers was ≥5LOD
(5): Number of pairs where the mean result for the two samplers was ≥5LOD and the RPD was > 50%

The volumes of the two samplers must agree within 15% to be used for precision calculations.
Sampler results were compared with LOD before volume correction.
Sampler differences were computed after volume correction.
Units used in calculations: picogram/m3
Maximum number of pairs found: 20

Table 4.3 (continued)
Sampling Precision

Precipitation-Empore:

Analyte	(1)	RSD	(2)	(3)	(4)	(5)
5+8	3	0.805	2	0	1	1
6	1		0	0	1	1
16+32	1		0	0	1	1
17	2	0.5977	1	0	1	1
18	2	0.6808	1	0	1	1
21	0		0	0	0	0
22	1		1	0	0	0
28+31	1		0	0	1	1
33	1		0	0	1	1
37+42	1		0	0	1	0
41+71+64	1		0	0	1	1
43	1		0	0	1	1
44	3	0.729	0	0	3	2
47+48	1		0	0	1	1
49	1		0	0	1	1
52	1		0	0	1	1
53	0		0	0	0	0
56+60	0		0	0	0	0
66	1		0	0	1	1
70+76	1		0	0	1	1
74	1		0	0	1	1
81	0		0	0	1	0
84+92	1		0	0	1	1
87	1		0	0	1	1
95	1		0	0	1	1
99	1		0	0	1	1
101	1		0	0	1	1
105+132+153	0		0	0	0	0
110	1		0	0	1	1
118	1		0	0	1	1
119	0		0	0	0	0
138+163	1		0	0	1	1
149	5	0.8654	4	0	1	1
Total PCBs	1		0	0	1	1

Table 4.3 (concluded)
Sampling Precision

Precipitation-Empore (continued)

Analyte	(1)	RSD	(2)	(3)	(4)	(5)
p,p' DDD	0		0	0	0	0
P,P' DDE	0		0	0	0 '	0
p,p' DDT	1		0	0	1	0
DIELDRIN	7	0.6279	5	0	2	1
HCB	1		1	0	0	0
a-HCH	14	1.5913	1	0	13	3
g-HCH	9	0.4146	2	0	7	1
ACENAPHTHENE	1		1	0	0	0
ACENAPHTHYLENE	0		0	0	0	0
ANTHRACENE	0		0	0	0	0
BENZO(a)ANTHRACENE	2	0.0381	2	0	0	0
BENZO(b)FLUORANTHENE	0		0	0	0	0
BENZO(k)FLUORANTHENE	6	0.1957	0	0	6	0
BENZO(ghi)PERYLENE	7	0.183	7	0	0	0
BENZO(a)PYRENE	0		0	0	0	0
CHRYSENE	9	0.5583	9	1	0	0
DIBENZO(ah)ANTHRACENE	0		0	0	0	0
FLUORANTHENE	4	0.1508	4	0	0	0
FLUORENE	1		1	0	0	0
INDENO(123,cd)PYRENE	4	0.2487	4	0	0	0
PHENANTHRENE	1		1	0	0	0
PYRENE	4	0.2945	4	0	0	0

(1): Number of pairs where both sampler results were > LOD
RSD: Relative standard deviation (see report text for definition)
(2): Number of pairs where the mean result for the two samplers was < 5LOD
(3): Number of pairs where the mean result for the two samplers was <5LOD and the RPD was > 100%
(4): Number of pairs where the mean result for the two samplers was ≥5LOD
(5): Number of pairs where the mean result for the two samplers was ≥5LOD and the RPD was > 50%

The volumes of the two samplers must agree within 15% to be used for precision calculations.
Sampler results were compared with LOD before volume correction.
Sampler differences were computed after volume correction.
Units used in calculations: picogram/m3
Maximum number of pairs found: 14

Table 4.4
Laboratory Matrix Spike (LMS)

All Matrices:

PCBs: congener #	*Target level (ng)*	*N*	*Average recovery (%)*	*Standard deviation (SD)*	*2 SD*
6	4.2	39	78.1	19.33	38.65
5+8	50	39	77.4	17.15	34.30
18	13	39	79.2	18.23	36.46
17	7.4	39	84.9	15.25	30.49
16+32	13.1	39	58.2	26.72	53.44
28+31	38	39	98.9	8.87	17.73
21	0.15	39	98.7	123.63	247.26
33	14	39	91.4	12.04	24.09
53	2.7	39	83.2	17.80	35.60
22	11	39	77.3	22.41	44.83
52	12	39	97.5	8.66	17.32
43	0.91	39	94.2	13.07	26.15
49	9	39	99.4	10.52	21.05
47+48	9	39	79.8	24.32	48.63
44	15	39	88.1	14.87	29.74
37+42	8.8	39	94.2	17.79	35.59
41+64+71	16.3	39	90.5	19.41	38.82
74	8.1	39	102.4	8.91	17.81
70+76	21	39	102.1	8.28	16.56
66	22	39	99.1	13.44	26.89
95	5.2	39	94.3	10.63	21.25
56+60	18	39	95.1	11.45	22.91
84+92	4.3	39	91.2	19.16	38.33
101	4.8	39	103.2	9.76	19.53
99	2.3	39	110.3	34.89	69.79
119	0.18	39	118.7	79.85	159.70
81	0.32	39	101.6	43.17	86.33
87	3	39	98.5	11.24	22.48
110	5.6	39	98.7	8.72	17.44
149	11	39	102.8	13.13	26.26
118	3.5	39	106.7	23.63	47.26
105+132+153	21.6	39	105.7	14.77	29.54
138+163	9.8	39	108.4	13.43	26.87
Total PCBs	610	39	88.2	8.77	17.54

Table 4.4 Laboratory Matrix Spike (LMS) (concluded)

Analyte	*Target level (ng)*	*N*	*Average recovery (%)*	*Standard deviation (SD)*	*2 SD*
alpha-hexachlorocyclohexane	20-84	74	**70.4**	28.67	57.34
gamma-hexachlorocyclohexane	5-20	74	**86.2**	29.24	58.48
dieldrin	5-20	73	**91.7**	31.84	63.68
p,p' DDT	20	61	**139.0**	74.98	149.97
p,p' DDD	20	61	**102.7**	28.06	56.11
p,p' DDE	20	26	**98.9**	14.12	28.24
hexachlorobenzene	5-20	26	**80.5**	7.81	15.61
acenaphthylene	10-5000	27	**49.4**	19.95	39.90
acenaphthene	10-5000	27	**48.1**	21.40	42.79
fluorene	10-5000	27	**60.0**	21.64	43.29
phenanthrene	10-5000	28	**68.1**	23.50	47.00
anthracene	10-5000	28	**69.2**	25.40	50.81
fluoranthene	10-5000	28	**80.5**	25.28	50.57
pyrene	10-5000	28	**84.7**	26.56	53.12
benzo(a)anthracene	10-5000	28	**67.7**	23.09	46.17
chrysene	10-5000	28	**102.9**	42.23	84.46
benzo(b)fluoranthene	10-5000	28	**96.6**	41.07	82.14
benzo(k)fluoranthene	10-5000	28	**87.4**	37.48	74.96
benzo(a)pyrene	10-5000	28	**85.6**	40.17	80.33
Indeno(123cd)pyrene	10-5000	28	**106.7**	61.28	122.57
dibenzo(ah)anthracene	10-5000	27	**108.6**	62.66	125.32
benzo(ghi)perylene	10-5000	28	**76.2**	38.75	77.51

Table 4.5
Laboratory Matrix Blanks (LB)

All Matrices

PCBs	n	Maximum (ng)	Minimum (ng)	Mean (ng)	Std. Dev.	% RSD
6	68	0.21	0	0.01	0.04	3.13
5+8	68	5.33	0	0.16	0.71	4.46
18	68	2.00	0	0.07	0.30	4.39
17	68	0.81	0	0.04	0.14	3.42
16+32	68	1.21	0	0.04	0.18	4.89
28+31	68	3.78	0	0.17	0.64	3.86
21	68	0.80	0	0.01	0.10	7.51
33	68	2.43	0	0.11	0.38	3.60
53	68	0.20	0	0.01	0.04	4.04
22	68	0.50	0	0.01	0.06	5.98
52	68	1.30	0	0.06	0.20	3.19
43	68	0.28	0	0.01	0.04	6.41
49	68	3.38	0	0.10	0.44	4.21
47+48	68	0.77	0	0.02	0.10	5.40
44	68	21.49	0	0.39	2.61	6.72
37+42	68	1.50	0	0.05	0.22	4.26
41+64+71	68	1.34	0	0.05	0.19	3.72
74	68	1.73	0	0.07	0.27	4.02
70+76	68	2.63	0	0.10	0.36	3.70
66	68	1.46	0	0.05	0.20	3.97
95	68	1.41	0	0.05	0.19	4.01
56+60	68	1.67	0	0.10	0.34	3.30
84+92	68	1.63	0	0.10	0.32	3.33
101	68	0.85	0	0.05	0.16	3.16
99	68	0.34	0	0.02	0.05	2.72
119	68	0.49	0	0.01	0.06	7.10
81	68	0.29	0	0.05	0.05	1.04
87	68	0.38	0	0.01	0.05	3.82
110	68	0.99	0	0.05	0.14	2.88
149	68	2.04	0	0.22	0.43	1.91
118	68	0.76	0	0.02	0.10	5.07
105+132+153	68	2.79	0	0.13	0.44	3.31
138+163	68	1.17	0	0.04	0.16	4.65
Total PCBs	68	52.27	0.13	4.21	8.30	1.97

Table 4.5 Laboratory Matrix Blanks (LB) (continued)

PESTICIDES	*n*	*Maximum (ng)*	*Minimum (ng)*	*Mean (ng)*	*Std. Dev.*	*% RSD*
a-HEXACHLOROCYCLOHEXANE	96	4.25	0	**0.25**	0.83	3.36
g-HEXACHLOROCYCLOHEXANE	96	4.93	0	**0.36**	1.01	2.78
DIELDRIN	96	27.29	0	**1.28**	4.77	3.74
p,p' DDT	96	15.89	0	**0.28**	1.86	6.74
p,p' DDD	96	5.05	0	**0.09**	0.53	6.12
p,p' DDE	53	18.87	0	**1.93**	5.15	267.39%
HEXACHLOROBENZENE	53	17.48	0	**2.22**	4.77	214.69%
PAHs						
ACENAPHTHYLENE	57	2.41	0	**0.04**	0.32	754.98%
ACENAPHTHENE	57	12.87	0	**0.42**	1.87	450.22%
FLUORENE	57	10.89	0	**0.95**	2.58	271.71%
PHENANTHRENE	57	39.16	0	**3.93**	7.71	196.50%
ANTHRACENE	57	13.51	0	**0.69**	2.52	365.48%
FLUORANTHENE	57	170.90	0	**11.18**	37.45	335.13%
PYRENE	57	123.60	0	**7.94**	23.45	295.19%
BENZO(A)ANTHRACENE	57	12.05	0	**1.14**	2.92	256.88%
CHRYSENE	57	19.36	0	**2.27**	4.95	217.78%
BENZO(B)FLUORANTHENE	57	19.69	0	**2.28**	5.35	234.37%
BENZO(K)FLUORANTHENE	57	16.45	0	**0.46**	2.51	547.22%
BENZO(A)PYRENE	57	19.31	0	**1.21**	4.45	368.38%
INDENO(123CD)PYRENE	57	29.71	0	**1.76**	5.92	335.93%
DIBENZO(AH)ANTHRACENE	57	10.41	0	**0.18**	1.38	754.98%
BENZO(GHI)PERYLENE	57	17.63	0	**0.60**	3.15	529.49%

Table 4.5 Laboratory Matrix Blanks (LB) (continued)

Glass Fiber Filters

PCBs	n	Maximum (ng)	Minimum (ng)	Mean (ng)	Std. Dev.	% RSD
6	7	0.04	0	0.01	0.01	2.65
5+8	7	0.07	0	0.02	0.03	1.71
18	7	0.04	0	0.01	0.02	1.89
17	7	0.04	0	0.01	0.02	1.27
16+32	7	0.03	0	0	0.01	2.65
28+31	7	0.14	0	0.04	0.06	1.73
21	7	0	0	0	0	
33	7	0.12	0	0.04	0.05	1.32
53	7	0	0	0	0	
22	7	0.05	0	0.01	0.02	1.85
52	7	0.11	0	0.04	0.05	1.28
43	7	0	0	0	0	
49	7	0.11	0	0.05	0.04	0.71
47+48	7	0.02	0	0	0.01	2.65
44	7	0.12	0	0.06	0.06	0.97
37+42	7	0.26	0	0.06	0.10	1.61
41+64+71	7	0.09	0	0.03	0.04	1.16
74	7	0.16	0	0.04	0.06	1.42
70+76	7	0.18	0	0.09	0.09	0.95
66	7	0.13	0	0.05	0.05	1.07
95	7	0.15	0	0.07	0.07	0.97
56+60	7	0.28	0	0.11	0.12	1.10
84+92	7	0.19	0	0.08	0.08	1.06
101	7	0.14	0	0.05	0.05	1.04
99	7	0.06	0	0.02	0.03	1.40
119	7	0	0	0	0	
81	7	0.08	0	0.04	0.04	0.96
87	7	0.11	0	0.03	0.04	1.36
110	7	0.20	0	0.09	0.07	0.77
149	7	1.03	0	0.19	0.37	1.92
118	7	0.19	0	0.03	0.07	2.31
105+132+153	7	0.44	0	0.08	0.16	1.92
138+163	7	0.06	0	0.01	0.02	1.84
Total PCBs	7	5.32	0.32	2.38	1.59	0.67

Table 4.5 Laboratory Matrix Blanks (LB) (continued)

PESTICIDES	*n*	*Maximum (ng)*	*Minimum (ng)*	*Mean (ng)*	*Std. Dev.*	*% RSD*
a-HEXACHLOROCYCLOHEXANE	17	4.15	0	**0.57**	1.29	2.26
g-HEXACHLOROCYCLOHEXANE	17	4.93	0	**0.85**	1.62	1.90
DIELDRIN	17	27.29	0	**3.73**	8.54	2.29
p,p' DDT	17	9.02	0	**0.57**	2.18	3.86
p,p' DDD	17	5.05	0	**0.30**	1.22	4.02
p,p' DDE	7	0.16	0	**0.057**	0.06	104.45%
HEXACHLOROBENZENE	7	0.10	0	**0.034**	0.03	103.27%
PAHs						
ACENAPHTHYLENE	10	0	0	**0**	0	
ACENAPHTHENE	10	0	0	**0**	0	
FLUORENE	10	7.57	0	**1.41**	2.99	211.51%
PHENANTHRENE	10	22.48	0	**6.72**	8.82	131.25%
ANTHRACENE	10	11.22	0	**1.72**	3.83	222.63%
FLUORANTHENE	10	20.45	0	**3.00**	6.82	227.66%
PYRENE	10	18.71	0	**2.60**	6.11	234.77%
BENZO(A)ANTHRACENE	10	10.38	0	**1.57**	3.31	210.70%
CHRYSENE	10	18.09	0	**4.43**	6.56	148.13%
BENZO(B)FLUORANTHENE	10	17.23	0	**2.82**	5.69	201.41%
BENZO(K)FLUORANTHENE	10	16.45	0	**1.65**	5.20	316.23%
BENZO(A)PYRENE	10	19.31	0	**3.65**	7.70	211.28%
INDENO(123CD)PYRENE	10	18.95	0	**3.77**	7.94	210.82%
DIBENZO(AH)ANTHRACENE	10	0	0	**0**	0	
BENZO(GHI)PERYLENE	10	17.63	0	**1.76**	5.58	316.23%

Table 4.5 Laboratory Matrix Blanks (LB) (continued)

PUF Cartridges:

PCBs:	n	Maximum (ng)	Minimum (ng)	Mean (ng)	Std. Dev.	% RSD
6	32	0	0	0	0	
5+8	32	0.26	0	0.02	0.07	2.75
18	32	0	0	0	0	
17	32	0.19	0	0.01	0.04	2.96
16+32	32	0.11	0	0	0.02	5.66
28+31	32	0.26	0	0.01	0.05	5.66
21	32	0	0	0	0	
33	32	0.44	0	0.02	0.08	3.53
53	32	0.06	0	0	0.01	5.66
22	32	0	0	0	0	
52	32	0.07	0	0.01	0.02	2.31
43	32	0	0	0	0	
49	32	0.15	0	0.01	0.03	3.39
47+48	32	0.22	0	0.01	0.05	3.35
44	32	21.49	0	0.69	3.80	5.54
37+42	32	0	0	0	0	
41+64+71	32	0.74	0	0.04	0.13	3.71
74	32	0.05	0	0	0.01	4.83
70+76	32	0.13	0	0.01	0.03	3.75
66	32	0.18	0	0.01	0.03	5.66
95	32	0.12	0	0	0.02	5.66
56+60	32	1.61	0	0.06	0.29	5.01
84+92	32	1.50	0	0.05	0.26	5.34
101	32	0.11	0	0.01	0.02	2.72
99	32	0.09	0	0.01	0.02	2.41
119	32	0.49	0	0.02	0.09	5.52
81	32	0.17	0	0.04	0.05	1.13
87	32	0	0	0	0	
110	32	0.09	0	0.01	0.02	2.12
149	32	2.04	0	0.29	0.50	1.73
118	32	0.76	0	0.02	0.13	5.66
105+132+153	32	0.88	0	0.03	0.16	4.87
138+163	32	0.49	0	0.02	0.09	4.42
Total PCBs	32	23.09	0.18	3.61	5.40	1.50

Table 4.5 Laboratory Matrix Blanks (LB) (continued)

PESTICIDES:	n	Maximum (ng)	Minimum (ng)	Mean (ng)	Std. Dev.	% RSD
a-HEXACHLOROCYCLOHEXANE	30	0.26	0	0.02	0.07	2.86
g-HEXACHLOROCYCLOHEXANE	30	3.16	0	0.13	0.58	4.60
DIELDRIN	30	1.18	0	0.07	0.24	3.16
p,p' DDT	30	0.56	0	0.02	0.10	4.72
p,p' DDD	30	0.93	0	0.09	0.26	2.71
p,p' DDE	20	15.60	0	2.38	5.48	229.78%
HEXACHLOROBENZENE	20	17.48	0	3.67	6.24	170.13%
PAHs:						
ACENAPHTHYLENE	32	0	0	0	0	
ACENAPHTHENE	32	12.87	0	0.53	2.37	443.82%
FLUORENE	32	3.77	0	0.17	0.72	425.47%
PHENANTHRENE	32	8.23	0	1.69	2.79	164.98%
ANTHRACENE	32	3.48	0	0.11	0.61	565.69%
FLUORANTHENE	32	170.90	0	7.47	30.27	404.96%
PYRENE	32	25.79	0	4.19	8.45	201.55%
BENZO(A)ANTHRACENE	32	7.38	0	0.36	1.38	379.77%
CHRYSENE	32	7.29	0	0.80	2.01	249.10%
BENZO(B)FLUORANTHENE	32	17.24	0	1.33	4.26	319.81%
BENZO(K)FLUORANTHENE	32	9.67	0	0.30	1.71	565.69%
BENZO(A)PYRENE	32	16.73	0	1.01	3.99	393.69%
INDENO(123CD)PYRENE	32	29.71	0	1.96	6.50	330.93%
DIBENZO(AH)ANTHRACENE	32	0	0	0	0	
BENZO(GHI)PERYLENE	32	16.29	0	0.51	2.88	565.69%

Table 4.5 Laboratory Matrix Blanks (LB) (continued)

XAD-2 Cartridge:

PCBs:	n	Maximum (ng)	Minimum (ng)	Mean (ng)	Std. Dev.	% RSD
6	15	0.21	0	0.03	0.06	1.90
5+8	15	0	0	0	0	
18	15	0.06	0	0.01	0.02	2.68
17	15	0.04	0	0	0.01	3.87
16+32	15	0.10	0	0.01	0.03	2.25
28+31	15	0.29	0	0.03	0.08	2.77
21	15	0	0	0	0	
33	15	0.05	0	0.01	0.02	2.14
53	15	0.01	0	0	0	3.87
22	15	0.03	0	0	0.01	3.87
52	15	0.09	0	0.01	0.03	1.88
43	15	0	0	0	0	
49	15	0.08	0	0.02	0.03	1.66
47+48	15	0	0	0	0	
44	15	0.34	0	0.06	0.10	1.59
37+42	15	0.06	0	0.01	0.02	2.85
41+64+71	15	0.12	0	0.02	0.04	2.21
74	15	0.03	0	0	0.01	3.87
70+76	15	0.13	0	0.02	0.04	1.74
66	15	0	0	0	0	
95	15	0.02	0	0	0	3.87
56+60	15	0.09	0	0.01	0.02	2.38
84+92	15	0.51	0	0.04	0.13	3.51
101	15	0.05	0	0.01	0.02	1.87
99	15	0.06	0	0.01	0.02	2.55
119	15	0.03	0	0	0.01	3.87
81	15	0.29	0	0.08	0.06	0.77
87	15	0.03	0	0	0.01	2.76
110	15	0.24	0	0.02	0.06	3.20
149	15	0.08	0	0.01	0.02	2.20
118	15	0.07	0	0	0.02	3.87
105+132+153	15	0.72	0	0.06	0.19	3.29
138+163	15	0	0	0	0	
Total PCBs	15	4.50	0.13	1.02	1.12	1.10

Table 4.5 Laboratory Matrix Blanks (LB) (continued)

PESTICIDES:	n	Maximum (ng)	Minimum (ng)	Mean (ng)	Std. Dev.	% RSD
a-HEXACHLOROCYCLOHEXANE	28	2.15	0	0.08	0.41	5.29
g-HEXACHLOROCYCLOHEXANE	28	2.85	0	0.15	0.58	3.85
DIELDRIN	28	6.84	0	0.49	1.38	2.81
p,p' DDT	28	0	0	0	0	
p,p' DDD	28	0	0	0	0	
p,p' DDE	15	18.87	0	2.20	5.84	265.20%
HEXACHLOROBENZENE	15	11.34	0	1.39	3.42	246.30%
PAHs:						
ACENAPHTHYLENE	4	0	0	0	0	
ACENAPHTHENE	4	0	0	0	0	
FLUORENE	4	0	0	0	0	
PHENANTHRENE	4	0	0	0	0	
ANTHRACENE	4	0	0	0	0	
FLUORANTHENE	4	0	0	0	0	
PYRENE	4	0	0	0	0	
BENZO(A)ANTHRACENE	4	0	0	0	0	
CHRYSENE	4	0	0	0	0	
BENZO(B)FLUORANTHENE	4	0	0	0	0	
BENZO(K)FLUORANTHENE	4	0	0	0	0	
BENZO(A)PYRENE	4	0	0	0	0	
INDENO(123CD)PYRENE	4	0	0	0	0	
DIBENZO(AH)ANTHRACENE	4	0	0	0	0	
BENZO(GHI)PERYLENE	4	0	0	0	0	

Table 4.5 Laboratory Matrix Blanks (LB) (continued)

XAD-2 Precipitation:

PCBs:	n	Maximum (ng)	Minimum (ng)	Mean (ng)	Std. Dev.	% RSD
6	10	0.15	0	0.03	0.05	1.80
5+8	10	0.43	0	0.06	0.14	2.27
18	10	0.14	0	0.02	0.05	2.19
17	10	0.14	0	0.02	0.05	2.73
16+32	10	0.03	0	0.01	0.01	2.11
28+31	10	0	0	0	0	
21	10	0.08	0	0.01	0.03	3.16
33	10	0.10	0	0.03	0.03	1.25
53	10	0	0	0	0	
22	10	0.06	0	0.01	0.02	2.19
52	10	0.34	0	0.04	0.10	2.49
43	10	0	0	0	0	
49	10	3.38	0	0.36	1.06	2.95
47+48	10	0	0	0	0	
44	10	0.40	0	0.06	0.12	2.12
37+42	10	0.03	0	0	0.01	2.25
41+64+71	10	0.05	0	0.01	0.02	2.11
74	10	0.17	0	0.02	0.05	2.94
70+76	10	0.10	0	0.03	0.04	1.44
66	10	0.05	0	0.01	0.02	3.16
95	10	0.05	0	0.01	0.02	2.28
56+60	10	1.42	0	0.16	0.44	2.71
84+92	10	0.24	0	0.03	0.07	2.93
101	10	0.01	0	0	0.01	1.61
99	10	0.07	0	0.01	0.02	2.33
119	10	0	0	0	0	
81	10	0.10	0	0.05	0.04	0.74
87	10	0.38	0	0.05	0.12	2.38
110	10	0.03	0	0.01	0.01	1.31
149	10	0.48	0	0.07	0.16	2.35
118	10	0	0	0	0	
105+132+153	10	0.02	0	0	0.01	3.16
138+163	10	0	0	0	0	
Total PCBs	10	7.84	0.31	1.91	2.40	1.26

Table 4.5 Laboratory Matrix Blanks (LB) (continued)

PESTICIDES:	n	Maximum (ng)	Minimum (ng)	Mean (ng)	Std. Dev.	% RSD
a-HEXACHLOROCYCLOHEXANE	18	0.64	0	**0.07**	0.17	2.42
g-HEXACHLOROCYCLOHEXANE	18	1.26	0	**0.14**	0.37	2.69
DIELDRIN	18	0.32	0	**0.10**	0.10	0.96
p,p' DDT	18	0.30	0	**0.02**	0.07	4.24
p,p' DDD	18	0.35	0	**0.02**	0.08	4.24
p,p' DDE	10	18.50	0	**2.02**	5.80	286.55%
HEXACHLOROBENZENE	10	12.11	0	**2.25**	4.61	204.45%
PAHs:						
ACENAPHTHYLENE	7	0	0	**0**	0	
ACENAPHTHENE	7	3.92	0	**0.56**	1.48	264.58%
FLUORENE	7	0	0	**0**	0	
PHENANTHRENE	7	2.51	0	**0.66**	1.14	171.56%
ANTHRACENE	7	0	0	**0**	0	
FLUORANTHENE	7	0	0	**0**	0	
PYRENE	7	7.87	0	**1.12**	2.98	264.58%
BENZO(A)ANTHRACENE	7	0	0	**0**	0	
CHRYSENE	7	0	0	**0**	0	
BENZO(B)FLUORANTHENE	7	0	0	**0**	0	
BENZO(K)FLUORANTHENE	7	0	0	**0**	0	
BENZO(A)PYRENE	7	0	0	**0**	0	
INDENO(123CD)PYRENE	7	0	0	**0**	0	
DIBENZO(AH)ANTHRACENE	7	10.41	0	**1.49**	3.93	264.58%
BENZO(GHI)PERYLENE	7	0	0	**0**	0	

5.0 Quality Assurance Records and Quality Control Samples

Quality assurance (QA) and quality control (QC) samples were added to sampling and laboratory procedures whenever possible. Site and laboratory QC/QC sampling sets were defined for the project.

5.1 Site Sample Set

QC samples from the IADN stations included: 1) one field blank (FB) per month per station for each matrix type, and 2) one pair of collocated field duplicate (CFD) samples per month from each master station for each matrix type.

5.2 Laboratory Sample Set

QC samples from the laboratory included: 1) a matrix FB, 2) a set of CFD samples, 3) a method/laboratory blank (LB), and 4) a laboratory matrix spike (LMS) for each matrix prepared.

5.3 Other QA/QC Samples

Additional QA/QC performance checks included: 1) instrument calibration checks, 2) analysis of laboratory surrogate spikes, 3) instrument linearity checks, and 4) analysis of interlaboratory performance check samples.

Internal QA procedures included: 1) the parallel analysis of old and new calibration and spiking standards before use of new solutions, 2) maintenance of laboratory records detailing sampling conditions, sample handling, instrument maintenance and calibration, standard and reagent preparation, and sample preparation, 3) initial investigations of the use of deuterated PAH surrogate standards (the addition of these new surrogates is expected in future method updates), and 4) documentation and identification of chromatographic coelution interferences whenever possible.

6.0 Protocol Changes

Sampling and analytical protocols were modified and improved as necessary as the monitoring project evolved.

6.1 Sampling Protocol

Particulate matter Quartz fiber filters (QFF) were used for particle sampling at the Eagle Harbor site only from November 1990 to November 1991. Analysis of QFF blanks resulted in high background levels for some analytes; as a result, their use was discontinued. Filter sample results from this site were not adversely affected. Glass fiber filters (GFF) were used for TSP/TOC samples, and these filters were substituted for the QFF for organic analyses for the sampling period affected. Only GFFs were used at all other sites. Beginning in early 1992, GFFs were routinely preconditioned at 450°C before use to avoid potential contaminants.

Precipitation The trapping agent for organics in precipitation samples was changed from Empore® disks to XAD-2 resin in February 1992.

Vapor In May 1992, the organic vapor trapping adsorbent was changed from polyurethane foam (PUF) to XAD-2 resin.

6.2 Laboratory Protocol

Laboratory extractions of field samples were initiated in the fall of 1991. Initial QC samples included matrix spikes, field blanks, lab blanks, and three PCB surrogate spikes. The matrix spike and lab blank materials were changed periodically to reflect those utilized for site samples (for example, XAD-2 was the matrix used for precipitation and vapor matrix quality control samples after March 1992, and June 1992, respectively). As the method evolved, matrix spike levels were adjusted to achieve concentrations closely reflecting those from site samples. As the project evolved, an increased number of quality control samples were added. By early 1992, every sample set extracted included matrix spikes for all analytes, a matrix lab blank, and surrogate standards whenever possible.

Additional analytes were added to the analytical method only after method development work indicated the procedures were valid for those analytes. Analytes added during the sampling interval covered by this report were:

Polychlorinated Bipheny/s (PCBs) Laboratory analysis of field samples was initiated in September 1991.

Pesticides In April 1991 alpha- and gamma-hexachlorocyclohexane, and dieldrin were added to the assay list. Four more pesticides (p,p' DDD, p,p' DDE, p,p' DDT, and hexachlorobenzene) were added in January 1992.

Po/ycyciic aromatic hydrocarbons (PAHs) Laboratory analysis for PAHs was initiated in late 1991 with gas chromatography-flame ionization detection (GC-FID). This approach was deemed unacceptable due to the low sensitivity and low selectivity of this detector. False positive results were highly suspected for site samples analyzed due to coeluting hydrocarbons. In March 1992, gas chromatography-mass spectroscopy (GC-MS) was selected as the method of choice due to its selectivity and improved sensitivity using selected ion monitoring procedures. All PAH results reported for this project utilized the GC-MS method. In June 1992, two deuterated PAH internal standards were added to the method, bringing the total number of internal standards to three.

All chromatographic methods were improved to obtain resolution of previously unresolved peaks and to identify interfering compounds. p,p' DDE was identified as a positive interference for PCB congener 77. Analytical method documentation included the determination of instrument linearity (Appendix C) and instrument detection limits (Table 4.1) for the gas chromatographic methods for all analytes.

6.3 Special Studies

6.3.1 Sample Storage before Analysis

6.3.1.1 Laboratory Storage

Some site samples were stored at -20° C for up to 12 months before extraction. Special studies to perform sample stability measurements were initiated in late 1992 to determine the effects of sample storage before extraction. Paired samples from collocated samplers were used for this determination. One of the paired samples was extracted within the storage time specified in the QAPjP (1-2 months for organics). A "twin" sample was stored for six months or one year before extraction. Results from the six months stability evaluation have been completed and preliminary

results reveal that no analyte losses occurred after six months of storage at -20°C. The results from the one-year stability evaluation are not yet available.

6.3.1.2 Field storage and shipment

Field samples were typically collected and stored at room temperature for up to two weeks during storage and shipment prior to receipt at the ISWS. Special studies were carried out to determine the effect of field storage conditions on sample integrity. Paired samples from collocated samplers in Champaign, IL, were used for this evaluation. One sample was frozen immediately after removal from the sampler while its "twin" sample was left at room temperature. Results from this study revealed no significant differences between freezer and room temperature storage for any analyte for up to two weeks.

7.0 References

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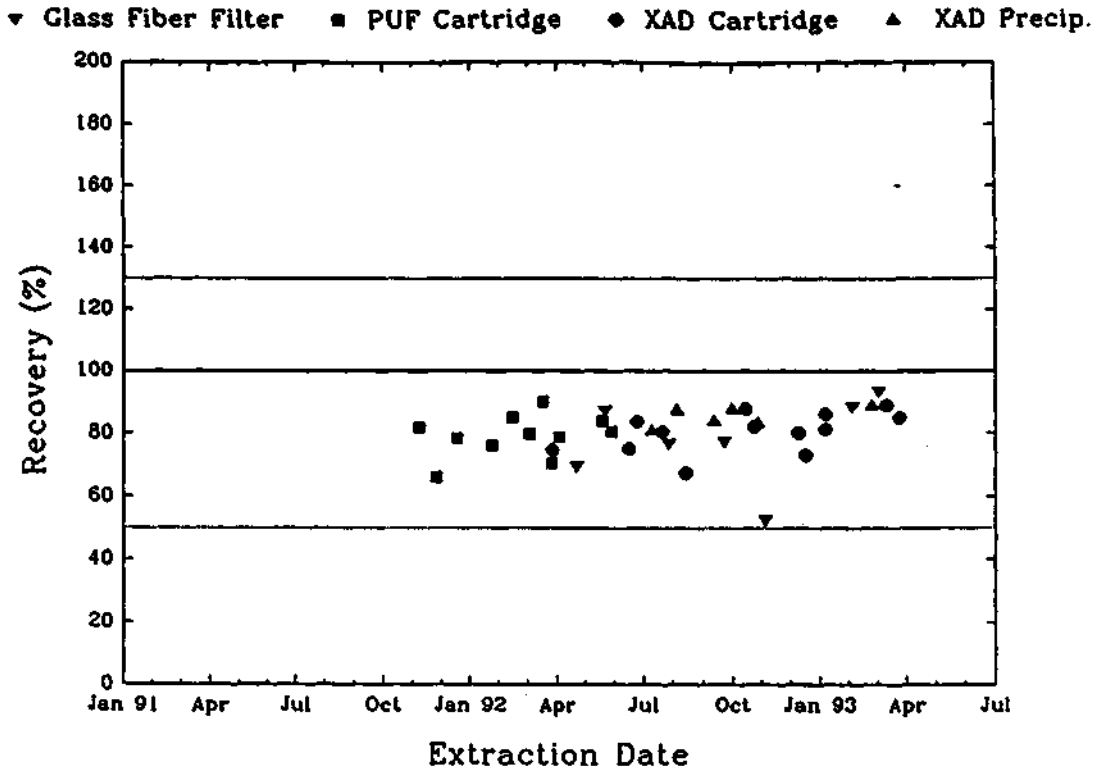
Appendices

Appendix A, Laboratory Matrix Spike (LMS) Control Charts
Appendix B, Interlaboratory Study, Phase I Data
Appendix C, Instrument Linearity Data
Appendix D, Quartz Fiber Filter (QFF) Field Blank and Lab Blank Data

Appendix A

Laboratory Matrix Spike (LMS) Control Charts

Total PCBs



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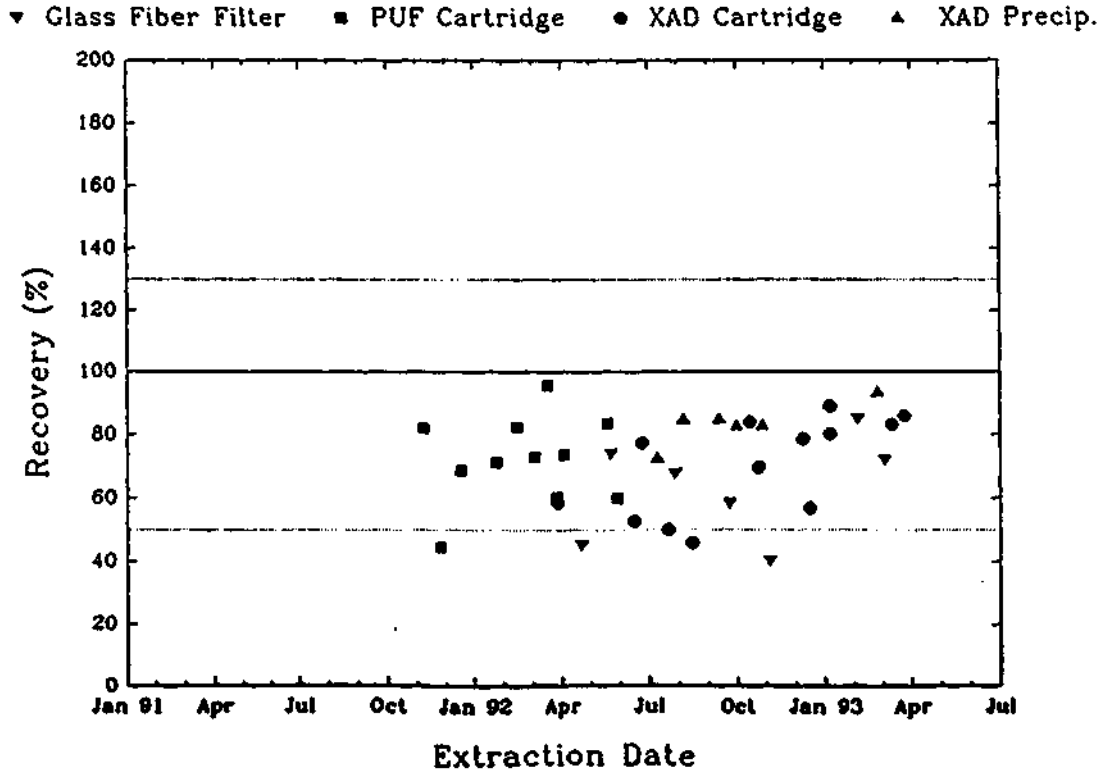

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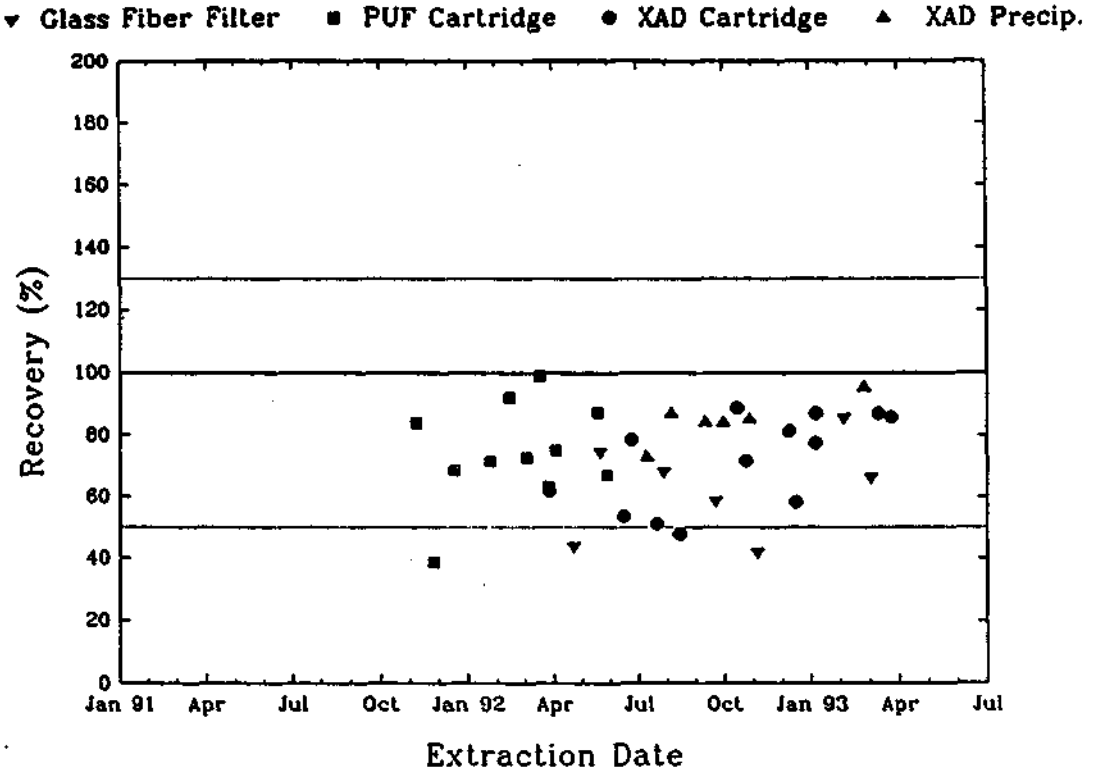

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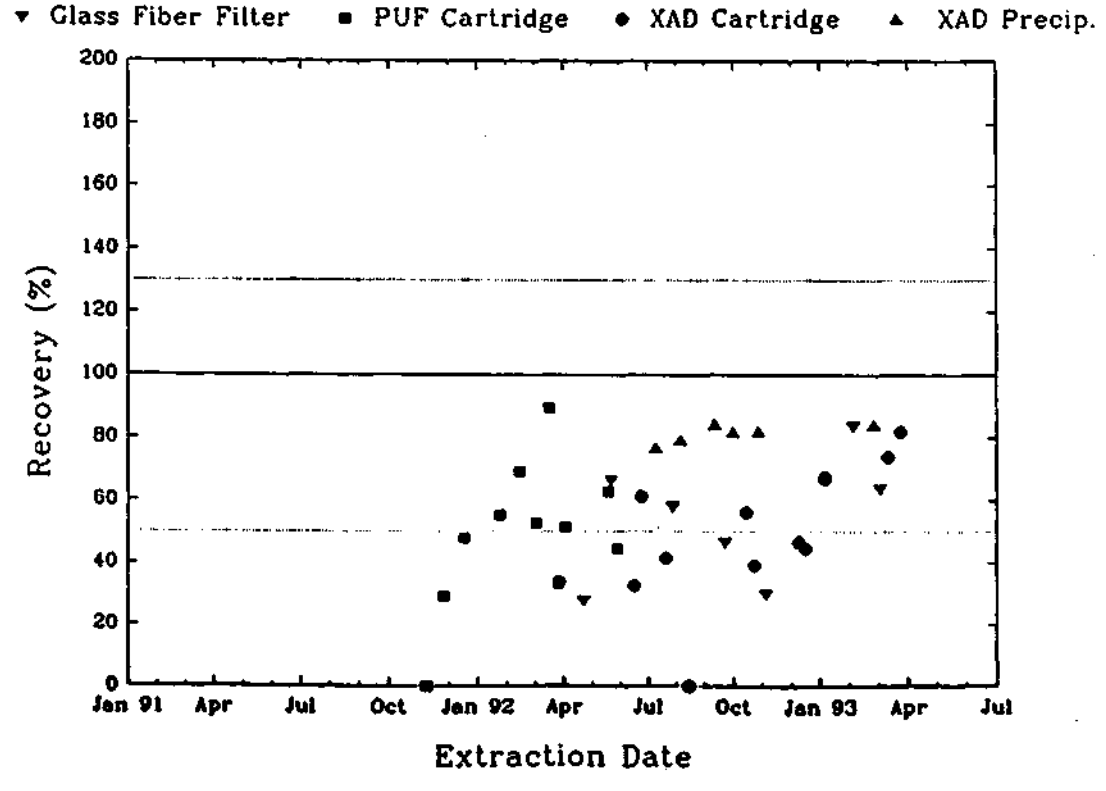

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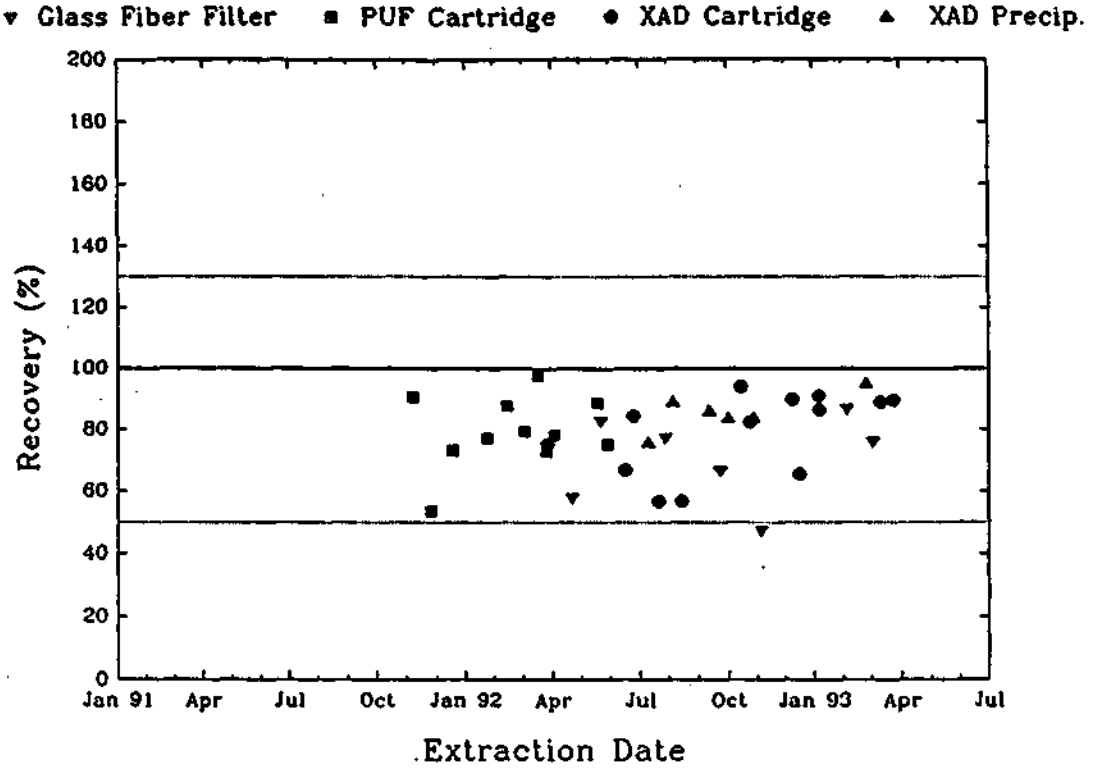

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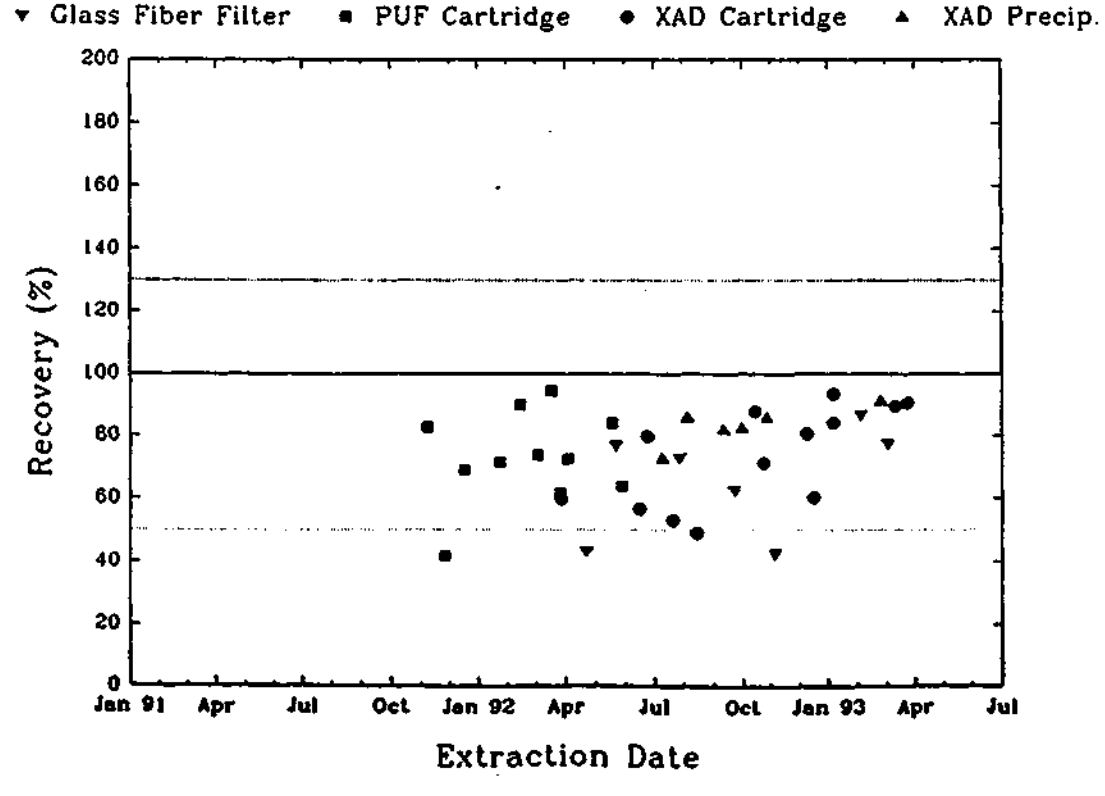

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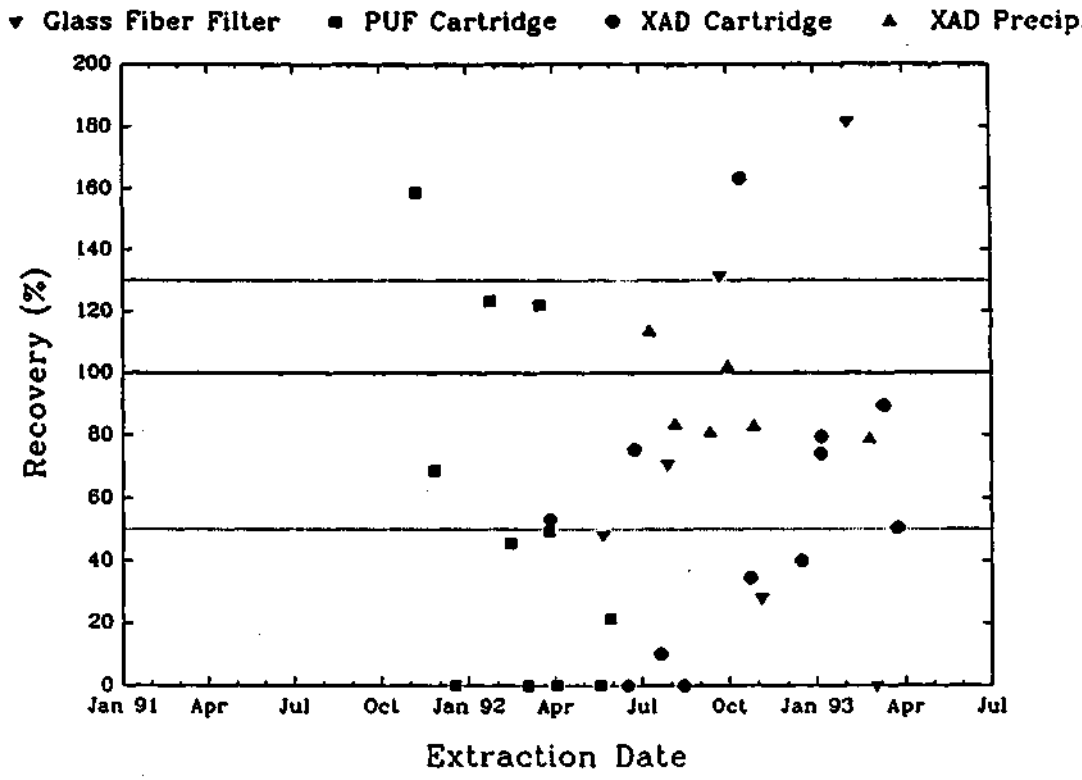

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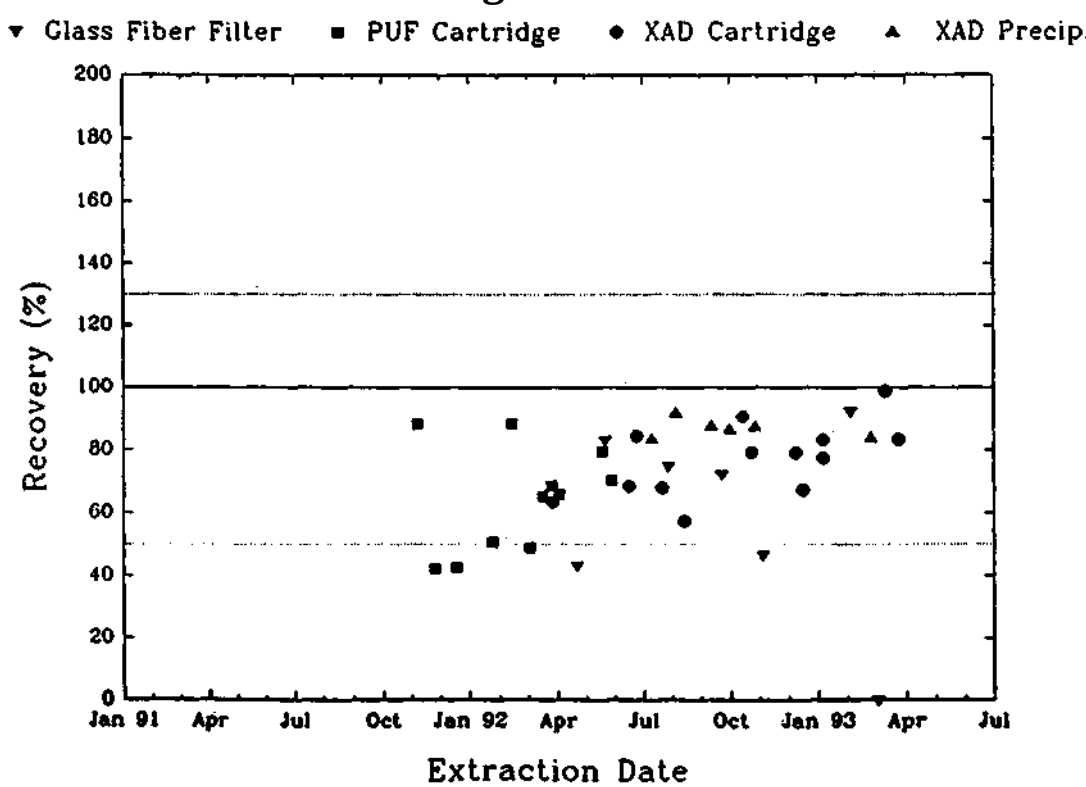

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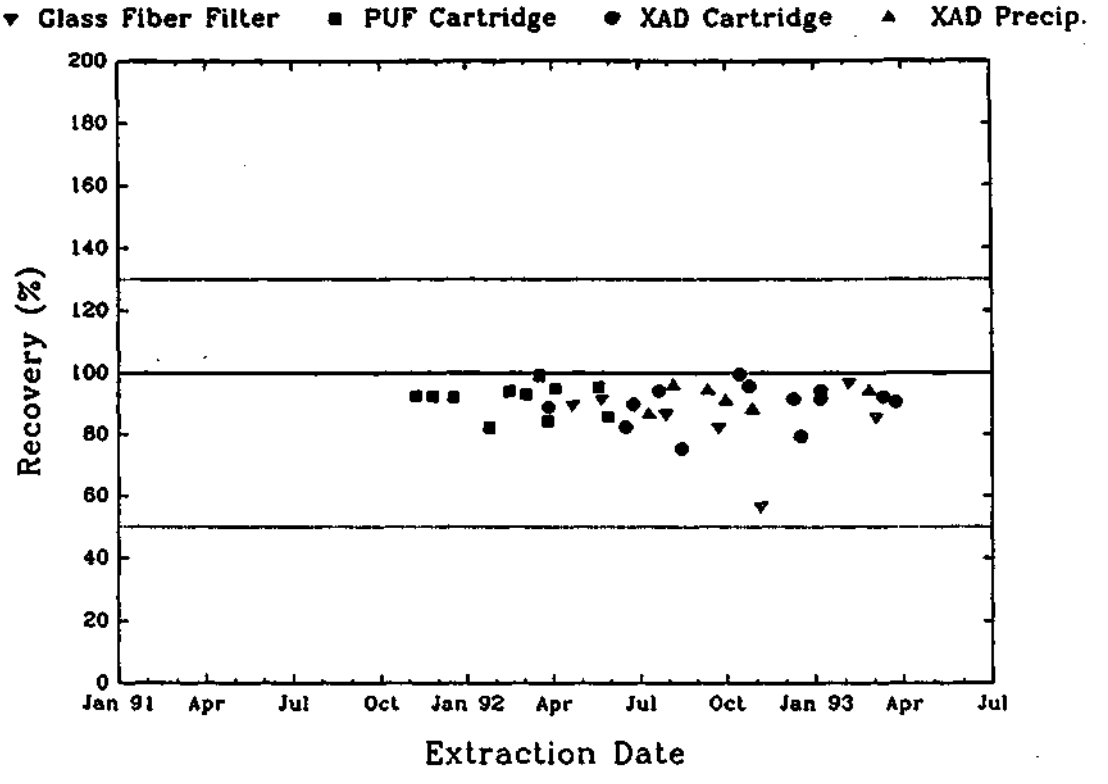

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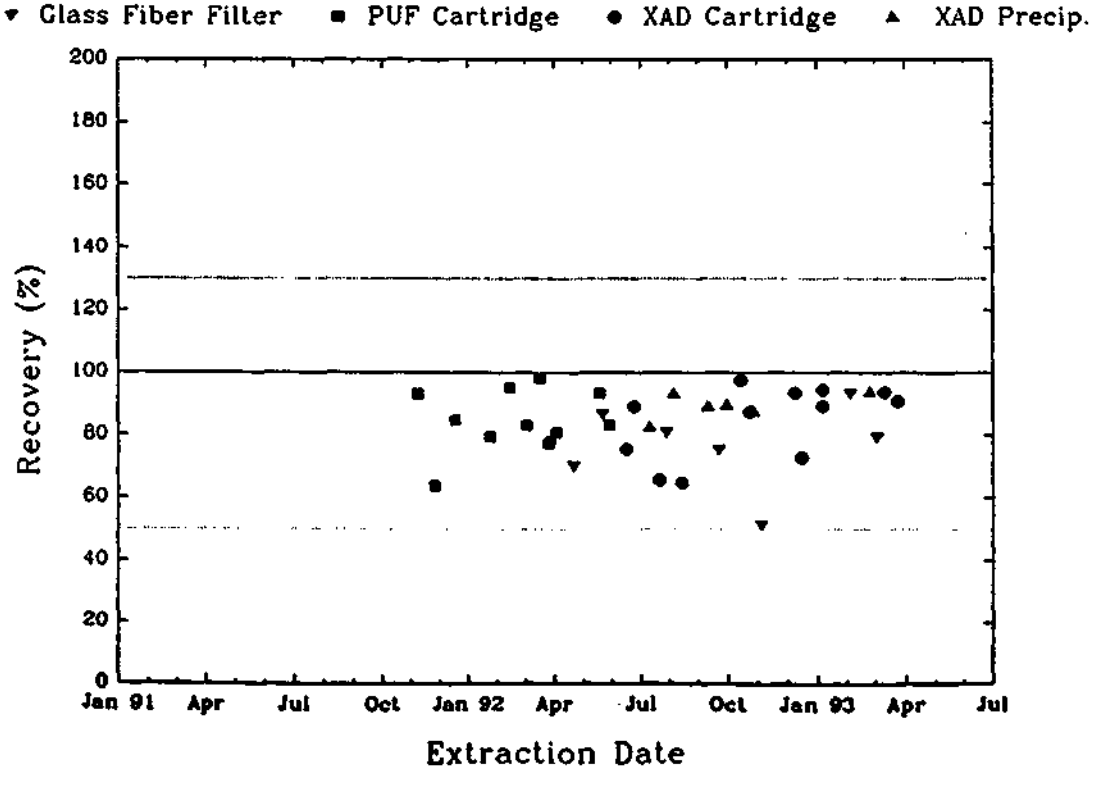

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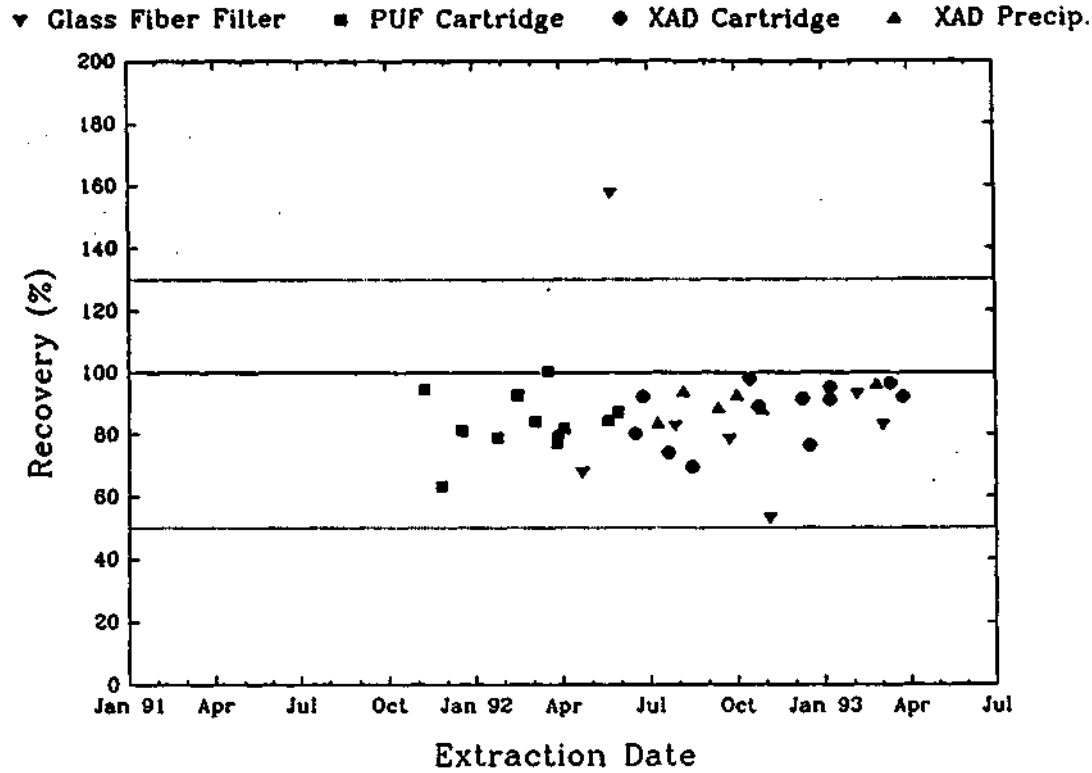

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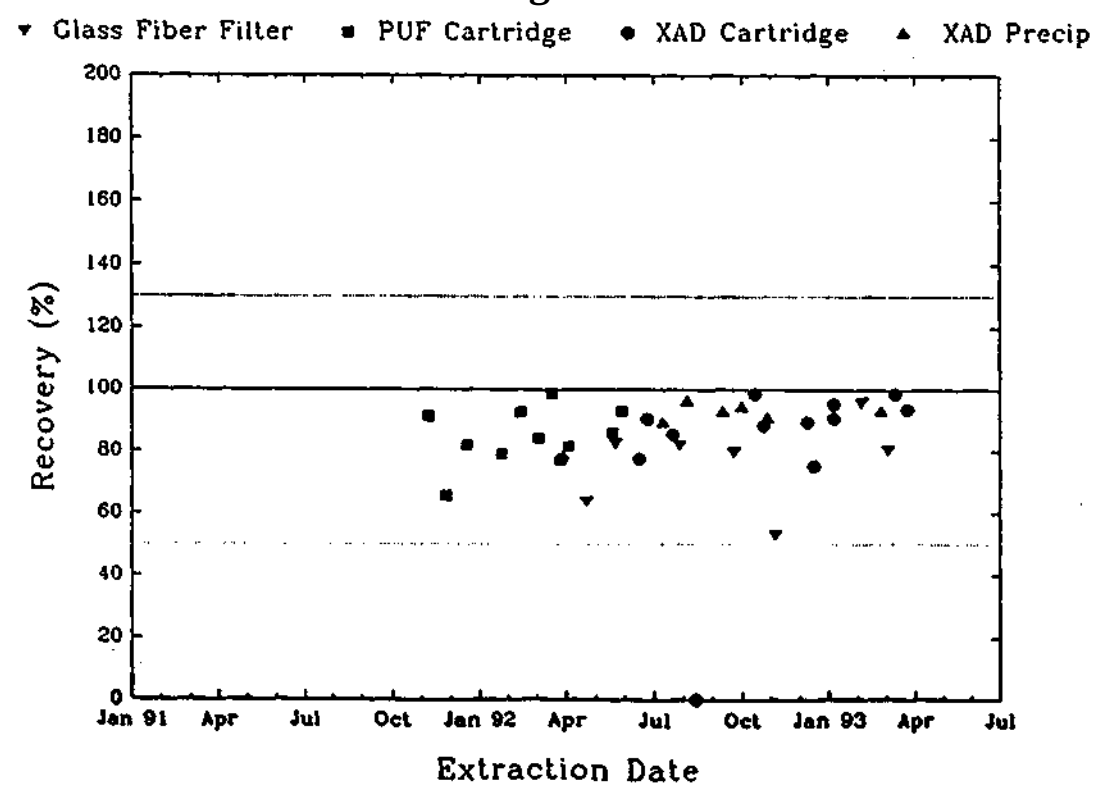

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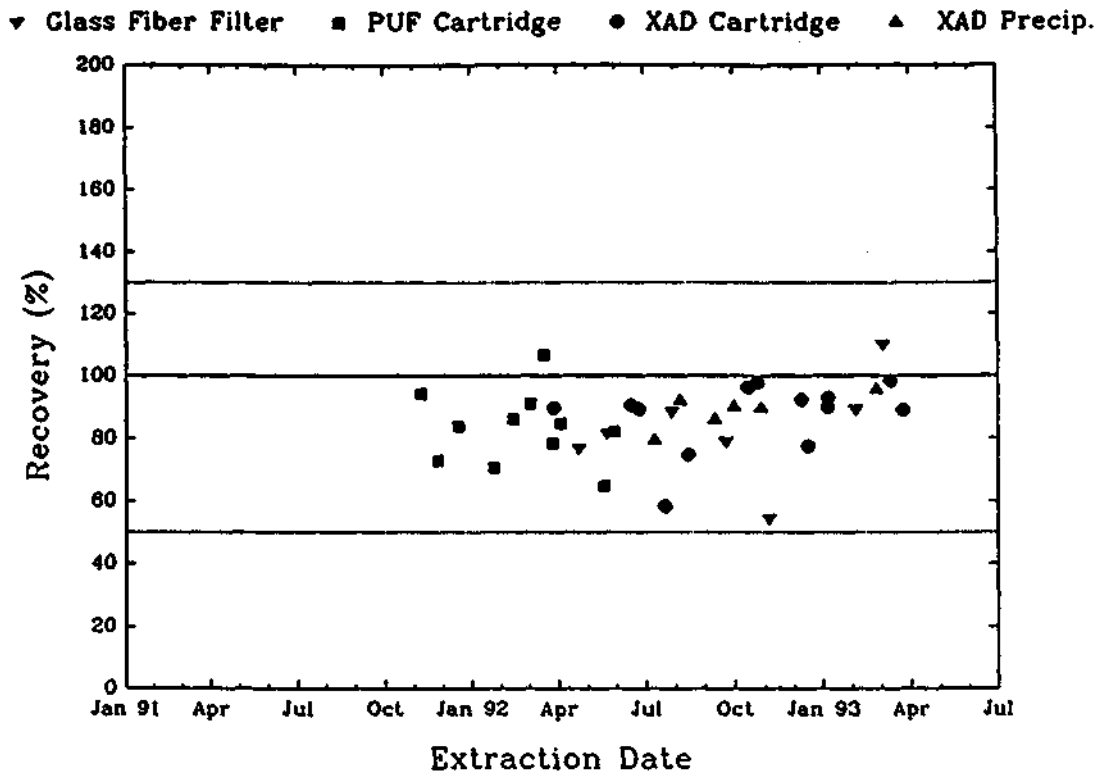

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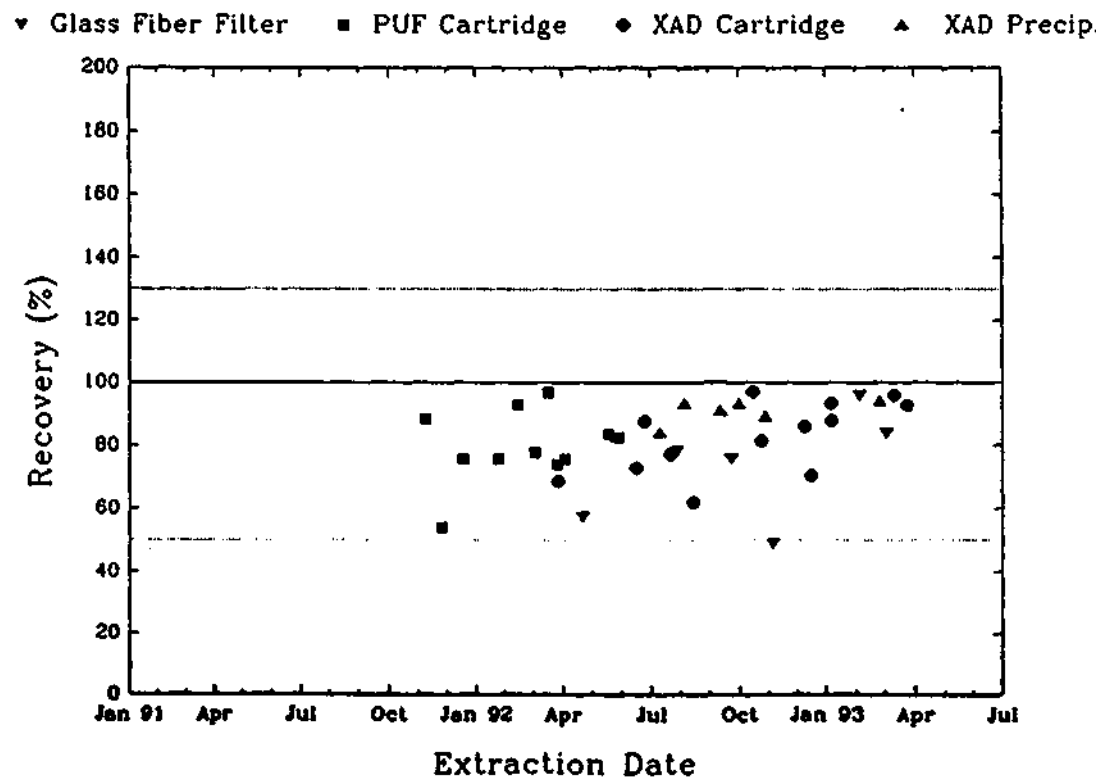

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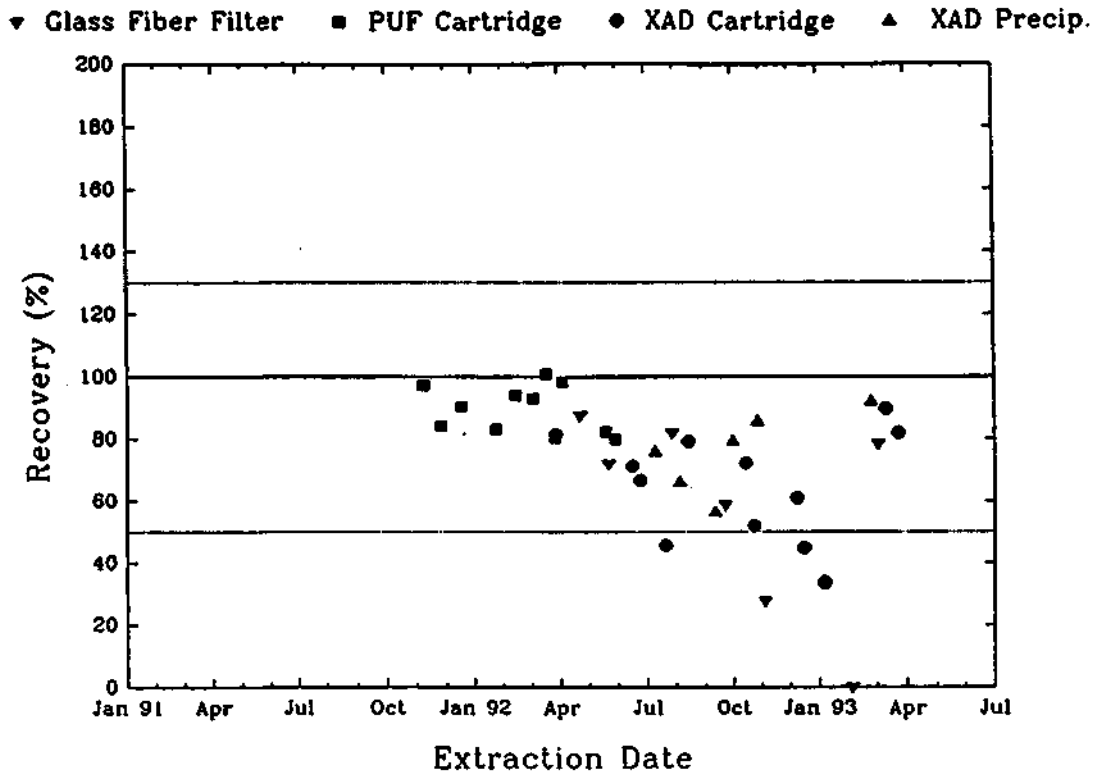

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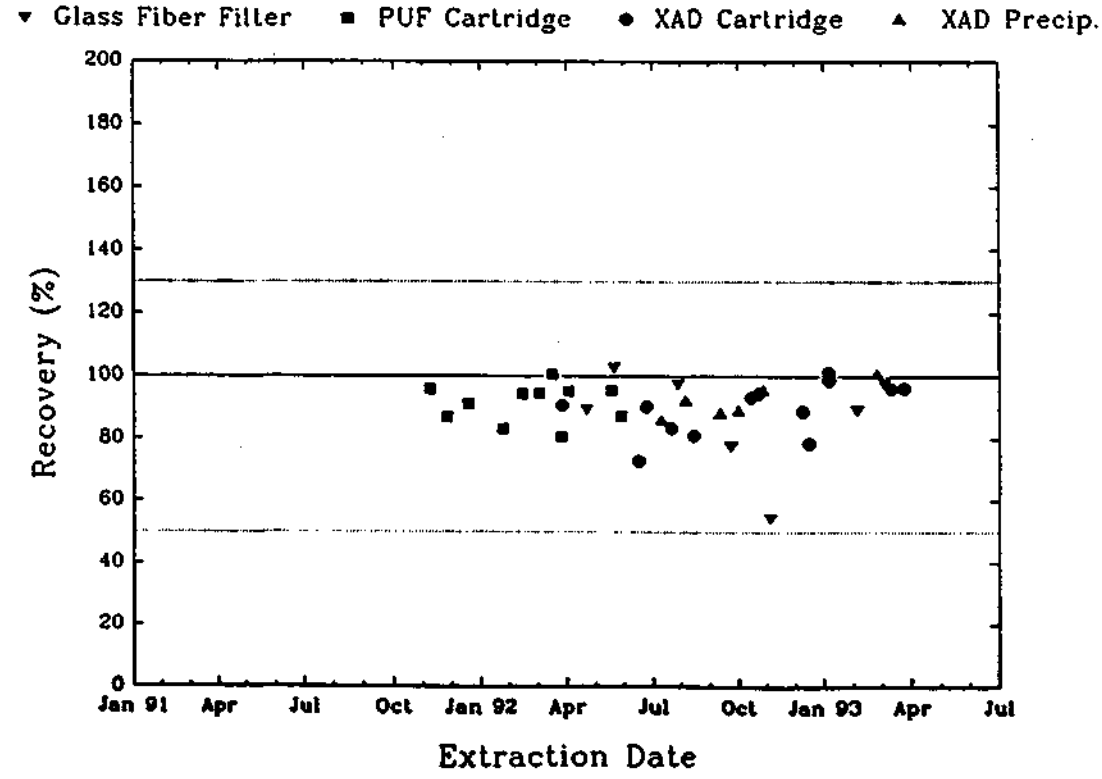

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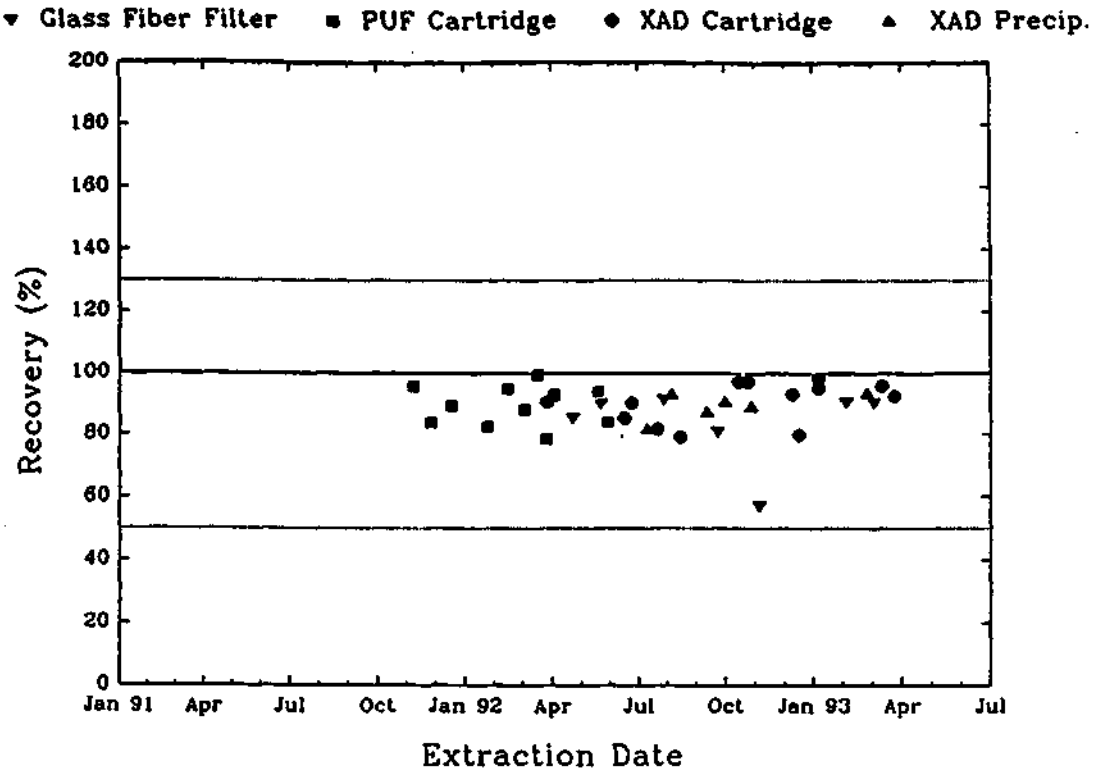

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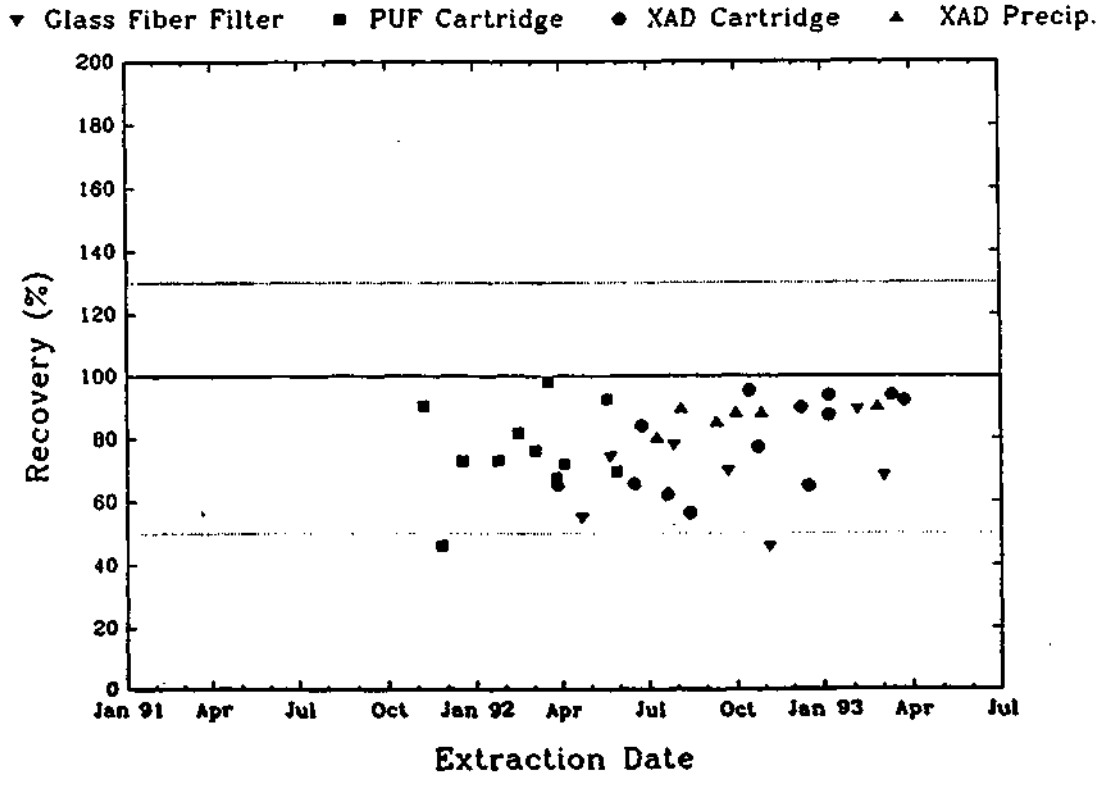

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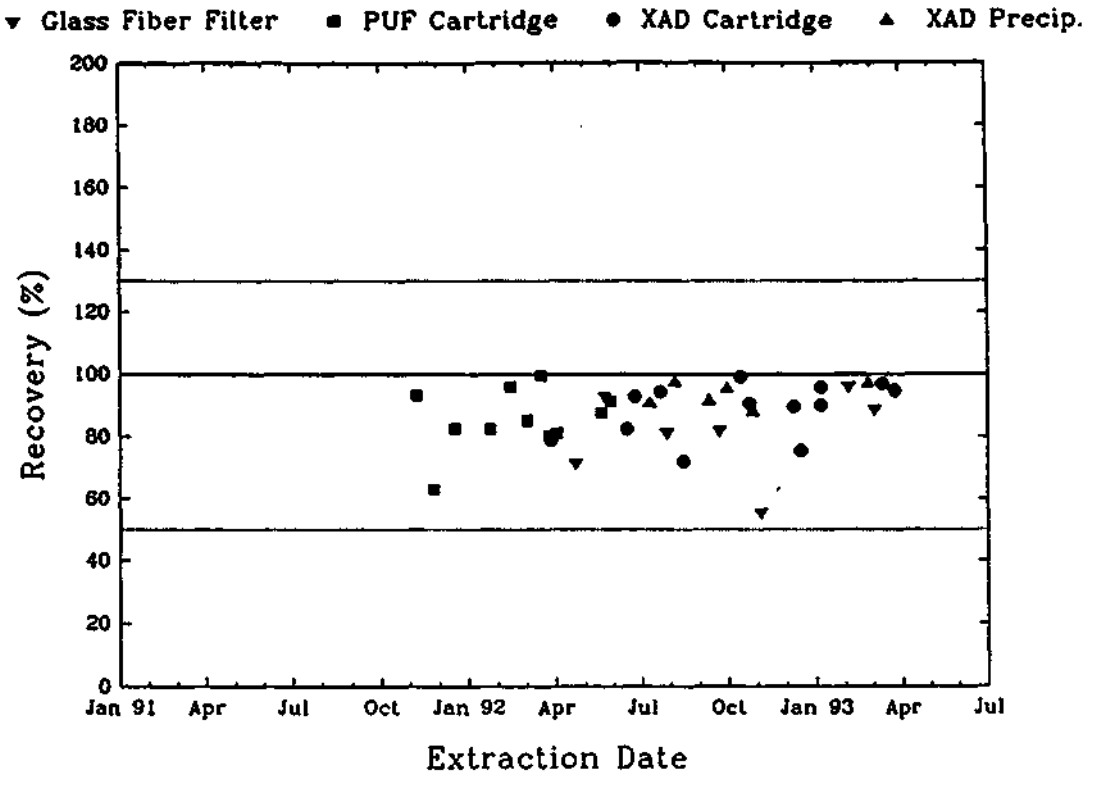

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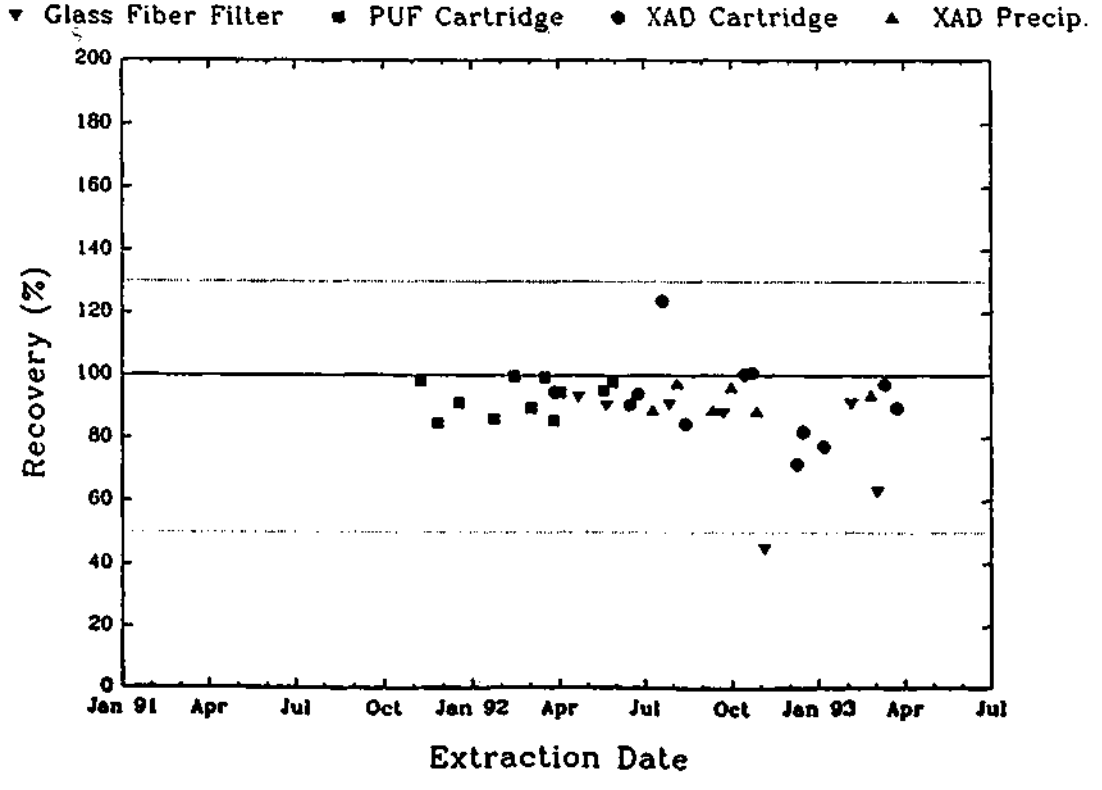

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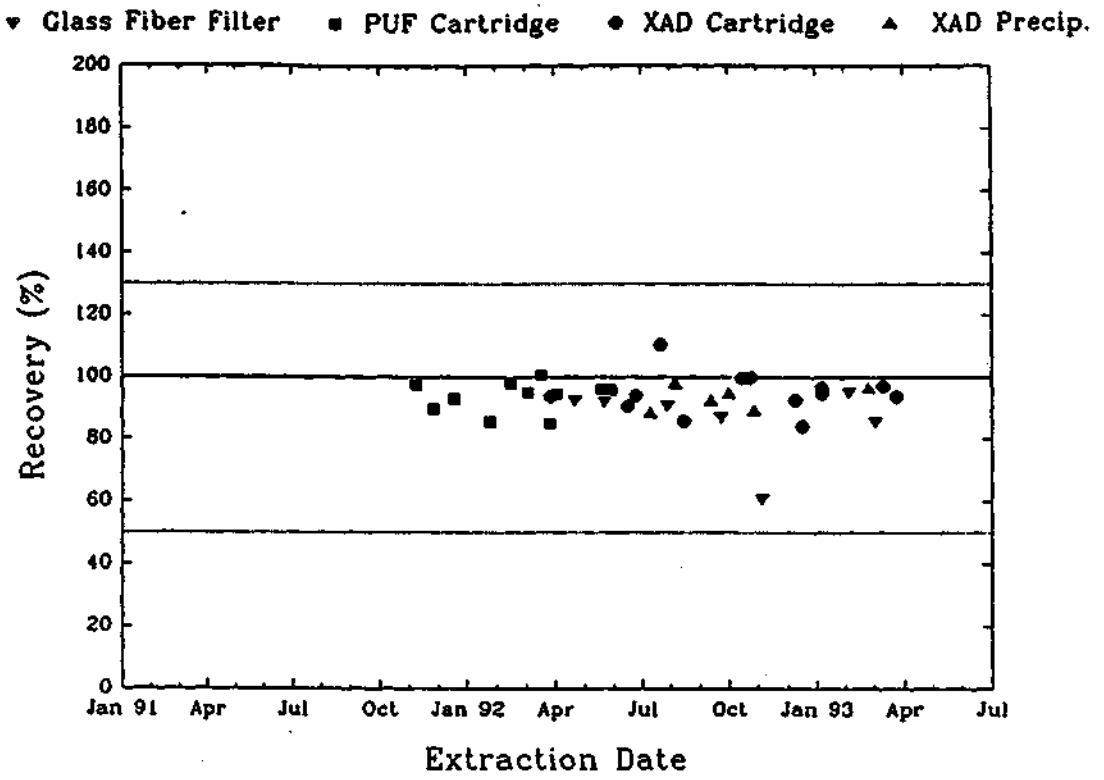

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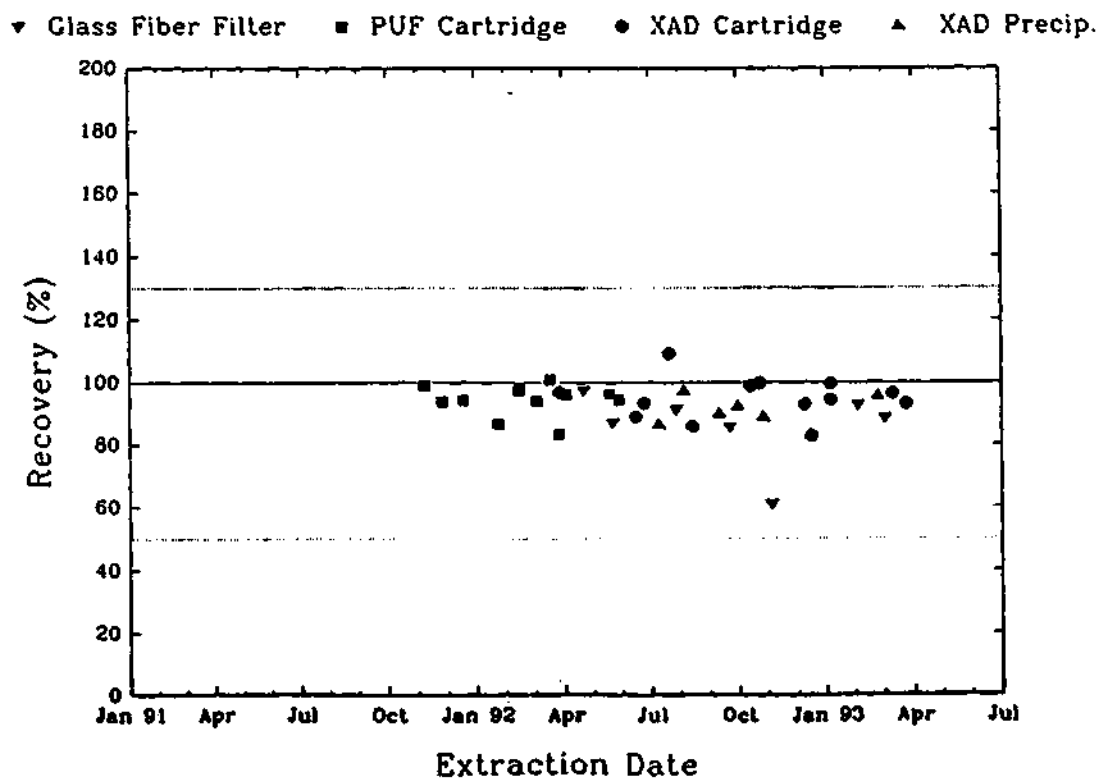

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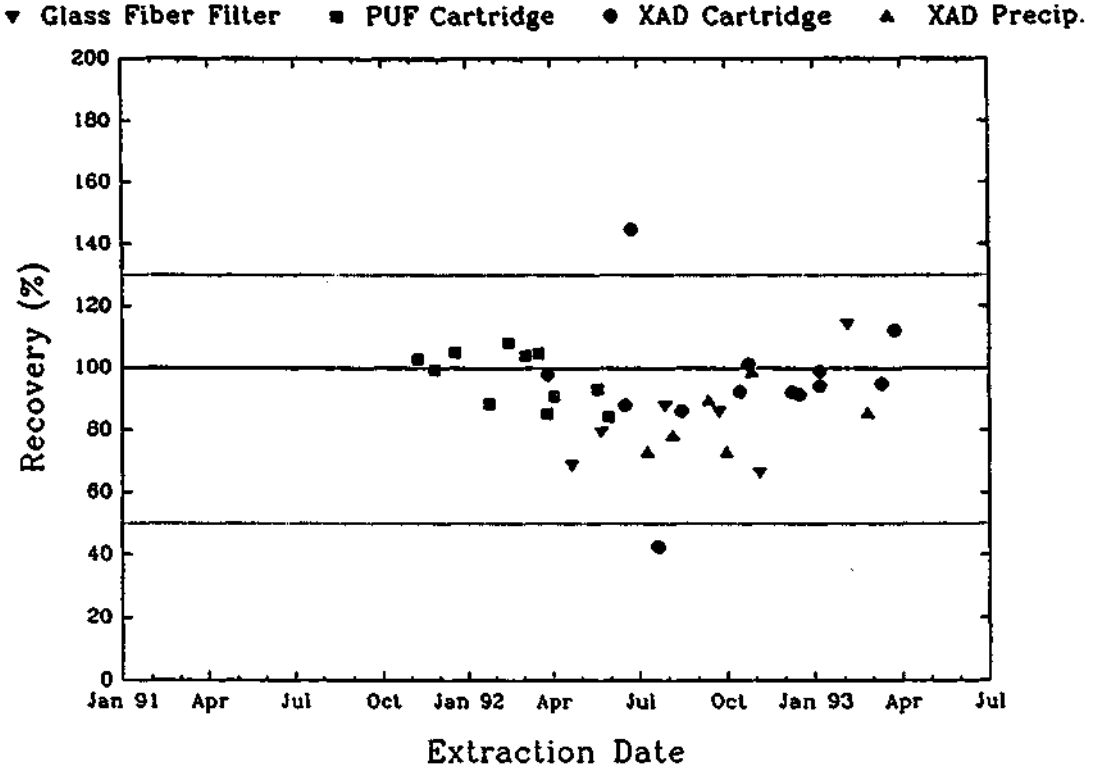

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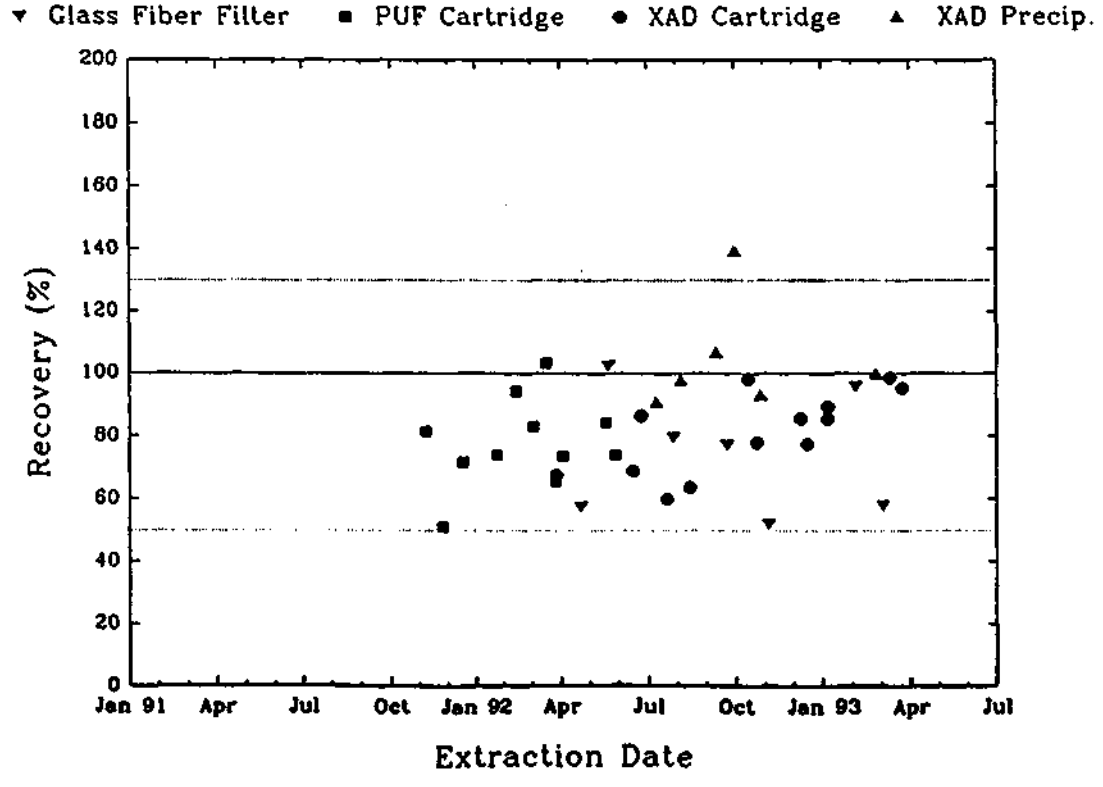

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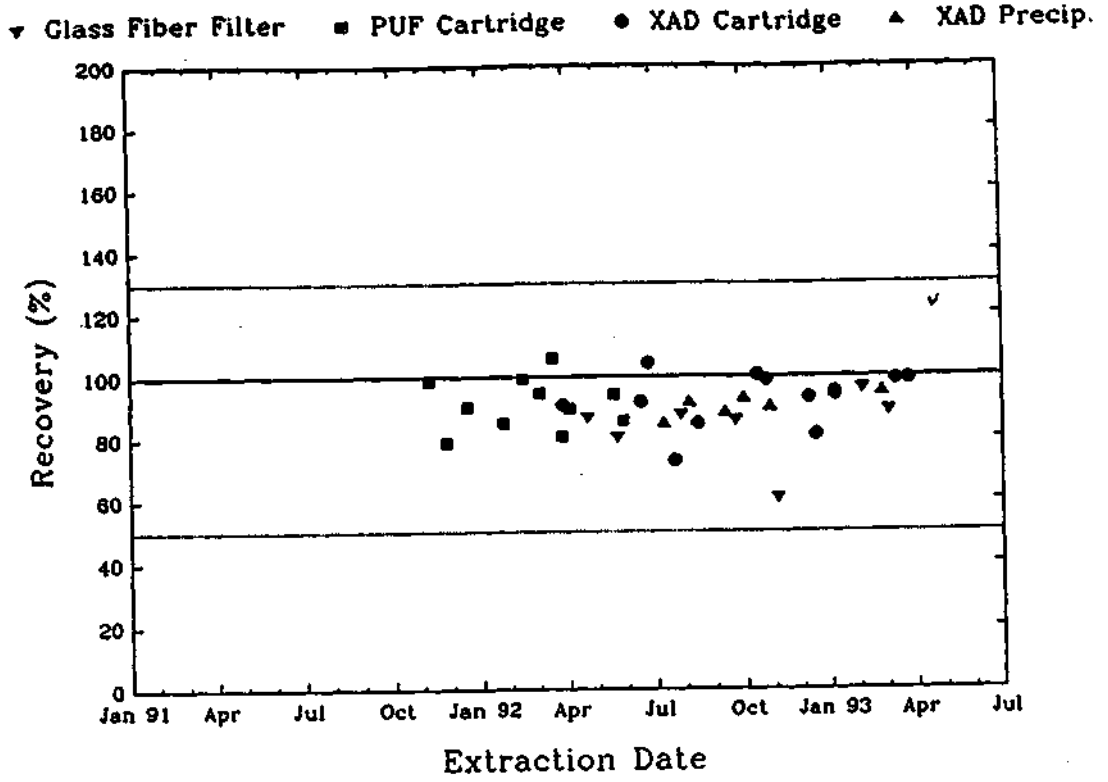

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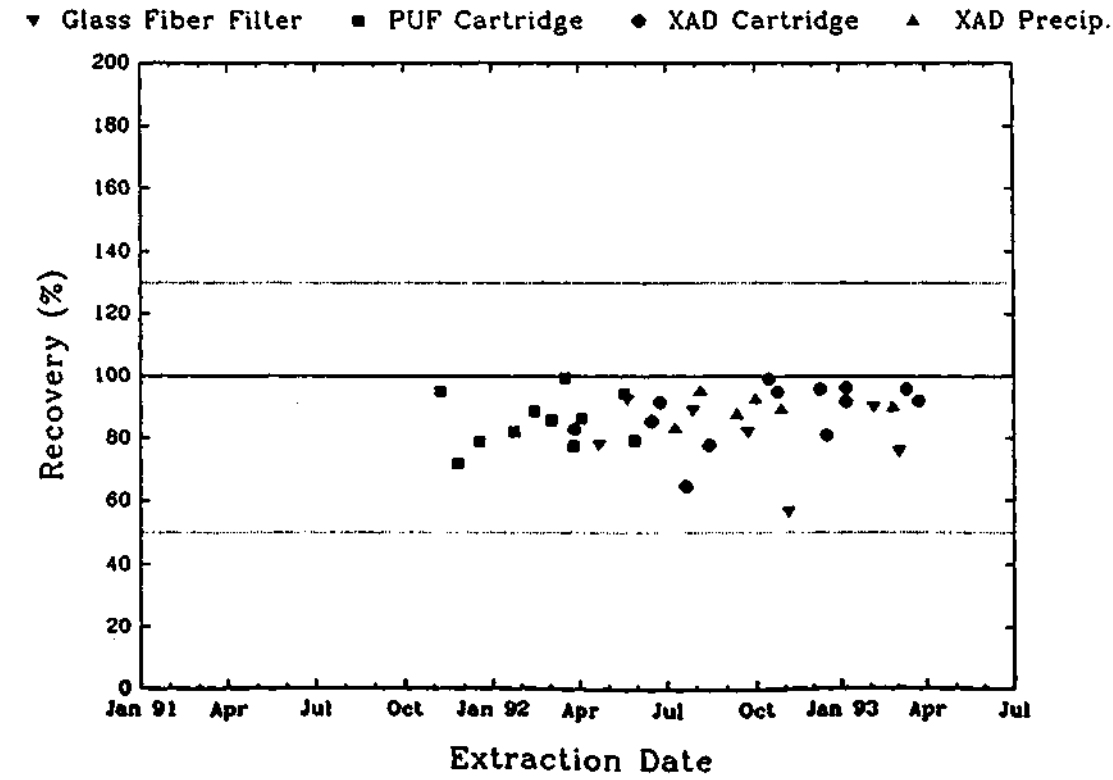

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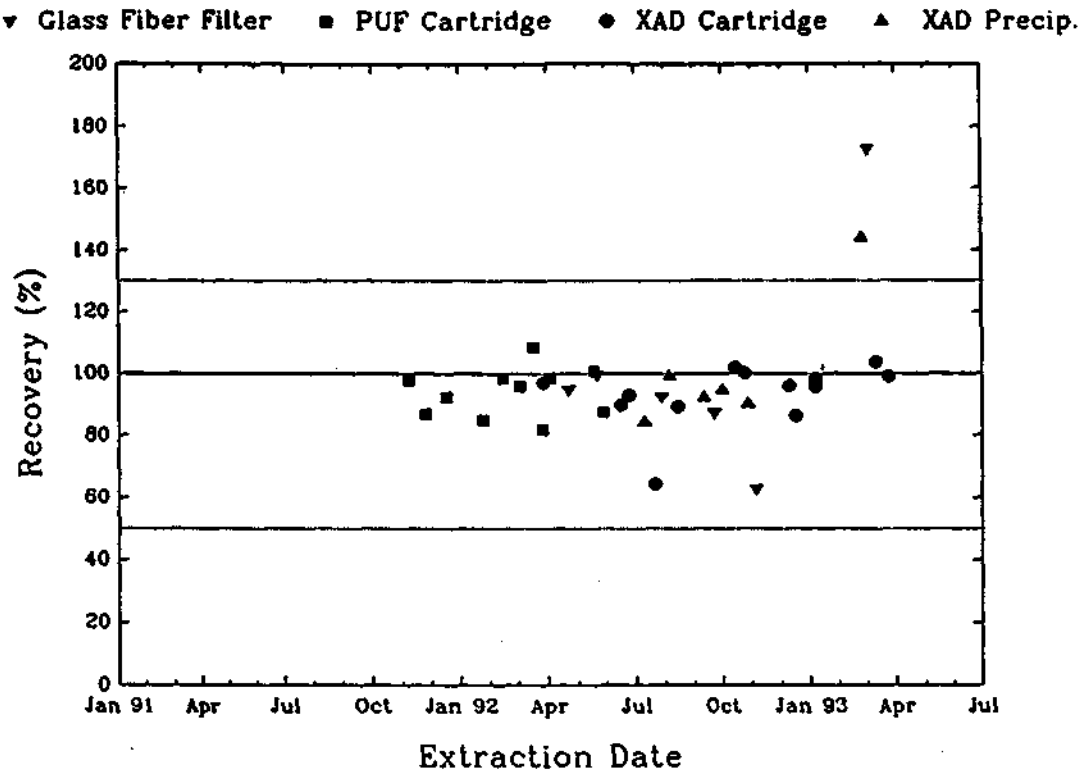

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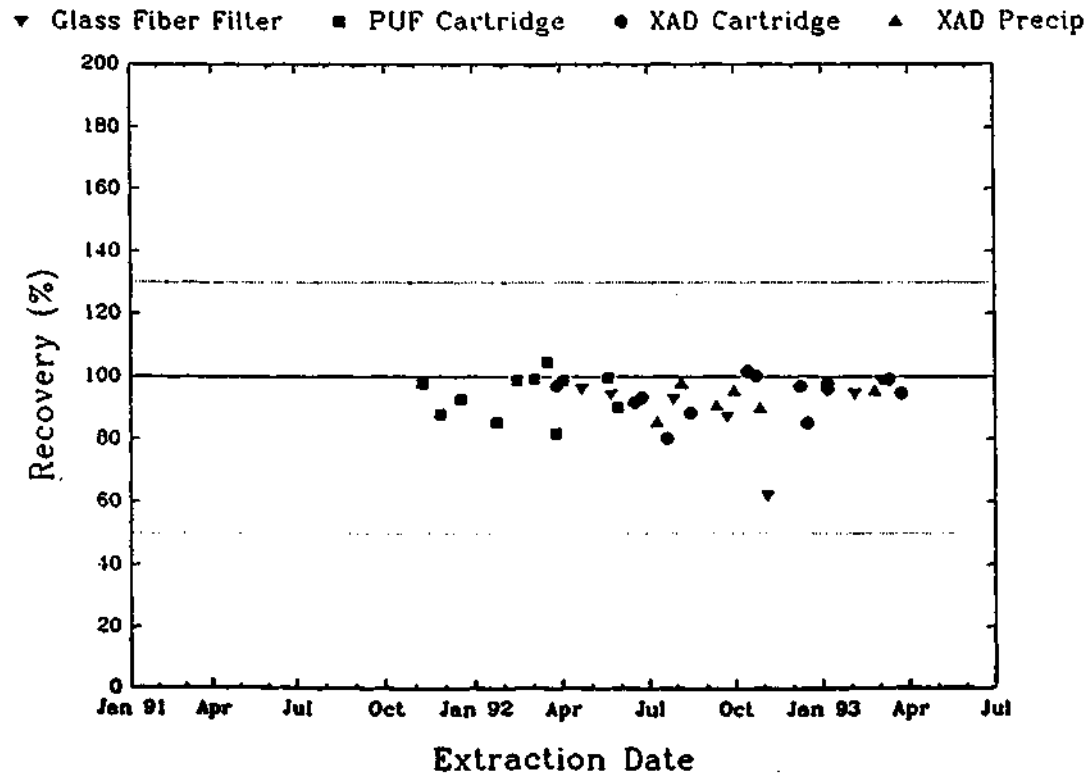

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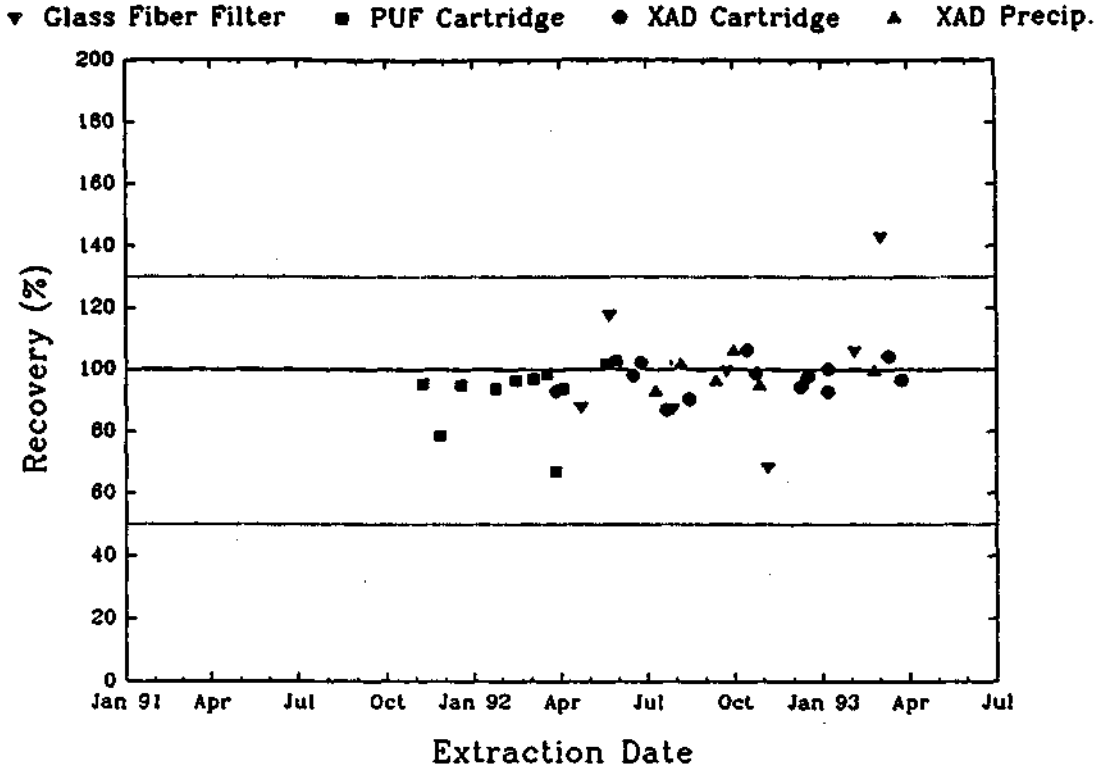

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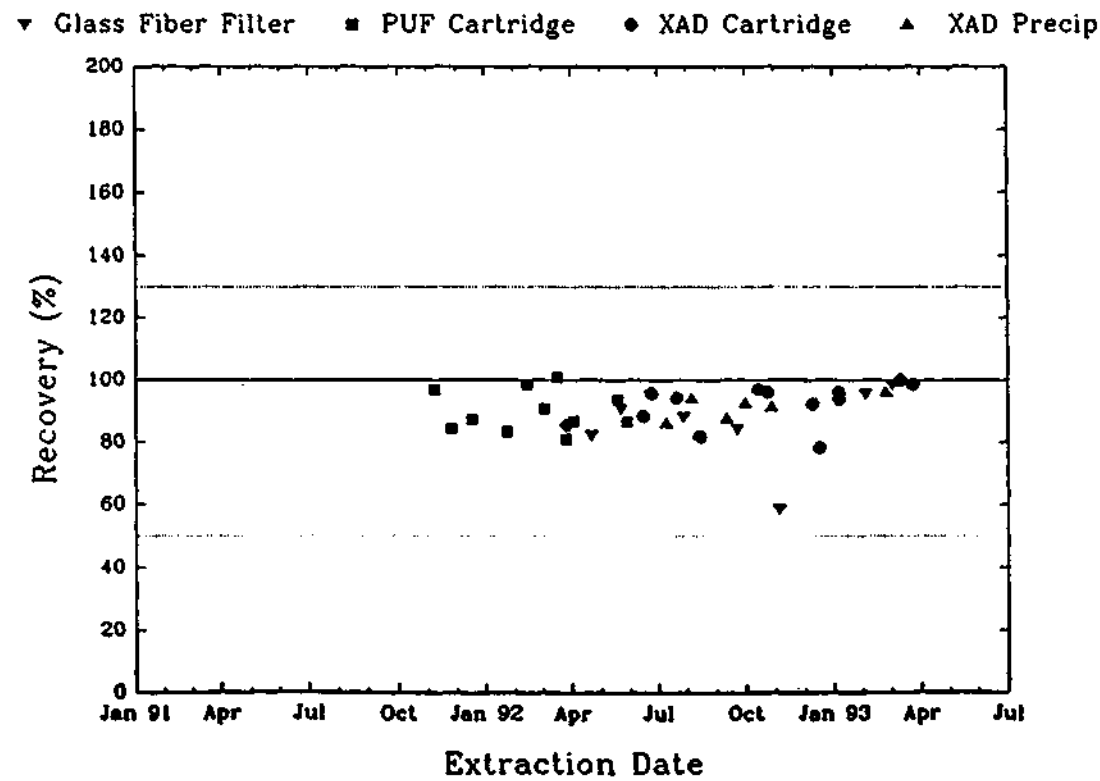

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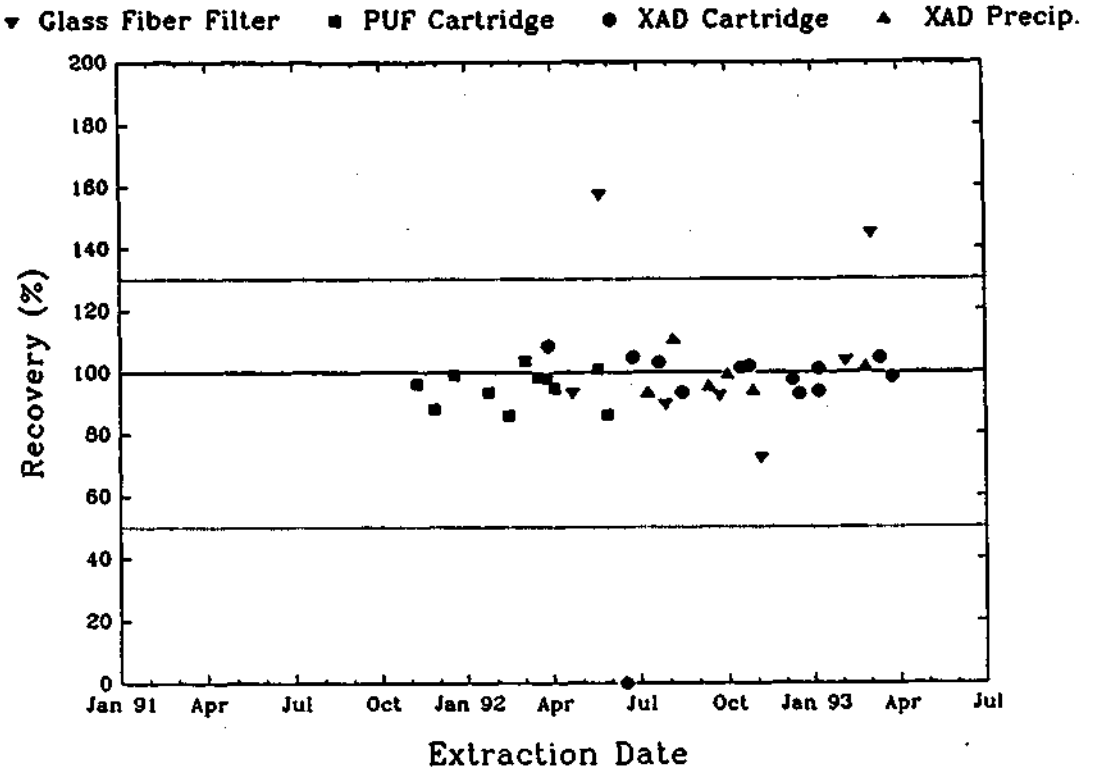

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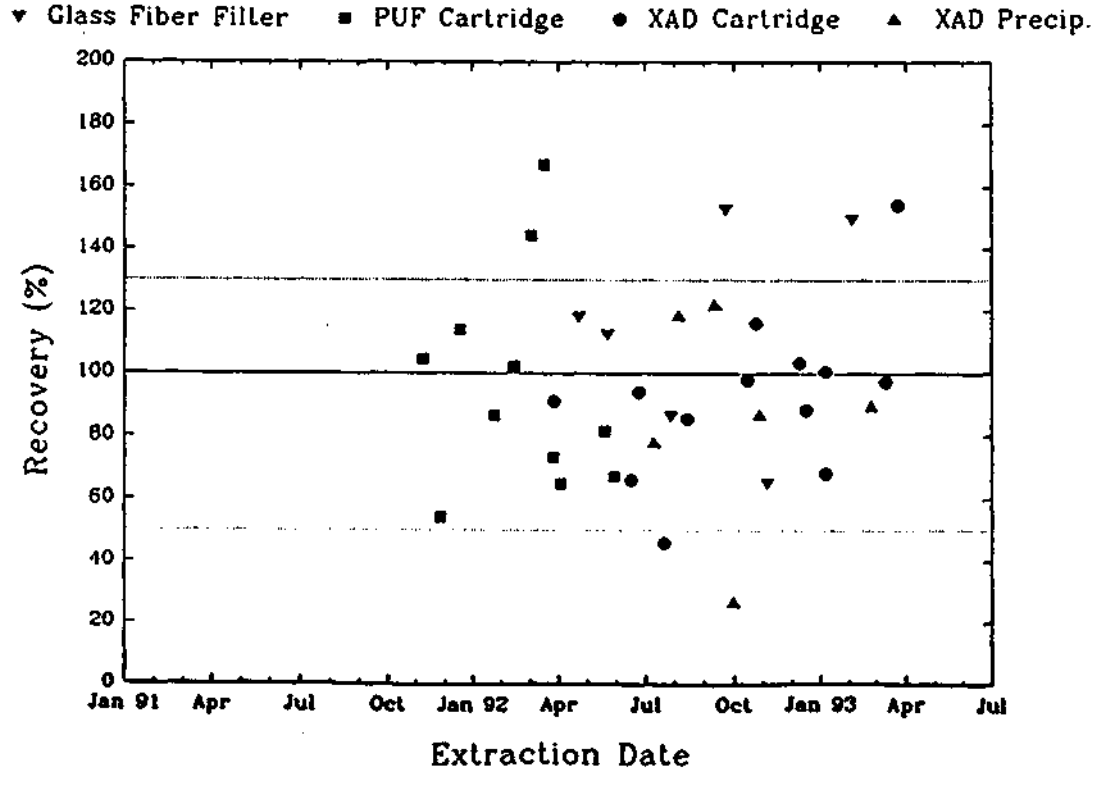

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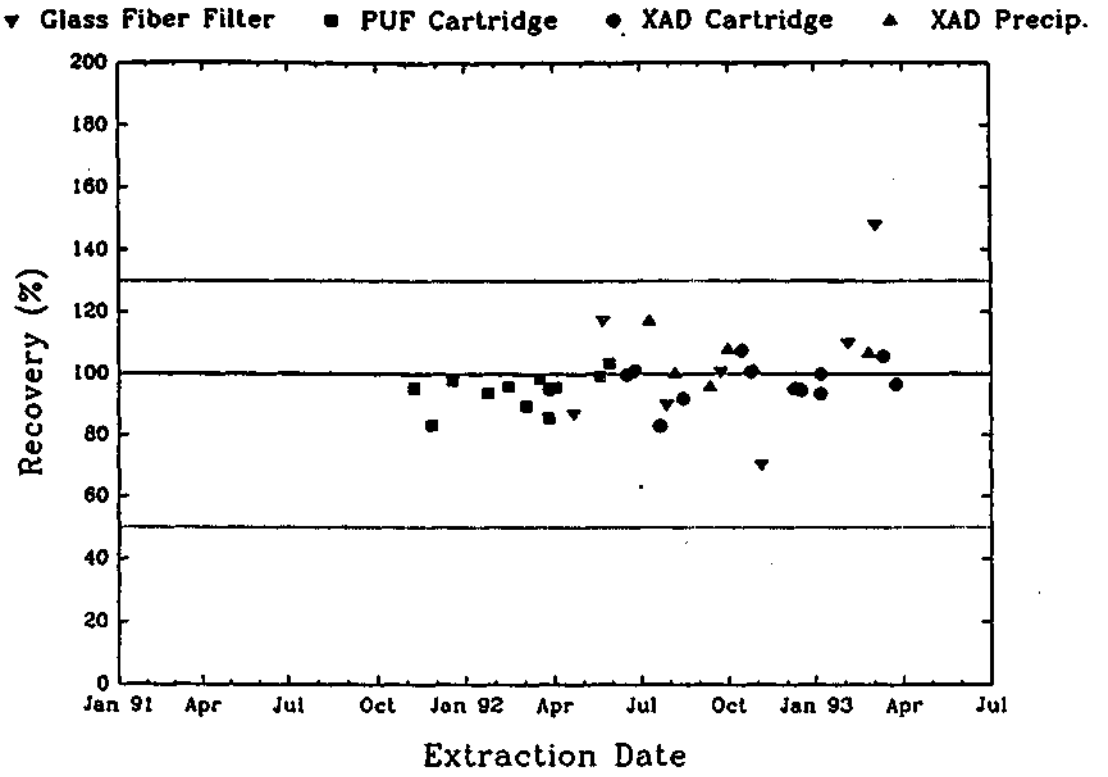

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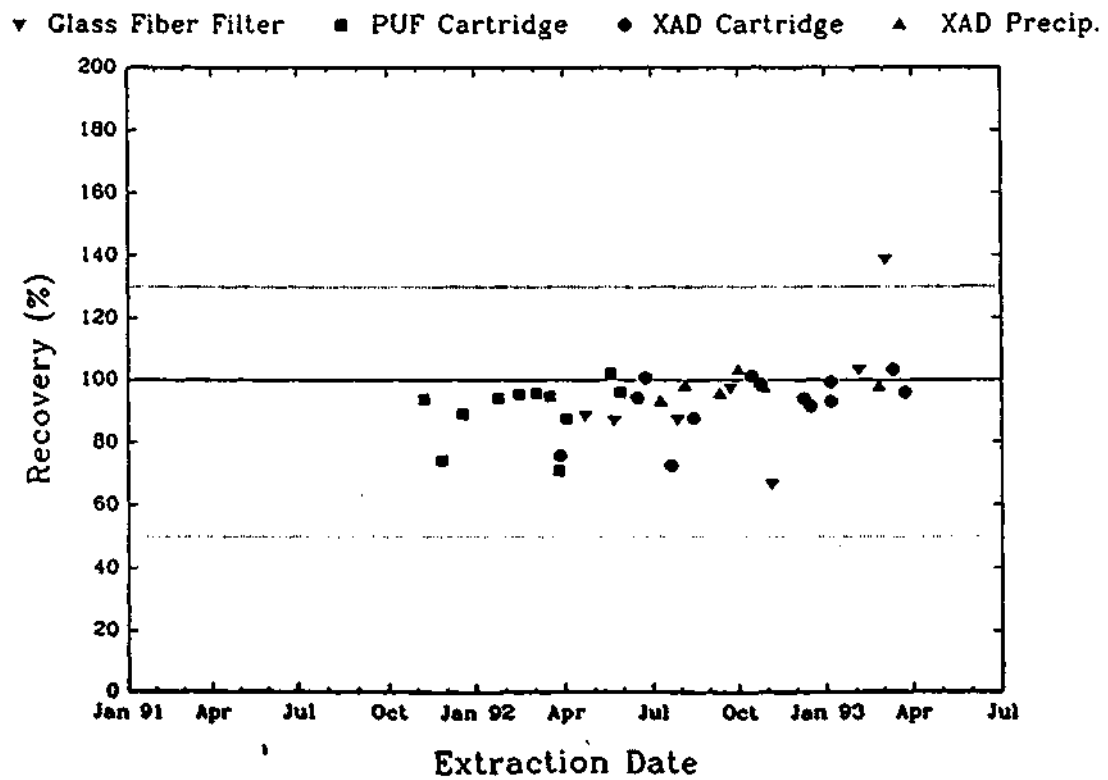
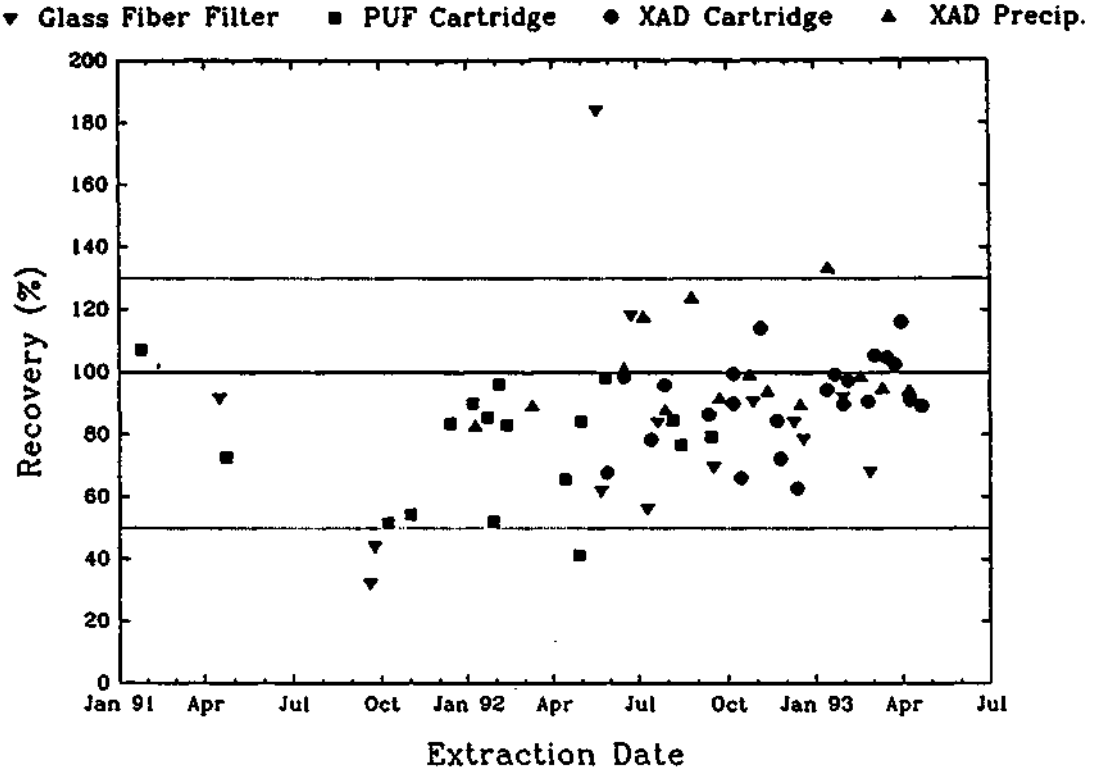


Pesticides - Dieldrin



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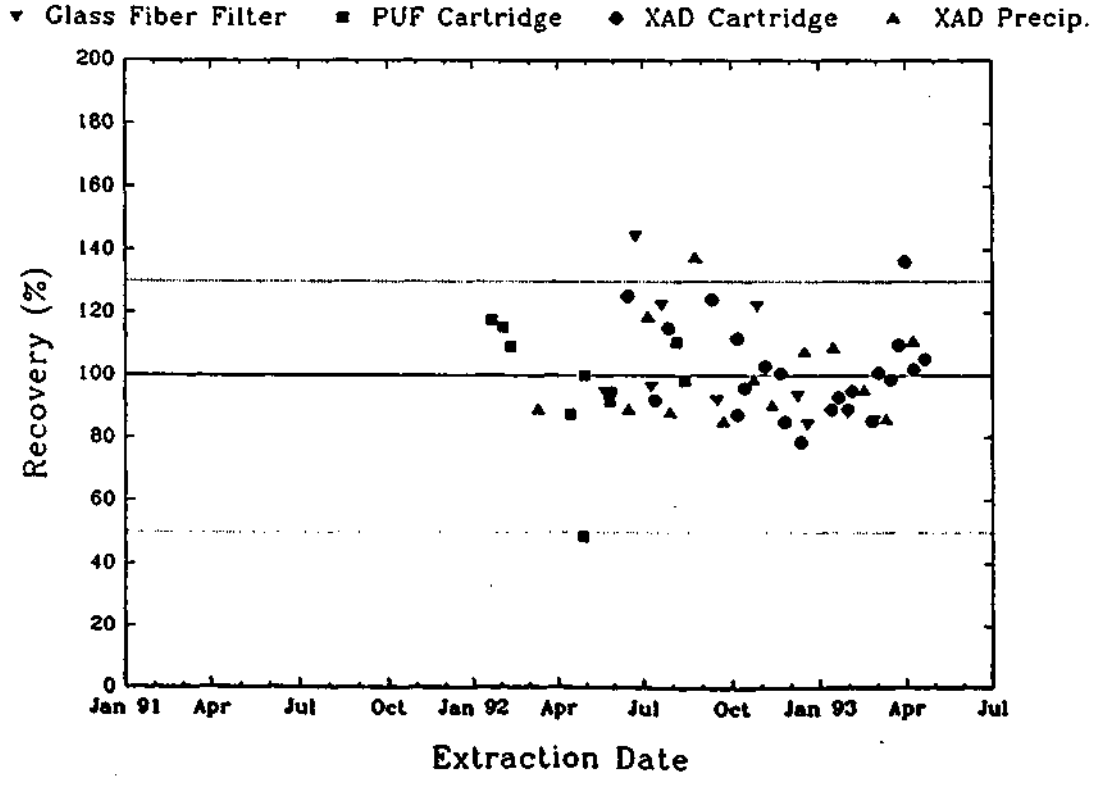

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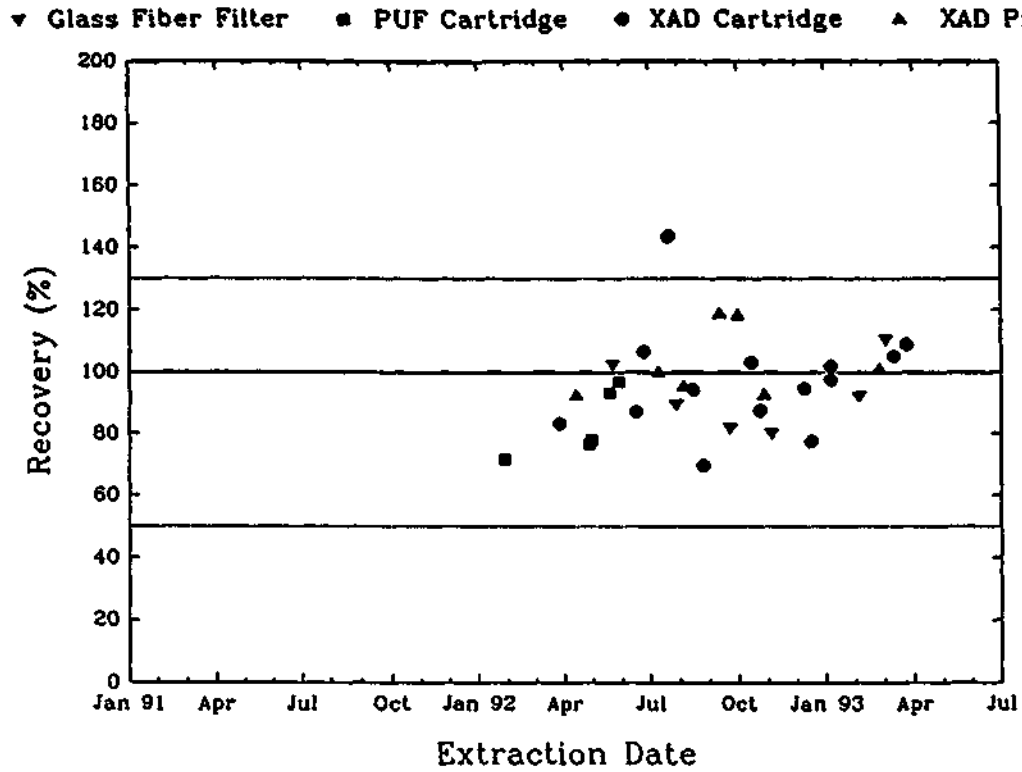
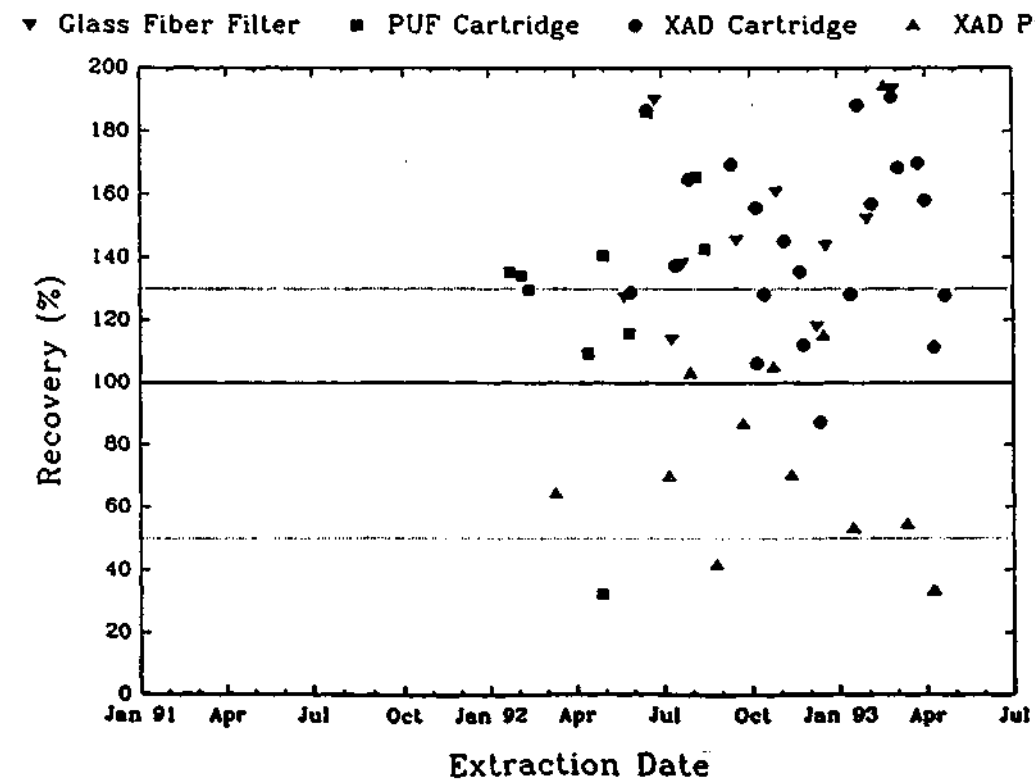
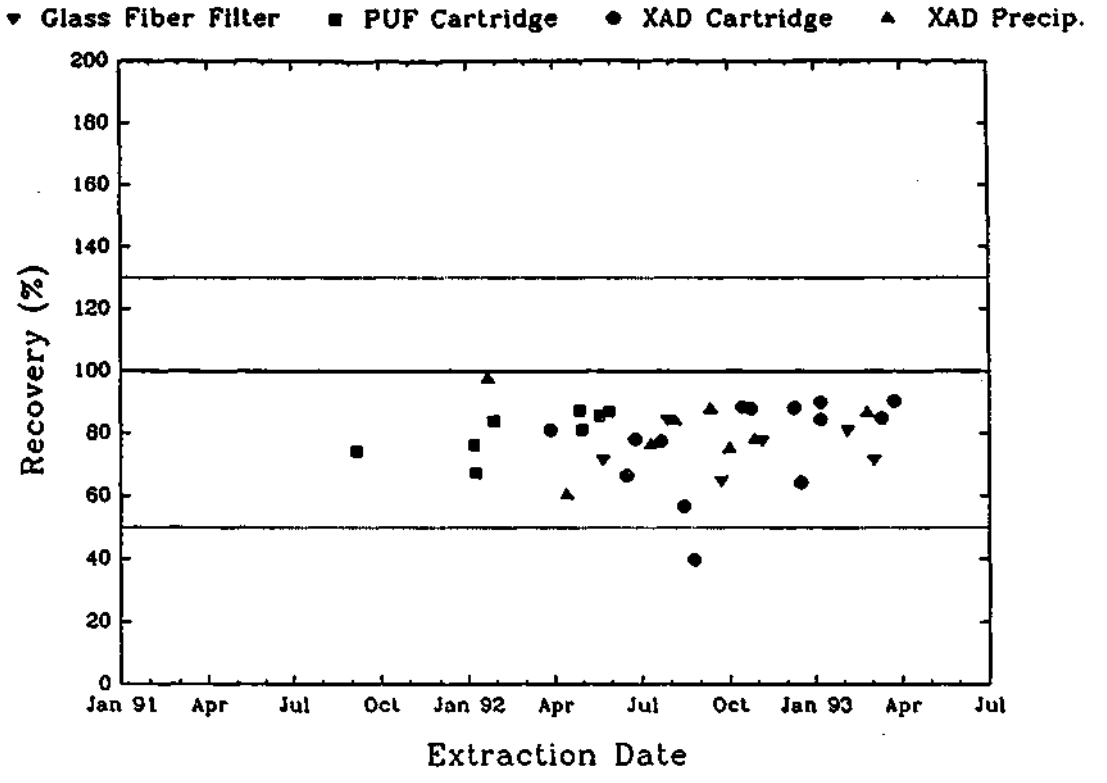


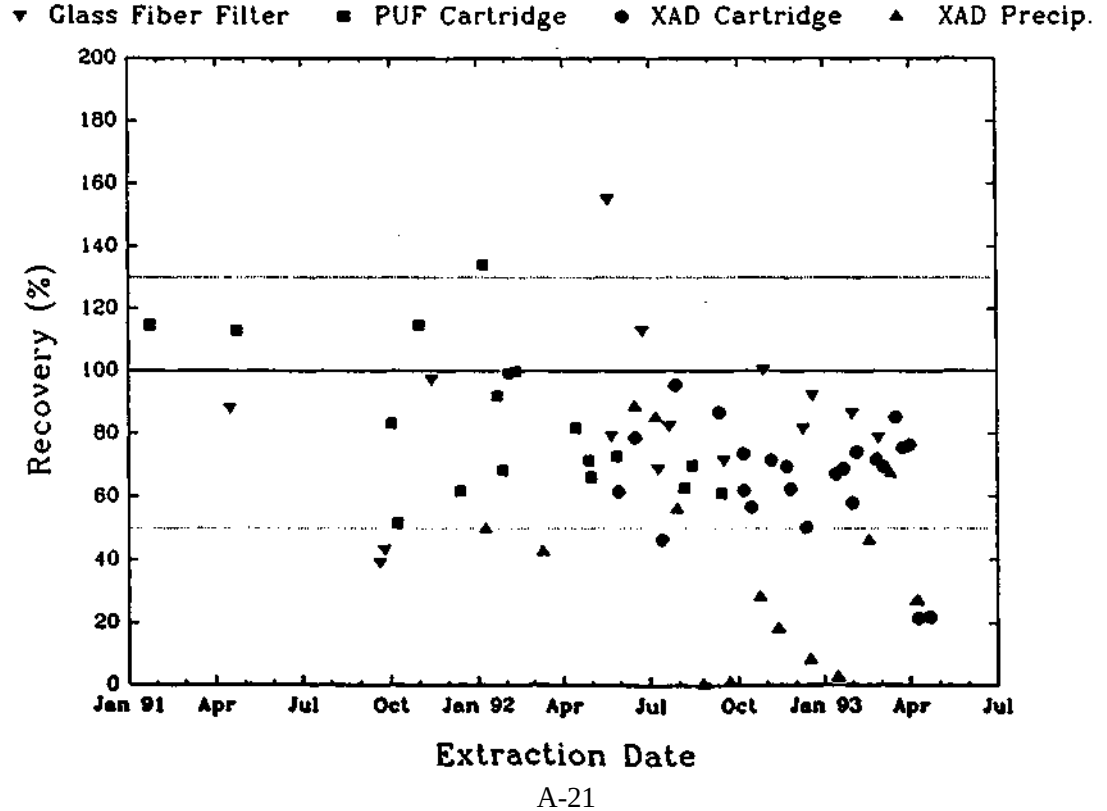
Pesticides - DDT



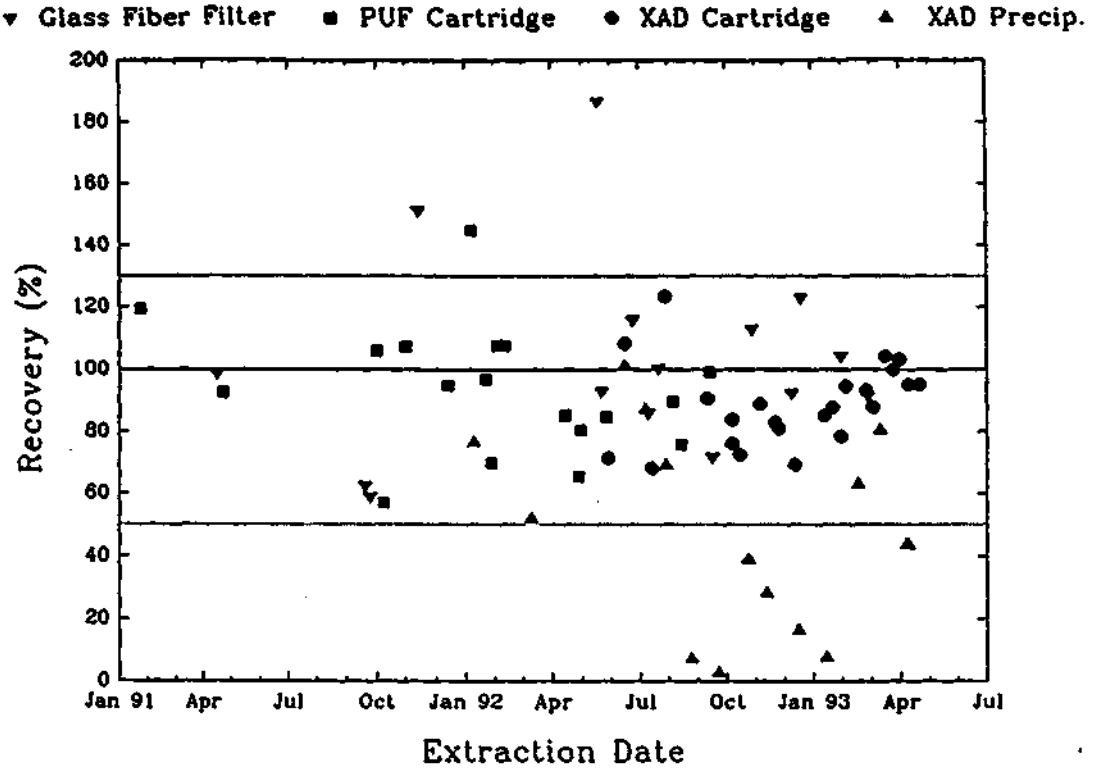
Pesticide - Hexachlorobenzene (HCB)



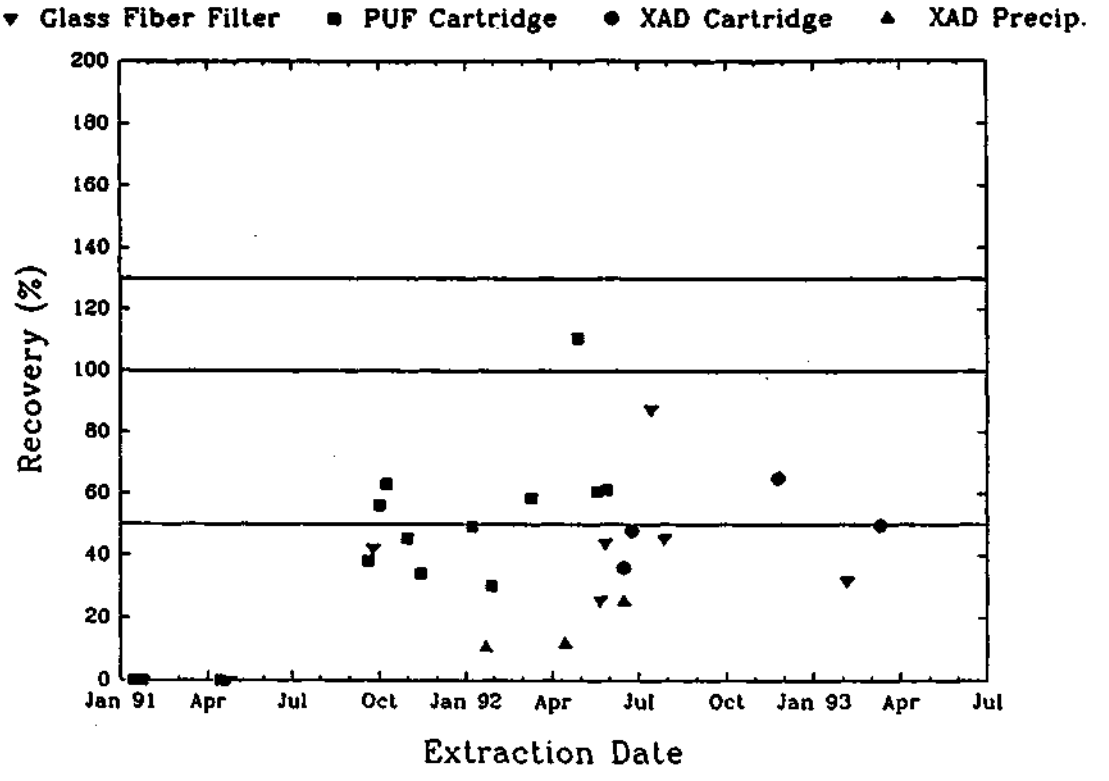
Pesticides - alpha HCH



Pesticides - gamma HCH



PAH - Acenaphthene



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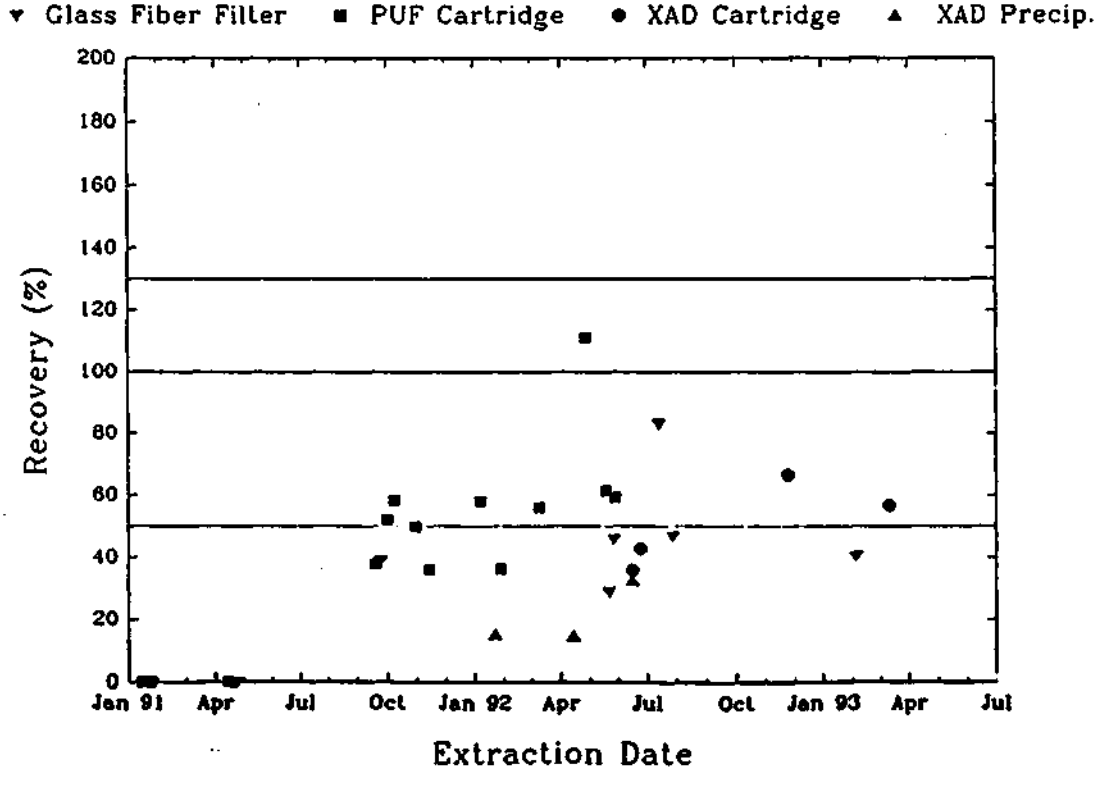
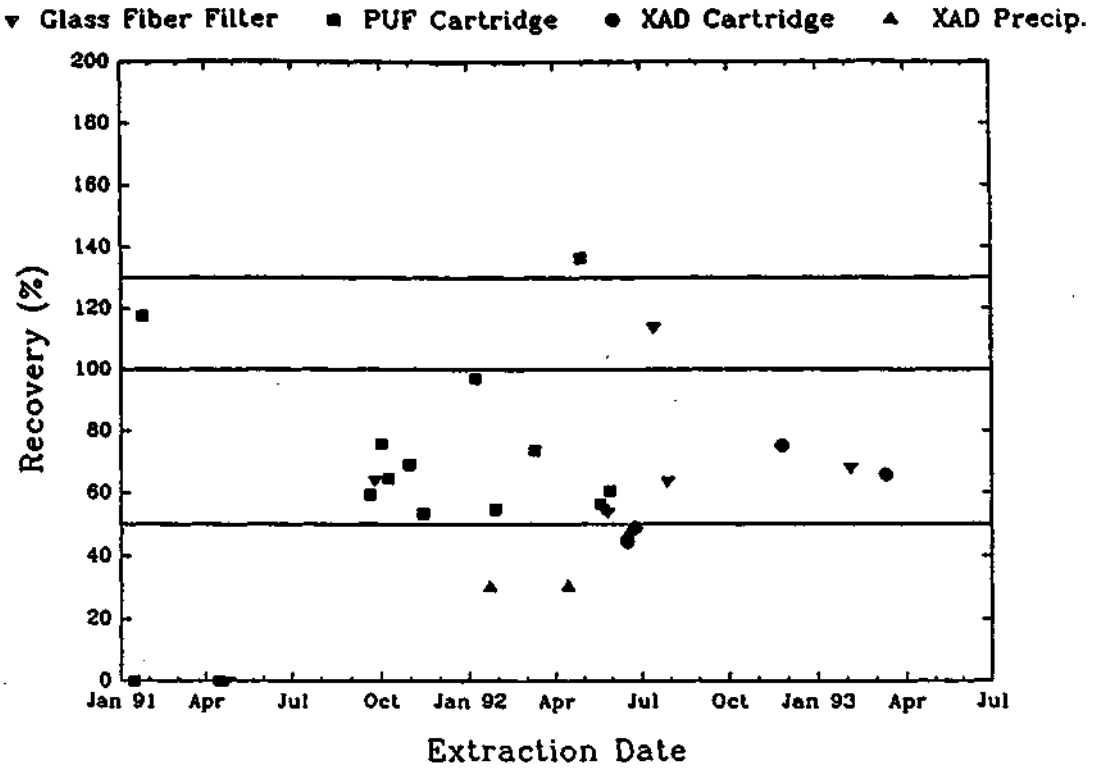
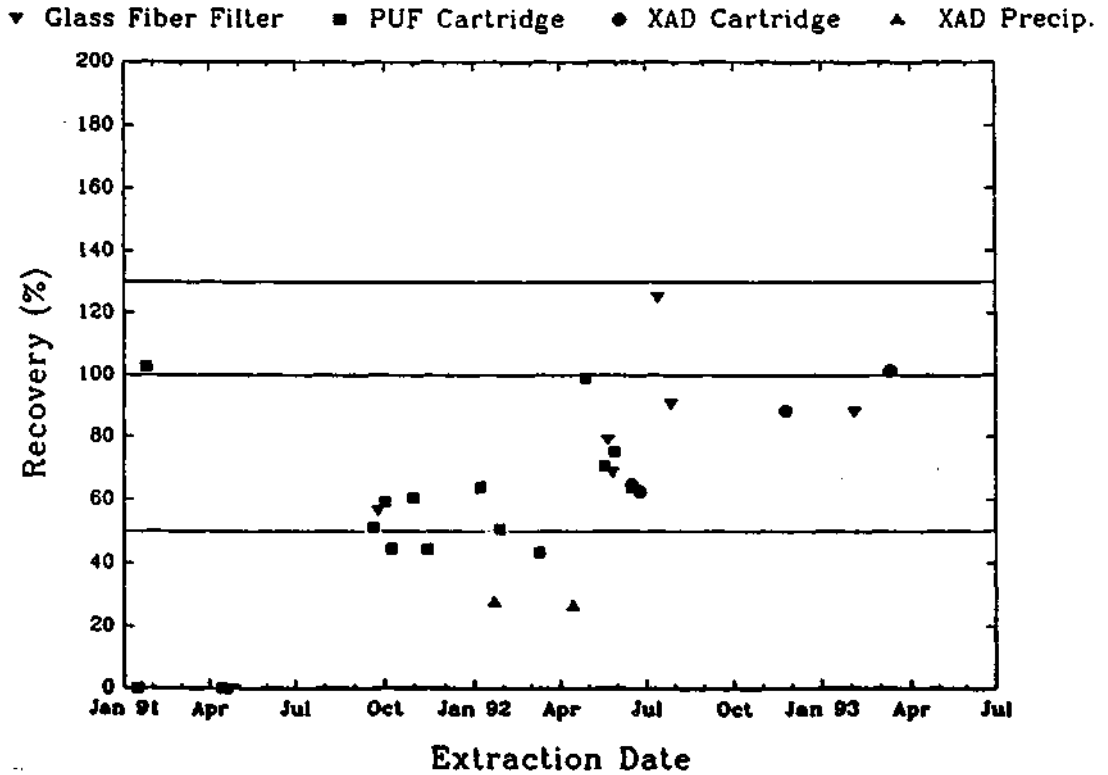


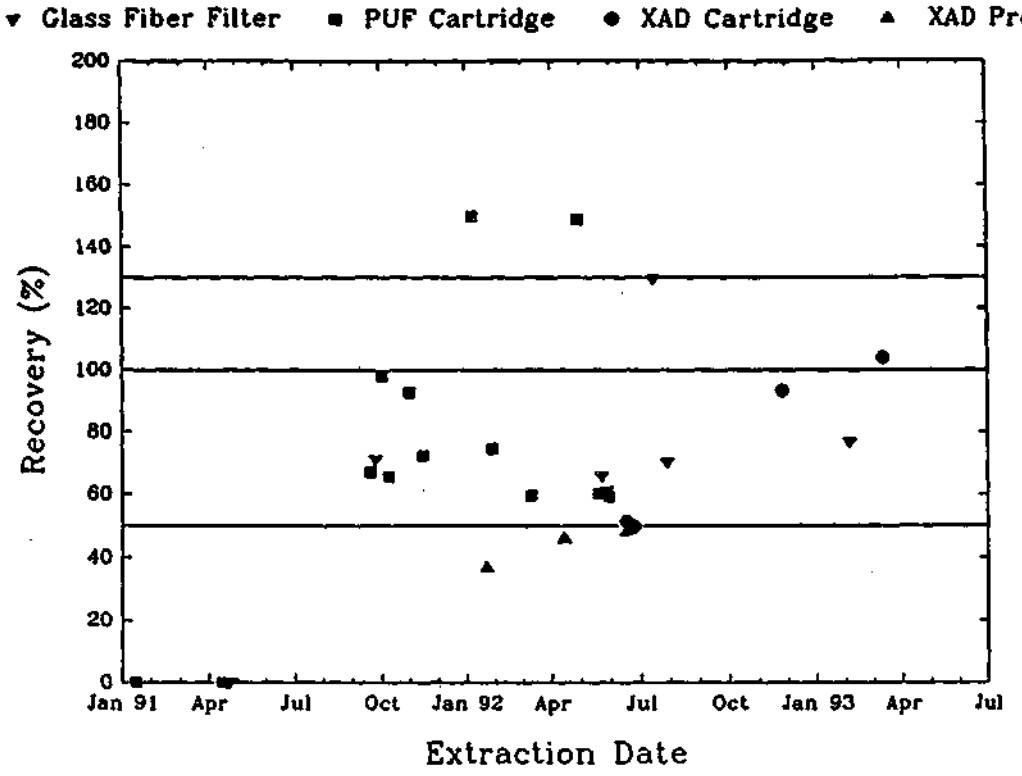
PAH - Anthracene



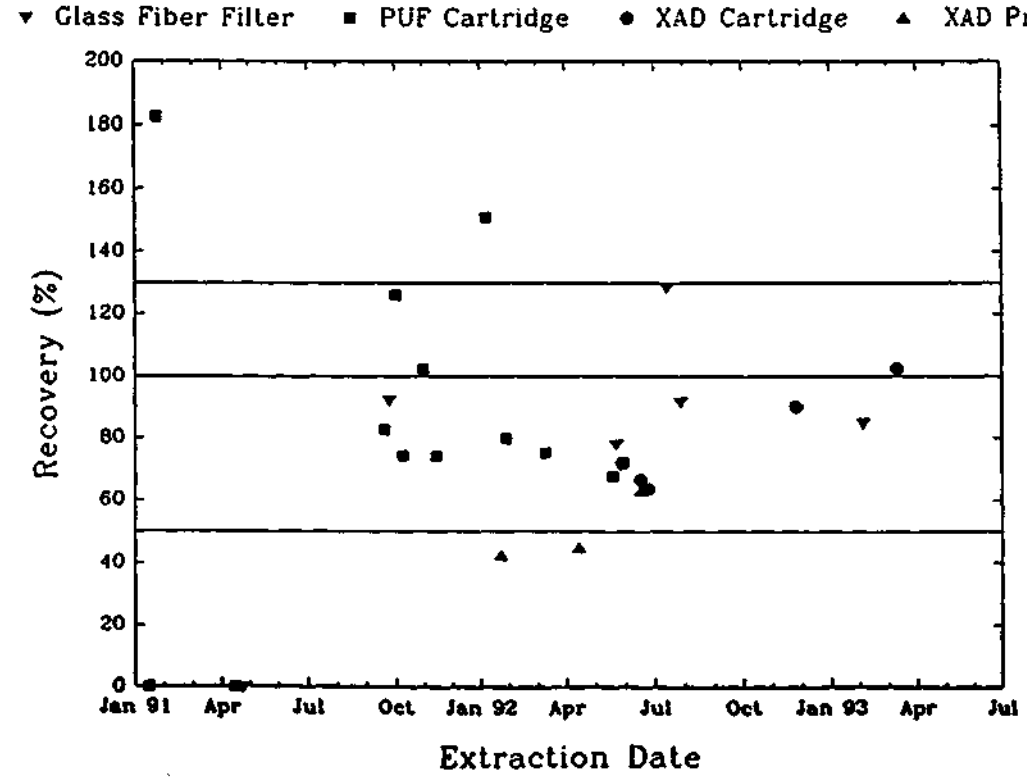
PAH - Benzo(a)anthracene



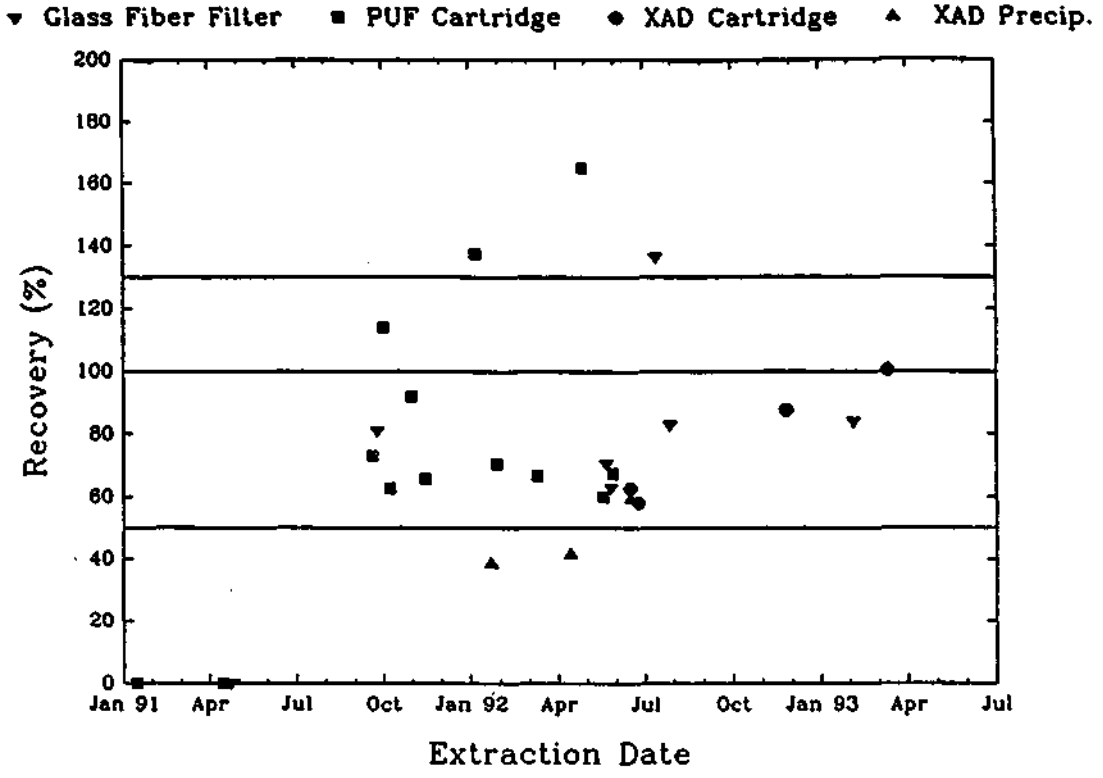
PAH - Benzo(a)pyrene



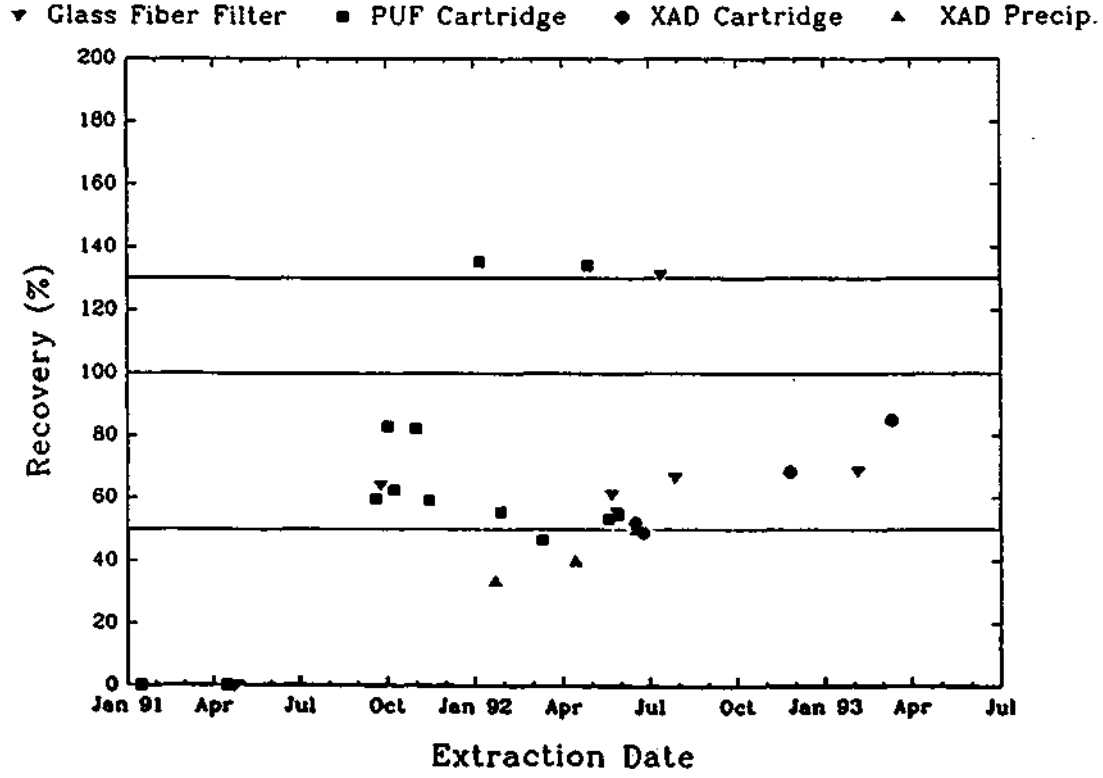
PAH - Benzo(b)fluoranthene



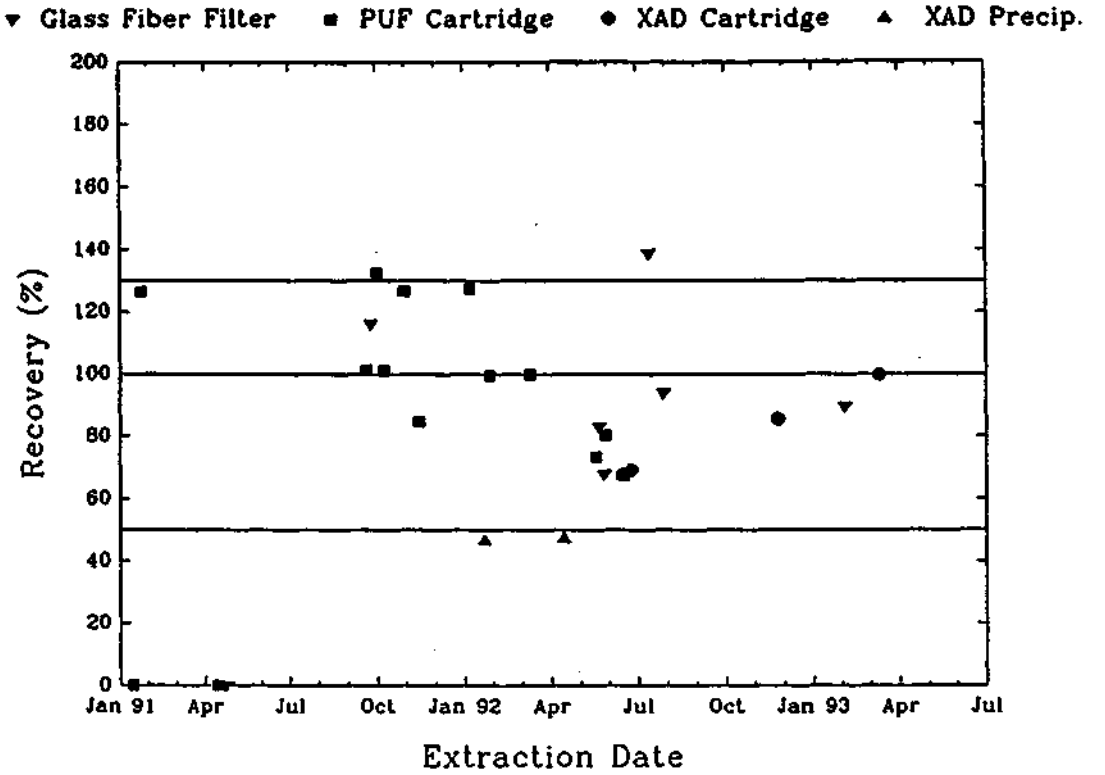
PAH - Benzo(k)fluoranthene



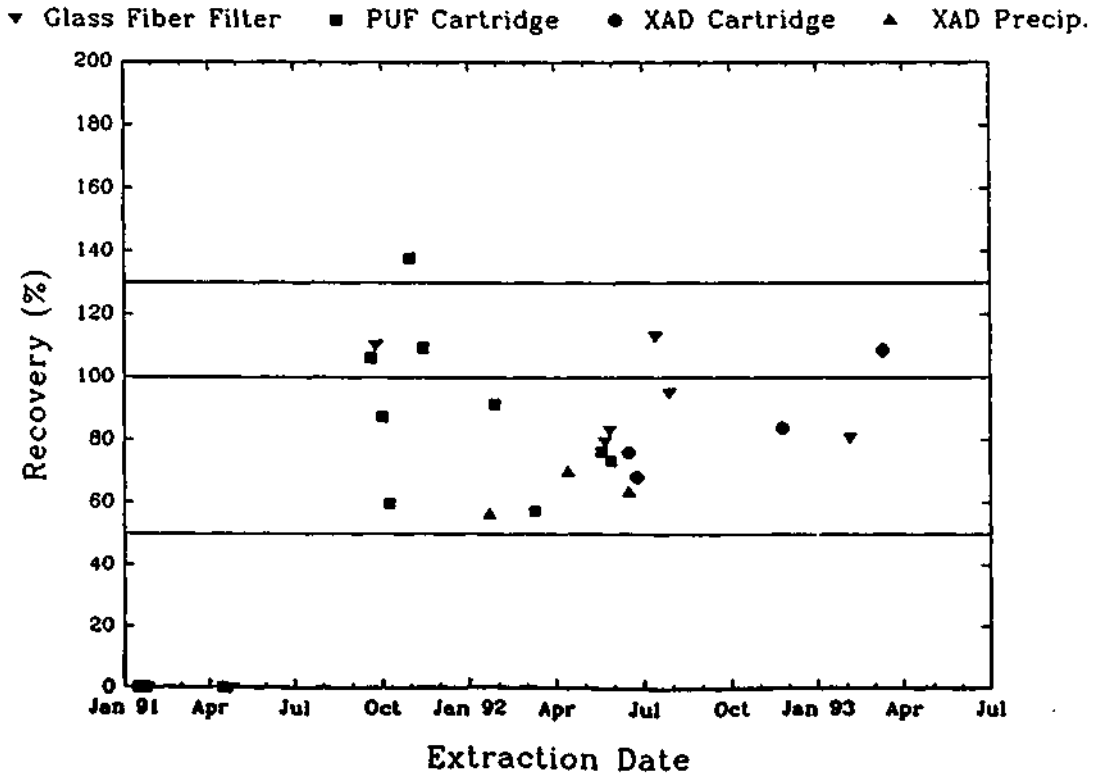
PAH - Benzo(ghi)perylene



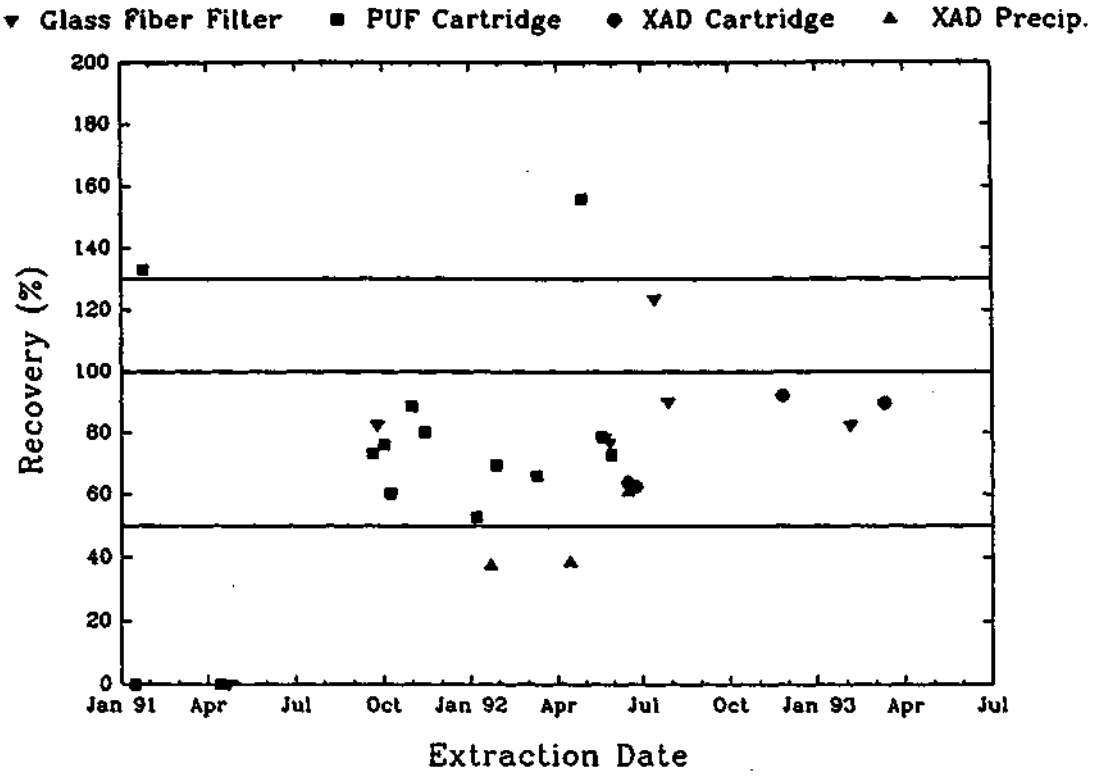
PAH - Chrysene



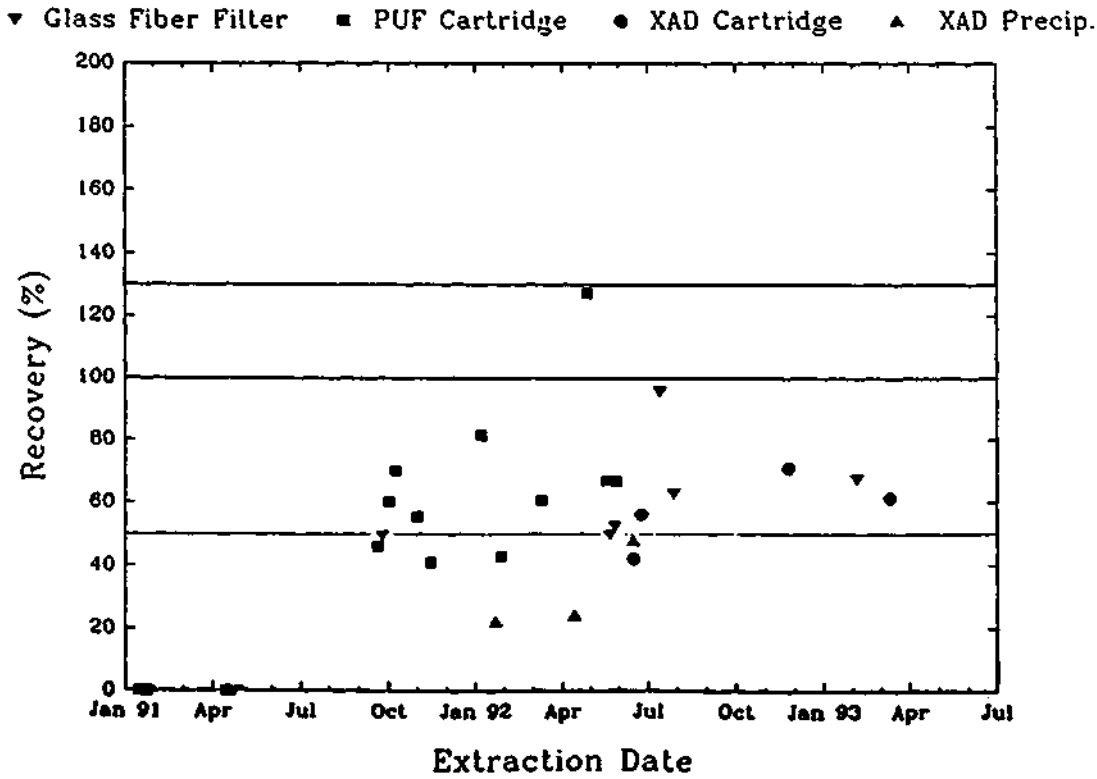
PAH — Dibenzo(ah)anthracene



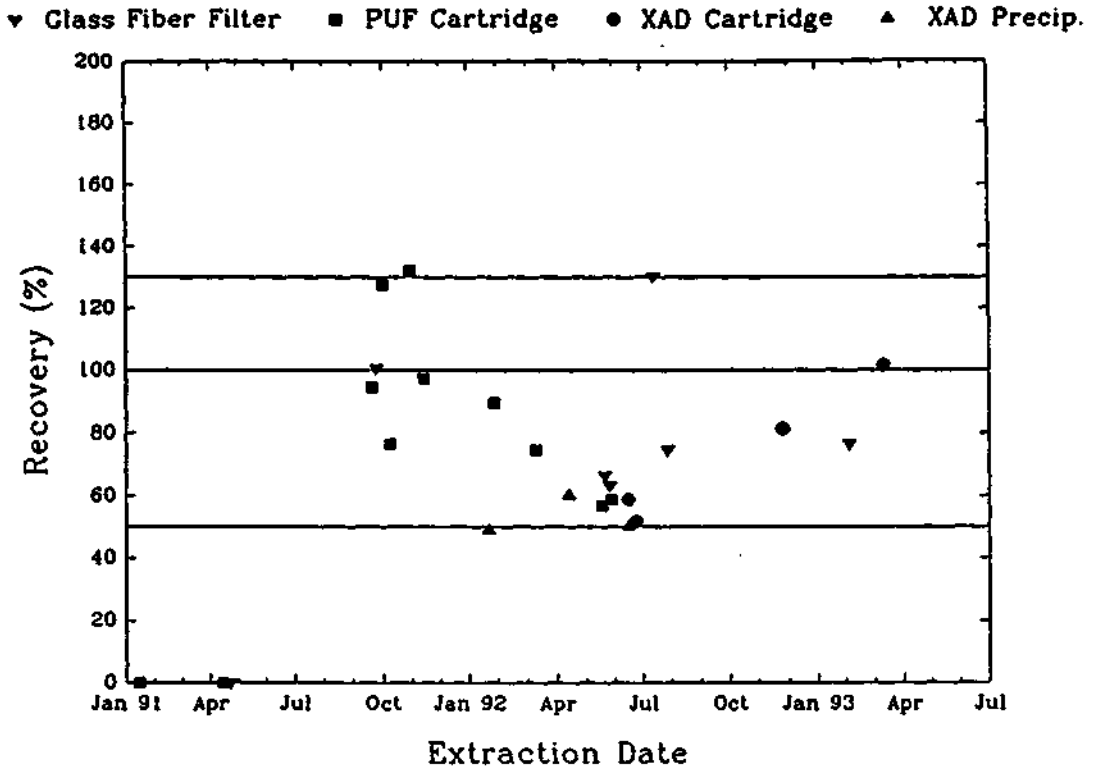
PAH - Fluoranthene



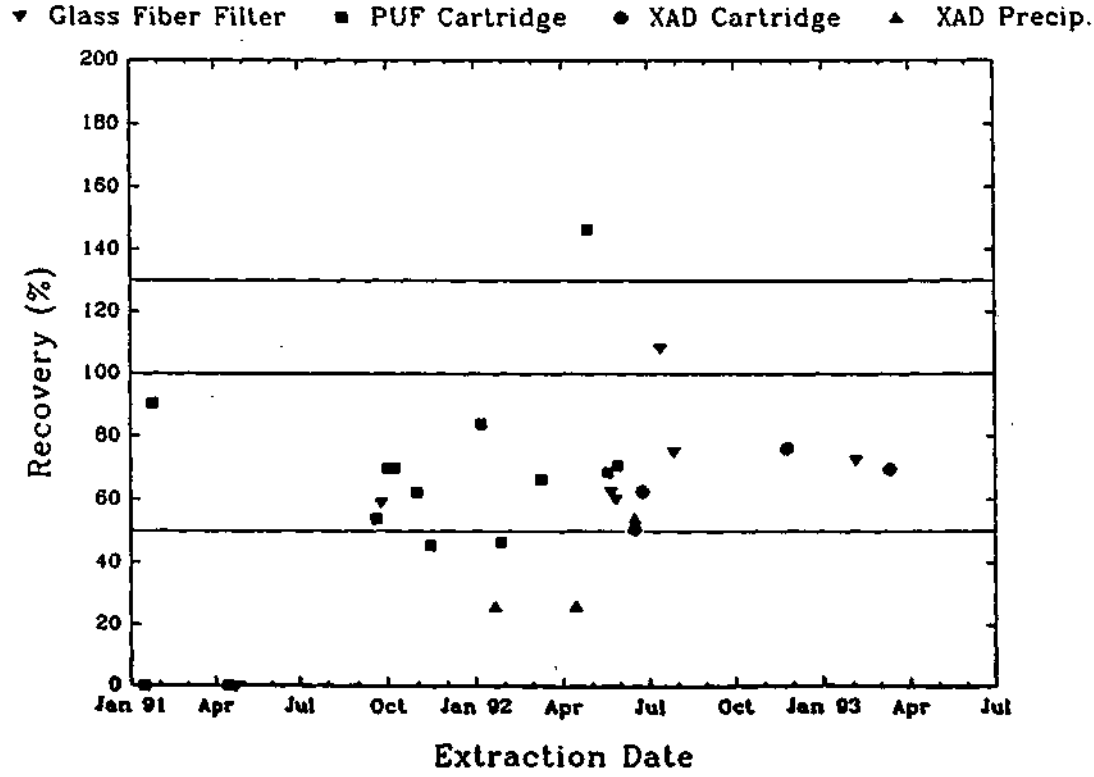
PAH - Fluorene



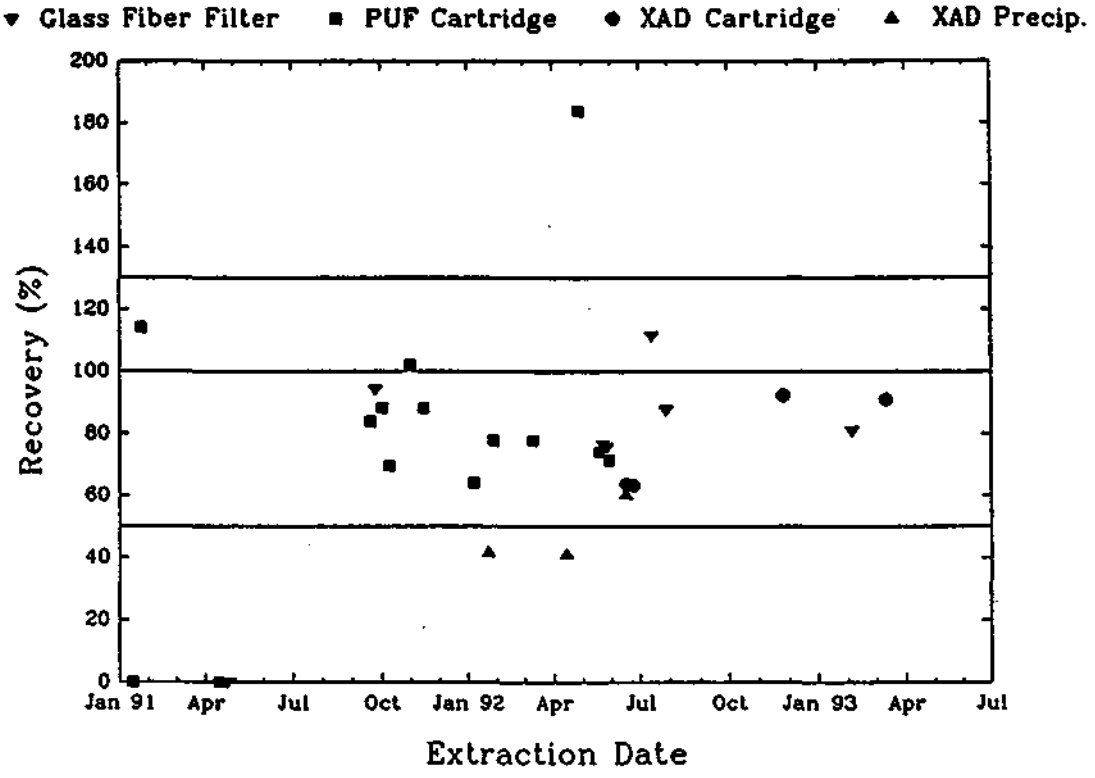
PAH - Indeno(l23,cd)pyrene



PAH - Phenanthrene



PAH - Pyrene


▼ Glass Fiber Filter
■ PUF Cartridge
◆ XAD Cartridge
▲ XAD Precip.
Recovery (%)
200
180
160
140
120
100
80
60
40
20
0
Jan 91
Apr
Jul
Oct
Jan 92
Apr
Jul
Oct
Jan 93
Apr
Jul
Extraction Date

Appendix B

Interlaboratory Study
1992 IADN Phase I Results

1992 IADN Interlaboratory Study Laboratory Identification Codes

Study	ISWS ID Code
Interlaboratory Study 92-1, PCB Isomers, Standard Solutions	9214
Interlaboratory Study 92-2, PAH, Standard Solutions	9222
Interlaboratory Study 92-3, OCs, Standard Solutions	9236
Interlaboratory Study 92-4, Trace Metal, Standard Solutions	9241, 9241A

ISBN 0-7778-2242-3

INTERLABORATORY STUDY 92-1

POLYCHLORINATED BIPHENYL (PCB) ISOMERS STANDARD SOLUTIONS

IN SUPPORT OF

THE INTEGRATED ATMOSPHERIC DEPOSITION NETWORK (IADN)

Interlaboratory Study 92-1, PCB Isomers, Standard Solutions ISWS Lab Code: 9214

SEPTEMBER 1992

Report Prepared by

Sylvia Cussion

for

Quality Management Unit
Laboratory Services Branch
Ontario Ministry of Environment and Energy

and

Air Quality Research Branch
Atmospheric Environment Service
Environment Canada
ARD Report: 93-11

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TABLE OF CONTENTS

1 SUMMARY OF INTERLABORATORY STUDY 92-1

Interlaboratory Study 92-1 was initiated in support of the integrated Atmospheric Deposition Network (IADN) to provide an initial assessment of between-laboratory variability for the analysis of Polychlorinated Biphenyl (PCB) isomers in precipitation and/or ambient air. Participation was limited to laboratories which contribute to the IADN database or related programs. This study was sponsored by the Canada-Ontario Agreement (COA) Air Toxics Workgroup, and conducted as a joint project between the Atmospheric Environment Service (AES) of Environment Canada and the Quality Management Unit (QMU), Laboratory Services Branch (LSB) of the Ontario Ministry of Environment and Energy (MOEE).

Six participating laboratories received a set of four ampouled standards that were ready for direct instrumental analysis. The parameter list consisted of 75 different PCB isomers. Ampoules 1, 2, and 3 contained subsets of the total target list and ampoule 4 contained all 75 isomers. One participant only reported a total value for each congener group. The remaining participants reported results for the individual isomers, though none of the participants had the capability of reporting results for every isomer on the target list.

The results from this study demonstrated interlaboratory means and medians that appear to agree with the target for PCB isomers that have three or more chlorine atoms. However, between-laboratory variability is frequently at a range of 20% or greater, which indicates poor agreement among the participants for may of the PCB isomers. This may introduce greater biases to the IADN database than may be acceptable. The use of a common reference standard by the participants should reduce this source of variability.

The participants demonstrated problems with the analysis of the mono- and di-chlorinated biphenyls. As these are more volatile compounds, sample losses may have occurred at the GC injection port. Differences in standards may also have contributed to between-laboratory variability.

Co-elution of PCB isomers also contributed to the between-laboratory variability and affected the accuracy of the results. As technology improves, resolution of different isomer pairs should help reduce between-laboratory variability.

At the time of this study, a final target list of PCB isomers had not been determined for the IADN program. Future interlaboratory studies will focus on the target list of the IADN program and attempt to determine performance criteria. Future studies will not only look at instrumental performance as in this study, but also attempt to address between-laboratory performance on the whole analytical method via sample extracts and spiked matrices.

2 INTRODUCTION

Interlaboratory performance studies are conducted to assess the comparability and accuracy of data among different laboratories. These studies are useful for the identification of biases, precision and accuracy problems. Participation in such studies can serve as a guide for improving individual laboratory performance and maintaining performance standards.

This study was designed to assess the analytical variability among laboratories contributing to the Integrated Atmospheric Deposition Network (IADN). IADN was established as a joint venture between Canada and the United States under the direction of the International Joint Commission[1]. The intent of IADN is to identify toxic airborne substances in the Great Lakes Basin, and by means of the network, quantify the total and net atmospheric loadings of these contaminants, and define spatial and temporal trends in the atmospheric deposition of these substances. Data from several participating agencies is to be merged into a central database. Comparability of these contributing data sets is an important component of the IADN Quality Assurance Implementation Plan[2]. This interlaboratory study provides information on the laboratory component of between agency differences, and can be used to help establish the comparability of the data sets. It is a recommended activity of the IADN Quality Assurance Program Plan[3]. Sponsorship of this interlaboratory study was through the Canada-Ontario Agreement (COA) Air Toxics Workgroup. Funding for the purchase of materials came from the Atmospheric Environment Service (AES) of Environment Canada. Co-ordination and implementation of the study was done by the Quality Management Unit (QMU) of Laboratory Services Branch (LSB) of the Ontario Ministry of Environment and Energy (MOEE).

Interlaboratory Study 92-1 targets laboratories analyzing for Polychlorinated Biphenyl (PCB) isomers in precipitation and/or ambient air. A target list of 75 PCB isomers was chosen for this study, comprising target lists from several contributing agencies. The aim of this study was to establish the comparability of instrumental calibration among the participating laboratories. Each participant received a set of ampouled standards ready for direct instrumental analysis. Ampoules 1, 2, and 3 contained subsets from the target list, while Ampoule 4 contained all of the parameters in the target list.

A list of participants is given in Appendix 2. Each participant was assigned a unique identification code for ease in data manipulation.

Section 3 describes sample preparation, sample distribution, analytical methodology, and data evaluation procedures. Final results are tabled in Appendix 1 and discussed in Section 4.

3 PROCEDURE

3.1 Preparation of Ampouled Standards

Neat PCB isomers of 99%+ purity were purchased from Ultra Scientific and AccuStandard by AES. All subsequent work was done by the QMU of LSB, MOEE. Concentrated stock solutions of each isomer were prepared in toluene and sealed into 5 mL amber ampoules. The stock concentrations were between 10 to 12 mg/L and verified using gas chromatography/mass spectrometry analysis by an analytical unit at LSB not involved in analysis of ambient air or

precipitation. Ampouled solutions were stored in a freezer at -20°C.

Solutions for the interlaboratory study were prepared from the concentrated stock solutions by diluting appropriate aliquots into a combined solution. All combined solutions for the study were prepared in iso-octane. Solutions 1, 2, and 3 were designed to consist of subsets of the complete target list. The isomers were distributed so that there would be approximately an equal number of each congener group in each solution and co-eluters or close eluters (based on relative retention time criteria defined by the National Research Council[4]) were in different solutions. Solution 4 contained all PCB isomers on the target list. Concentration levels were designed to fall in the routine analytical range of most participants. As each isomer was present in two different solutions, one solution had a "low" concentration level and the other a "high" concentration level. All solutions were sealed into 5 mL amber ampoules and stored in a freezer at -20°C until shipped to the participants. The ampoules were labelled IADN PCBs 1-4. In the following Discussion, the ampoules are referred to as Ampoules 1-4.

3.2 Sample Distribution

Samples were packed into styrofoam shipping containers and shipped by Purolator Courier to the participating laboratories. A list of the laboratories receiving sample sets is given in Appendix 2. Samples were shipped on September 28, 1992. A copy of all correspondence is also included in Appendix 2.

3.3 Analytical Methodology

Participating laboratories were requested to analyze the samples using their routine in-house methods used to analyze precipitation and/or ambient air samples for the IADN program. Participants were requested on the report form provided (Appendix 2) to summarize their Instrument and Detector used for the analysis. Information regarding the gas chromatograph column was requested at a later date. All participants were assigned a unique identification code that does not correspond with the order the participants are listed in Appendix 2.

3.4 Data Reporting

Results were submitted to the QMU, LSB in written form. All data were manually entered by laboratory code into an electronic spreadsheet.

The participating laboratories were mailed a copy of the tables of results on February 25, 1993. Two participants reported two data sets, using two different instruments. One participant submitted a revised data set after the release of the tables of results, with an explanatory note provided below in the Discussion. Both values are included in the tables, though the corrected results are used in the evaluation.

The interlaboratory mean, median, standard deviation (SD), and relative standard deviation (%RSD) were calculated for each isomer in each ampoule for which there were 2 or more laboratories reporting results and included in Tables 1-4, Appendix 1. As the data set is small, these calculated values are provided as an approximate indicator of the spread of the data and may not necessarily

be statistically correct.

4 DISCUSSION

OVERVIEW OF INTERLABORATORY PERFORMANCE

Laboratory 9211 reported only total congener groups. In the following discussion on the study results, this laboratory is not included. Their performance is evaluated in the section on individual participants' results.

The list of PCB Isomers selected for this study included target isomers in the IADN Implementation Plan[3], isomers on the current target lists of the participating laboratories (based on response forms from the invitation to participate), and a summation of potential toxic isomers or those found in the environment that have been cited in the literature (P. Yang, Internal Memorandum, 1992, LSB, MOEE). A total list of 75 isomers was assembled. Out of this list, 22 isomers were on the target list of all participants (Table 5). There were 3 isomers included in the study for which no results were reported (i.e. they were not on the target list of any of the participants - see Table 5). An additional 3 isomers were on the target list of only one participant (Table 5). Other combinations of PCB Isomers on the target lists of 3, 4, and 5 participants are not included in Table 5.

The interlaboratory mean and median appear to demonstrate good agreement with the target values for most isomers of the tri-chlorinated and higher chlorinated congener groups (PCB16 and up). However, due to the small size of the data set. and the "not normal" distribution of most of the results, the statistical calculations are not reliable indicators of the data quality. There are several cases where the interlaboratory mean |s biased particularly low relative to the target due to the "ND" or 0 reported by one or more participant (e.g. PCB157 in Ampoule 1, PCB77 in Ampoule 3, and PCB27 in Ampoule 4).

The range of results among the different labs was frequently quite high, with a %RSD for many of the isomers greater than 20%, emphasizing the "not normal" distribution of the data. Of particular note is the %RSD of 155% for PCB8 in Ampoule 4, which has a bimodal distribution. This suggests poor agreement among the participating laboratories. While the biased high and biased low participants compensate each other when calculating the interlaboratory mean for this interlaboratory study results, problems can occur when merging data sets from these laboratories. To reduce the possibility of laboratories contributing data sets to the central IADN database differing by 20% or more, the use of a common reference standard can minimize this source of variability.

Results for the mono- and di-chlorinated isomers indicated that all of the participants had difficulties with the analysis of these compounds. The results for several of these isomers indicate a bimodal distribution among the participants. For PCB4 Laboratories 9213 (A&B) and 9214 agreed with each other, and Laboratories 9212 (-V & -HP) and 9215 agreed with each other, but differed from the other two labs by an order of magnitude. Laboratory 9216 did not have any of the mono- or di-chlorinated congeners on their target list, except for PCB15, which was not on the target list of the other participants. Therefore no comparison could be made of Laboratory 9216's performance with the other participants for the mono- and di-chlorinated PCB isomers. The range of variability was high, with the %RSD being greater than 50% in several cases. The statistical calculations included in Tables 1-4 for these isomers are not

valid from a statistical point of view, and are provided only as a very general indicator of the spread of the data. These PCB's have higher vapour pressures[5] than the more chlorinated isomers, making them more susceptible to vaporization at the high temperature point of the gas chromatograph injection port, with subsequent sample loss. This may be a source of low bias for PCB4 by Laboratories 9213 (A&B) and 9214.

A major source of variation among the laboratories is the problem of co-elution of PCB isomers of various congener groups. Several participants reported results that were a combination of two isomers, such for PCB71 and PCB41 in Tables 2 and 4. For the purposes of calculating an interlaboratory mean, median, and standard deviation, the total value reported for a combination of isomers was divided equally among the isomers and these values were flagged in Tables 1-4. This proportioning of the reported result may not be analytically correct, as the area of the analytical peak may actually be divided 40-60 between the two isomers, or some other proportion. This can introduce biases when evaluating the "accuracy" of the interlaboratory mean of some of the isomers.

The study design attempted to avoid as many co-eluters as possible in Ampoules 1, 2, and 3 and thereby avoid identification errors. However, there were still some problems for some of the participants. As an example, in Ampoule 1, PCB163 was present, but PCB138, a close eluter to PCB163[4], was not included in this ampoule. Two participants reported a positive response for PCB 138 and indicated that PCB163 was not part of their target list (Table 1). In Ampoule 4, where both isomers were present together, these two participants reported a value for PCB 138 that corresponds to the sum of PCB138 and PCB163 in this ampoule (Table 4). This type of incorrect identification and quantitation due to co-eluters will introduce between-laboratory bias. Further instrumental research and development is required to attempt to eliminate the co-elution problem.

As an alternate way of evaluating the results, a graphical technique was used for those isomers with 6 or 7 results. As each isomer had a "pair" of results, one from either Ampoule 1, 2, or 3, and the other from Ampoule 4, these results may be plotted on an X-Y plot using the Youden technique[8]. The result from Ampoule 1, 2, or 3 is plotted on the vertical axis and the result from Ampoule 4 is plotted on the horizontal axis. The graphs are divided into four quadrants, with the intersection point at the target values. The data points should cluster around the target if random error is the only source of variability. Results in the upper right quadrant are considered biased high and those in the lower left quadrant are biased low. The main source of this type of variability is a difference in analytical standards or inadequate calibration practices. Data points that fall in the lower right or upper left quadrants are considered erratic or out-of-control. Sources of this type of error are more difficult to ascertain. In this study, the participants were analyzing ampoules for direct instrumental injection. Sources of erratic performance could be poor sample injection into the gas chromatograph, a septum leak, poor chromatography if contamination remained from a previous sample, or other instrumental problems. Within-laboratory precision may be assessed by drawing a line between the origin and the intersection of the target values. The closer the data point is to this diagonal line, the better the within-laboratory precision.

The Youden plots for 36 of the PCB isomers in this study are found in Appendix 1, Figures 1 - 36. Isomers such as PCB44 (Fig. 9), PCB49 (Fig. 11), PCB52 (Fig. 12), PCB70(Fig. 14),PCB101 (Fig. 17),PCB114 (Fig. 19), PCB137 (Fig. 23), PCB118 (Fig.

20). PCB158 (Fig. 27). PCB180 (Fig. 30). PCB187 (Fig. 31), and PCB198 (Fig. 35). demonstrate between-laboratory differences that can usually be attributed to differences in standards. All of these figures demonstrate the spread of the participants' results in the upper right and lower left quadrants along the diagonal line between the origin and the target. As noted above, the use of a common reference standard by all of these laboratories would reduce this type of variation. The participants do demonstrate good within-laboratory precision for these isomers, as the data points are close to the diagonal line between the origin and target for almost all of the laboratories.

The results for PCB4 (Fig. 1) also demonstrates a spread of results in the lower left quadrant. However, as discussed above, the low bias may be due to vaporization at the high temperature point of the GC injection port. Further investigation is required by the participants with low biases to determine if the problems are with their analytical standards or instrumental conditions.

Several isomers demonstrate a pattern of a parallel line to the line passing between the origin and target (PCB 18, Fig. 3, PCB31, Fig. 5, PCB97, Fig. 16, PCB 136, Fig. 22, PCB153, Fig. 25, and PCB158, Fig. 27). These laboratories are precise to this parallel line, suggesting a consistent bias in all of these participants. This may possibly be due to an error in the ratios of concentration to response factors. Only Laboratory 9214 reported two of these isomers as co-eluting with another isomer (PCB31 with PCB28 and PCB153 with PCB105), so a co-elution effect does not appear to be the source of error.

Other isomers such as PCB8 (Fig. 2), PCB33 (Fig. 6), PCB42 (Fig. 8), PCB47 (Fig. 10), PCB66 (Fig. 13), PCB 77 (Fig. 15), PCB128 (Fig. 21), PCB138 (Fig. 24), and PCB190 (Fig. 32) show more erratic performance among the participants. The sources of these types of variation are more difficult to identify, as noted above. Co-elution problems may be the main source of variability for isomers such as PCB8 and PCB 138.

Many of the Youden plots re-emphasize the spread in results among the participants, despite the good within-laboratory precision. The interlaboratory mean and median showed agreement with the target for isomers such as PCB18, PCB42, PCB52, PCB101, PCB190, and PCB198. However the plots for these isomers' results (Figures 3,8,12,17,32, and 35 respectively) demonstrate a wide spread of results among the participants.

INDIVIDUAL LABORATORY PERFORMANCE

To give an overview of the individual participant's agreement with the target values, the results for all of the isomers from all of the ampoules were grouped according to percentage of target. These results are presented in Table 7 and Figure 37 (excluding Laboratory 9211).

Laboratory 9211

Laboratory 9211 reported only total congener groups, and as noted above, they were not included in the interlaboratory performance evaluation. When comparing their results of the total congener groups (based on the number of isomers present in each ampoule), they agree with the target totals within ± 20% for the majority of congener groups, with a few results within 30% of the target (Table 8). The only congener group that they had consistent problems in quantitation was the octachlorobiphenyls.

In all four ampoules they recognized the correct number of isomers present, but their quantification was low compared to the target and the other participants. They should investigate the accuracy of the standard they use for this congener group.

Laboratory 9211 was the only participant to use a Mass Spectrometer as the detection system.

The IADN program requires isomer specific analysis as well as total congener group results[3]. This laboratory will need to develop the capability for isomer-specific analysis to be a future contributor to the IADN program.

Laboratory 9212

This laboratory reported two sets of results, using two different instruments, as described in Table 6. The results in Tables 1-4 have been designated "V" for the Varian 3400 and "HP" for the Hewlett-Packard 5890. Both instruments used the same type of capillary columns and the same calibration standard was used.

The performance of the two systems is not identical. There were several instances of a positive identification on one instrument and not on the other, particularly for the lower concentration ampoules (1, 2, and 3). PCB190, which was identified correctly on the Varian and had good agreement with the target, was not identified on the HP in Ampoule 3, and had a co-elution problem in Ampoule 4. The reported result from the HP in Ampoule 4 was divided equally between PCB170 and PCB190. Based on the non-identification in Ampoule 3 of PCB 190, the correct identification of PCB170 in Ampoule 1, and the value of the combined result in Ampoule 4 corresponding to the target value of only 1 of the 2 isomers (ie. half of the total), the result on the HP for the combined PCB170 and PCB190 probably is attributable to only PCB170.

As seen in Table 7 and displayed in Figure 37, the distribution of sample concentrations on the Varian and HP are different in the ranges 75-90% and 90-110%. Using the Varian, 54.7% and 33.7% of the results were in the ranges 75-90% and 90-100% respectively, as compared to using the HP where 19.8% and 46.5% were in the 75-90% and 90-110% range of target. As noted above, the same calibration standard was used for both analytical systems. The differences between the two sets of results appear to be instrument related, possibly due to differences in temperature programming, gas flow rates, detectors, calibration factors or integration software. Laboratory 9212 should investigate further the differences in performance of the two instrumental systems so that they can report a consistent data set using either analytical system.

The within-laboratory precision is generally consistent (see Figures 1 - 36) in Appendix 1, though there are some instances of missed results in the "low" ampoules (1, 2, and 3). As detection limits were not provided, some of the "low" concentration levels may have been near the detection limits for some of the isomers.

Laboratory 9213

Laboratory 9213 analyzed the ampoules using a Varian 3400 with a SPI (Septum Programmable Injector). They repeated their analysis of the PCB ampoules using the Varian Vista 6000. Both systems used the same capillary column and the same calibration standard was used. Results from the Varian 3400 are labelled "A" and results from the Varian 6000 are labelled "B".

The results from the two systems are not identical. As seen in Table 7 and Figure 37, 44.6% of the results from the Varian 3400 ("A") are within 90-110% of the target, while only 20.7% of the results from the Varian 6000 ("B") are in the same range. The majority of results from the Varian 6000 are in the range 75-90% of target (Table

Within-laboratory precision was good for many of the isomers. However there was inconsistent performance for some of the isomers, such as PCB33 (Fig. 6), PCB47 (Fig. 10), PCB 128 (Fig. 21), and PCB177 (Fig. 29). The Varian 3400 performed slightly better than the Varian 6000 in this regard.

As with Laboratory 9212, who also reported results from two different analytical systems, Laboratory 9213 used the same calibration standard on both systems. As noted for Laboratory 9212, differences in temperature programming, gas flow rates, detectors or integration software may be potential sources of variability between the two systems. Further investigation of the differences in performance of the two instrumental systems should be conducted so that this laboratory can report a consistent data set using either analytical system.

Laboratory 9214 - ISWS

Laboratory 9214 had the highest proportion of results that were greater than the target value as well as the results of other participants (Table 7 and Figure 37). Evaluation of their standard to a reference standard should help to resolve these differences. They also had problems with the analysis of the mono- and di-chlorobiphenyls. Several results are either very low (eg. PCB4 in Ampoules 2 and 4) or high (eg. PCB5 in Ampoule 3). Better performance (i.e. agreement with the target) was achieved on the more highly chlorinated isomer groups. Investigation of their initial GC conditions may help improve performance for the lower chlorinated groups which elute near the beginning of the GC scan.

They also had the largest number of co-eluters, as compared to the other participants. While they were not the only laboratory to use a 30 m capillary column (Table 6), switching to a 60 m column may help eliminate some of the co-elution problems.

Within-laboratory precision is very good for almost all of the isomers (Figures 1 - 36), despite some of the other problems noted above. Isomers which had less precise within-laboratory performance generally were co-eluters such as PCB105 (Fig. 18) and PCB153(Fig. 25).

Laboratory 9215

Laboratory 9215 had 39.7% of its results within 90-110% of the target. They had no co-elution problems with Ampoules 1, 2, and 3, but they had some interference problems for PCB17 and PCB149 in Ampoule 4. They demonstrated good within-laboratory precision for all the isomers (Figures 1 - 36) except PCB18 (Fig. 3) and PCB194 (Fig. 33).

Laboratory 9216

Laboratory 9216 had run out of their own calibration standards when the ampoules were received. To try and meet the study deadline, they borrowed calibration standards that had been cross-checked to the same external sources that they used.

When they received the table of results from this study, they felt that their performance could have been better. Upon comparing the borrowed standards with their own new standards. Laboratory 9216 felt that the borrowed standards were the source of bias in their performance. They reanalysed the ampouled solutions using their new calibration standards. Both sets of results are included in Tables 1-4, but the revised results are used in the calculations of interlaboratory mean, median and standard deviation. The following discussion of their performance refers to the revised set of results.

Laboratory 9216 had 48% of their results within 90-110% of the target (Table 7 and Figure 37). They tended to be biased high, as 30% of their results were in the range 110-130% of the target. They had the fewest number of interlaboratory study PCB isomers on their target list, as compared with the other participants, though they provided a list of the different isomers that are on their target list. They particularly didn't have many of the mono-, di-, and tri-chlorobiphenyls on their own target list.

Within-laboratory precision was variable. For some isomers (eg. PCB44 (Fig. 9), PCB101 (Fig. 17), PCB105 (Fig. 18), PCB114 (Fig. 19). PCB187 (Fig. 31), and PCB209 (Fig. 36)), they had excellent within-laboratory precision. For others (eg. PCB31 (Fig. 5), PCB40 (Fig. 7), PCB77 (Fig. 15), and PCB138 (Fig. 24)) they had more erratic performance. It is difficult to determine the possible sources of this variability, as the different isomers were all part of a combined solution. More of the variability appears to be in Ampoule 4, which contained all of the isomers in the study target list. While Laboratory 9216 did not note any co-elution problems, integration of GC peaks of closely eluting isomers may have been more difficult, contributing to the increased variability of the results from Ampoule 4.

5 CONCLUSION

The results from this study demonstrate an interlaboratory mean and median that appear to agree with the target for PCB isomers that have three or more chlorine atoms. However, the between-laboratory variability is frequently at a range of 20% or greater, indicating a spread of results that suggest poor agreement among the participating laboratories. This may introduce greater biases to the IADN database than may be acceptable. The use of a common reference standard by the participants should reduce this source of variability.

The participants demonstrated problems with the analysis of the mono- and di-chlorinated biphenyls. As these are more volatile compounds, sample losses may have occurred at the GC injection port. Differences in standards may also contribute to between-laboratory variability.

Co-elution of PCB isomers also contributes to the between-laboratory variability and affects the accuracy of the results. The participants were not asked to provide copies of their chromatograms nor details of their analytical conditions (i.e. retention times, resolution, etc.), so the degree of co-elution contributing to between-laboratory variability cannot be determined for this study. Future studies may attempt to address the degree of this effect in greater detail. As technology improves, resolution of different isomer pairs should help reduce between-laboratory variability.

At the time of this study, the IADN Implementation Committee had not selected a final list of PCB isomers to be the target list for IADN. The broad range of isomers used in

the study was intended to cover all the possibilities. When a final parameter list is chosen, future studies will focus on those PCB isomers so that more definitive performance criteria may be developed.

6 REFERENCES

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7 APPENDIX 1 - RESULTS AND GRAPHS

TABLE 1 - Ampoule PCBs 1
Results in µg/L

PCB ISOMER	TARGET	8211	#	8212-V	8212-HP	8213A	8213B	8214	8215	8216	MEAN	MEDIAN	SD	n	%RSD	8216 $
PCB3	232			N/A	N/A	234.91	155.92	166.408	227.01	N/A	196.1	196.71	40.65	4	20.73%	N/A
TOTAL MONO	232	210	1	-	-	234.91	155.92	166.408	227.01	-						-
PCB4/10								0.081								
PCB5						16.31		40.559	16.59							
PCB7	300			N/A	N/A	379.66	167.48	123.851	263.52	N/A	238.6	225.5	115.7	4	48.47%	N/A
PCB16	11.3			N/A	N/A	10.84	8.86	7.598	11.43	N/A	9.682	9.85	1.772	4	18.30%	N/A
TOTAL DI	311.3	260	2	-	-	406.61	176.34	172.069	311.54	-						-
PCB18	10.4			9.8	10.7	8.65	6.65	6.961	12.62	12.3	9.654	9.8	2.406	7	24.93%	19.68
PCB19	10.4			N/A	N/A	9.53	7.61	5.912	10.93	N/A	8.496	8.57	2.195	4	25.84%	N/A
PCB24	9.4			N/A	N/A	10.78	13.13 &	7.955 &	6.26	N/A	9.531	9.37	3.038	4	31.88%	N/A
PCB29	16.4			14.0	14.6	N/A	N/A	12.351	16.30	N/A	14.11	14.4	1.291	4	9.15%	N/A
PCB33						8.67										
TOTAL TRI	46.6	41	5	23.8	25.5	37.63	27.39	33.079	45.11	12.3						19.68
PCB40	10.8			12.6	10.9	12.47	10.67	11.737	11.17	10.8	11.51	11.17	0.85	7	7.39%	16.53
PCB44	11.0			10.3	11.2	9.69	8.47	11.484	11.11	10.9	10.45	10.9	1.064	7	10.18%	16.61
PCB46	10.1			N/A	N/A	9.14	7.74	9.671	8.93	N/A	8.87	9.04	0.815	4	9.19%	N/A
PCB52	9.9			10.1	10.2	9.33	7.58	8.058	10.51	12.0	9.683	10.1	1.51	7	15.60%	17.51
PCB53	10.5			0.0	0.0	N/A	N/A	9.135	8.08	N/A	4.304	4.04	4.988	4	115.90%	N/A
PCB56/60						0.22										
PCB70	13.5			0.0	14.2	14.80	11.87	17.752	14.04	N/A	12.11	14.12	6.227	6	51.42%	N/A
PCB77								0.253								
PCB81	9.7			N/A	N/A	N/A	N/A	6.932	9.95	N/A	8.441	8.44	2.134	2	25.28%	N/A
TOTAL TETRA	76.5	78	7	33.2	46.5	55.65	46.33	76.022	73.79	33.7	-					50.65
PCB84/92								0.046								
PCB87							5.11									
PCB95								0.030								
PCB97	12.8			12.0	13.0	13.91	ND	11.024	10.11	N/A	10.01	11.51	5.066	6	50.62%	N/A
PCB105	9.5			7.7	9.2	8.39	6.50	9.488	8.77	9.4	8.493	8.77	1.08	7	12.72%	10.67
PCB114						0.21		0.093								
PCB118	10.1			8.5	10.2	10.90	8.41	10.200	9.92	ND	8.304	9.92	3.776	7	45.47%	ND
PCB126	12.0			N/A	N/A	N/A	N/A	N/A	N/A	N/A	-					N/A
TOTAL PENTA	44.4	34	4	28.2	32.4	33.41	20.02	30.681	28.60	9.4	-					10.67
PCB129/178							6.08 $									
PCB130/176						1.01 $										
PCB136	20.0			15.8	17.2	20.15	17.77	12.087	18.71	N/A	16.95	17.49	2.794	6	16.48%	N/A
PCB137/176								0.234								
PCB138						11.23	11.10			11.25						13.01
PCB146						0.20										
PCB149	12.2			N/A	N/A	11.46	10.30	11.270	12.66	N/A	11.47	11.37	1.055	4	9.20%	N/A
PCB157	14.8			0.0	0.0	16.54	12.99	0.000	N/A	N/A	5.906	0.0	8.184	5	138.57%	N/A

TABLE 1 - Ampoule PCBs 1
Results in µg/L

PCB ISOMER	TARGET	9211	#	9212-V	9212-HP	9213A	9213B	9214	9215	9216	MEAN	MEDIAN	SD	n	%RSD	9216 §
PCB163	10.6			N/A	N/A	N/A	N/A	11.654 *	12.91	N/A	12.28		0.888	2	7.23%	N/A
PCB156	21.9			N/A	N/A	N/A	N/A	20.606	N/A	N/A						N/A
TOTAL HEXA	79.7	81	5	15.6	17.2	60.59	56.24	55.853	44.48	11.25	-					13.01
PCB170	13.3			11.5	11.6	11.83	10.43	22.470 @	11.86	14.5	13.46	11.83	4.163	7	30.94%	15.26
PCB176/130						1.01 $										
PCB177				0.2		0.07		0.138								
PCB178/129							6.08 $									
PCB180								0.036								
PCB187/182								0.070								
PCB189							0.14	0.126								
TOTAL HEPTA	13.3	6.9	1	11.7	11.6	12.91	16.65	22.841	11.86	14.5	-					15.26
PCB194	11.0			9.2	11.8	9.55	10.70	10.307	12.08	11.4	10.72	10.70	1.105	7	10.31%	11.25
TOTAL OCTA	11.0	6.6	1	9.2	11.8	9.55	10.70	10.307	12.08	11.4	-					11.25

Laboratory 9211 reported only total congener groups. The values in the adjacent column indicate the total number of analytical peaks detected by this laboratory.

&, @, * These isomers were reported as co-eluting with another isomer. In this ampoule, the co-eluting isomer was not present, so the value reported may be attributed to the one isomer only.

$ These isomers were reported as co-eluting with another isomer. The result is equally divided among both isomers.

N/A Laboratory does not calibrate for this isomer.

ND Participant did not detect this isomer, which was present in the ampoule, and reported as Not Detected.

Participants that did not report a result for an isomer that was present in the ampoule, and did not mark the report form with an "ND", were assigned a "0".

§ Original set of results reported by Laboratory 9216. They had run out of their own calibration standards when the ampoules were received. To try and meet the study deadline, they borrowed calibration standards that had been cross-checked to the same external sources that they used. When they received the table of results from this study, they did felt that their performance could have been better. Upon comparing the borrowed standards with their own new standards, Laboratory 9216 felt that the borrowed standards were the source of variability in their performance. They reanalysed the ampouled solutions using their new calibration standards. The revised results are used in the calculations of mean and standard deviation.

Laboratories 9212 and 9213 provided two sets of results using two different instruments. See Table 6 for description.

TABLE 2 - Ampoule PCBs 2
Results in µg/L

PCB ISOMER	TARGET	9211	#	9212-V	9212-HP	9213A	9213B	9214	9215	9216	MEAN	MEDIAN	SD	n	%RSD	9216 ß
PCB4	246			208.6	205.6	27.29	20.29	26.103	188.37	N/A	113.0	108.2	96.48	6	85.35%	N/A
PCB7							3.02									
PCB8	226			226.1	227.4	147.83	112.97	363.986	230.18	N/A	219.1	226.8	66.66	6	30.75%	N/A
TOTAL DI	474	320	2	434.7	433.0	175.12	136.26	392.089	418.55	-	-					-
PCB16						14.60										
PCB17	9.9			N/A	N/A	N/A	8.54	9.961	7.06	N/A	8.854	9.54	1.568	3	17.71%	N/A
PCB25	10.8			N/A	N/A	10.92	9.80	9.872	9.45	N/A	10.01	9.84	0.634	4	6.33%	N/A
PCB28	14.5			11.4	0.0	12.24	10.92	15.426 @	11.68	N/A	10.28	11.54	5.264	6	51.42%	N/A
PCB31							0.29									
PCB32	10.4			N/A	N/A	N/A	12.61 +	21.405	11.58	N/A	15.2	12.61	5.4	3	35.53%	N/A
PCB33	10.3			0.0	9.0	10.95	9.84	11.737	10.28	N/A	8.635	10.06	4.332	6	50.17%	N/A
TOTAL TRI	55.9	43	5	11.4	9.0	48.61	53	68.401	50.05	-	-					-
PCB40							0.73			3.41						
PCB41	10.4			N/A	N/A	6.215 ¥	5.60 ¥	16.154 ¥	4.48 ¥	N/A	8.112	5.91	5.409	4	66.68%	N/A
PCB44							0.68									
PCB47						15.31	11.82	10.829								
PCB49	9.9			7.7	9.2	9.36	7.41	8.623	8.43	11.0	8.816	8.62	1.199	7	13.59%	18.18
PCB52							0.43	0.040								
PCB56/60						0.24				2.1						
PCB61	10.6			10.6	9.8	N/A	N/A	N/A	N/A	N/A	10.2	-	0.566	2	5.55%	N/A
PCB64						19.07	14.09									
PCB71	11.1			N/A	N/A	6.215 ¥	5.60 ¥	16.154 ¥	4.48 ¥	N/A	8.112	5.91	5.409	4	66.68%	N/A
PCB74						15.92										
PCB75	10.4			12.3	12.1	N/A	N/A	N/A	N/A	N/A	12.2	-	0.141	2	1.16%	N/A
TOTAL TETRA	52.4	60	4	30.6	31.1	72.33	46.36	51.800	26.35	16.51	-					18.18
PCB84/92								0.584								
PCB95	13.3			N/A	N/A	13.25	10.62	14.142	14.59	N/A	13.15	13.70	1.777	4	13.51%	N/A
PCB97							0.7	0.090								
PCB100	11.4			N/A	N/A	N/A	N/A	15.765	11.87	N/A	13.82	-	2.754	2	19.93%	N/A
PCB101							0.56	0.144								
PCB110	11.0			N/A	N/A	7.84	6.16	9.039	8.87	N/A	7.982	8.36	1.313	4	16.45%	N/A
PCB118	12.4			N/A	N/A	N/A	N/A	14.286	12.19	N/A	13.24		1.482	2	11.20%	N/A
TOTAL PENTA	48.1	38	4	-	-	21.09	16.06	54.040	47.52	-	-					-
PCB128	16.7			15.4	16.2	14.06	12.66	27.188	16.95	17.2	17.38	16.95	4.731	7	27.22%	21.56
PCB130/176						1.96										
PCB132							1.37									
PCB136							0.95									
PCB138	9.9			8.5	0.0	9.17	8.20	10.861 *	6.18	11.2	7.673	9.17	3.845	7	48.83%	12.65
PCB149							1.03	0.037								
PCB155	10.9			N/A	N/A	N/A	N/A	N/A	N/A	N/A						N/A

TABLE 2 - Ampoule PCBs 2
Results in µg/L

PCB ISOMER	TARGET	9211	#	9212-V	9212-HP	9213A	9213B	9214	9215	9216	MEAN	MEDIAN	SD	n	%RSD	9216 §
PCB157/201							0.81									
PCB167								0.082								
PCB169	9.5			N/A	N/A	N/A	N/A	N/A	7.67	N/A						N/A
TOTAL HEXA	47.0	42	4	23.9	18.2	25.19	26.03	38.168	31.00	43.6	-					34.21
PCB175						0.06	1.13									
PCB177	15.1			14.9	17.0	14.53	16.54	17.011	16.61	N/A	16.10	16.58	1.095	6	6.80%	N/A
PCB187/182							0.31	0.054								
PCB189	11.1	-		N/A	N/A	11.89	ND	9.629	11.55	12.8	9.214	11.55	5.262	5	57.11%	13.45
TOTAL HEPTA	26.2	20	2	14.9	17.0	0.19	17.98	26.894	28.16	12.8	-					13.45
PCB194						26.69	0.61									
PCB198	13.9			11.8	13.8	13.76	15.30	18.235	8.20	N/A	13.52	13.79	3.371	6	24.93%	N/A
TOTAL OCTA	13.9	6	1	11.8	13.8	40.47	15.91	18.235	8.20	-						
PCB209	11.8			9.2	11.6	10.39	10.09	14.526	10.58	11.6	11.14	10.58	1.715	7	15.39%	11.00
TOTAL DECA	11.8	13	1	9.2	11.6	10.39	10.09	14.526	10.58	11.6	-					11.00

Laboratory 9211 reported only total congener groups. The values in the adjacent column indicate the total number of analytical peaks detected by this laboratory.

&, @, °, ▸ These isomers were reported as co-eluting with another isomer. In this ampoule, the co-eluting isomer was not present, so the value reported may be attributed to the one isomer only.

¢ These isomers were reported as co-eluting with another isomer. The result is equally divided among both isomers.

N/A Laboratory does not calibrate for this isomer.

ND Participant did not detect this isomer, which was present in the ampoule, and reported as Not Detected.

Participants that did not report a result for an isomer that was present in the ampoule, and did not mark the report form with an "ND", were assigned a "0".

§ Original set of results reported by Laboratory 9216. They had run out of their own calibration standards when the ampoules were received. To try and meet the study deadline, they borrowed calibration standards that had been cross-checked to the same external sources that they used. When they received the table of results from this study, they did felt that their performance could have been better. Upon comparing the borrowed standards with their own new standards, Laboratory 9216 felt that the borrowed standards were the source of variability in their performance. They reanalysed the ampouled solutions using their new calibration standards. The revised results are used in the calculations of mean and standard deviation.

Laboratories 9212 and 9213 provided two sets of results using two different instruments. See Table 6 for description.

TABLE 3 - Ampoule PCBs 3
Results in µg/L

PCB ISOMER	TARGET	9211	#	9212-V	9212-HP	9213A	9213B	9214	9215	9216	MEAN	MEDIAN	SD	n	%RSD	9216 §
PCB3				N/A	N/A			1.041								
TOTAL MONO								1.041								
PCB4/10							1.24	0.089								
PCB5	234			N/A	N/A	244.76 ♦	218.36 ♦	560.844	214.33	N/A	309.6	231.6	168.1	4	54.29%	N/A
PCB7						0.29	0.65	0.249								
PCB15	198			N/A	N/A	N/A	N/A	N/A	N/A	263.0						331.3
TOTAL DI	432	360	2	-	-	245.05	220.25	561.182	214.33	263.0	-					331.3
PCB16							0.64	0.164								
PCB17							32.10									
PCB22	13.4			N/A	N/A	13.47	11.55	20.676	11.91	N/A	14.4	12.69	4.265	4	29.62%	N/A
PCB24						10.53										
PCB25							0.61	0.206								
PCB26	10.6			N/A	N/A	12.92	11.82	9.795	12.94	N/A	11.87	12.37	1.478	4	12.45%	N/A
PCB27	12.8			N/A	N/A	ND	12.61 ♦	8.841 &	14.09	N/A	8.885	10.73	6.322	4	71.15%	N/A
PCB31	12.1			10.6	11.6	11.27	9.85	11.500 @	11.16	12.6	11.23	11.27	0.856	7	7.62%	19.78
PCB33						0.54	1.84	0.225								
PCB37	9.5			N/A	N/A	N/A	N/A	7.020	13.48	N/A	10.25	-	4.568	2	44.56%	N/A
TOTAL TRI	58.4	50	5	10.6	11.6	48.73	81.02	58.427	63.58	12.6	-					19.78
PCB40				4.1	4.0	4.21	3.90	3.682		-						
PCB41/71							0.46	0.074								
PCB42	13.9			13.2	15.4	16.92	14.15	13.147	12.74	N/A	14.26	13.68	1.616	6	11.33%	N/A
PCB47	13.7			11.2	11.6	16.02	11.10	14.168	11.80	N/A	12.65	11.7	2.000	6	15.81%	N/A
PCB49							0.33	0.057								
PCB52								0.027								
PCB56/60						1.71	2.51									
PCB64							0.94									
PCB66	14.8			10.5	12.6	ND	11.44	20.916	16.41	N/A	12.01	12.12	7.016	6	58.42%	N/A
PCB70/76								0.059						*		
PCB74	10.5			N/A	N/A	9.95	10.88	8.990	14.09	N/A	11.00	10.47	2.213	4	20.11%	N/A
PCB77	10.6			0.0	9.6	ND	ND	11.904	13.27	15.0	7.111	9.6	6.644	7	96.25%	19.35
TOTAL TETRA	63.5	78	6	39.0	53.4	48.81	55.63	73.024	68.31	15.0	-					19.35
PCB84	13.0			10.4	11.4	0	0	20.448	15.03	N/A	9.546	10.9	8.19	6	85.79%	N/A
PCB95						16.72										
PCB100								0.531								
PCB101	10.5			8.7	9.4	11.00	20.06	8.480	11.83	12.2	11.67	11.00	3.985	7	34.16%	13.95
PCB110							4.66	0.258								
PCB114	13.1			13.1	12.0	14.05	14.10	0.000	15.31	12.5	11.58	13.1	5.225	7	45.12%	15.02
PCB118								0.197								
PCB119								0.026								
PCB123	11.4			N/A	N/A	N/A	N/A	N/A	N/A	N/A						N/A

TABLE 3 - Ampoule PCBs 3
Results in µg/L

PCB ISOMER	TARGET	9211	#	9212-V	9212-HP	9213A	9213B	9214	9215	9216	MEAN	MEDIAN	SD	n	%RSD	9216 §
TOTAL PENTA	48.0	40	4	32.2	32.8	41.77	38.62	29.942	42.17	24.7	-					28.97
PCB126						10.88	13.50	0.132								
PCB132							1.36									
PCB137	13.1			11.8	12.6	14.71	16.74	0.000	8.57	12.9	10.9	12.6	5.321	7	48.80%	16.7
PCB138/163						0.19		0.096								
PCB146						13.90										
PCB149							15.36									
PCB151						0.23										
PCB153	19.5			15.8	16.8	18.92	16.06	23.232	17.73	19.8	18.33	17.73	2.609	7	14.23%	25.22
PCB156	14.2			0.0	11.5	13.41	14.55	0.000	15.42	15.2	10.01	13.41	6.964	7	69.56%	16.55
PCB157/201							0.10									
PCB158	9.6			8.4	8.5	9.57	11.66	16.727	12.26	N/A	11.19	10.62	3.152	6	28.18%	N/A
PCB167	12.8			10.1	13.1	N/A	N/A	11.687	15.94	N/A	12.71	12.40	2.479	4	19.51%	N/A
TOTAL HEXA	69.2	72	5	46.1	62.5	81.61	88.32	51.874	69.92	47.9	-					58.47
PCB177							1.29	0.066								
PCB180	11.7			10.0	10.8	10.73	9.25	12.567	8.80	12.9	10.72	10.73	1.556	7	14.52%	13.33
PCB187	13.9			12.0	13.3	13.45	12.08	13.957	11.63	14.6	13	13.3	1.117	7	8.59%	15.97
PCB189							0.99									
PCB190	10.0			9.5	0.0	9.74	12.55	15.843	10.73	N/A	9.727	10.24	5.311	6	54.60%	N/A
TOTAL HEPTA	35.6	30	3	31.5	24.1	33.92	36.16	42.433	31.16	27.5	-					29.3
PCB195	12.7			11.2	11.5	11.70	10.56	29.862	14.18	12.3	14.47	11.70	6.882	7	47.56%	13.23
PCB198							0.85									
TOTAL OCTA	12.7	6.2	1	11.2	11.5	11.70	11.41	29.862	14.18	12.3	-					13.23
PCB209							0.44									

\# Laboratory 9211 reported only total congener groups. The values in the adjacent column indicate the total number of analytical peaks detected by this laboratory.

¢, &, @, ▸ These isomers were reported as co-eluting with another isomer. In this ampoule, the co-eluting isomer was not present, so the value reported may be attributed to the one isomer only.

N/A Laboratory does not calibrate for this isomer.

ND Participant did not detect this isomer, which was present in the ampoule, and reported as Not Detected.

Participants that did not report a result for an isomer that was present in the ampoule, and did not mark the report form with an "ND", were assigned a "0".

§ Original set of results reported by Laboratory 9216. They had run out of their own calibration standards when the ampoules were received. To try and meet the study deadline, they borrowed calibration standards that had been cross-checked to the same external sources that they used. When they received the table of results from this study, they did felt that their performance could have been better. Upon comparing the borrowed standards with their own new standards, Laboratory 9216 felt that the borrowed standards were the source of variability in their performance. They reanalysed the ampouled solutions using their new calibration standards. The revised results are used in the calculations of mean and standard deviation.

Laboratories 9212 and 9213 provided two sets of results using two different instruments. See Table 6 for description.

TABLE 4 - Ampoule PCBs 4
Results in µg/L

PCB ISOMER	TARGET	9211	#	9212-V	9212-HP	9213A	9213B	9214	9215	9216	MEAN	MEDIAN	SD	n	%RSD	9216 §
PCB3	346			N/A	N/A	360.79	250.30	231.156	298.44	N/A	285.2	274.4	57.82	4	20.27%	N/A
TOTAL MONO	346	330	1			360.79	250.30	231.156	298.44	-	-					-
PCB4	369			292.4	259.2	37.80	29.05	36.256	265.26	N/A	153.3	148.5	130.8	6	85.32%	N/A
PCB6	361			N/A	N/A	657.35	73.26 +	625.532 +	352.69	N/A	427.25	439.2	222.7	4	63.63%	N/A
PCB7	450			N/A	N/A	642.58	238.56	176.314	378.67	N/A	359.0	309.12	207.2	4	57.71%	N/A
PCB8	342			0.0	0.0	0.00	73.26 +	625.532 +	267.98	N/A	161.12	36.3 **	250.1	6	155.20%	N/A
PCB15	297			N/A	N/A	N/A	N/A	N/A	N/A	440.0						654.1
TOTAL DI	1809	1490	4	292.4	259.2	1337.73	415.13	1462.634	1264.80	440.0	-					654.1
PCB16	22.6			N/A	N/A	43.64	18.25 +	14.045	22.21	N/A	24.54	20.23	13.16	4	53.66%	N/A
PCB17	19.6			N/A	N/A	N/A	56.75	78.644	INT	N/A	67.65	-	15.41	2	22.78%	N/A
PCB18	20.6			16.6	19.3	15.87	12.64	10.948	29.94	20.6	18.04	16.6	6.279	7	34.80%	27.1
PCB19	20.6			N/A	N/A	17.68	14.56	11.156	19.67	N/A	15.82	16.23	3.758	4	23.75%	N/A
PCB22	26.6			N/A	N/A	24.99	20.20	41.913	23.19	N/A	27.57	24.09	9.762	4	35.40%	N/A
PCB24	18.6			N/A	N/A	35.94	27.84 +	16.997	12.27	N/A	23.26	22.42	10.67	4	45.88%	N/A
PCB25	21.6			N/A	N/A	21.81	18.01	20.290	19.78	N/A	19.97	20.04	1.567	4	7.85%	N/A
PCB26	21.2			N/A	N/A	23.75	20.84	19.487	26.74	N/A	22.46	22.30	2.822	4	12.57%	N/A
PCB27	25.6			N/A	N/A	ND	27.86 +	16.997 &	25.37	N/A	17.56	21.18	12.59	4	71.73%	N/A
PCB28	29.0			23.5	24.1	24.66	19.38	28.256 @	24.77	N/A	24.11	24.38	2.852	6	11.83%	N/A
PCB29	32.6			25.4	27.6	N/A	N/A	25.292	28.53	N/A	26.71	26.5	1.616	4	6.05%	N/A
PCB31	24.2			19.3	19.1	17.22	16.83	28.256 @	21.06	ND	17.4	19.1	8.572	7	49.26%	ND
PCB32	20.6			N/A	N/A	N/A	18.25 +	43.837	18.72	N/A	26.94	18.72	14.64	3	54.35%	N/A
PCB33	20.6			26.6	17.1	35.65	29.44	23.205	21.36	N/A	25.59	25.00	6.529	6	25.51%	N/A
PCB37	19.0			N/A	N/A	N/A	N/A	11.160	22.49	N/A	16.84	-	7.997	2	47.50%	N/A
TOTAL TRI	344.4	270	12	111.6	107.2	261.41	300.87	390.404	315.10	20.6	-					27.1
PCB40	21.6			25.0	22.3	27.09	23.97	29.028	24.71	29.3	25.91	25.0	2.635	7	10.17%	35.98
PCB41	20.6			N/A	N/A	12.87 §	10.15 §	32.511 §	8.90 §	N/A	16.11	11.51	11.06	4	68.66%	N/A
PCB42	27.6			25.6	21.0	32.47	24.89	28.580	25.05	N/A	26.3	25.43	3.877	6	14.74%	N/A
PCB44	22.0			18.6	20.6	17.77	15.70	22.976	20.97	22.7	19.93	20.6	2.681	7	13.45%	28.81
PCB47	27.4			24.6	0.0	70.27	47.38	35.999 +	23.43	N/A	33.6	30.25	23.9	6	71.13%	N/A
PCB48	20.2			N/A	N/A	0.00	0.00	35.999 +	17.42	N/A	13.35	8.71	17.19	4	128.68%	N/A
PCB49	19.6			15.0	16.0	17.22	13.73	16.990	17.04	22.2	16.88	16.99	2.667	7	15.80%	29.46
PCB52	19.8			19.0	19.8	17.34	14.35	15.700	18.70	25.0	18.56	18.70	3.431	7	18.49%	30.63
PCB53	21.0			0.0	0.0	N/A	N/A	17.254	14.96	N/A	8.054	7.48	9.346	4	116.05%	N/A
PCB56/60						3.58										
PCB61	21.2			13.9	20.2	N/A	N/A	N/A	N/A	N/A	17.05	-	4.455	2	26.13%	N/A
PCB64						34.19	25.96									
PCB66	29.6			36.6	46.6	0.00	0.00	42.651	28.08	N/A	25.69	32.44	20.85	6	81.17%	N/A
PCB70	27.0			0.0	25.3	28.40	22.47	35.787	27.69	N/A	23.27	26.50	12.24	6	52.58%	N/A
PCB71	22.2			N/A	N/A	12.87 §	10.14 §	32.511 §	8.90 §	N/A	16.11	11.51	11.06	4	68.69%	N/A
PCB74	21.0			N/A	N/A	56.92	15.78	17.788	26.61	N/A	29.27	22.20	19.02	4	64.98%	N/A

TABLE 4 - Ampoule PCBs 4
Results in µg/L

PCB ISOMER	TARGET	9211	#	9212-V	9212-HP	9213A	9213B	9214	9215	9216	MEAN	MEDIAN	SD	n	%RSD	9216 ß
PCB75	20.8			17.4	20.9	N/A	N/A	N/A	N/A	N/A	19.15	-	2.475	2	12.92%	N/A
PCB77	21.2			13.8	16.8	ND	ND	23.940	25.70	68.7	21.26	16.8	23.3	7	109.50%	100.8
PCB81	19.4			N/A	N/A	N/A	N/A	13.603	22.59	N/A	18.1	-	6.355	2	35.12%	N/A
TOTAL TETRA	382.8	440	13	209.8	229.7	330.19	224.52	401.320	326.53	167.9	-					225.7
PCB84	26.0			20.0	20.1	24.19	5.12	42.226	28.43	N/A	23.34	22.15	12.14	6	52.01%	N/A
PCB87							9.89									
PCB95	26.6			N/A	N/A	68.22	47.73	27.469	29.03	N/A	43.11	38.38	19.1	4	44.31%	N/A
PCB97	25.6			22.4	23.4	25.07	22.67	22.243	16.00	N/A	22	22.64	3.11	6	14.14%	N/A
PCB100	22.8			N/A	N/A	N/A	N/A	31.933	23.85	N/A	27.89	-	5.716	2	20.49%	N/A
PCB101	21.0			17.1	18.1	20.90	35.11	17.310	23.05	26.2	22.54	20.90	6.468	7	28.70%	28.03
PCB105	19.0			16.0	17.8	16.32	11.70	32.591 ◄	16.36	19.4	18.6	16.36	6.603	7	35.51%	21.52
PCB110	22.0			N/A	N/A	26.17	16.75	18.357	15.04	N/A	19.08	17.55	4.917	4	25.77%	N/A
PCB114	26.2			25.5	25.5	26.29	25.17	0.141	29.54	28.2	22.91	25.5	10.17	7	44.39%	27.59
PCB118	20.2			18.1	20.2	21.12	15.56	20.341	17.78	ND	16.16	18.1	7.374	7	45.64%	ND
PCB119	24.8			N/A	N/A	N/A	N/A	29.189	22.84	N/A	26.01	-	4.489	2	17.26%	N/A
PCB123	22.8			N/A	N/A	N/A	N/A	N/A	N/A	N/A						N/A
PCB126	24.0			N/A	N/A	N/A	N/A	N/A	N/A	N/A						N/A
TOTAL PENTA	261	220	12	119.1	125.1	226.26	169.9	274.391	221.92	73.8	-					77.14
PCB128	33.4			28.6	33.2	58.41	42.40	57.328	32.46	39.4	41.69	39.4	11.96	7	28.69%	39.68
PCB129/178							11.32 ►									
PCB135/144						0.27										
PCB136	40.0			26.2	28.4	36.66	33.16	23.373	32.78	N/A	30.1	30.59	4.958	6	16.48%	N/A
PCB137	26.2			22.2	24.4	25.75	27.19	0.000	16.09	27.6	20.46	24.4	9.836	7	48.07%	27.51
PCB138	19.8			0.0	34.4	48.34	32.00	22.524 *	12.12 *	45.8	27.88	32.00	17.58	7	63.04%	45.6
PCB146						1.04										
PCB149	24.4			N/A	N/A	41.66	42.37	21.739	INT	N/A	35.26	41.66	11.71	3	33.22%	N/A
PCB151						0.60										
PCB153	39.0			29.0	31.6	35.29	27.82	32.591 ◄	33.34	40.7	32.91	32.591	4.273	7	12.99%	45.63
PCB155	21.6			N/A	N/A	N/A	N/A	N/A	N/A	N/A						N/A
PCB156	28.4			25.2	23.2	32.64	25.72	0.216	29.21	32.2	24.06	25.72	11.1	7	46.16%	31.34
PCB157	29.6			24.8	23.4	32.34	25.29	0.000	N/A	N/A	21.17	24.8	12.33	5	58.25%	N/A
PCB158	19.2			17.0	16.4	18.55	20.25	32.621	22.80	N/A	21.27	19.4	6.026	6	28.33%	N/A
PCB163	21.6			N/A	N/A	N/A	N/A	22.524 *	12.12 *	N/A	17.31	-	7.36	2	42.52%	N/A
PCB166	43.8			N/A	N/A	N/A	N/A	43.782	N/A	N/A						N/A
PCB167	25.6			19.6	24.2	N/A	N/A	23.597	32.62	N/A	25	23.90	5.472	4	21.88%	N/A
PCB169	19.0			N/A	N/A	N/A	N/A	N/A	16.03	N/A						N/A
TOTAL HEXA	391.8	380	11	192.6	239.2	331.55	267.52	247.704	253.79	185.7	-					189.6
PCB170	26.6			19.9	10.55 ▲	21.65	19.94	41.514 ▲	21.46	30.3	23.64	21.46	9.754	7	41.25%	30.23
PCB177	30.2			27.7	29.3	27.56	29.36	34.528	31.33	N/A	29.96	29.33	2.623	6	8.75%	N/A
PCB178/129							11.32 ►									

TABLE 4 - Ampoule PCBs 4
Results in µg/L

PCB ISOMER	TARGET	9211	#	9212-V	9212-HP	9213A	9213B	9214	9215	9216	MEAN	MEDIAN	SD	n	%RSD	9216 §
PCB180	23.4			21.6	19.2	20.12	16.52	25.109	16.12	27.3	20.85	20.12	4.177	7	20.03%	24.99
PCB187	27.6			21.5	25.4	26.67	20.13	27.554	23.96	29.4	24.94	25.4	3.313	7	13.28%	29.03
PCB189	22.2			N/A	N/A	23.40	23.33	20.429	22.59	27.0	23.35	23.33	2.368	5	10.14%	23.67
PCB190	20.0			16.6	10.55 ▲	18.85	19.66	41.514 ▲	20.58	N/A	21.29	19.26	10.54	6	49.50%	N/A
TOTAL HEPTA	150.2	110	5	87.4	95.0	138.45	140.26	190.848	136.04	114	-					107.9
PCB194	22.0			17.6	18.6	19.77	20.53	21.238	20.39	23.9	20.29	20.39	2.016	7	9.93%	21.95
PCB195	25.4			21.8	21.5	22.41	18.97	62.069	26.75	24.6	28.33	22.41	15.09	7	53.27%	21.62
PCB198	27.8			24.2	23.4	26.76	28.26	37.578	15.65	N/A	25.98	25.49	7.167	6	27.59%	N/A
TOTAL OCTA	75.2	34	3	63.6	63.5	68.96	67.75	120.905	62.79	48.7	-					
PCB209	23.6			17.1	17.8	20.10	18.59	30.674	20.50	22.8	21.11	20.10	4.708	7	22.30%	22.42
TOTAL DECA	23.6	24	1	17.1	17.8	20.10	18.59	30.674	20.50	22.8	-					65.99

Laboratory 9211 reported only total congener groups. The values in the adjacent column indicate the total number of analytical peaks detected by this laboratory.

+, &, @, °, ‡, ►, ◄, ▲, ▼, «, • These isomers were reported as co-eluting with another isomer. Results are equally divided between the two isomers.

N/A Laboratory does not calibrate for this isomer.

ND Participant did not detect this isomer, which was present in the ampoule, and reported as Not Detected.

Participants that did not report a result for an isomer that was present in the ampoule, and did not mark the report form with an "ND", were assigned a "0".

§ Original set of results reported by Laboratory 9216. They had run out of their own calibration standards when the ampoules were received. To try and meet the study deadline, they borrowed calibration standards that had been cross-checked to the same external sources that they used. When they received the table of results from this study, they did felt that their performance could have been better. Upon comparing the borrowed standards with their own new standards, Laboratory 9216 felt that the borrowed standards were the source of variability in their performance. They reanalysed the ampouled solutions using their new calibration standards. The revised results are used in the calculations of mean and standard deviation.

****** Distribution of results bimodal. Mean, Median, SD and %RSD unreliable.

INT Interference(s) for this isomer. Could not quantitate the peak area.

Laboratories 9212 and 9213 provided two sets of results using two different instruments. See Table 6 for description.

TABLE 5: Distribution of PCB Isomers on Participants' Target Lists

Number on Target List	PCB Isomer
All participants (6)	PCB18 PCB31 PCB40 PCB44 PCB49 PCB52 PCB77 PCB101 PCB105 PCB114 PCB118 PCB128 PCB137 PCB138 PCB153 PCB156 PCB170 PCB180 PCB187 PCB194 PCB195 PCB209
Target List of 1 Participant Only	PCB15 PCB61 PCB75 PCB166 PCB169
Not on any Participant's Target List	PCB123 PCB126 PCB155

TABLE 6: Instruments and GC Columns

Lab Code	9211	9212-V	9212-HP	9213	9214	9215	9216
Instrument	GC/MSD: HP	GC/ECD: Varian 3400	GC/ECD: HP5890	A: GC/ECD: Varian 3400 B: GC/ECD: Varian Vista 6000	GC/ECD: HP5890	GC/ECD: HP5890	GC/ECD: HP3890
Column	DB-5, 30 m	DB-5, 60 m DB-1701, 60 m	DB-5, 60 m DB-1701, 60 m	DB-5, 60 m	DB-5, 30 m	DB-5, 60 m DB-17, 30 m	DB-1, 30 m DB-5, 30 m

NOTE 1: Laboratory 9213 analyzed the ampoules using the Varian 3400 with a SPI (Septum Programmable Injector). They repeated their analysis of the PCB ampoules using the Varian Vista 6000. Both sets of results are included in Tables 1-4 as marked.

NOTE 2: Laboratory 9216 had run out of their own calibration standards when the ampoules were received. To try and meet the study deadline, they borrowed calibration standards that had been cross-checked to the same external sources that they used. When they received the original table of results, they did not feel that their performance could have been better. Upon investigating the borrowed standards with their new standards, they felt that the borrowed standards were the source of variability in their performance. They reanalysed the ampouled solutions using their new calibration standards. Both sets of results are included in Tables 1-4 as marked.

TABLE 7: Distribution of Participants' Results Relative to Target

Lab ID Code	9212-V		9212-HP		9213A		9213B		9214		9215		9216	
Percent of Target	n	%	n	%	n	%	n	%	n	%	n	%	n	%
<60%	10	11.6%	10	11.6%	14	12.5%	20	17.2%	17	12.7%	8	6.1%	5	10%
60-75%	7	8.1%	2	2.3%	4	3.6%	19	16.4%	11	8.2%	12	9.2%	0	0%
75-90%	47	54.7%	29	33.7%	20	17.9%	35	30.2%	20	14.9%	34	26.0%	0	0%
90-110%	17	19.8%	40	46.5%	50	44.6%	24	20.7%	36	26.9%	52	39.7%	24	48%
110-130%	4	4.7%	3	3.5%	13	11.6%	8	6.9%	12	9.0%	22	16.8%	15	30%
>130%	1	1.2%	2	2.3%	11	9.8%	10	8.6%	38	28.4%	3	2.3%	6	12%

n - number of results falling in range (includes results from all four ampoules)

TABLE 8 - Performance of Laboratory 9211

CONGENER GROUP	TARGET	RESULT	% OF TARGET	# PEAKS PRESENT	# PEAKS REPORTED
IADN PCBs 1					
TOTAL MONO	232	210	90.5%	1	1
TOTAL DI	311.3	260	83.5%	2	2
TOTAL TRI	46.6	41	88.0%	4	5
TOTAL TETRA	75.5	78	103.3%	7	7
TOTAL PENTA	44.4	34	76.6%	4	4
TOTAL HEXA	79.7	81	101.6%	5	5
TOTAL HEPTA	13.3	6.9	51.9%	1	1
TOTAL OCTA	11	6.6	60.0%	1	1
IADN PCBs 2					
TOTAL DI	474	320	67.5%	2	2
TOTAL TRI	55.9	43	76.9%	5	5
TOTAL TETRA	52.4	60	114.5%	5	4
TOTAL PENTA	48.1	38	79.0%	4	4
TOTAL HEXA	47	42	89.4%	4	4
TOTAL HEPTA	26.2	20	76.3%	2	2
TOTAL OCTA	25.7	6	23.3%	1	1
TOTAL DECA	11.8	13	110.2%	1	1
IADN PCBs 3					
TOTAL DI	432	360	83.3%	2	2
TOTAL TRI	58.4	50	85.6%	5	5
TOTAL TETRA	63.5	79	124.4%	5	6
TOTAL PENTA	48	40	83.3%	4	4
TOTAL HEXA	69.2	72	104.0%	5	5
TOTAL HEPTA	35.6	30	84.3%	3	3
TOTAL OCTA	12.7	6.2	48.8%	1	1
IADN PCBs 4					
TOTAL MONO	348	330	94.8%	1	1
TOTAL DI	1809	1490	82.4%	5	4
TOTAL TRI	344.4	270	78.4%	15	12
TOTAL TETRA	382.8	440	114.9%	17	13
TOTAL PENTA	281	220	78.3%	12	12
TOTAL HEXA	391.8	380	97.0%	14	11
TOTAL HEPTA	150.2	110	73.2%	6	5
TOTAL OCTA	75.2	34	45.2%	3	3
TOTAL DECA	23.6	24	101.7%	1	1

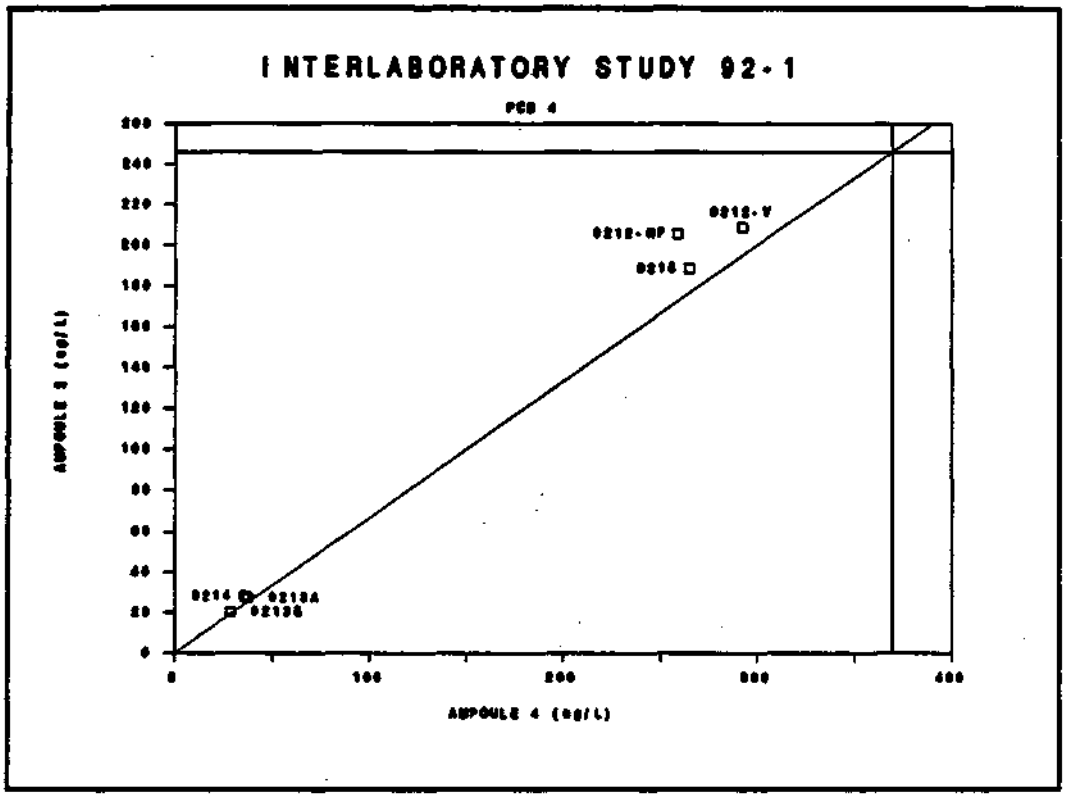

Figure 1 - PCB4

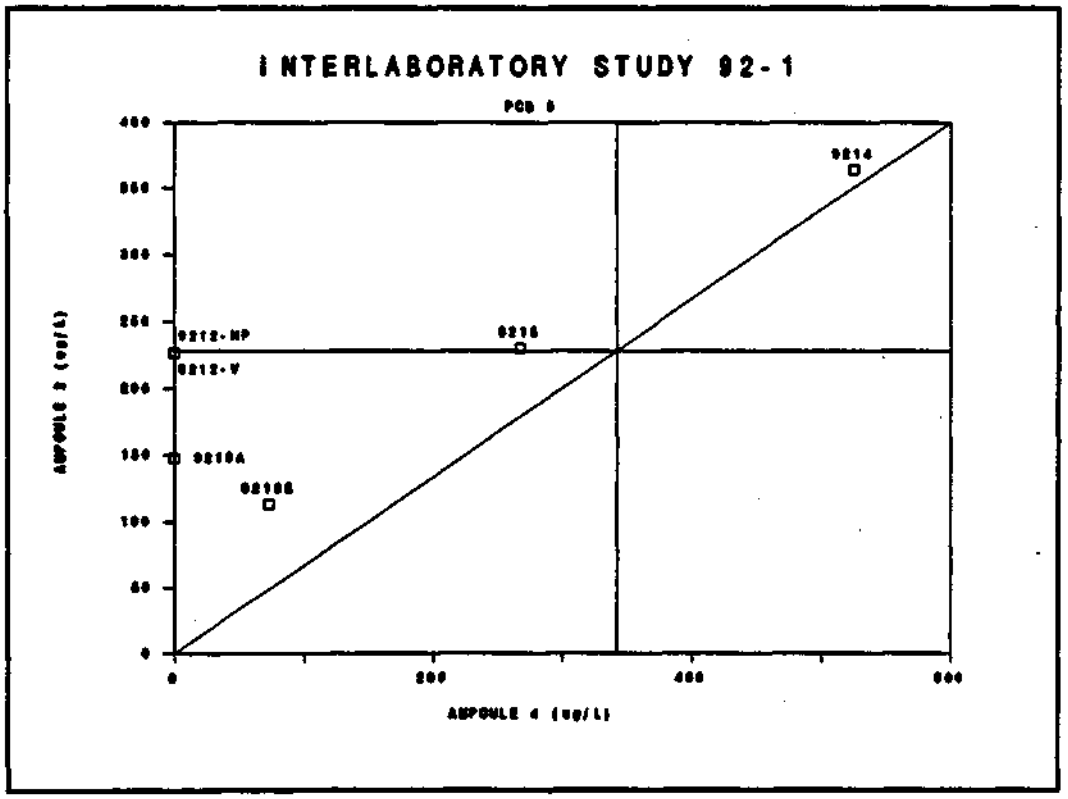

Figure 2 - PCB8

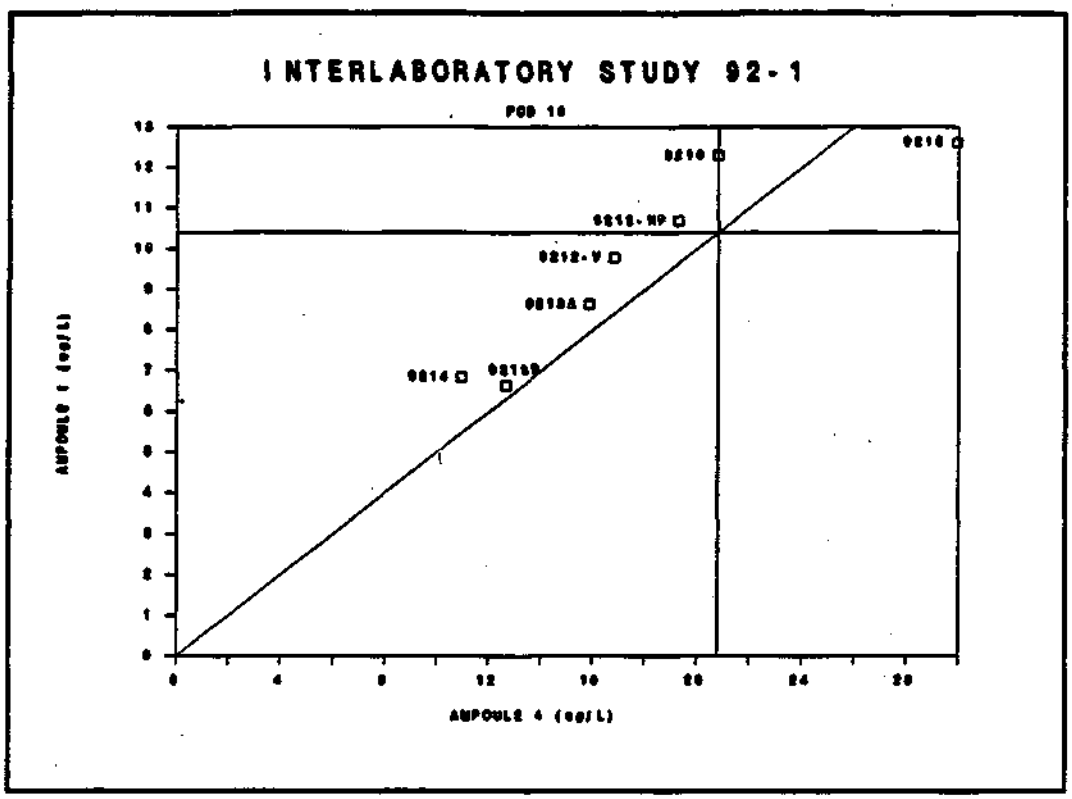

Figure 3 - PCB18

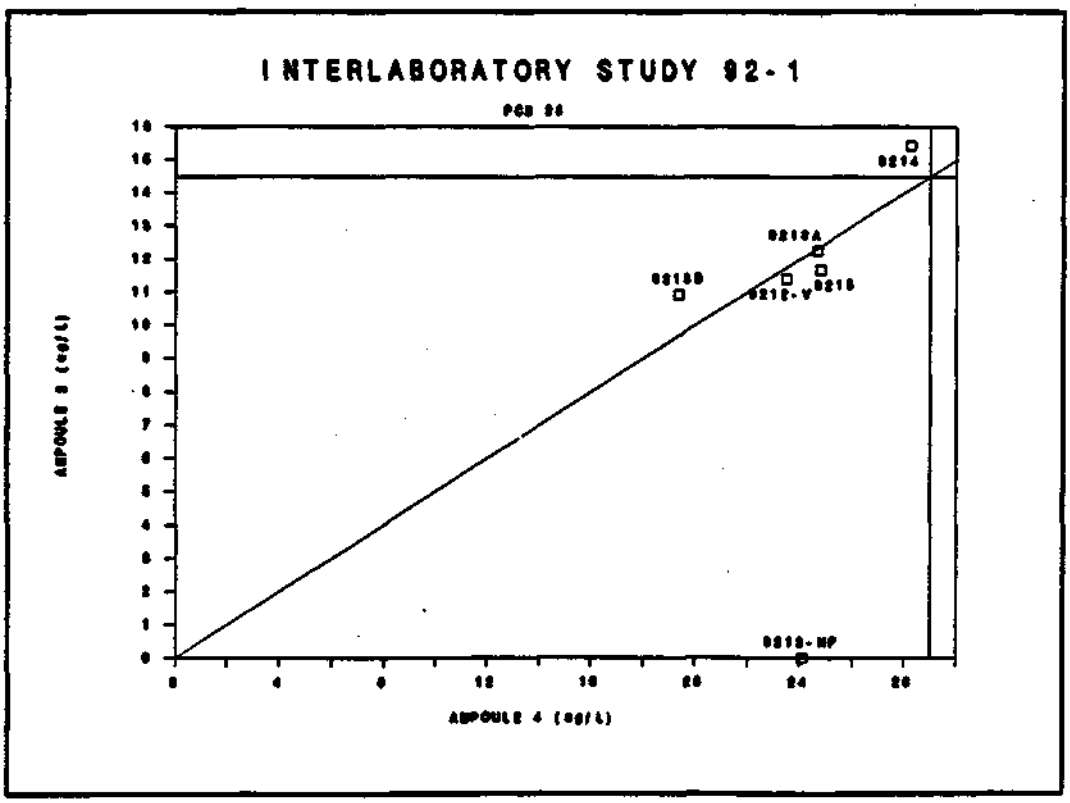

Figure 4 - PCB28

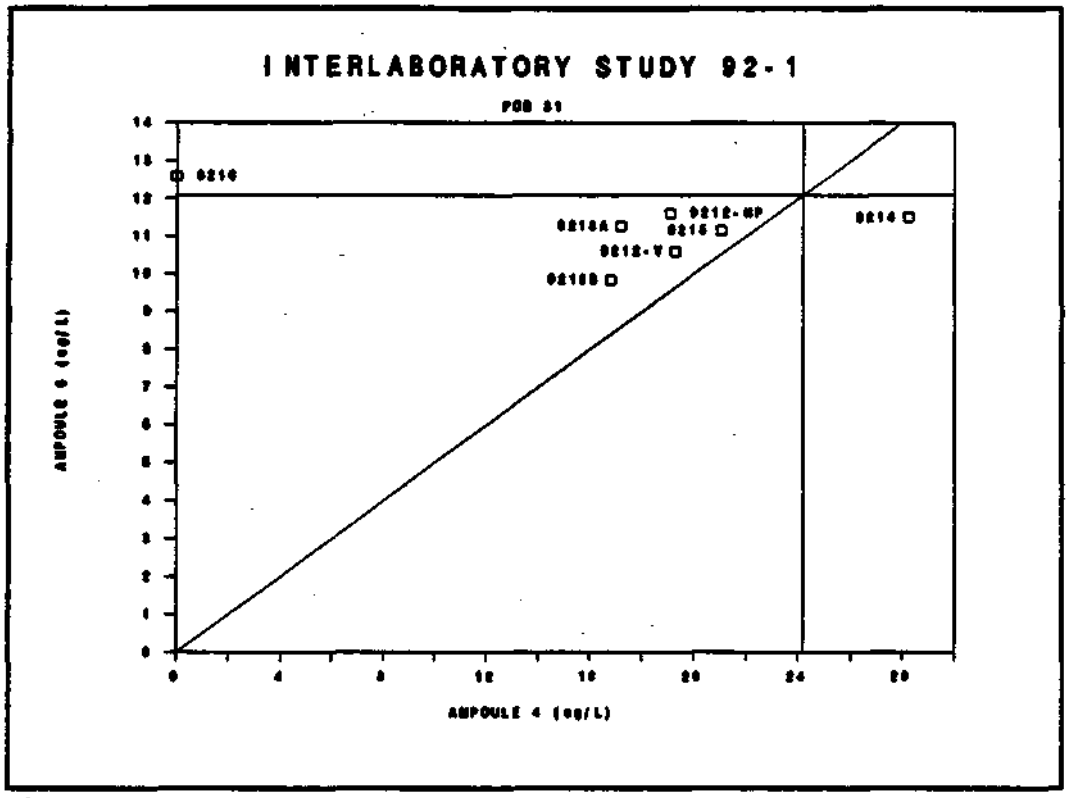

Figure 5 - PCB31

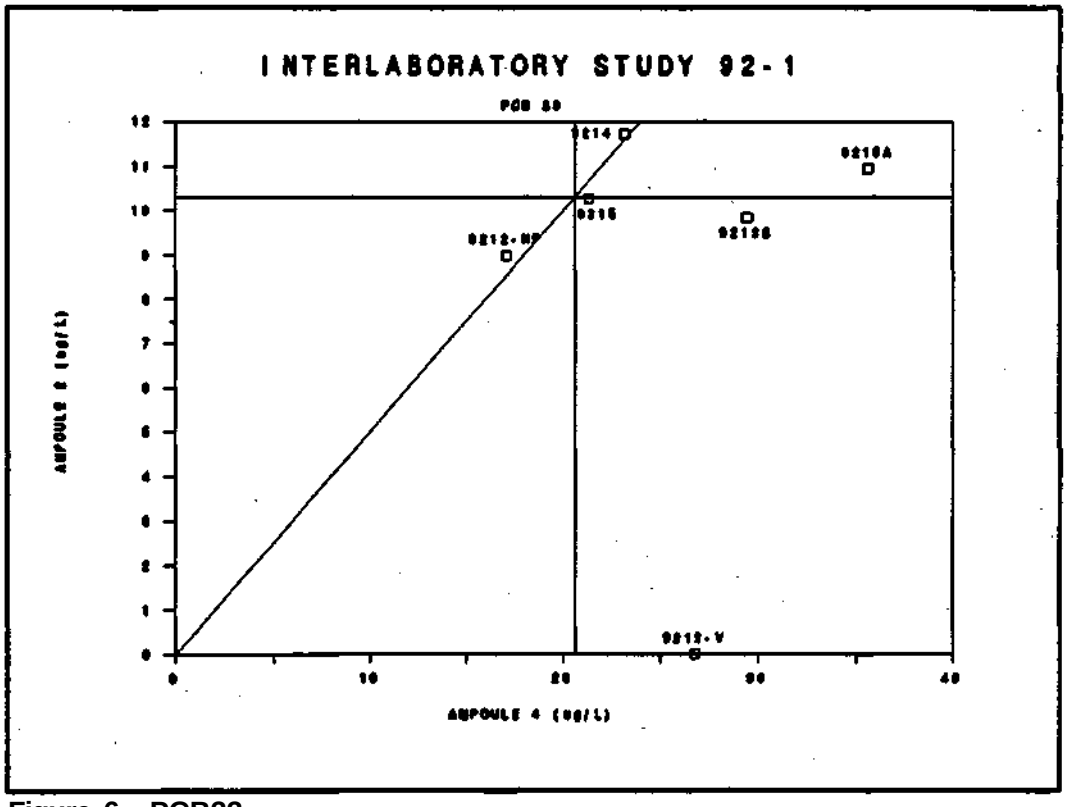

Figure 6 - PCB33

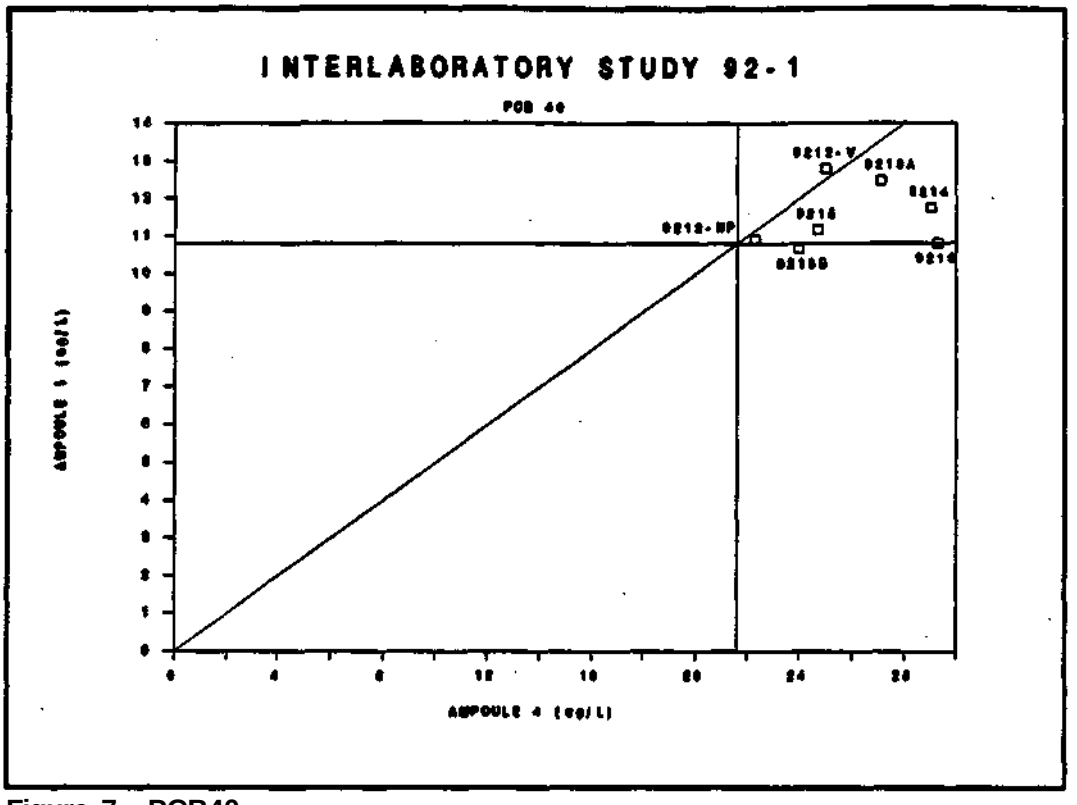

Figure 7 - PCB40

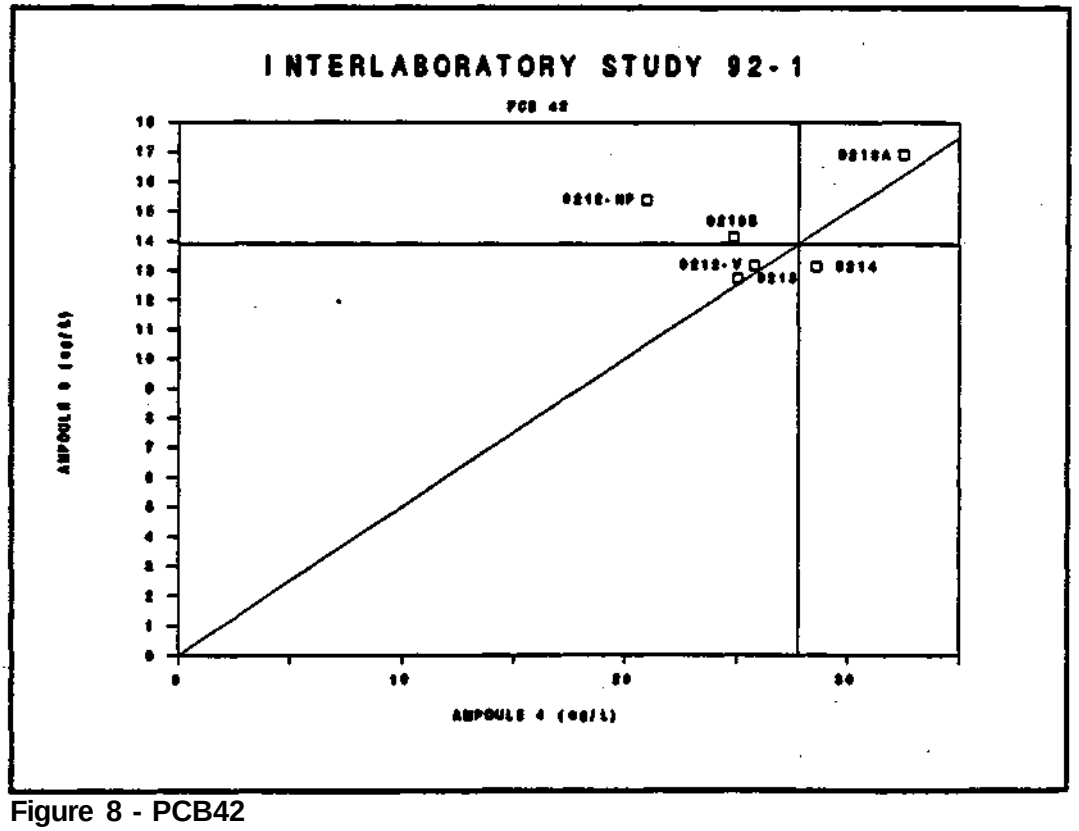

Figure 8 - PCB42

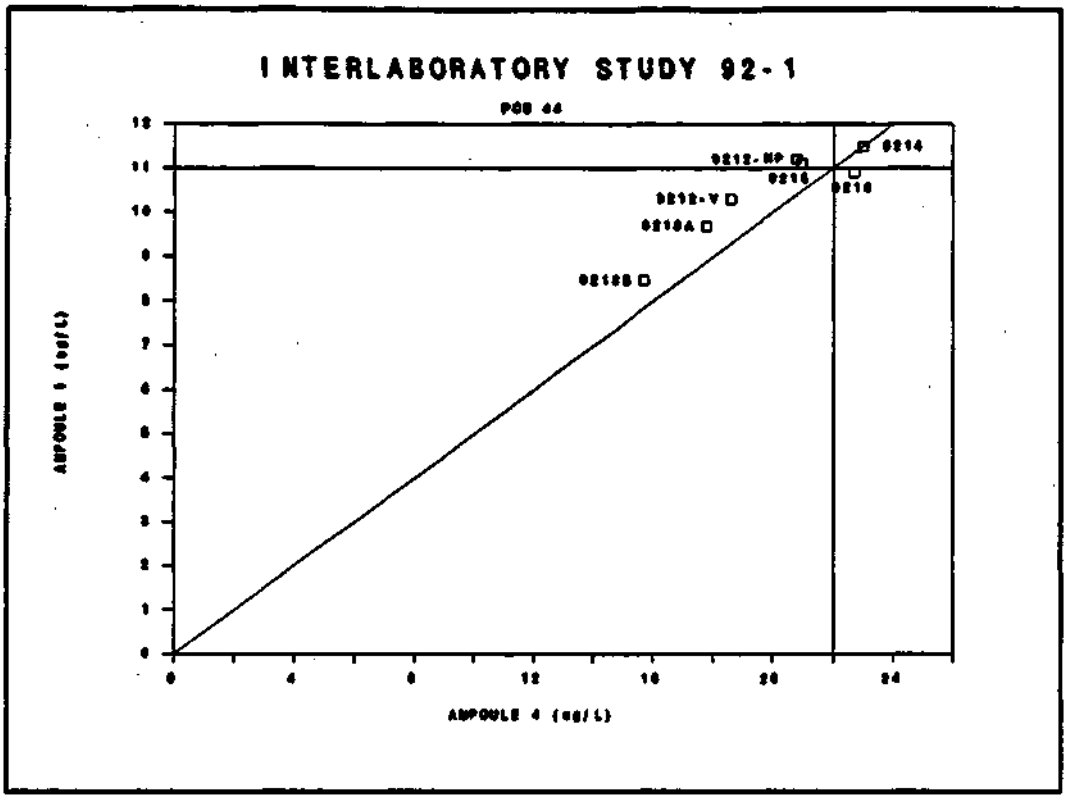

Figure 9 - PCB44

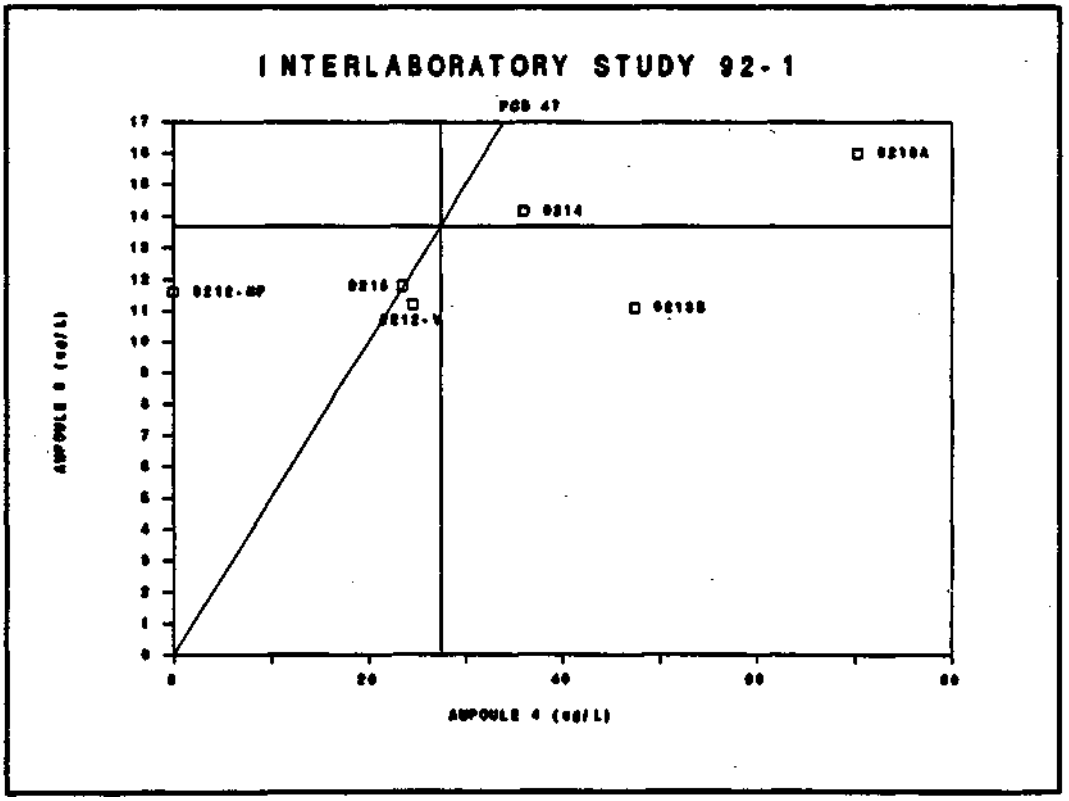

Figure 10 - PCB47

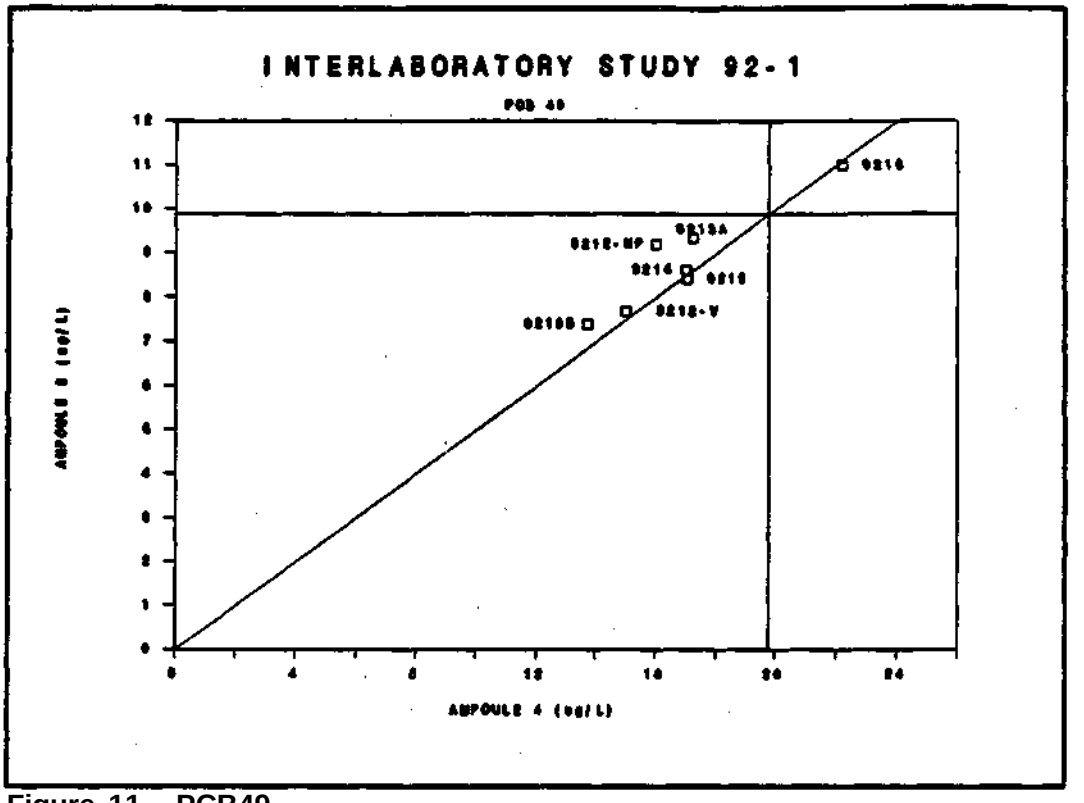

Figure 11 - PCB49

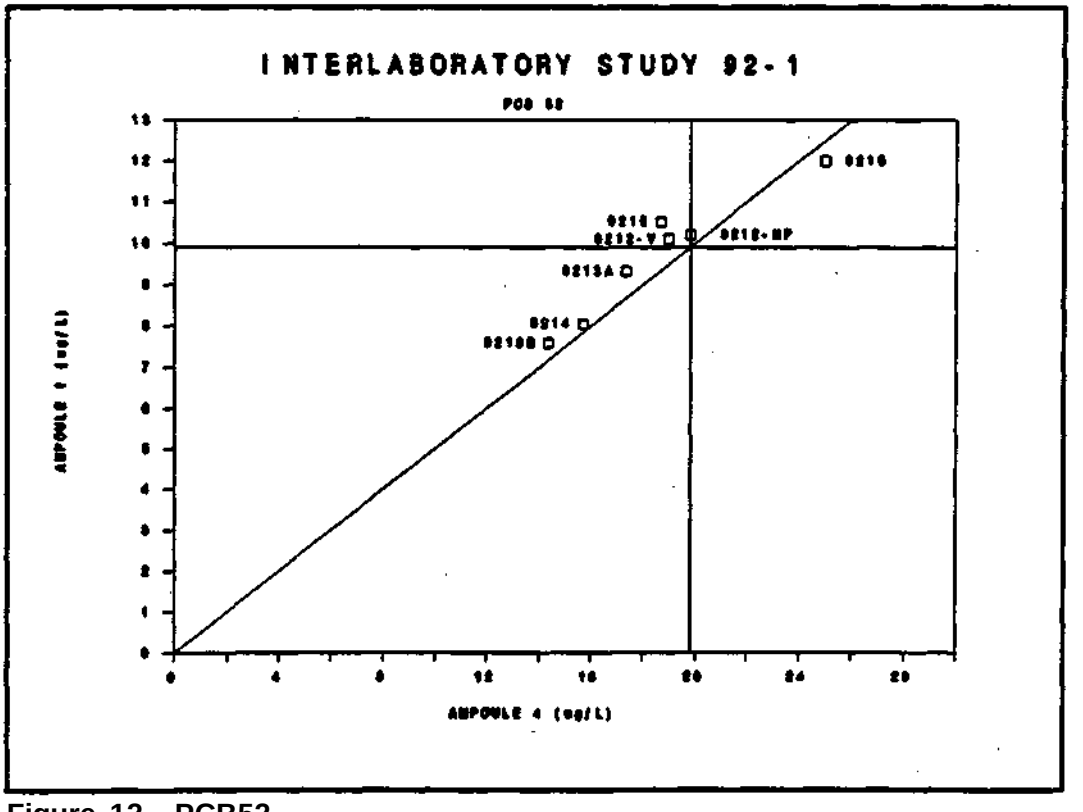

Figure 12 - PCB52

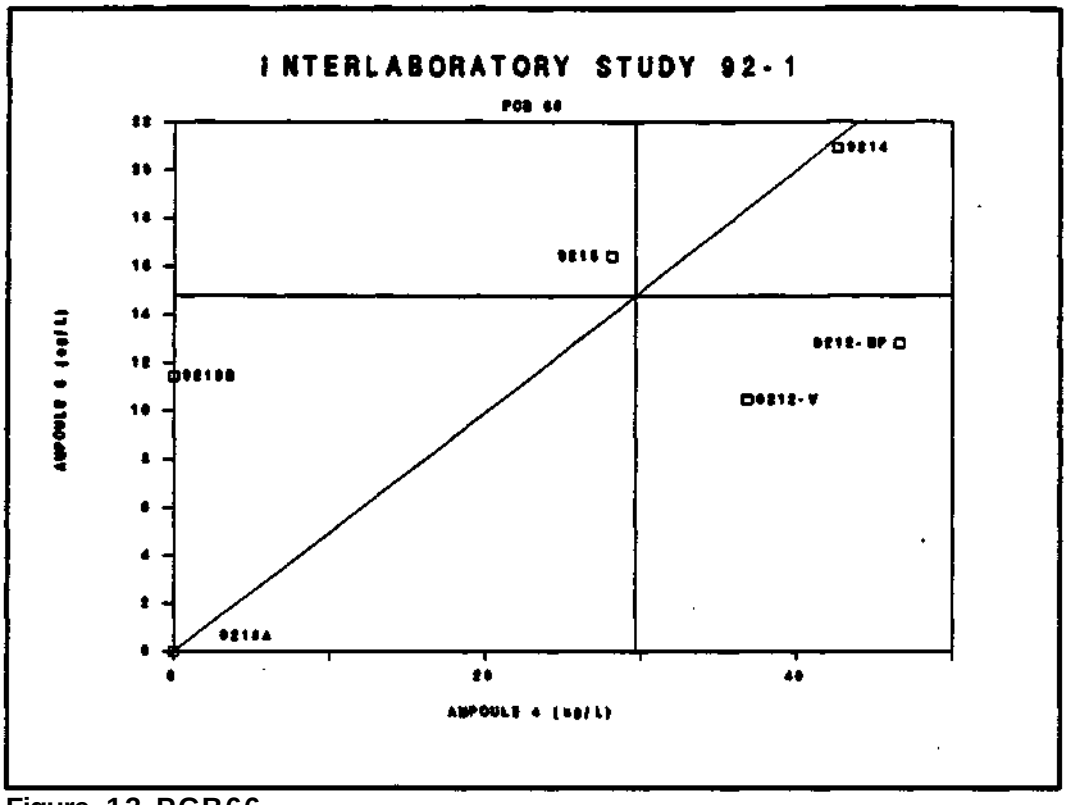

Figure 13-PCB66

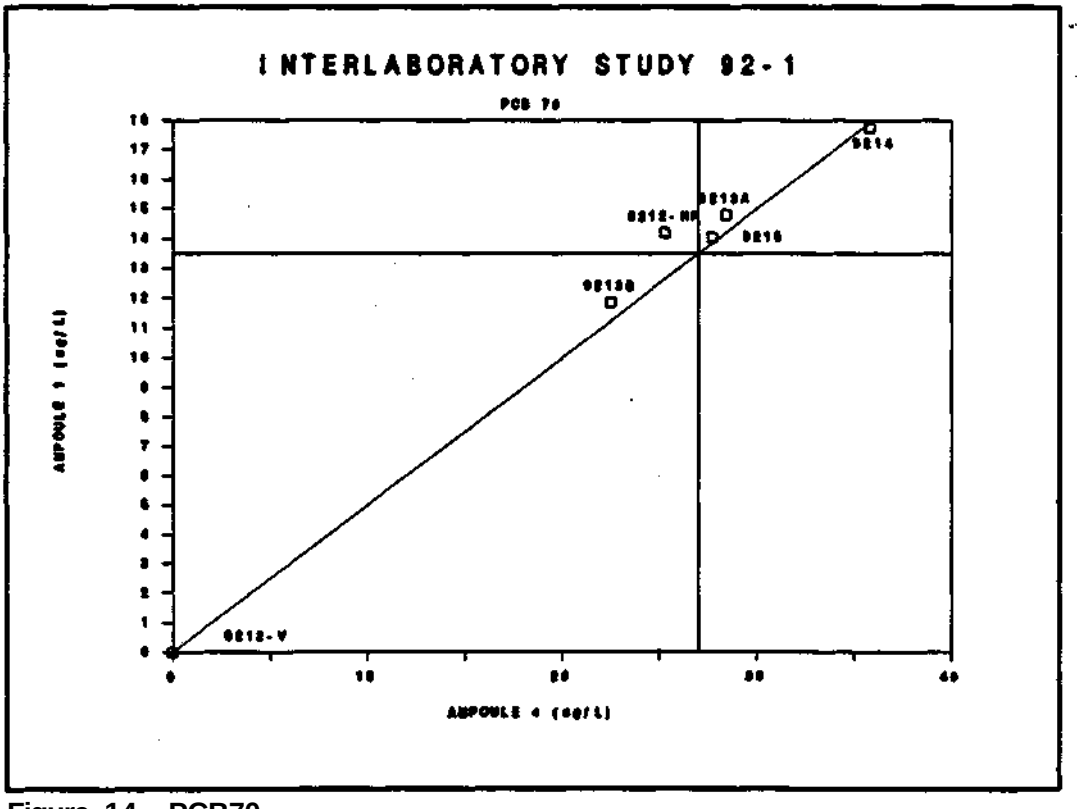

Figure 14 - PCB70

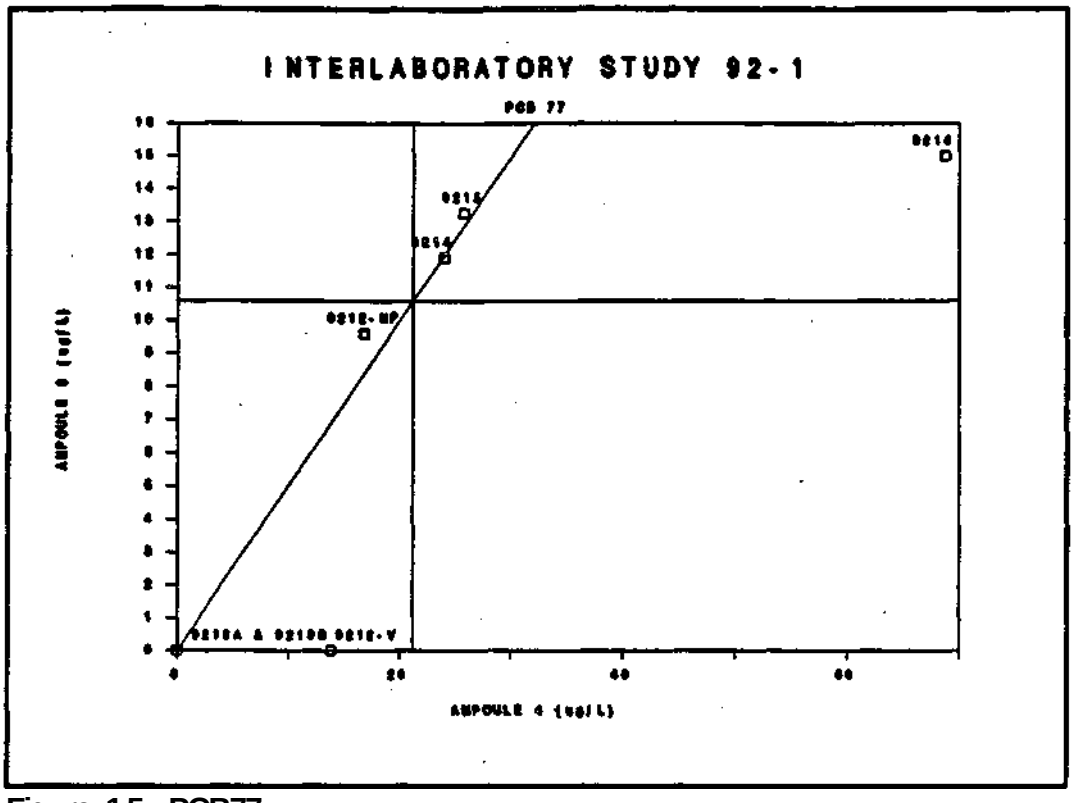

Figure 15- PCB77

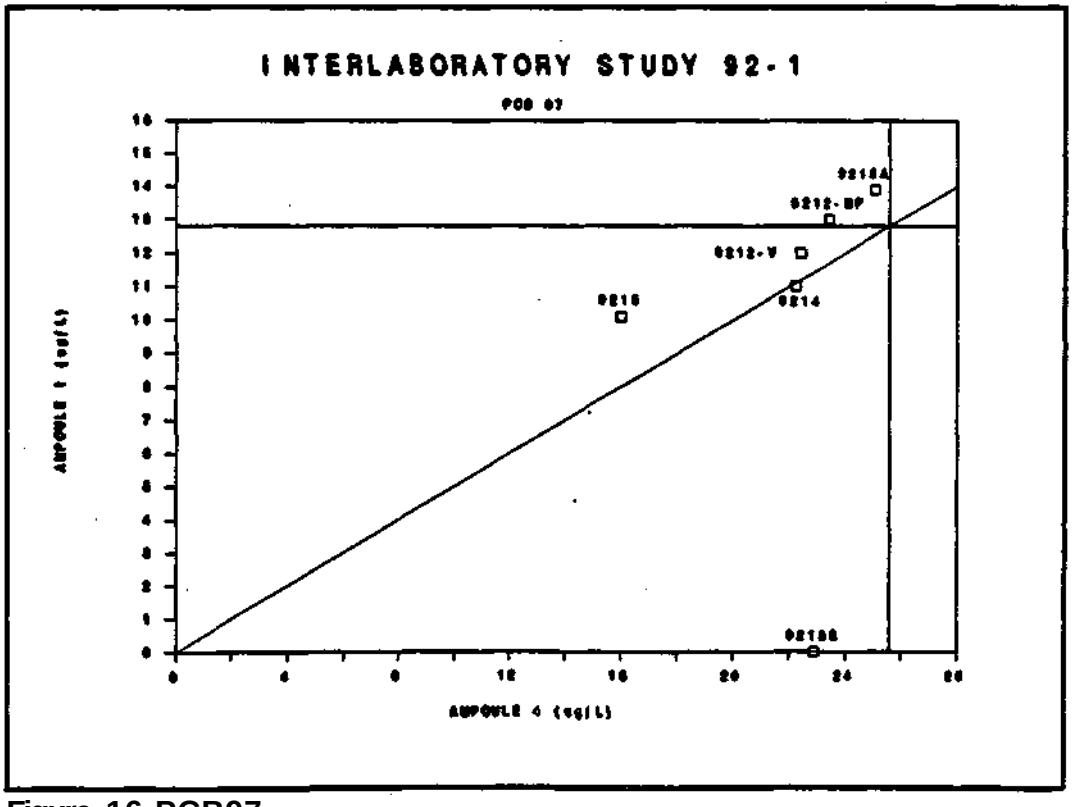

Figure 16-PCB97

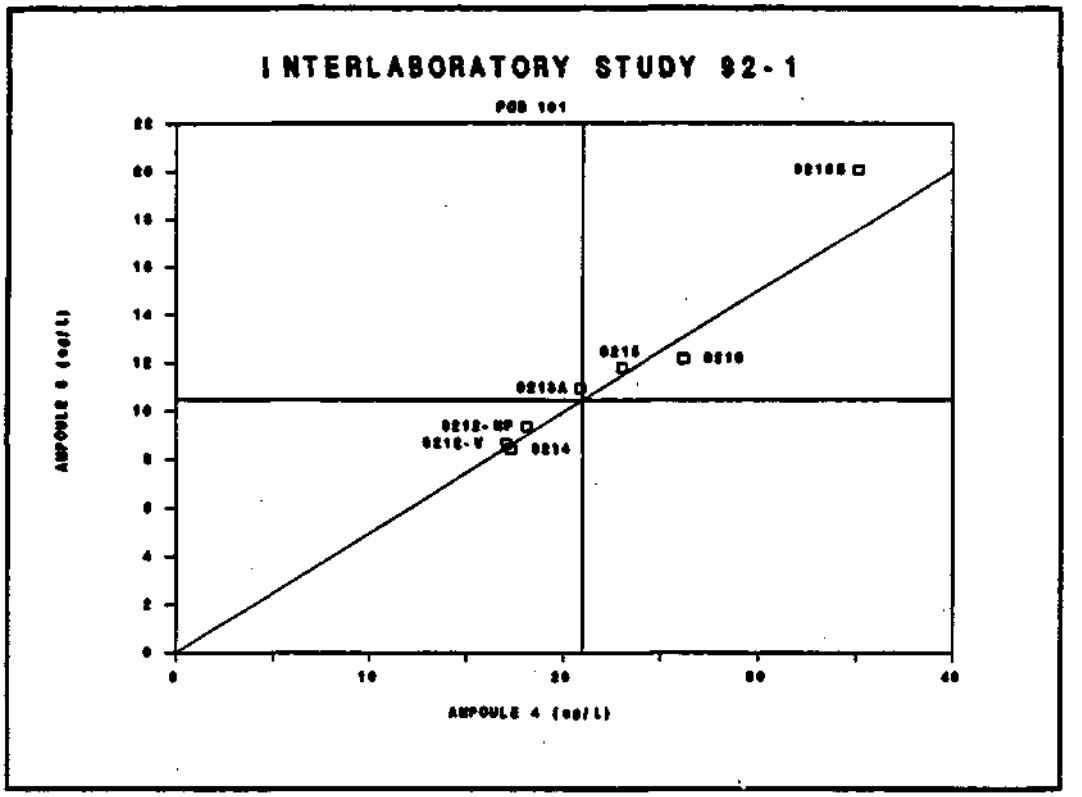

Figure 17 - PCB101

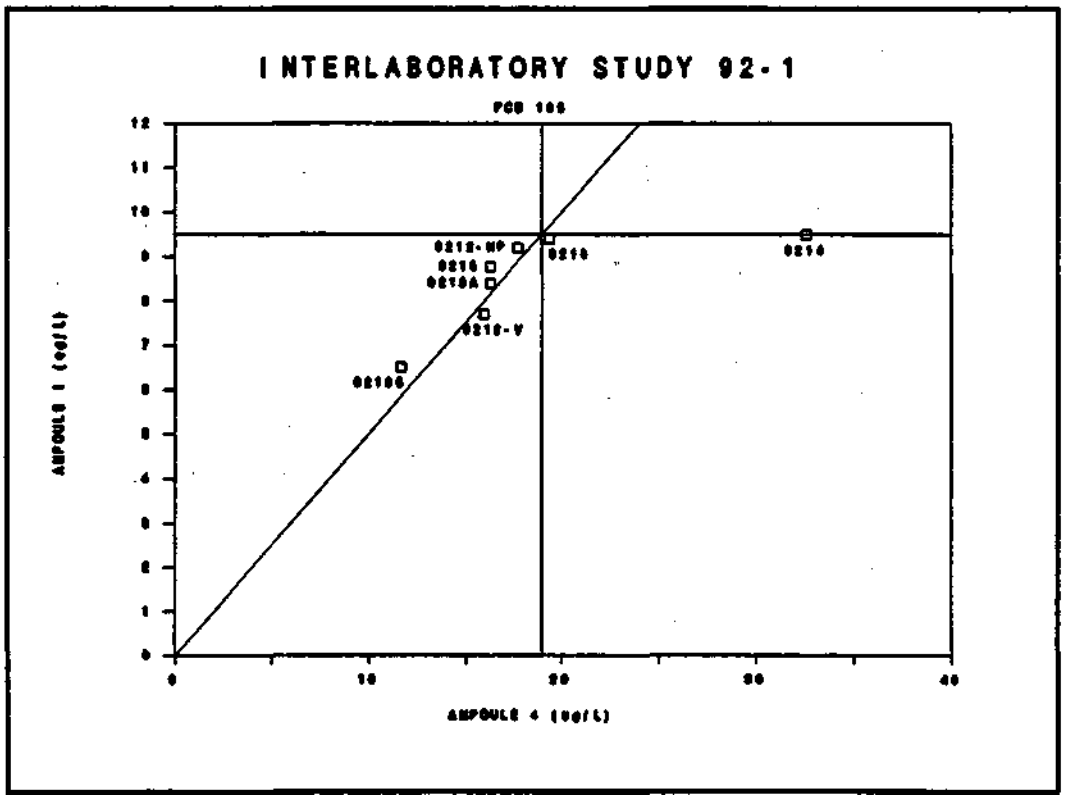

Figure 18 - PCB105

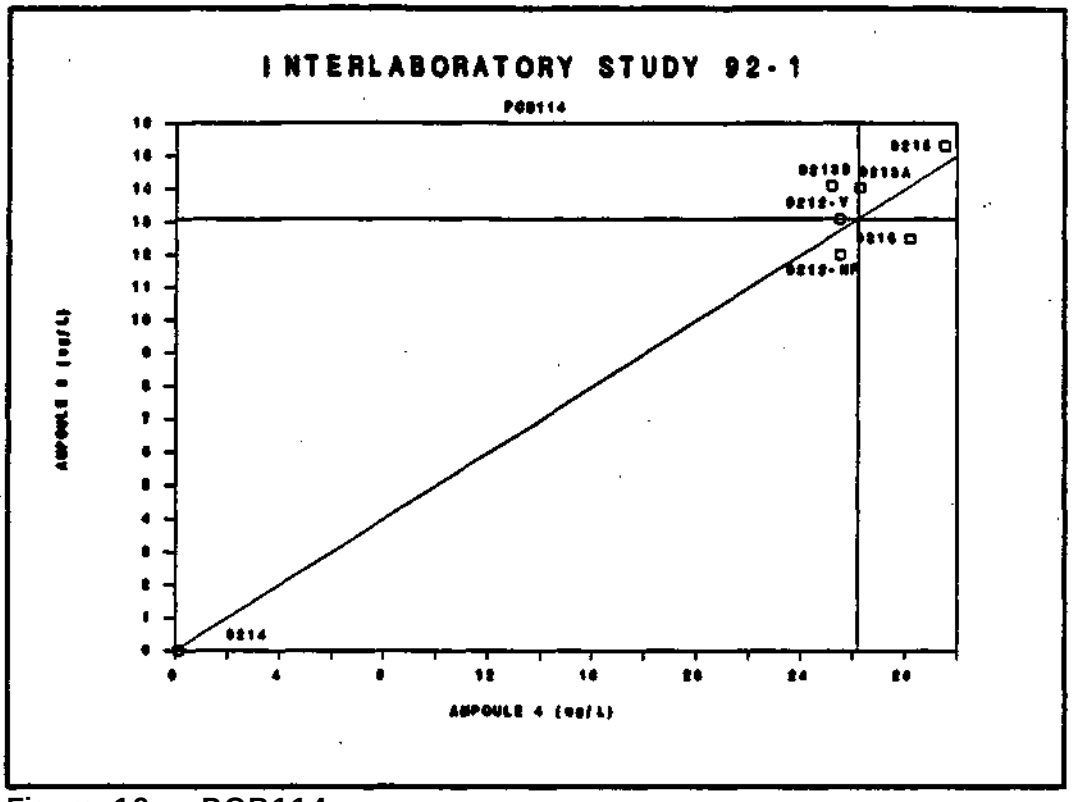

Figure 19 - PCB114

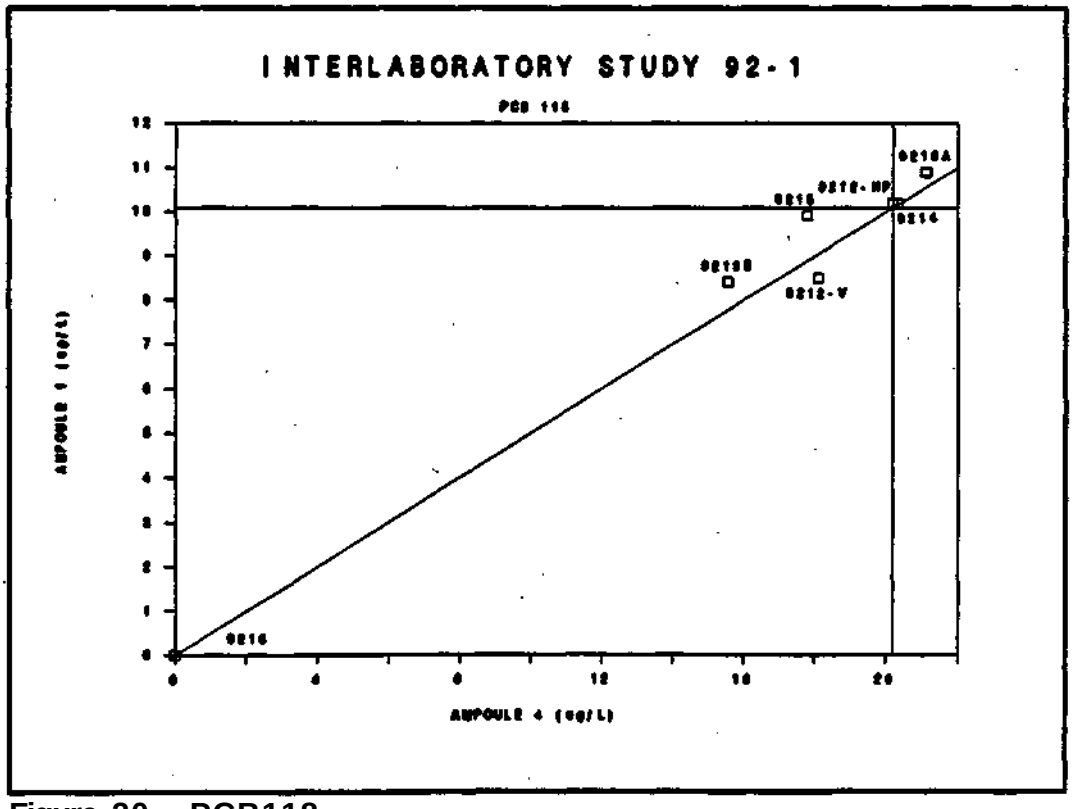

Figure 20 - PCB118

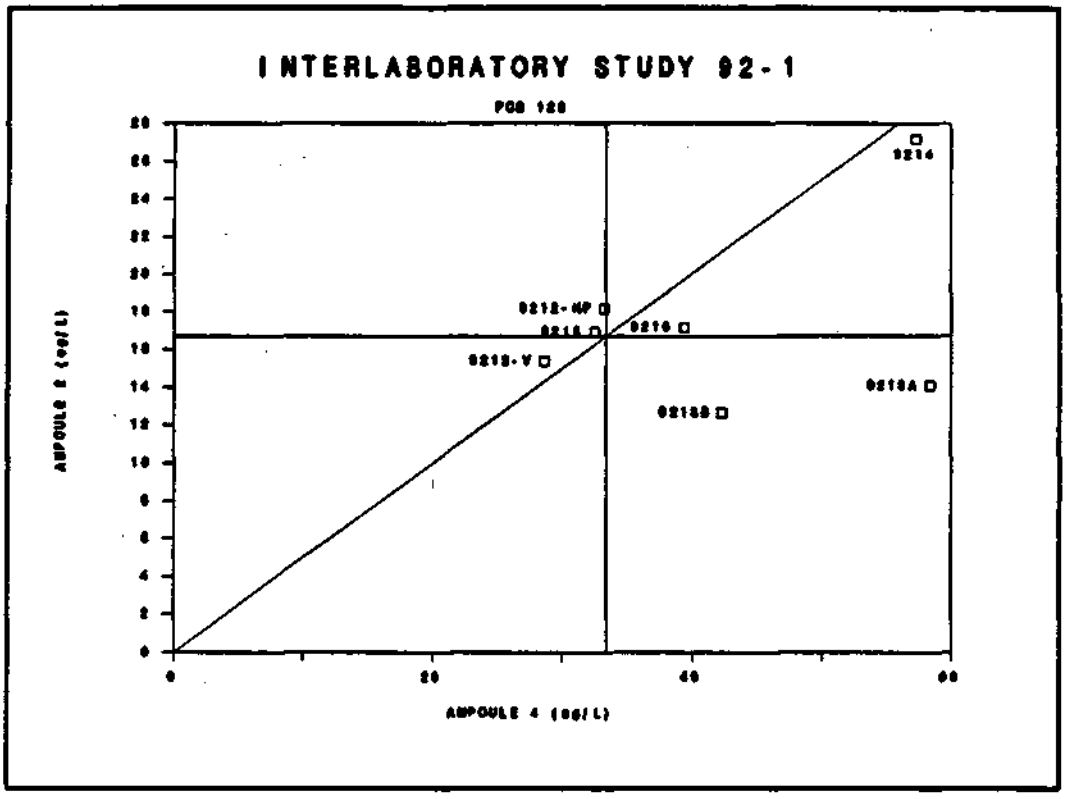

Figure 21 - PCB128

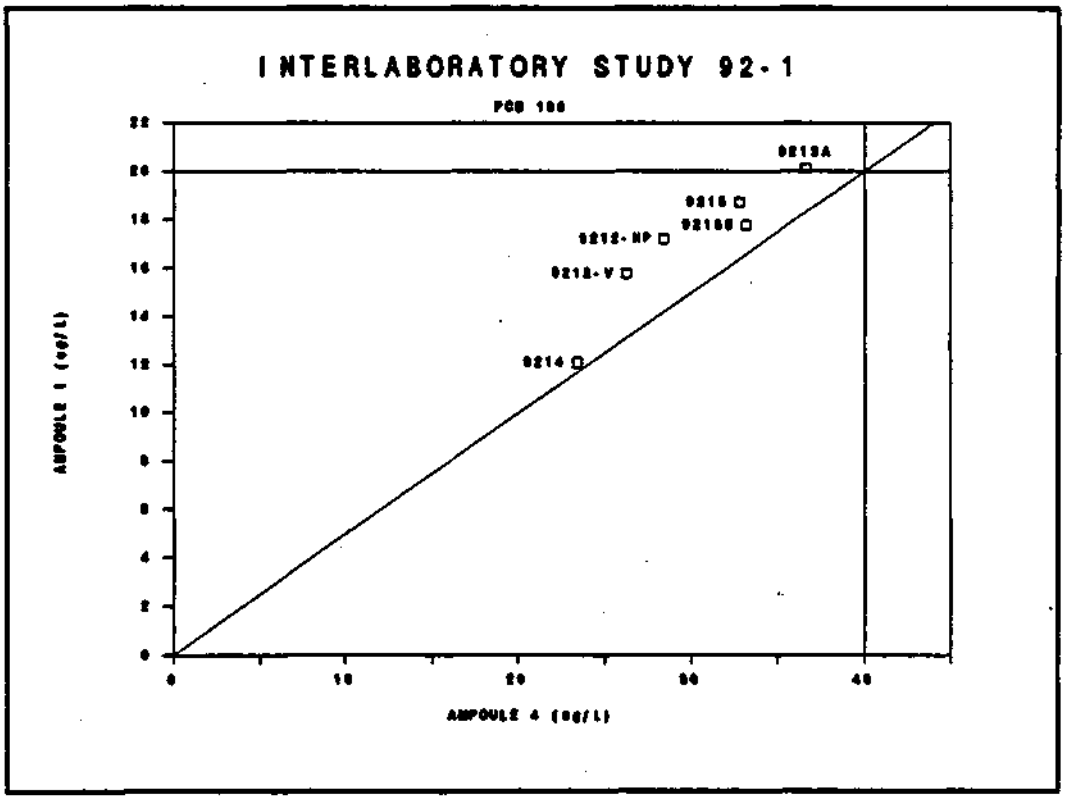

Figure 22 - PCB136

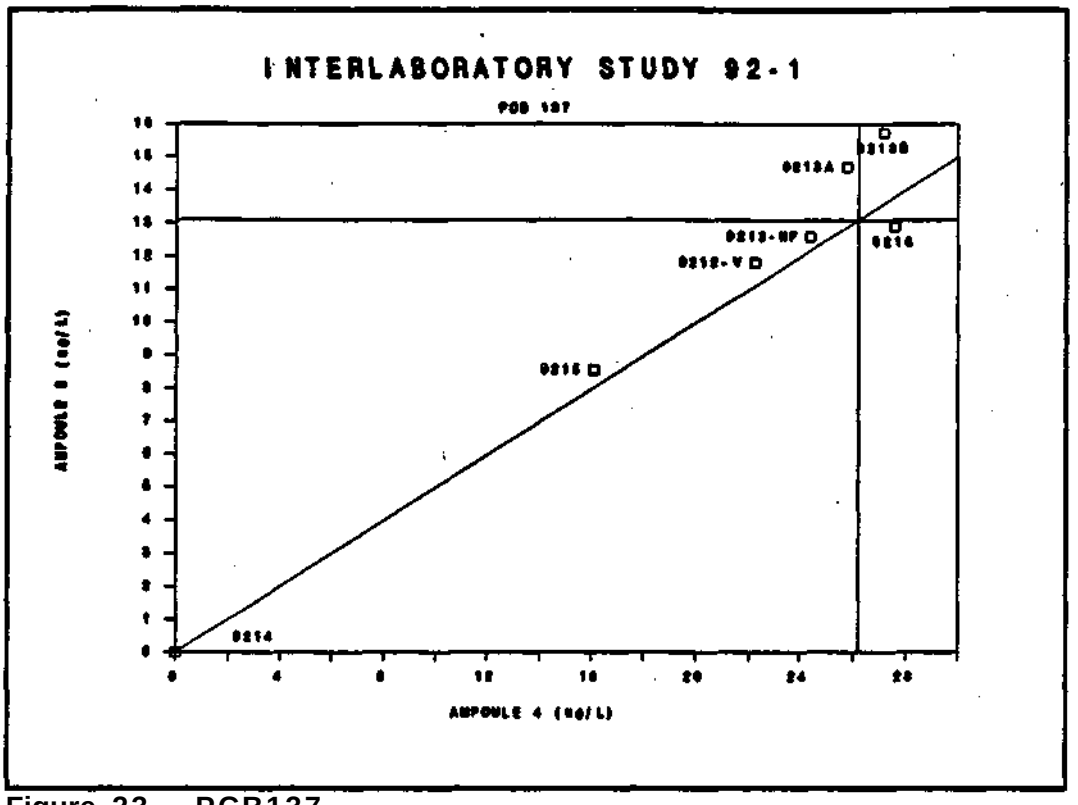

Figure 23 - PCB137

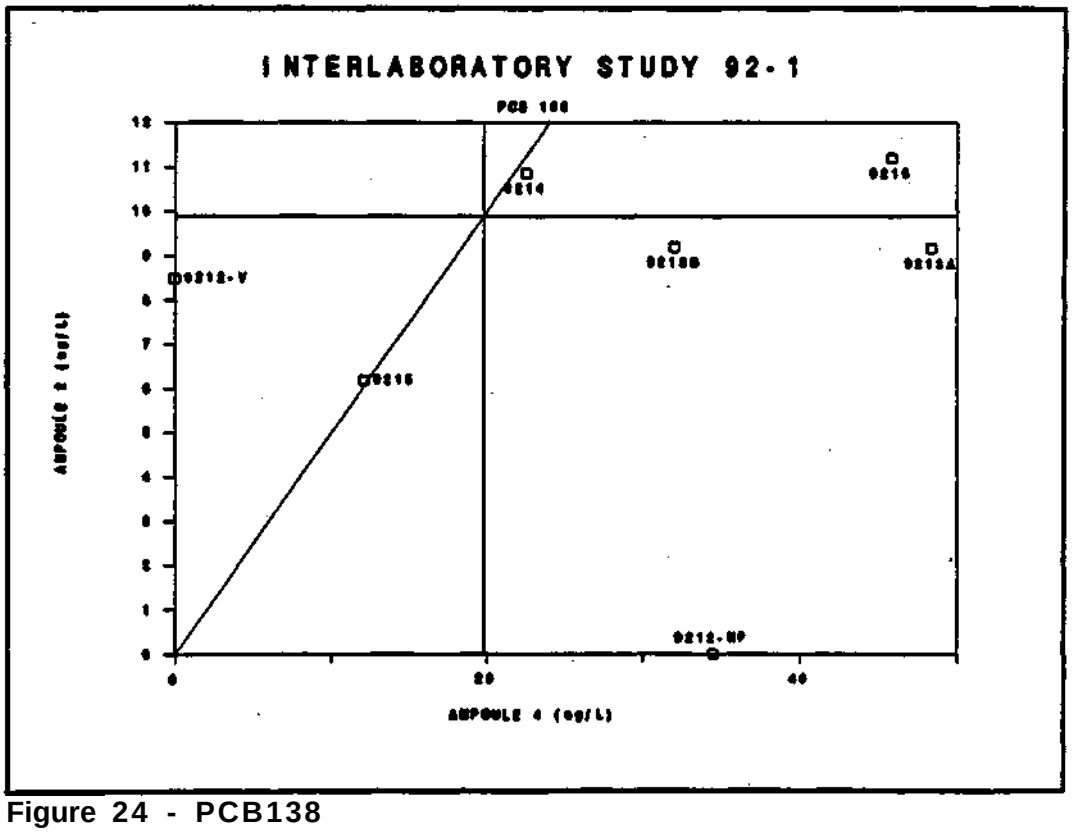

Figure 24 - PCB138

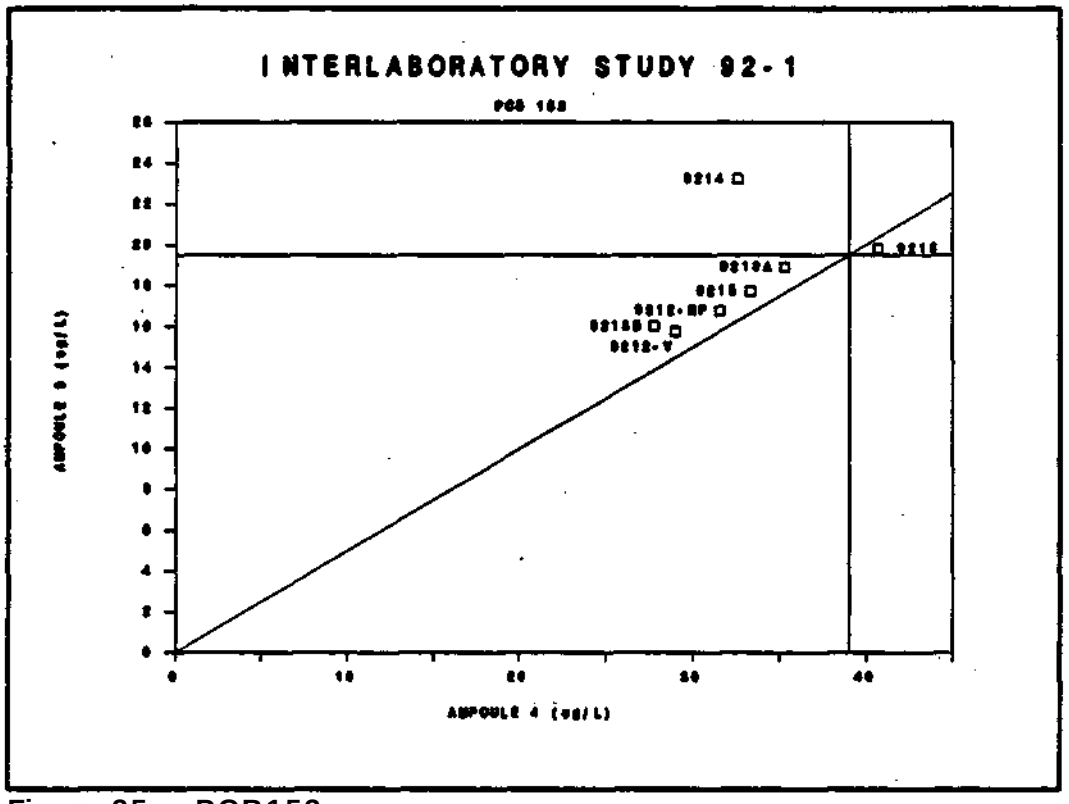

Figure 25 - PCB153

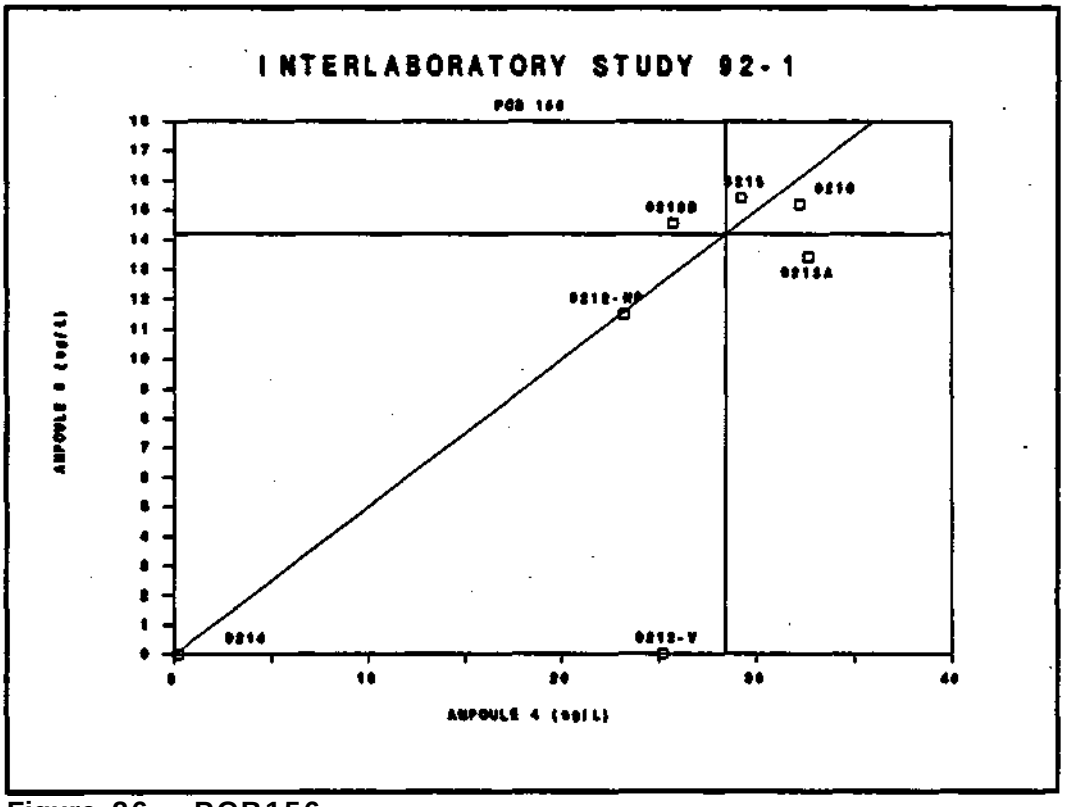

Figure 26 - PCB156

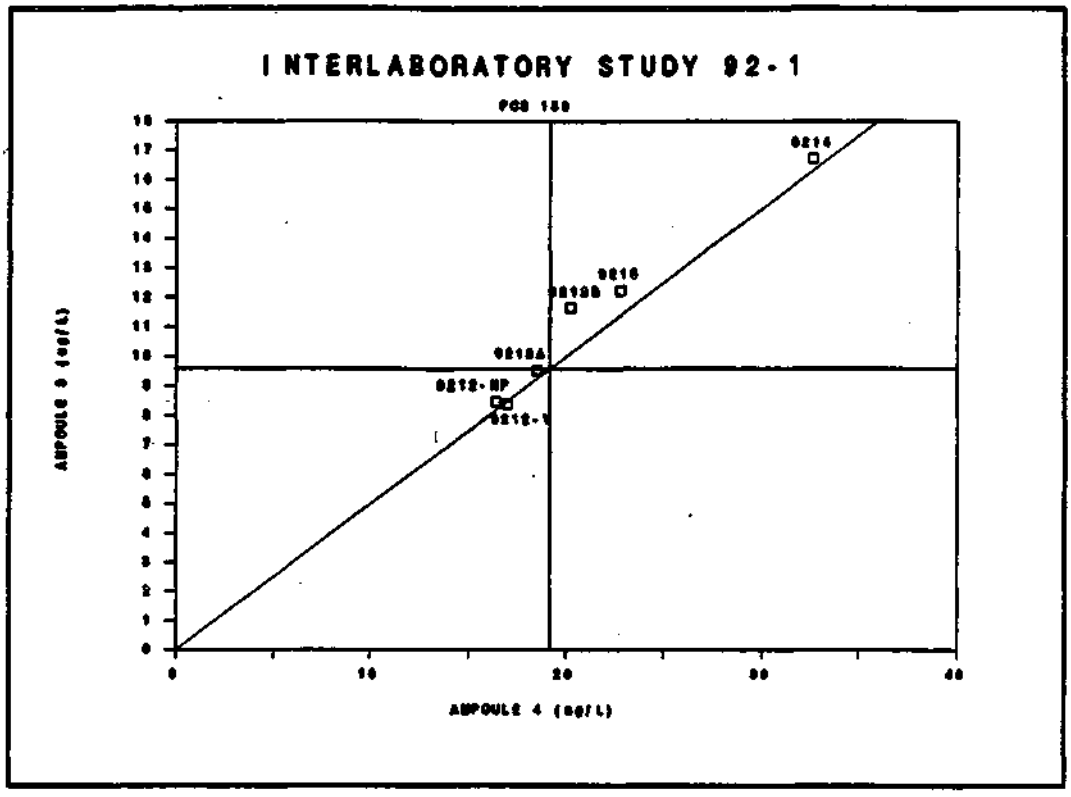

Figure 27 - PCB158

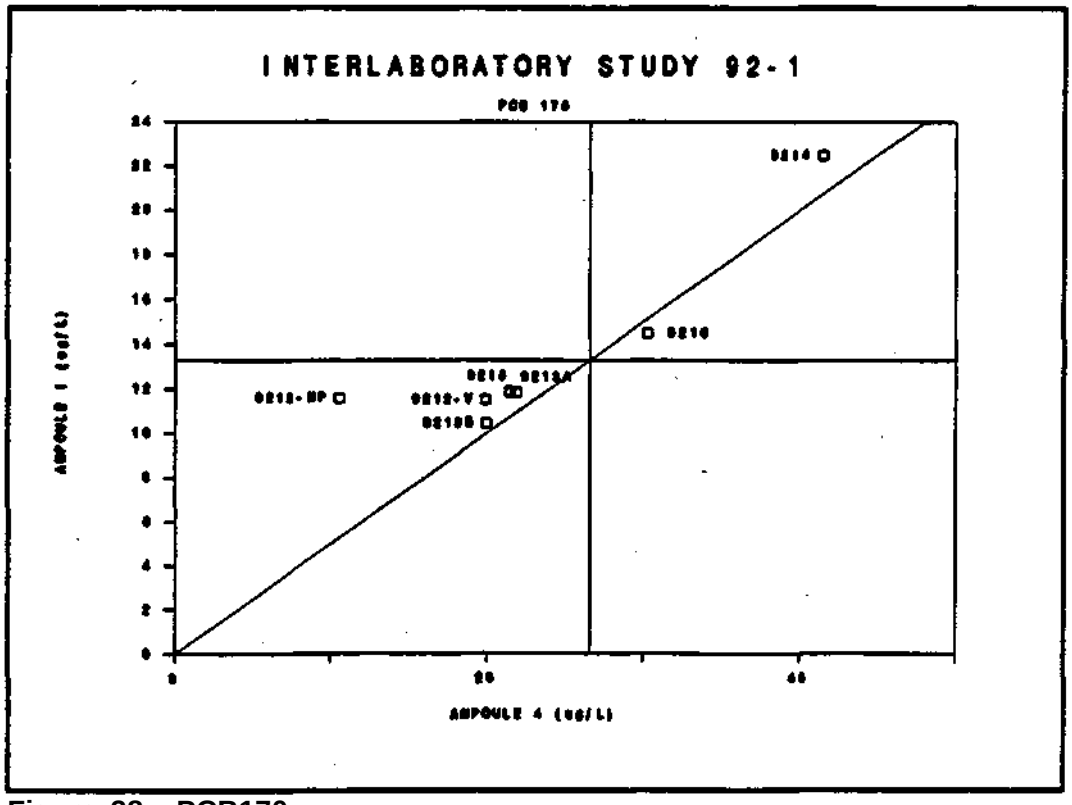

Figure 28 - PCB170

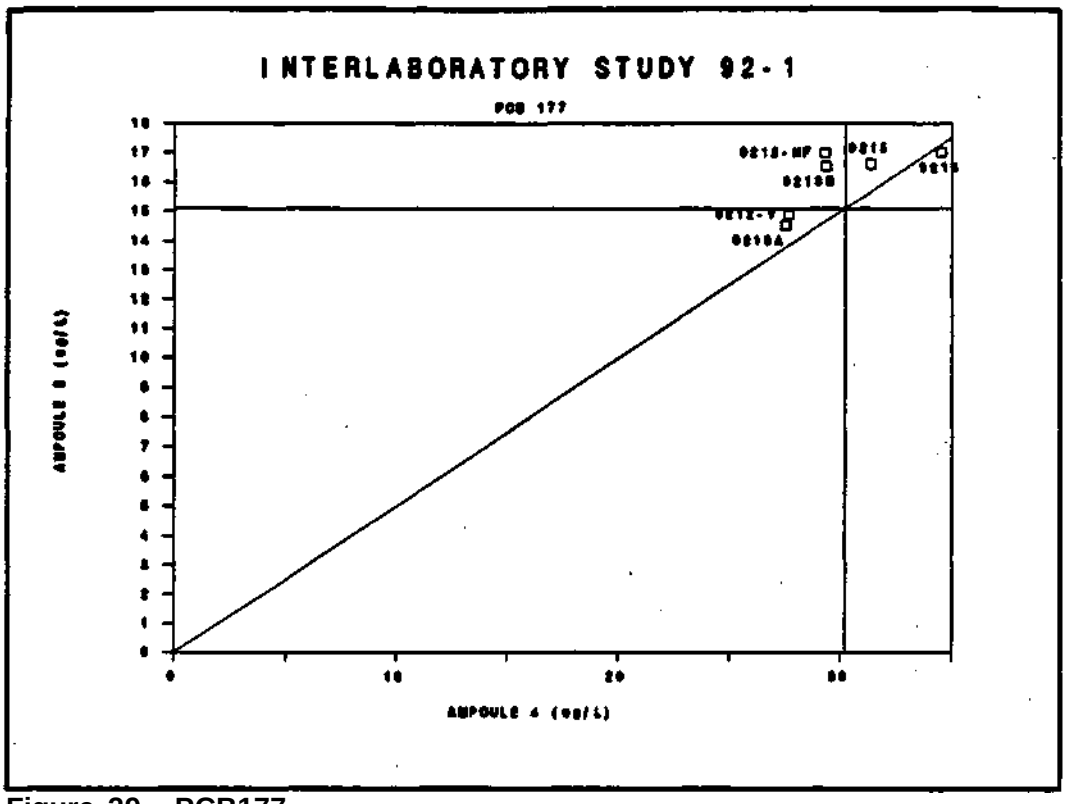

Figure 29 - PCB177

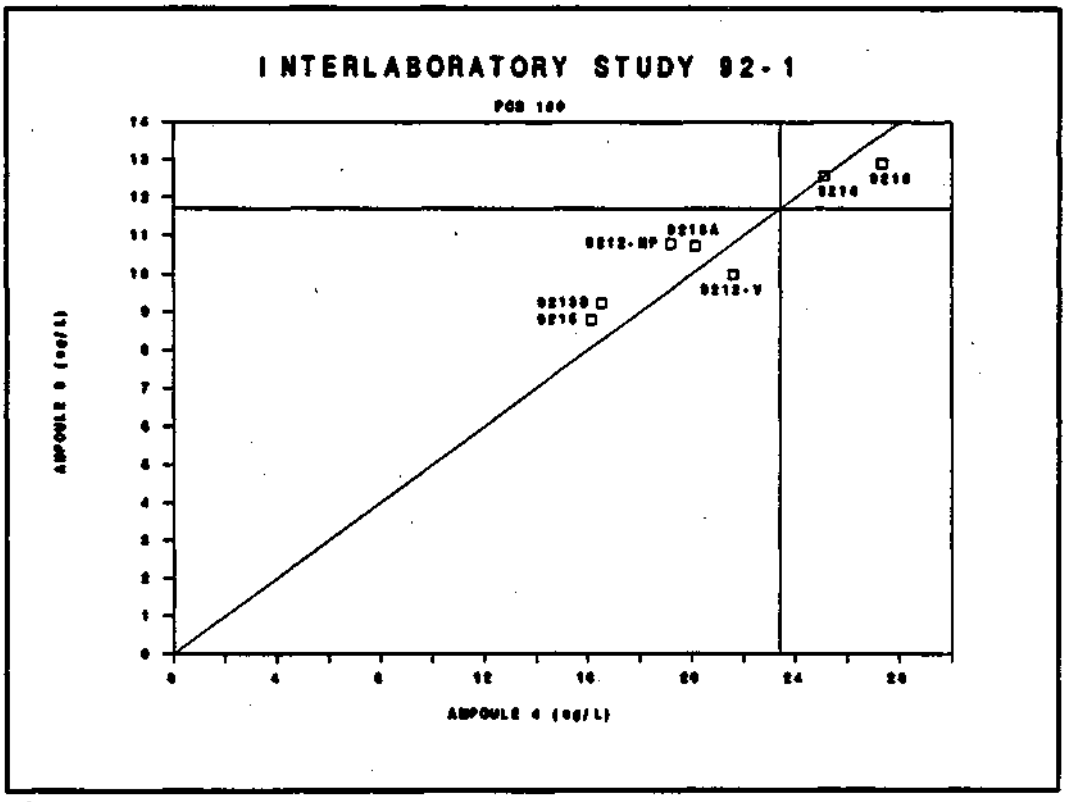

Figure 30 - PCB180

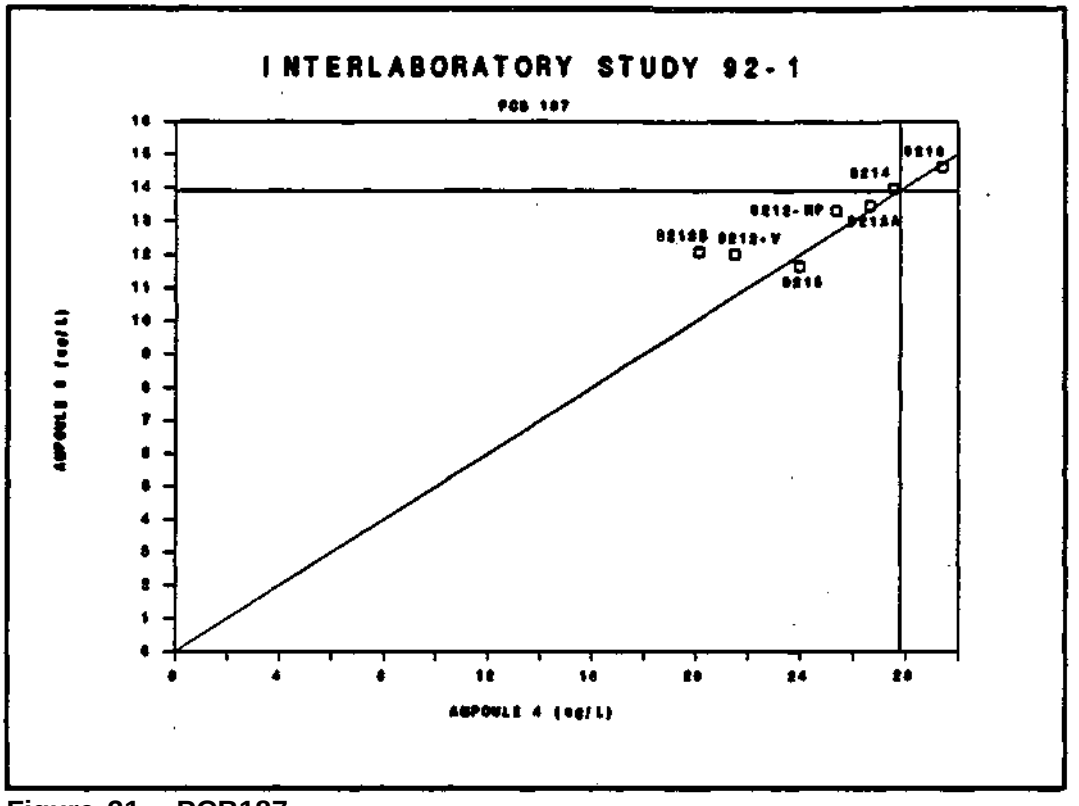

Figure 31 - PCB187

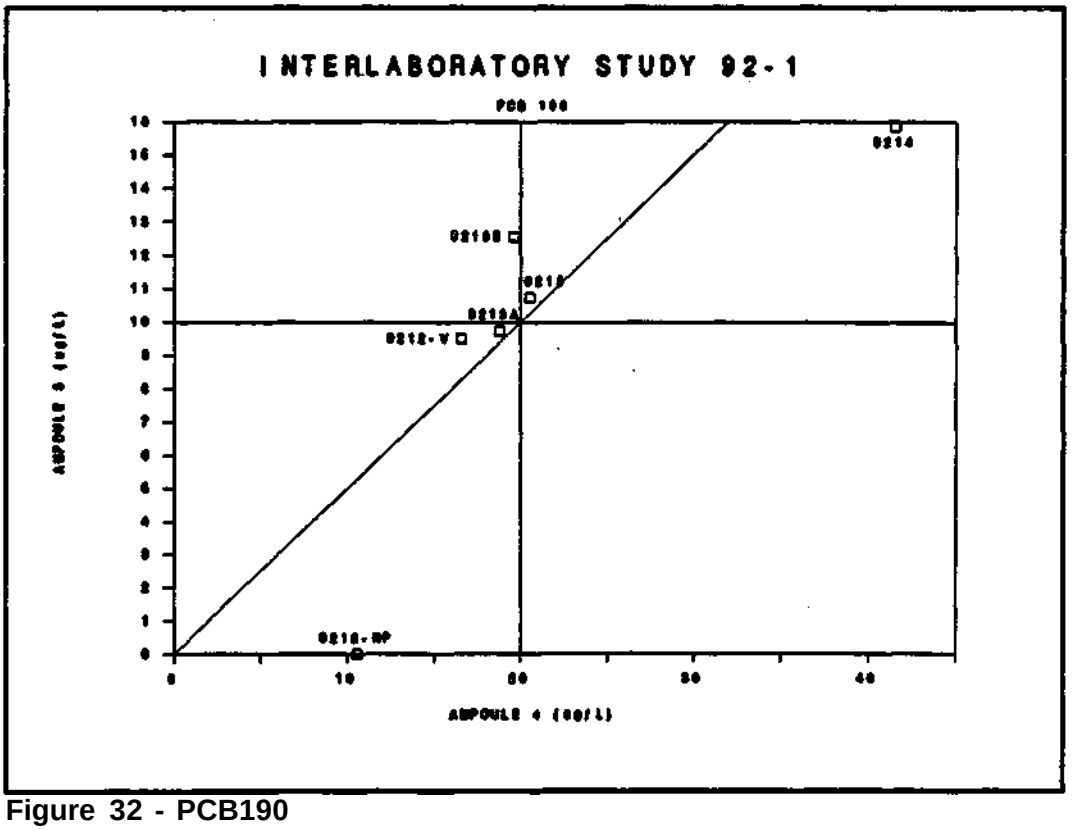

Figure 32 - PCB190

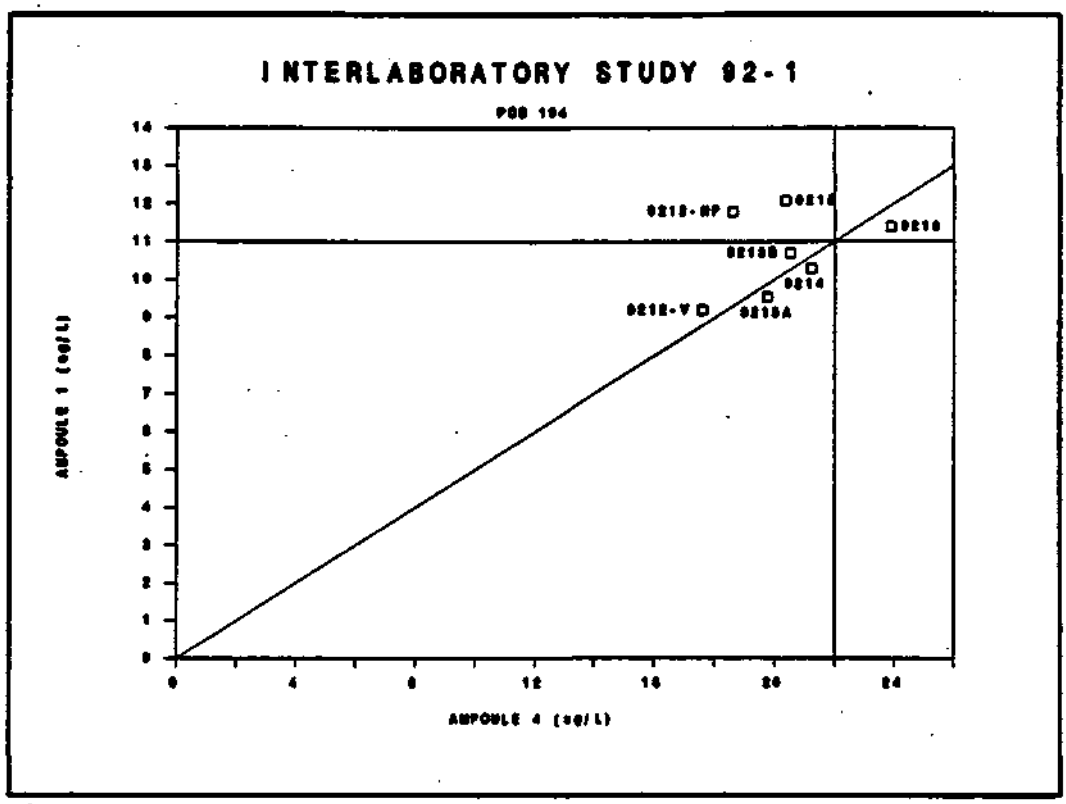

Figure 33 - PCB194

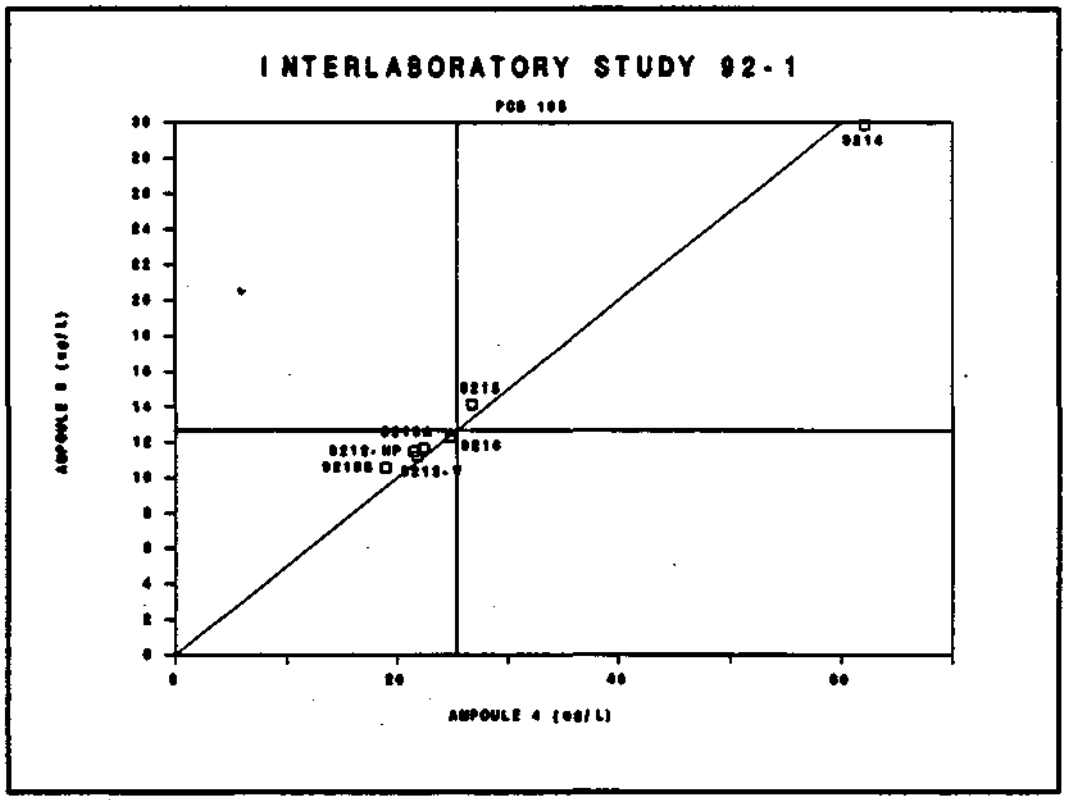

Figure 34 - PCB195

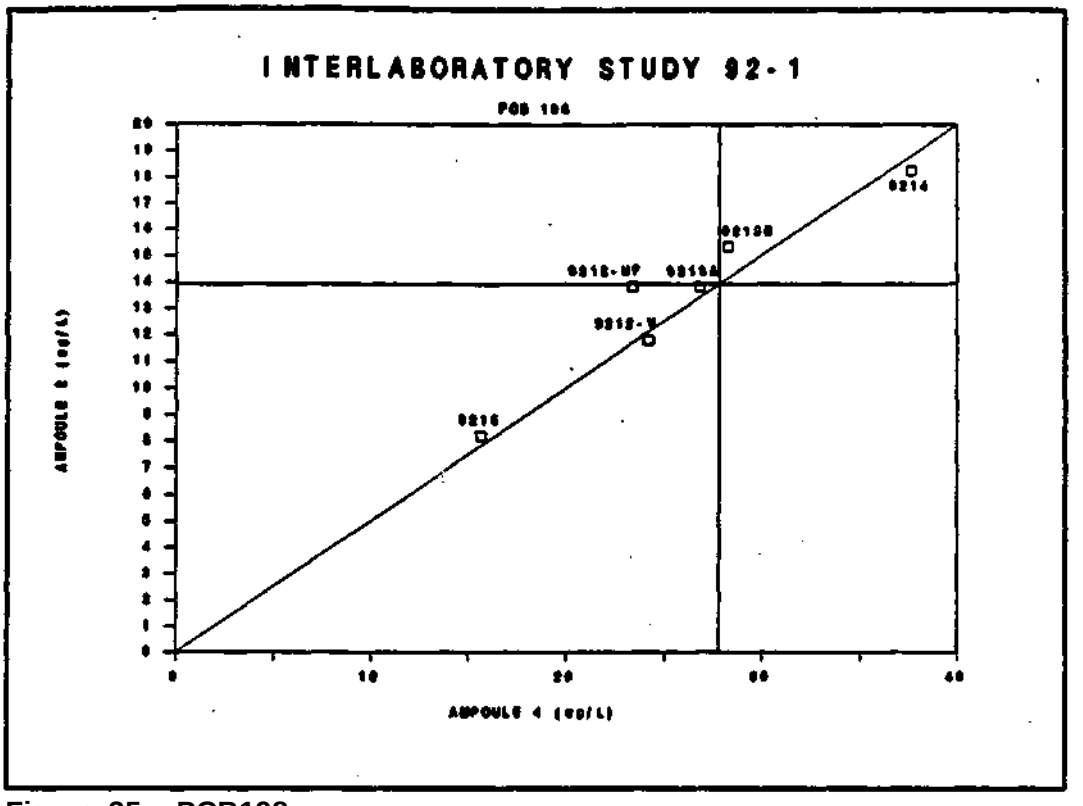

Figure 35 - PCB198

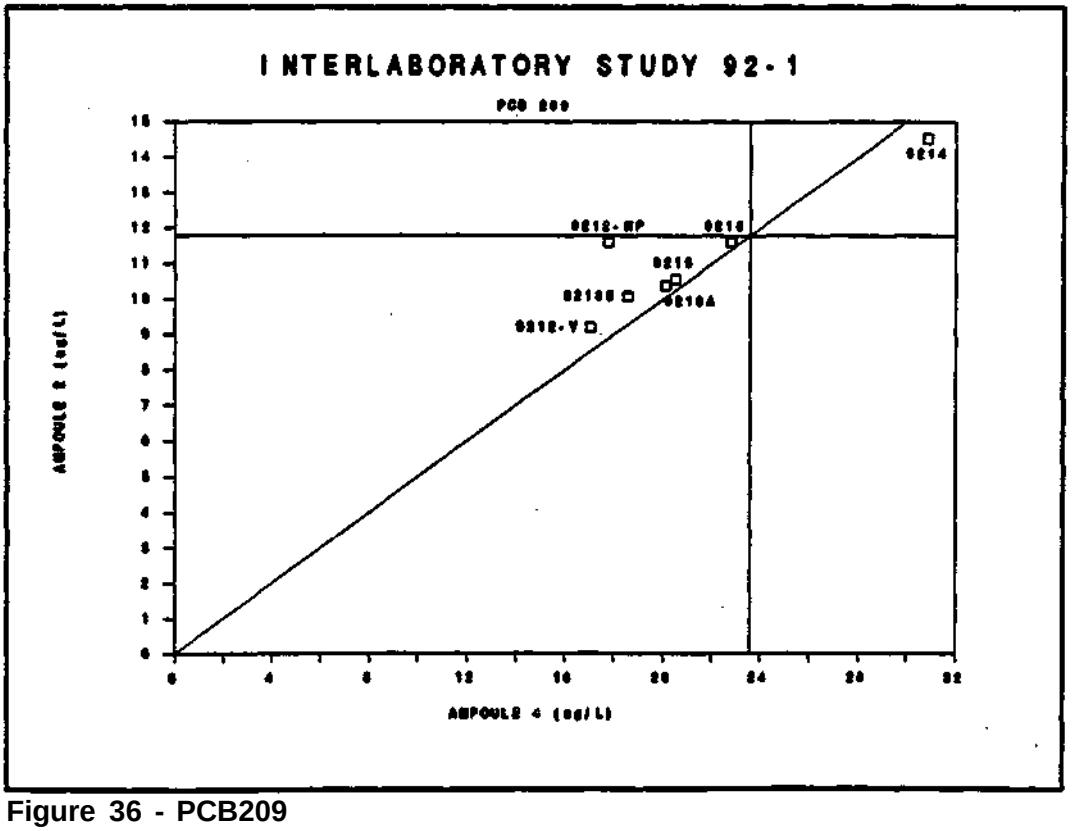

Figure 36 - PCB209

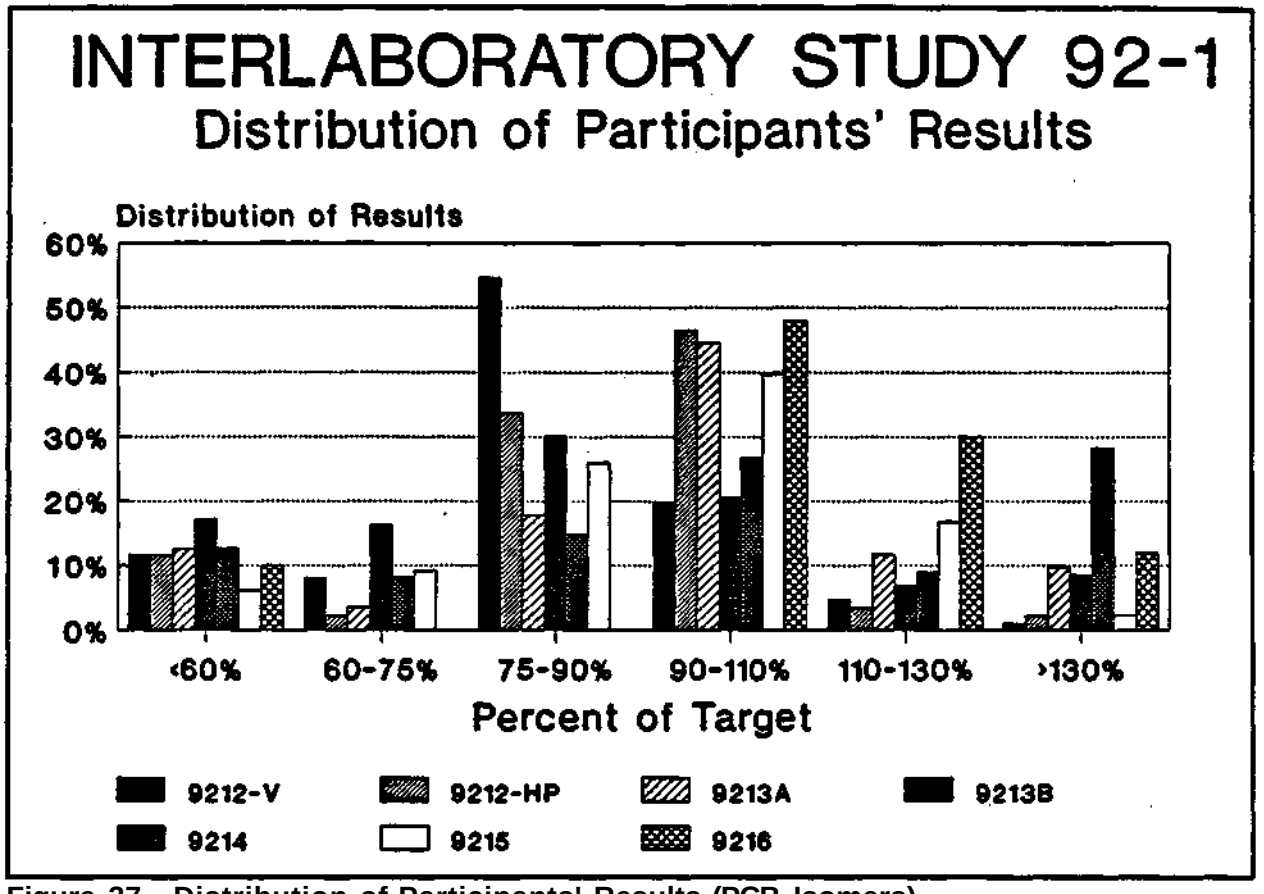

Figure 37 - Distribution of Participants' Results (PCB Isomers)

8 APPENDIX 2 - PARTICIPANTS AND CORRESPONDENCE

List of Participants

William Strachan/Debbie Burniston
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Environmental Technology Centre
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K1G 3N3
(613)990-8560

Quality Management Office

September 28, 1992

Dear Interlaboratory Study 92-1 Participant,

Please find enclosed four 5 mL ampoules for the analysis of Polychlorinated Biphenyl Isomers (PCB's). The ampoules are labelled IADN PCBs 1, IADN PCBs 2, IADN PCBs 3, and IADN PCBs 4. The solvent is Iso-octane. If you are missing any of the ampoules or they have broken in transit, please contact me at (416) 235-5842 immediately for replacement.

The ampoules are ready for direct instrumental analysis. Break open the ampoule on the scored mark and transfer the contents to the appropriate sample container for your analytical system. No dilutions should be required, but if you do so, please mark the dilution factor used on the accompanying report form. The parameters present are indicated on the form. Please note that each ampoule does not necessarily contain all of the isomers.

Please report all results on the accompanying form by October 16. 1992.

Thank you for your participation in this study.

Your identification code is:

Sylvia Cussion
Laboratory Quality Audit Scientist
(416)235-5842
FAX (416) 235-6110

INTERLABORATORY STUDY 92-1

PCB ISOMERS FOR THE INTEGRATED ATMOSPHERIC DEPOSITION NETWORK

Identification Code:

Units:

PCB ISOMER	IADN PCBs 1	IADN PCBs 2	IADN PCBs 3	IADN PCBs 4
PCB3				
PCB4				
PCB5				
PCB7				
PCB8				
PCB15				
PCB16				
PCB17				
PCB18				
PCB19				
PCB22				
PCB24				
PCB25				
PCB26				
PCB27				
PCB28				
PCB29				
PCB31				
PCB32				
PCB33				
PCB37				
PCB40				
PCB41				
PCB42				
PCB44				
PCB48				
PCB49				

PCB ISOMER	IADN PCBs 1	IADN PCBs 2	IAON PCBs 3	IADN PCBs 4
PCB52				
PCB53				
PCB61				
PCB66				
PCB70				
PCB71				
PCB74				
PCB75				
PCB77				
PCB81				
PCB84				
PCB95				
PCB97				
PCB100				
PCB101				
PCB105				
PCB110				
PCB114				
PCB118				
PCB119				
PCB123				
PCB126				
PCB128				
PCB136				
PCB137				
PCB138				
PCB149				
PCB153				
PCB155				
PCB156				
PCB157				
PCB158				
PCB163				

PCB ISOMER	IADN PCBs 1	IADN PCBs 2	IADN PCBs 3	IADN PCBs 4
PCB166				
PCB167				
PCB169				
PCB170				
PCB177				
PCB180				
PCB187				
PCB189				
PCB190				
PCB194				
PCB195				
PCB198				
PCB209				

INSTRUMENT AND DETECTOR USED FOR ANALYSIS:

125 Resources Rd.
Etobicoke, Ontario, M9P 3V6
Phone: (416) 235-5842
FAX: (416) 235-6107

February 25, 1993

TO: PARTICIPANTS OF INTERLABORATORY STUDY 92-1

Thank you for your participation in Interlaboratory Study 92-1 for the analysis of PCB Isomers in ampouled standards. This study was in support of the integrated Atmospheric Deposition Network (IADN) program. I apologize for the delay in reporting results, but one participant did not report their final results until last week.

The results are provided in the attached tables. Target values are provided. Please inform me of any transcription errors by March 12, 1993.

Each participant received a set of ampoules prepared from the same stock solution, prepared in iso-octane.

One participant did not report individual isomer results, but only total congener groups. To provide a comparison with the other participants, the results for each congener group have been summed for all participants. The target value for each congener group sum has also been provided.

The Quality Assurance Working Group of the Canada-Ontario Agreement (COA) has been the directing force for these interlaboratory studies. They wish to know the identities of the participating laboratories for the purposes of data comparison for IADN. The Program Managers and Principle Investigators (U.S. and Canadian) for IADN also wish to have the laboratories identified. As the original invitation for this study indicated that laboratory codes were confidential, I am asking each participant to give me permission to reveal their identities to these groups of data users. Please notify me in writing with your permission to reveal your study code.

A date has not yet been set for the next set of ampouled standards in this series of IADN studies, but hopefully will take place in April or early May. A letter will be sent out giving several weeks notice.

Your identification code is:

Sylvia Cussion
Laboratory Quality Audit Scientist

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INTERLABORATORY STUDY 92-2

POLYCYCLIC AROMATIC HYDROCARBON (PAH) STANDARD SOLUTIONS

IN SUPPORT OF
THE INTEGRATED ATMOSPHERIC DEPOSITION NETWORK (IADN)

Interlaboratory Study 92-2, PAH, Standard Solutions *ISWS Lab Code: 9222*

SEPTEMBER 1992

Report Prepared by

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for

Quality Management Unit
Laboratory Services Branch
Ontario Ministry of Environment and Energy
PIBS No. 3079

and

Air Quality Research Branch
Atmospheric Environment Service
Environment Canada
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TABLE OF CONTENTS

1 SUMMARY OF INTERLABORATORY STUDY 92-2

Interlaboratory Study 92-2 was initiated in support of the Integrated Atmospheric Deposition Network (IADN) to provide an initial assessment of between-laboratory variability for the analysis of Polycyclic Aromatic Hydrocarbons (PAH's). Participation was limited to laboratories which contribute to the IADN database or related programs. This study was sponsored by the Canada-Ontario Agreement (COA) Air Toxics Workgroup, and conducted as a joint project between the Atmospheric Environment Service (AES) of Environment Canada and the Quality Management Unit (QMU), Laboratory Services Branch (LSB) of the Ontario Ministry of Environment and Energy (MOEE).

Six participating laboratories received a set of four ampouled standards that were ready for direct instrumental analysis. The parameter list consisted of 20 different PAH's. Ampoule 1 contained ail 20 compounds, while Ampoules 2, 3, and 4 contained subsets of the total target list. Results were received from all of the participants.

The results from this study indicate a low bias relative to the target values for many of the parameters, though at least one participant was close to the target for each parameter. The use of a common reference standard by all of the participants would help determine the accuracy of their standards and improve the consensus among the laboratories.

The variability among the participants differed among the target parameters, with no clear pattern. Co-elution of some compounds contributes to between-laboratory variability and may be an important source of between-laboratory bias for the IADN database. Participants that have only one of a pair of known co-eluting compounds in their calibration standard may be misidentifying a peak in a real sample. Even when correction for misidentified peaks can be made using 50% of the response if both co-eluters are present, some laboratories may still report biased high results while others will report biased low results. If no corrections are made for mis-identified or co-eluting peaks, the value assigned to the unknown peak may consist of contributions from more than one compound. A biased high value for the one target analyte will be that laboratory's contribution to the IADN database.

The need to prepare individual sample sets in different solvents, may also contribute to the between-laboratory variability, due to slight variations in sample preparation and solvent effects. However, compared to the overall analytical variability, this contribution is minor.

The goal of interlaboratory studies such as this is to help participating laboratories identify possible sources of variability and help achieve greater comparability among the participants. As this was the first study of this kind among this group of laboratories, the results provide a starting point from which better agreement can be the goal. Future studies should show improved comparability among the laboratories who participated in this study.

2 INTRODUCTION

Interlaboratory performance studies are conducted to assess the comparability and accuracy of data among different laboratories. These studies are useful for the identification of biases, precision and accuracy problems, as well as ensuring overall data quality. Participation in such studies can serve as a guide for improving individual laboratory performance and maintaining performance standards.

This study was designed to assess the analytical variability among laboratories contributing to the Integrated Atmospheric Deposition Network (IADN). IADN was established as a joint venture between Canada and the United States under the direction of the International Joint Commission[1]. The intent of IADN is to identify toxic airborne substances in the Great Lakes Basin, and by means of the network, quantify the total and net atmospheric loadings of these contaminants, and define spatial and temporal trends in the atmospheric deposition of these substances. Data from several participating agencies is to be merged into a central database. Comparability of these contributing data sets is an important component of the IADN Quality Assurance Implementation Plan[2]. This interiaboratory study provides information to help establish the comparability of data sets. Sponsorship of this interiaboratory study was through the Canada-Ontario Agreement (COA) Air Toxics Workgroup. Funding for the purchase of materials came from the Atmospheric Environment Service (AES) of Environment Canada. Co-ordination and implementation of the study was done by the Quality Management Unit (QMU) of Laboratory Services Branch (LSB) of the Ontario Ministry of Environment and Energy (MOEE).

Interiaboratory Study 92-2 targets laboratories analyzing for Polycyclic Aromatic Hydrocarbons (PAH's) in precipitation and/or ambient air. A target list of 20 PAH's was chosen for this study, comprising target lists from several contributing agencies. The aim of this study was to establish the comparability of instrumental calibration among the participating laboratories. Each participant received a set of ampouled standards ready for direct instrumental analysis. Ampoule 1 contained all of the parameters in the target list, while Ampoules 2, 3, and 4 contained subsets from the target list.

A list of participants is given in Appendix 2. Each participant was assigned a unique identification code for ease in data manipulation.

Section 3 describes sample preparation, sample distribution, analytical methodology, and data evaluation procedures. Final results are tabled in Appendix 1 and discussed in Section 4.

3 PROCEDURE

3.1 Preparation of Ampouled Standards

Neat PAH's of 99% + purity were purchased from Ultra Scientific and Supelco by AES. All subsequent work was done by the QMU of LSB, MOEE. Concentrated stock solutions of each compound were prepared in toluene and sealed into 5 mL amber ampoules. The stock concentrations were between 10 to 15 mg/L and verified using gas chromatography/mass spectrometry analysis by an analytical unit at LSB not involved in analysis of ambient air or precipitation. Ampouled solutions were stored in a freezer at -20°C.

Solutions for the interlaboratory study were prepared from the concentrated stock solutions by diluting appropriate aliquots into a combined solution in toluene. Solution 1 contained all the PAH's on the target list. Solutions 2, 3, and 4 were designed to consist of subsets of the complete target list. The compounds were distributed so that known co-eluters or close eluters were in different solutions. This series of solutions were sealed in 5 mL amber ampoules and labelled IADN1, IADN2, IADN3, and IADN4. They were in a concentration range of μg/mL (See Tables 1-4). This concentration range was suitable only for one of the participants.

To achieve concentration levels that fell in the routine analytical range of the other participants, an aliquot of each of ampoules IADN1, IADN2, IADN3, and IADN4 was diluted to the ng/mL range. Each of the five participants requiring the more dilute solutions required a different solvent for their calibration standards, so separate dilute solutions were prepared in four different solvents. Each participant received a set of four ampoules prepared from the IADN1-4 ampoules, and diluted in the required solvent. The solvents used for each participant are given in Table 5. Each set was at the same concentration level and were labelled IADN1a, IADN2a, IADN3a, and IADN4a.

As each compound was present in two different solutions, one solution had a "low" concentration level and the other a "high" concentration level. All ampoules were stored in a freezer at -20°C until shipped to the participants.

3.2 Sample Distribution

Samples were packed into styrofoam shipping containers and shipped overnight by Purolator Courier to the participating laboratories. A list of the laboratories receiving sample sets is given in Appendix 2. Samples were shipped on September 21, 1992. A copy of all correspondence is also included in Appendix 2.

3.3 Analytical Methodology

Participating laboratories were requested to analyze the samples using their routine in-house methods used to analyze precipitation or ambient air samples for the IADN program. Participants were requested on the report form provided (Appendix 2) to summarize their Instrument and Detector used for the analysis. Information regarding the stationary phase used for separation was requested at a later date. All participants were assigned a unique identification code.

3.4 Data Reporting

Results were submitted to the QMU, LSB in written form. All data were manually entered by laboratory code into an electronic spreadsheet.

The participating laboratories were mailed a copy of the tables of results on January 4, 1993. One participant submitted some notes regarding co-elution results and a possible mis-identification in Ampoule IADN2a. These comments are noted as foot-notes to the tables and in the individual laboratory review.

The interlaboratory mean, median, standard deviation (SD), and relative standard deviation (%RSD) were calculated for each parameter in each of the

"A" series ampoules for which there were 2 or more results reported, and are included in Tables 1-4, Appendix 1. As the data set is small, these calculated values are provided as an approximate indicator of the spread of the data and may not necessarily be statistically correct.

4 DISCUSSION

OVERVIEW OF INTERLABORATORY PERFORMANCE

The between laboratory variability is more difficult to evaluate in this study because of the need to prepare individual solutions for each participant. Conventional interlaboratory study design normally involves the distribution of the same material to all of the participants[4]. While one combined set of solutions was prepared (the IADN1-4 ampoules), only 1 participant analyzed this set of solutions (Laboratory 9225). All of the other participants analyzed their own dilution from this "intermediate" set of solutions. As each participant required a different solvent, five different dilution sets were prepared. This resulted in the possible introduction of preparation errors that could contribute to the overall between-laboratory variability. While every care was taken to minimize preparation errors, slight variations of glassware may have introduced a 1-2% variation among the different solutions.

The differences in solvents may also contribute to between-laboratory variability. As noted in Section 3.1, the individual stock solutions were prepared in toluene, as were the combined solutions (IADN1-4). For Laboratory 9225 analyzing the series IADN1-4, there should have been no solvent effect. For Laboratory 9221, who received their ampoules also in toluene, there also should have been no solvent effect. The other four participants received their solutions prepared in different solvents. Depending on the ampoule, this resulted in 1-8% toluene combined with the other solvent. While only Laboratory 9224reported a problem with the toluene peak at the front end of their chromatographs, this solvent effect may have affected quantitation of the early eluting compounds for other participants.

As Laboratory 9225 was the only participant to analyze the IADN1-4 series, their performance is discussed separately in the individual laboratory section below. All of the remaining discussion is for the five participants analyzing the "A" series of ampoules.

Two parameters, Benzo(a)fluorene and Benzo(b)fluorene, were on the target list of only one participant. For all other compounds, the interlaboratory mean, median, standard deviation (SD) and relative standard deviation (%RSD) were calculated and included in Tables 1-4. As these calculations were done on a small data set, they are only a very approximate estimate of the data distribution and are not necessarily reliable statistical estimators.

The interlaboratory mean and median were low relative to the target value except for Triphenylene (IADN1a & IA0N4a), Dibenzo(a,c)anthracene (IADN1a & IADN2a), Chrysene (IADN1 a) and Benzo(e)pyrene (IADN3a). Except for Benzo(e)pyrene, the high bias in these parameters may be attributed to co-elution problems. The distribution of the participants' results relative to the target also indicate an overall low bias (Table 6 and Figure 35). While this may appear to indicate a possible problem in the preparation of the interlaboratory study solutions, for almost all of the parameters in the study, at least one participant agreed with the target (within 10%), though not

always the same participant. For many of the parameters two of the participants agreed with the target, while the other three participants reported lower values. For Acenaphthene (IADN1a & IADN4a), Anthanthrene (IADN1a & IADN3a), and Dibenzo(a,c)anthracene (IADN1 a & IADN2a), none of the participants were within 10% of the target. Only two participants reported results for Anthanthrene and Dibenzo(a,c)anthracene, and in both cases, one participant was higher than the target and the other was lower than the target. Further intercomparisons are necessary to establish agreement among the laboratories.

The most common source of bias in an interlaboratory study is a difference in calibration standards. This could be a particular problem for PAH's which are vulnerable to photodegradation. The solutions used in this study were freshly prepared, so there had not been time for any significant degradation to occur between preparation and sample distribution. The age of the participants' calibration solutions was not known, so there may have been some aging effects for an individual participant. This could have contributed to the bias in the interlaboratory study results. While some participants reported results after the requested date (see letter in Appendix 2), all results were reported within 7 weeks of sample shipment. This is well within the normal lifetime of analytical standards (one year), so there should have been no aging of the study solutions. Other sources of between laboratory bias may include the variation in preparation or solvent effect, as noted above.

Another source of between-laboratory variability and difference from the target is the effect of co-elution. This was a potential source of variability particularly in Ampoule IADN1a and IADN1 (Table 1). One laboratory reported co-elution of Benzo(b)fluoranthene and Benzo(k)fluoranthene, two laboratories reported co-elution of Dibenzo(a,c)anthracene and Dibenzo(a,h)anthracene, and four participants had co-elution of Chrysene and Triphenylene. In all cases, the combined result was evenly divided among the two compounds for the purposes of calculating the interlaboratory mean, median and standard deviation. However this may not actually be analytically correct, as the peak area may have been distributed 40-60 between the two compounds, or some other proportion. This may affect the agreement with the target, as well as the between-laboratory variability. Even though 50% of the reported value was used, Chrysene and Triphenylene show high bias by Laboratories 9221 and 9222, but a low bias for Laboratory 9226, with all three laboratories reporting co-elution of the two compounds.

The problem of co-elution also affects correct identification. In Ampoule IADN2a, two participants reported a positive response for Dibenzo(a,h)anthracene, which was not present in that ampoule, but the close or co-eiuting Dibenzo(a,c)anthracene was present (Table 2). One of the participants qualified their result after receiving the initial tables of results (see individual laboratory review). Similarly, in IADN4a, Laboratory 9222 reported a positive response for Chrysene, which was not present in that ampoule (Table 4). Triphenylene, which co-elutes with Chrysene, was present in this ampoule. The value reported by this participant should have been identified as Triphenylene, not Chrysene. For the purposes of preparing the Youden plots (see below). Laboratory 9222's reported "Chrysene" result was assigned to Triphenylene for ampoule IADN4a. As welt, several participants reported a combined result for Chrysene/Triphenylene in ampoules IADN2, IADN2a, IADN4, and IADN4a when only one of the compounds was present. For the purposes of interlaboratory comparison, the result was assigned to the. "correct" parameter. This can only be done in a situation such as an interlaboratory study, where the target compounds are known. In the case of real environmental samples, these laboratories would not be able to

correctly identify the peak unless some other confirmatory technique such as High-Resolution Mass Spectrometry was used.

In all of these cases, the participants were using Gas Chromatography/Mass Selective Detector (GC/MSD) as their analytical technique and detector. The only participant who did not have any co-elution problems was Laboratory 9224, who used High Pressure Liquid Chromatography (HPLC) as their analytical technique. (Laboratory 9223 did not include any of the above co-eluting compounds as part of their target list.)

The selection of GC versus HPLC for the analysis of PAH's may be influenced by various factors. GC is generally used for PAH's up to 24 carbons due to their higher volatility, while HPLC is the choice when PAH's with higher number of carbons are the compounds of interest[5]. (The choice of 24 carbons is somewhat arbitrary.) Larger or more non-volatile PAH's will not elute using GC or may get trapped in the injection port. Several PAH's may also decompose or rearrange pyrolytically to other structures in the high temperature of the GC injection port[5]. These latter reasons support the choice of HPLC. However GC has greater resolving power for the smaller PAH's. Many of the more toxic PAH's fall into this category, influencing the selection of GC as the analytical method. At the time of this study, the IADN program did not specify an analytical method for PAH's. Data produced by the network may indicate a need to specify an analytical method in the future.

As an alternate method of evaluating the results, a graphical technique was used for those parameters with 4 or 5 results from the "A" set of ampoules. As each parameter had a "pair" of results, one from either Ampoule 2, 3, or 4, and the other from Ampoule 1, these results may be plotted on an X-Y plot using the Youden technique[4]. The result from the "low" ampoule is plotted on the vertical axis and the result from the "high" ampoule is plotted on the horizontal axis. The graphs are divided into four quadrants, with the intersection point at the target values. The data points should cluster around the target if random error is the only source of variability. Results in the upper right quadrant are considered biased high and those in the lower left quadrant are biased low. The main source of this type of variability is a difference in analytical standards or inadequate calibration practices. Data points that fall in the lower right or upper left quadrants are considered erratic or out-of-control. Sources of this type of error are more difficult to ascertain. In this study, the participants were analyzing ampoules for direct instrumental injection. Sources of erratic performance could be poor sample injection into the gas chromatograph, a septum leak, poor chromatography if contamination remained from a previous sample, or other instrumental problems. Within-laboratory precision may be assessed by drawing a line between the origin and the intersection of the target values. The closer the data point is to this diagonal line, the better the within-laboratory precision.

The majority of the parameters plotted using the Youden technique (Figures 1-15) demonstrate a low bias by most of the participants, though as noted above, at least one participant agreed with the target for almost all of the parameters (except for Acenaphthene, as noted above). In many cases, two of the participants agreed with the target. The low bias may be attributed to a difference in standards between the participants. The majority of results fall on the line drawn between the target and the origin, indicating that most participants demonstrated good within-laboratory precision. The results for Acenaphthylene (Figure 2), Benzo(b)fluoranthene (Figure 5), Benzo(k)fluoranthene (Figure 6), Chrysene (Figure 9), Triphenylene (Figure 10), Fluorene (Figure 12), Phenanthrene (Figure 14) show more erratic performance by the

participants. Variable performance for Chrysene and Triphenylene may be attributed to co-elution effects, as noted above. Further studies would be required to determine the possible source(s) of the within-laboratory precision problems for the other three compounds mentioned above.

INDIVIDUAL LABORATORY PERFORMANCE

Laboratory 9221

Laboratory 9221 noted with their results for IADN4a, that the relative retention time for the peak identified as Chrysene was not acceptable based on their in-house protocol, and suggested that it could be Triphenylene. As noted above in the Overview section, several participants identified the peak in IADN4a as Chrysene or as Chrysene/Triphenylene, when only Triphenylene was present. The reported "Chrysene" values in Ampoule IADN4a for this laboratory (as well as the other participants) was assigned to Triphenylene (see comment above).

One parameter was mis-identified in Ampoule IADN2a. Dibenzo(a,c)anthracene was not on their target list but was present in that ampoule. They identified the peak as Dibenzo(a,h)anthracene, a close eluter to Dibenzo(a,c)anthracene. They did not add any further qualifying comments to their results after receiving the tables or results.

Within-laboratory precision was good for most parameters, though they did have some problems with Anthracene (Figure 3), Benzo(b)fluoranthene (Figure 5), Dibenzo(a,h)anthracene (Figure 8), Chrysene (Figure 9), Triphenylene (Figure 10), and Phenanthrene (Figure 14).

Laboratory 9222 - ISWS

Laboratory 9222 noted with their results that six of the target compounds in the interlaboratory study were not on their target list. Based on their own reference material, they noted that their results for Indenod ,2,3-c,d)pyrene (on their target list) may have been elevated by the presence of Anthanthracene (not on their target list). Similarly, the presence of Benzo(e)pyrene (not on their target list) could affect their results for Benzo(b)fluoranthene, Benzo(k)fluoranthene, or Benzo(a)pyrene (all on their target list). The presence of Dibenzo(a,c)anthracene (not on their list) could affect their quantitation of Dibenzo(a,h)anthracene (on their list), as well as the presence of Triphenylene (not on their list) could affect their quantitation of Benzo(a)anthracene or Chrysene (on their list). As noted above in the Overview, the "Chrysene" result reported in IADN4a was actually due to the presence of Triphenylene and assigned as such for the purposes of preparing the Youden plot.

When Laboratory 9222 received the table of results, they responded back with some additional notes to their results. In Ampoule IADN1 a, the result reported for Chrysene had suspected co-elution with Triphenylene, and the result for Dibenzo(a,h)anthracene had suspected co-elution with Dibenzo(a,c)anthracene. Dividing the reported values between the two co-eluters would bring their results into agreement with the other participants that reported the same co-elution problems (these revisions are noted in Table 1 of this report). In Ampoule IADN2a, they reported a positive result for Dibenzo(a,h)anthracene, which was not present in the ampoule. After checking their chromatograph and mass tables, they feel that the value reported should have been assigned to Dibenzo(a,c)anthracene, which was present in the ampoule.

While these modifications to Laboratory 9222's interlaboratory study data set have been made for the purposes of comparing their results to the other participants, this could not be applied to real samples without the use of additional analytical techniques. Knowledge of historical data may suggest when an individual data point may be anomalous, but modifying that point must be approached with care. By not having both of the known co-eluting compounds in their calibration standard. Laboratory 9222 cannot be certain of the identification of a peak without some other supporting confirmation data. This can lead to biases in a data set, both due to misidentification and attributing a greater value to a compound than is actually present (i.e. quantifying a peak that is a combination of Chrysene and Triphenylene, but assigning the total value only to Chrysene).

They had good agreement with the target values for most of the parameters (Table 6 and Figure 35). Problem parameters were the co-eluting pairs of Chrysene/Triphenylene and Dibenzo(a,c)/(a,h)anthracene, which were biased high. Further method development work may help improve performance for these co-eluting parameters. Within-laboratory precision was good except for Benzo(a)pyrene (Figure 7), Chrysene (Figure 9) and Fluorene (Figure 12).

Laboratory 9223

Laboratory 9223 had the fewest number of compounds in the study on their target list. They were biased low for all their results except Indeno(1,2,3-d,c)pyrene and Phenanthrene in Ampoule IADN2a and Acenaphthylene in Ampoule IADN3a. They also tended to have lower results than most of the other participants, with 60% of their results less than 75% of the target (Table 6 and Figure 35). Comparison of their standards with reference materials should help them improve this bias. They had acceptable within-laboratory precision except for Acenaphthylene (Figure 2), Fluorene (Figure 12) and Phenanthrene (Figure 14).

Laboratory 9224

Laboratory 9224 noted that the presence of toluene in the solutions could have an affect on their results for Acenaphthene and Fluorene. Their original set of results had a very high value reported for Fluorene, that was significantly different from the target and the other participants. Before the results were released, they were contacted and asked to investigate this result. Their original chromatograph showed a very distorted Fluorene peak. For many of the compounds in this study, the levels were higher than their normal analytical range, so that dilution of the ampouled solution may have influenced their original Fluorene result. They repeated the analysis with an undiluted aliquot of Ampoule IADN1a and reported a revised result for Fluorene, which is included in Table 1.

They noted the potential interference for Acenaphthene and Fluorene due to the presence of toluene in the ampoules. Their results for these two compounds were biased low and this may be attributed to the solvent effect.

Laboratory 9224 agreed within 75-110% of the target values for most parameters (Table 6 and Figure 35). In ampoules IADN1a, they had the greatest number of results within 10% of the target for all of the participants (11 out of 18 on their target list). The lack of co-elution problems due to the use of HPLC may contribute to their good performance. They also demonstrated good within-laboratory precision, except for

Fluorene (Figure 12) which can be attributed to the solvent effect as already noted, and Benzo(a)anthracene (Figure 4) and Fluoranthene (Figure 11).

laboratory 9225

Laboratory 9225 was the only participant to analyze the undiluted IADN1 -4 ampoules.

Most of their results were within 75-90% of the target (Table 6 and Figure 35). Their low bias may be attributed to a difference in their calibration standards from the interlaboratory study solutions. Comparison with a reference standard may improve this difference. Problem compounds were Acenaphthene, Acenaphthylene, and Benzo(a)fluorene in Ampoule IADN1, and Dibenzo(a,h)anthracene in IADN1 and IADN4. The low result for Dibenzo(a,h)anthracene is most probably due to co-elution with Dibenzo(a,c)anthracene.

As they had a different target value from the other participants, Laboratory 9225's results could not be included in the Youden plots (Figure 1-15) prepared for ampoules IADN1a-4a. A separate set of plots showing Laboratory 9225's within-laboratory precision were prepared (Figures 16 - 34). Within-laboratory precision was good for most parameters except for Chrysene (Figure 26) and Dibenzo(a,c)anthracene (Figure 28).

Laboratory 9226

Laboratory 9226 noted that for their analytical working range, the concentration levels in Ampoules IADN1a, IADN2a, and IADN4a were either at or near their detection limit. They anticipated their analytical precision and accuracy to be poor. While all the participants were consulted by telephone regarding the concentration range appropriate for this study, it is possible that there were some misunderstandings on this point. The concentration levels in Ampoules IADN1 -4 (as analyzed by Laboratory 9225) may have been more appropriate for Laboratory 9226.

Many of Laboratory 9226's results were biased low. As noted above, the concentration levels for most of the ampoules were near their detection limits. This may be considered the most likely source for their low bias.

Except for Anthracene (Figure 3), Benzo(b)fluoranthene (Figure 5), Benzo(k)fluoranthene (Figure 6), Benzo(a)pyrene (Figure 7), and Chrysene (Figure 9), they demonstrated good within-laboratory precision. One value for all of these parameters was in the three ampoules that Laboratory 9226 noted as being close to their detection limit. The poorer within-laboratory precision for these parameters may most likely be attributed to the low concentration levels and the associated increase in analytical variability.

5 CONCLUSIONS

The results from this study indicate a low bias relative to the target values for many of the parameters. The use of a common reference standard by all of the participants would help determine the accuracy of their standards and improve the consensus among the laboratories.

The variability among the participants differed among the target parameters, with no clear pattern. Co-elution of some compounds contributes to between-laboratory variability and may be an important source of between-laboratory bias for the IADN database. Participants that have only one of a pair of known co-eluting compounds in their calibration standard may be misidentifying a peak in a real environmental sample. Even when correction for misidentified peaks can be made using 50% of the response if both co-eluters are present, some laboratories may still report biased high results while others will report biased low results. If no corrections are made for mis-identified or co-eluting peaks, the value assigned to the unknown peak may consist of contributions from more than one compound. A biased high value for the one target analyte will be that laboratory's contribution to the IADN database.

The need to prepare individual sample sets in different solvents, may also contribute to the between-laboratory variability, due to slight variations in preparation and solvent effects. However, compared to the overall analytical variability, this contribution is minor.

As this was the first interlaboratory study between this group of participants involved in the IADN program, it serves as a starting point for establishing comparability. Future studies should demonstrate improvements among this group of laboratories.

6 REFERENCES

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7 APPENDIX 1 - RESULTS AND GRAPHS

TABLE 1 - Results for IADN1 and IADNIa

AMPOULE/LAB CODE	IADN1	9225	IADN1a	9221	9222	9223	9224	9226	MEAN	MEDIAN	SD	n	%RSD
PARAMETER	µg/mL	µg/mL	ng/mL	ng/mL	ng/mL	ng/mL	ng/mL	ng/mL	ng/mL	ng/mL			
ACENAPHTHENE	0.66	0.48	52.8	40.7	45	43	32.22	44	40.98	43	5.152	5	12.6%
ACENAPHTHYLENE	0.51	0.36	40.8	30.3	40	33	40.74	38	36.41	38	4.559	5	12.5%
ANTHANTHRENE	0.54	NA	43.2	NA	NA	NA	49.66	24	36.93	-	18.286	2	49.5%
ANTHRACENE	0.605	0.50	48.4	43.0	44	NA	45.29	40	43.07	43.5	2.253	4	5.2%
BENZO(A)ANTHRACENE	0.64	0.54	51.2	33.7	46	NA	50.31	32	40.50	39.85	9.037	4	22.3%
BENZO(B)FLUORANTHENE	0.605	0.45	48.4	35.6	45	21	47.66	55 &	40.89	45	13.116	5	32.1%
BENZO(K)FLUORANTHENE	0.7	0.58	56.0	54.4	48	29	58.68	55 &	49.06	54.4	11.672	5	24.2%
BENZO(A)FLUORENE	0.54	0.34	43.2	NA	NA	NA	NC	33	-	-	-	1	-
BENZO(B)FLUORENE	0.755	0.68	60.4	NA	NA	NA	NC	44	-	-	-	1	-
BENZO(A)PYRENE	0.515	0.47	41.2	34.6	33	18	38.78	37	32.28	34.6	8.282	5	25.7%
BENZO(E)PYRENE	0.495	0.50	39.6	43.4	NA	NA	35.77	33	37.39	35.77	5.386	3	14.4%
CHRYSENE	0.51	0.56 *	40.8	57.5 *	66 *	NA	34.95	43 *	50.36	50.25	13.991	4	27.8%
DIBENZO(A,C)ANTHRACENE	0.51	0.50 $	40.8	NA	61.5 $	NA	NC	32 $	46.75	-	20.860	2	44.6%
DIBENZO(A,H)ANTHRACENE	0.715	0.50 $	57.2	64.2	61.5 $	NA	52.35	32 $	52.51	56.925	14.585	4	27.8%
FLUORANTHENE	0.755	0.51	60.4	50.4	50	22	44.38	53	43.96	50	12.670	5	28.8%
FLUORENE	0.64	0.53	51.2	39.2	47	41	52.45 @	43	44.53	43	5.292	5	11.9%
INDENO(1,2,3-C,D)PYRENE	0.545	0.52	43.6	22.4	41	31	49.55	27	34.19	31	10.991	5	32.1%
PHENANTHRENE	0.575	0.44	46.0	40.9	42	39	42.24	39	40.63	40.9	1.570	5	3.9%
PYRENE	0.75	0.65	60.0	54.4	51	22	60.06	50	47.49	51	14.783	5	31.1%
TRIPHENYLENE	0.635	0.56 *	50.8	57.5 *	66 *	NA	49.60	43 *	54.03	53.55	9.943	4	18.4%

NOTES (apply to all 4 data tables)

*	Chrysene and Triphenylene co-elute; half of total assigned to each parameter
#	result reported as combination of Chrysene/Triphenylene; only one compound present in ampoule, so value was assigned to "correct" parameter
##	reported a positive response for Chrysene, which was not included in this ampoule; Triphenylene was present and co-elutes with Chrysene
&	co-elute: half of total value assigned to each parameter
$	co-elute: half of total value assigned to each parameter
@	result qualified: suspect due to peak distortion
* *	originally reported as Dibenzo(a,h)anthracene; may have been mis-identified as they co-elute
NA	Not available
NC	Not calibrated for

TABLE 2 - Results for IADN2 and IADN2a

AMPOULE/LAB CODE	IADN2	9225	IADN2a	9221	9222	9223	9224	9226	MEAN	MEDIAN	SD	n	%RSD
PARAMETER	µg/mL	µg/mL	ng/mL	ng/mL	ng/mL	ng/mL	ng/mL	ng/mL	ng/mL	ng/mL			
ACENAPHTHYLENE				16.8									
ANTHRACENE				6.2									
BENZO(A)ANTHRACENE	1.024	0.94	28.672	20.6	25	NA	24.22	18	21.96	22.41	3.260	4	14.8%
BENZO(K)FLUORANTHENE	1.12	0.85	31.36	25.4	25	20	32.15	41	28.71	25.4	8.116	5	28.3%
BENZO(A)FLUORENE	0.864	0.54	24.192	NA	NA	NA	NC	18	-	-	-	1	-
BENZO(A)PYRENE	0.824	0.76	23.072	17.7	25	10	20.33	14	17.41	17.7	5.761	5	33.1%
CHRYSENE	0.816	0.73 #	22.848	21.2	24	NA	18.72	16 #	19.98	19.96	3.419	4	17.1%
DIBENZO(A,C)ANTHRACENE	0.816	0.67	22.848	NA	36	NA	NC	12	24.00	-	16.971	2	70.7%
DIBENZO(A,H)ANTHRACENE				17.6	**								
FLUORANTHENE				3.3									
FLUORENE				13.1									
INDENO(1,2,3-C,D)PYRENE	0.872	0.90	24.416	10.2	26	15	30.78	12	18.80	15	9.083	5	48.3%
PHENANTHRENE	0.92	0.70	25.76	28.0	23	27	22.77	23	24.75	23	2.533	5	10.2%
PYRENE	1.2	1.02	33.6	29.8	32	11	33.60	26	26.48	29.8	9.111	5	34.4%

TABLE 3 - Results for IADN3 and IADN3a

AMPOULE/LAB CODE	IADN3	9225	IADN3a	9221	9222	9223	9224	9226	MEAN	MEDIAN	SD	n	%RSD
PARAMETER	µg/mL	µg/mL	ng/mL	ng/mL	ng/mL	ng/mL	ng/mL	ng/mL	ng/mL	ng/mL			
ACENAPHTHENE						2	1.56						
ACENAPHTHYLENE	1.02	0.77	204	178	207	209	187.99	180	192.40	187.99	14.742	5	7.7%
ANTHANTHRENE	1.08	NA	216	NA	NA	NA	243.88	140	191.94	-	73.454	2	38.3%
ANTHRACENE				4.4									
BENZO(E)PYRENE	0.99	1.03	198	272	NA	NA	183.13	210	221.71	210	45.578	3	20.6%
FLUORANTHENE	1.51	1.10	302	295	257	136	299.48	280	253.50	280	67.744	5	26.7%
FLUORENE	1.28	1.12	256	223	272	232	233.61	220	236.12	232	20.872	5	8.8%
PHENANTHRENE				6.4									

TABLE 4 - Results for IADN4 and IADN4a

AMPOULE/LAB CODE	IADN4	9225	IADN4a	9221	9222	9223	9224	9226	MEAN	MEDIAN	SD	n	%RSD
PARAMETER	µg/mL	µg/mL	ng/mL	ng/mL	ng/mL	ng/mL	ng/mL	ng/mL	ng/mL	ng/mL			
ACENAPHTHENE	1.056	0.75	29.568	21.4	25	25	18.35	22	22.35	22	2.787	5	12.5%
ANTHRACENE	0.968	0.66	27.104	16.4	23	NA	24.85	14	19.56	19.7	5.187	4	26.5%
BENZO(B)FLUORANTHENE	0.968	0.75	27.104	27.2	30	10	26.04	42	27.05	27.2	11.445	5	42.3%
BENZO(B)FLUORENE	1.208	0.95	33.824	NA	NA	NA	NC	26					
DIBENZO(A,H)ANTHRACENE	1.144	0.75	32.032	19.8	32	NA	25.94	17	23.69	22.87	6.663	4	28.2%
TRIPHENYLENE	1.016	0.89 #	28.448	44.7 #	##	NA	30.74	20 #	31.81	30.74	12.385	3	38.9%
CHRYSENE					40 ##								

TABLE 5 - Analytical Conditions

Lab Code	9221	9222	9223	9224	9225	9226
Ampoule Solvent	Toluene	Hexane	Iso-octane	Acetonitrile	Toluene	Benzene
Instrument/ Detector	GC/MSD: HP5890/HP5970	GC/MSD: HP5890/HP5970S	GC/MSD: HP5970	HPLC/Fluorescent/UV: HP1090/HP1046A/HP1050	GC/MSD: HP5890A/HP5970	GC/MSD: HP
Stationary & Mobile Phase	DB-5, 30 m	DB-5, 30 m	DB-5, 30 m	Reverse-phase gradient ($ACN/H_2O/C_{18}$); 16 cm X 4.6 mm; 5 µm particle size	DB-5, 60 m	DB-5, 30 m

TABLE 6 - Distribution of Participants' Results

Range of Target	9225		9221		9222		9223		9224		9226	
< 60%	0	0.0%	2	6.3%	0	0.0%	9	45.0%	0	0.0%	6	15.0%
60-75%	11	28.9%	7	21.9%	0	0.0%	3	15.0%	10	29.4%	10	25.0%
75-90%	17	44.7%	11	34.4%	12	37.5%	5	25.0%	16	47.1%	16	40.0%
90-110%	10	26.3%	7	21.9%	14	43.8%	3	15.0%	5	14.7%	5	12.5%
110-130%	0	0.0%	2	6.3%	2	6.3%	0	0.0%	1	2.9%	1	2.5%
> 130%	0	0.0%	3	9.4%	4	12.5%	0	0.0%	2	5.9%	2	5.0%

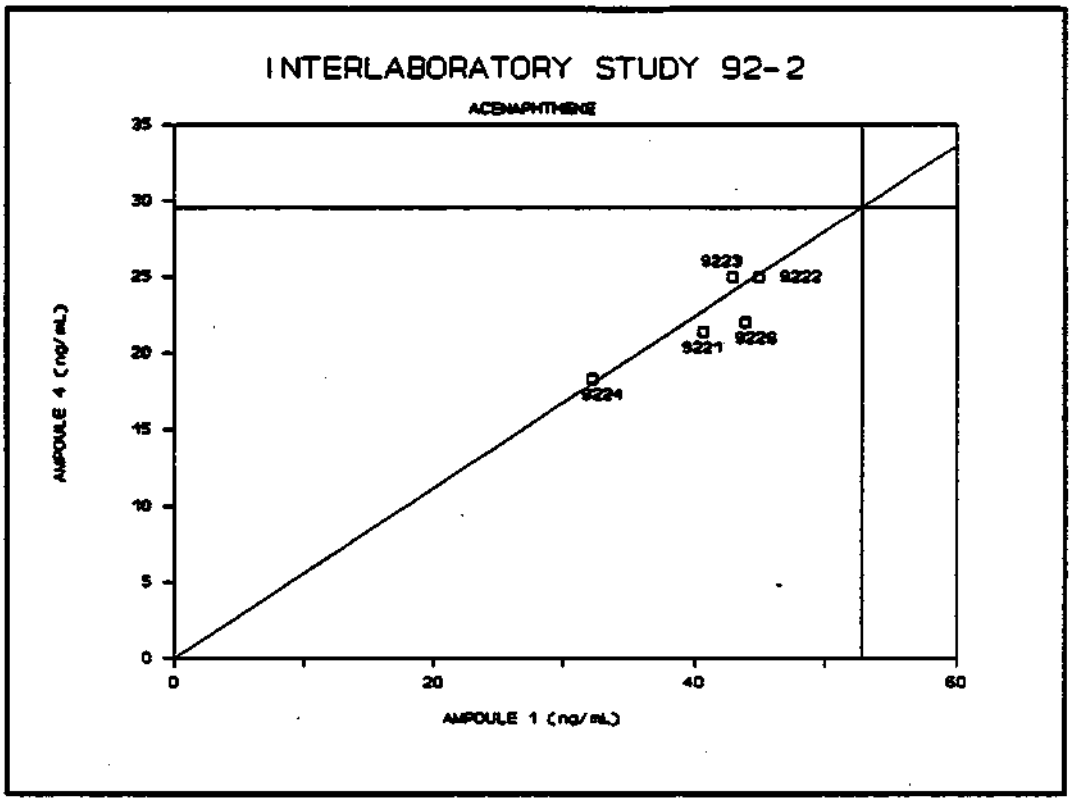

Figure 1 - Acenaphthene (IADN1a & IADN4a)

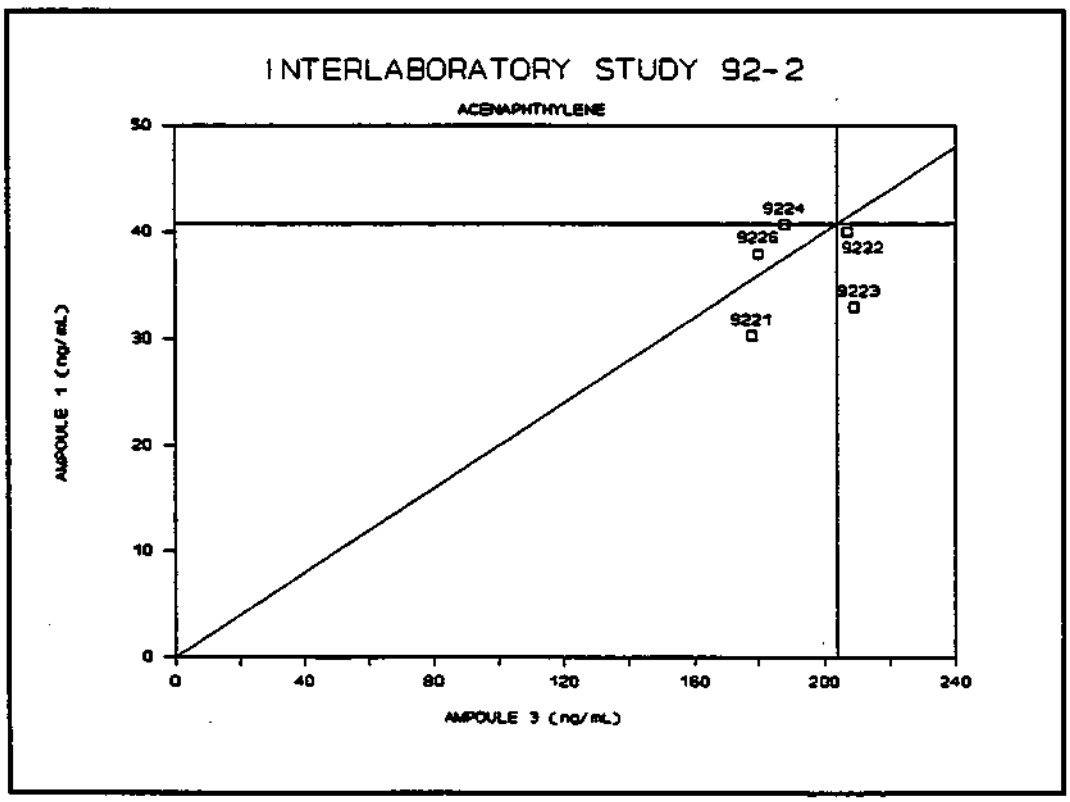

Figure 2 - Acenaphthylene (IADNIa & IADN3a)

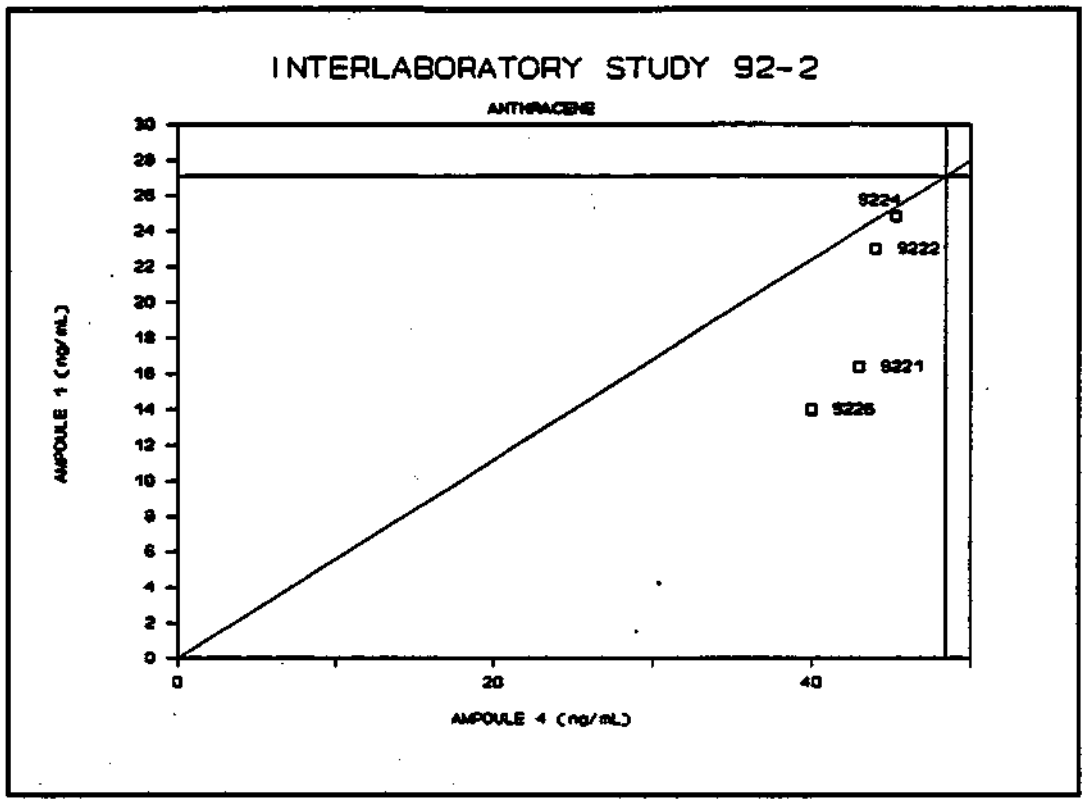

Figure 3- Anthracene (IADN1a & IADN4a)

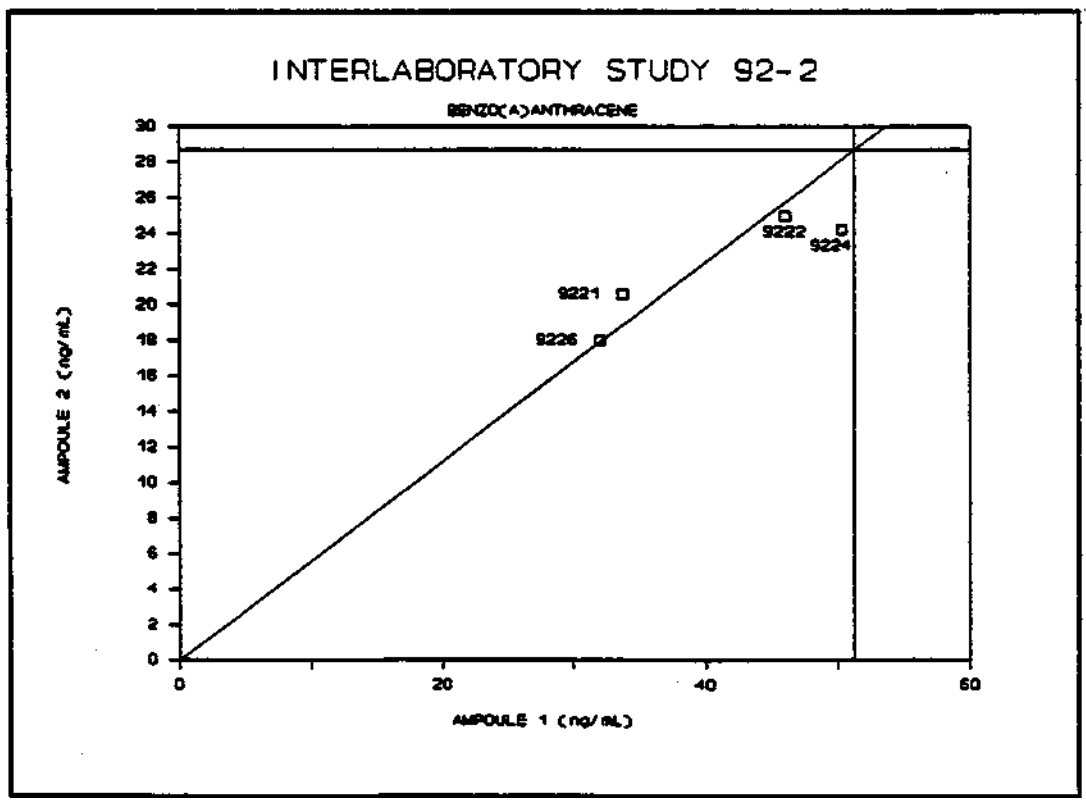

Figure 4 - Benzo(a)anthracene (IADN1a & IADN2a)

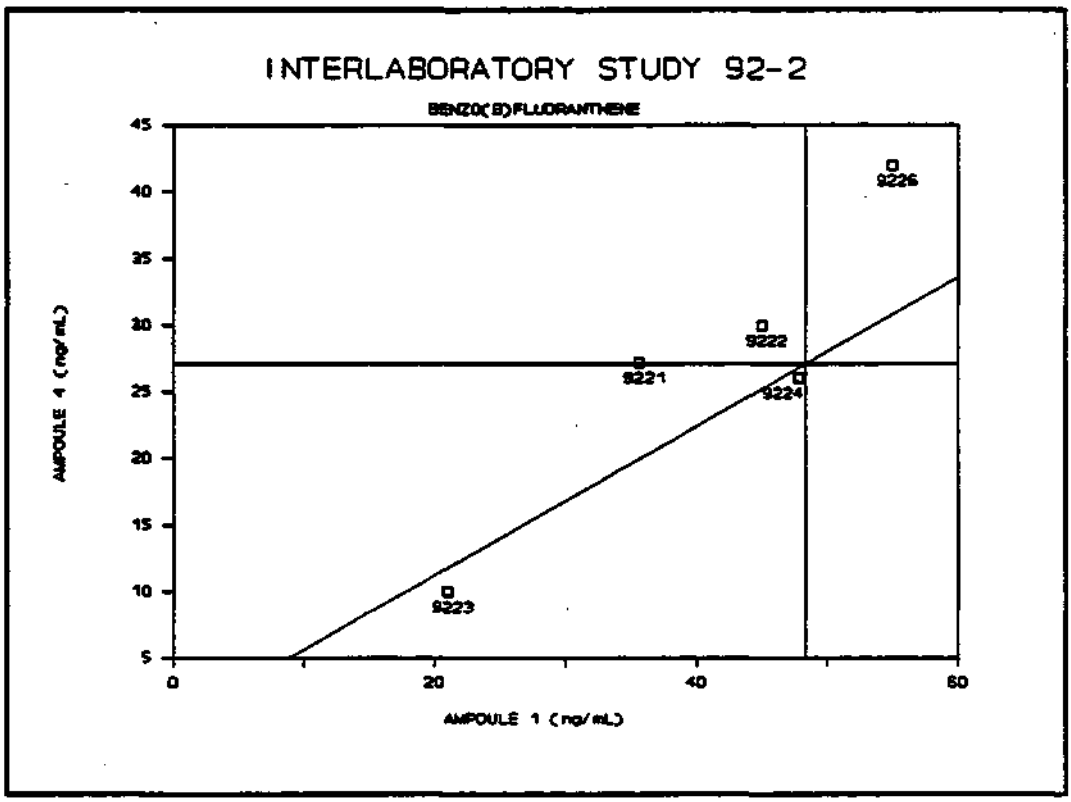

Figure 5 - Benzo(b)fluoranthene (IADN1a & IADN4a)

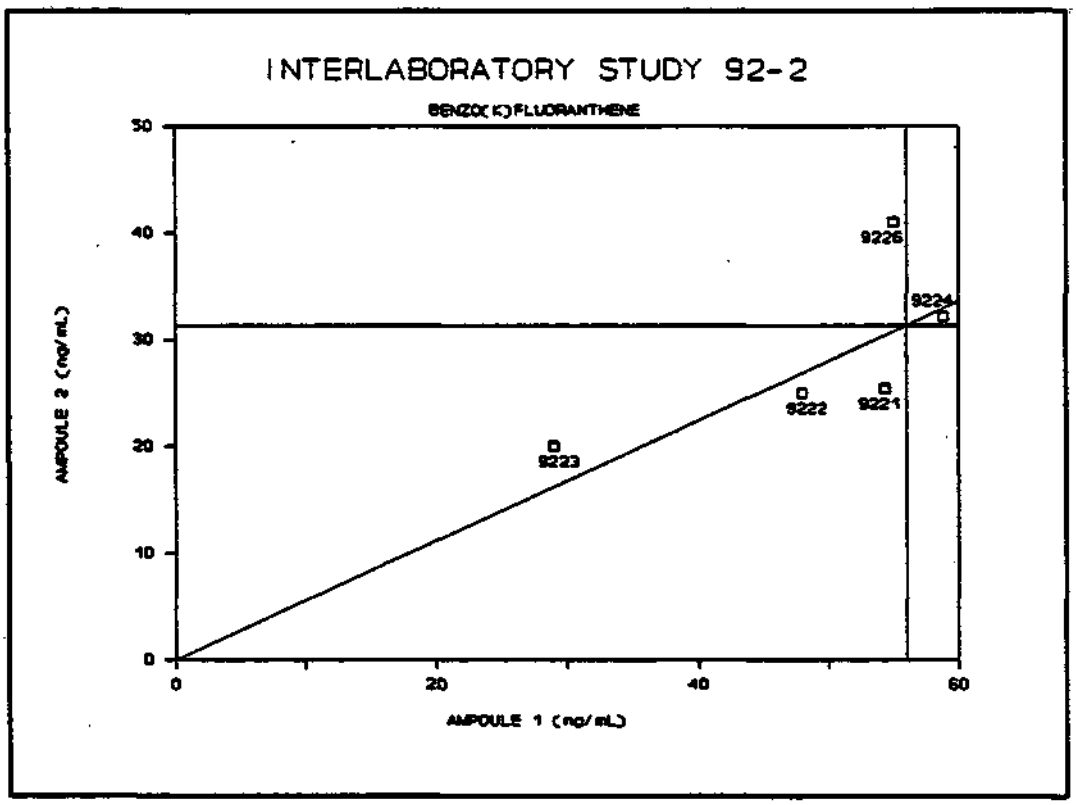

Figure 6 - Benzo(k)fluoranthene (IADN1a & IADN2a)

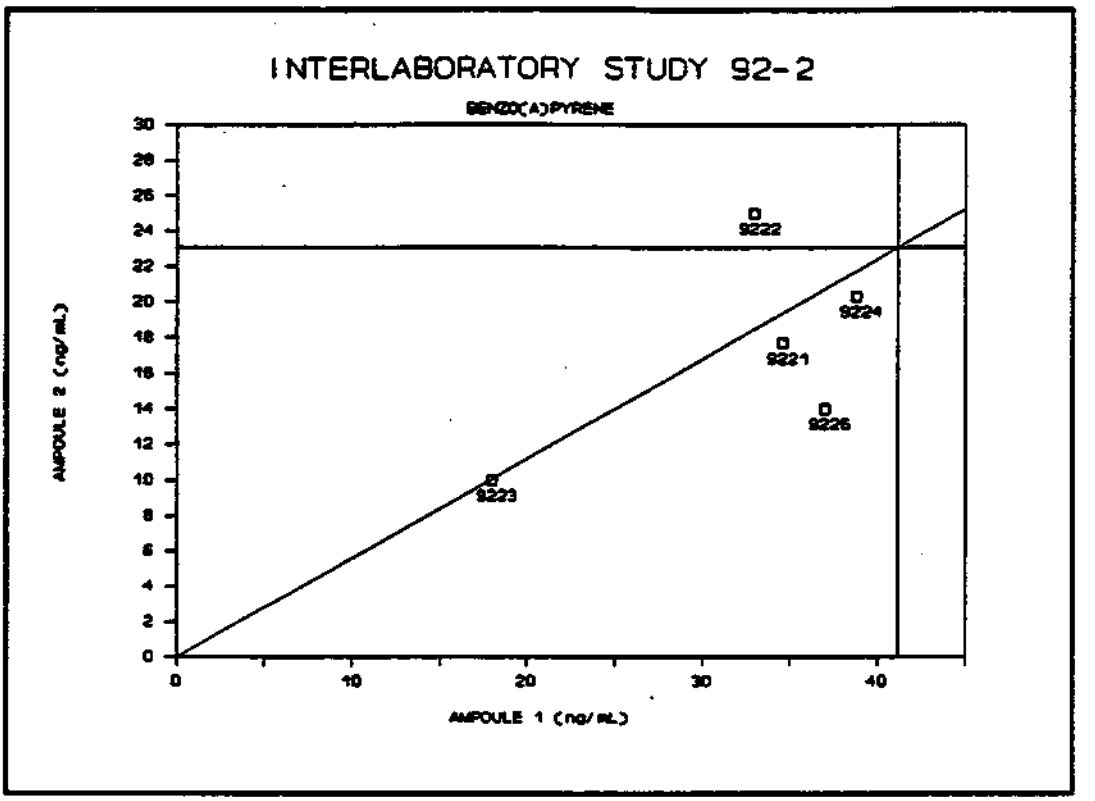

Figure 7 - Benzo(a)pyrene (IADN1a & IADN2a)

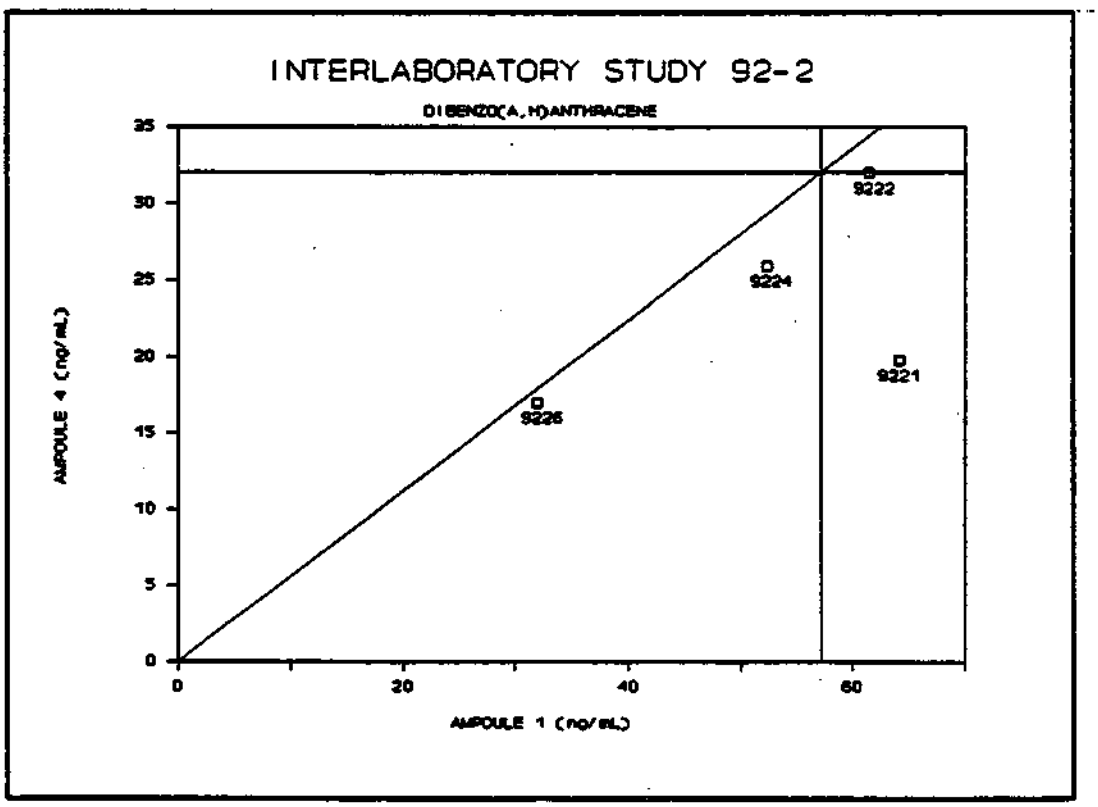

Figure 8 - Dibenzo(a,h)anthracene (IADN1a & IADN4a)

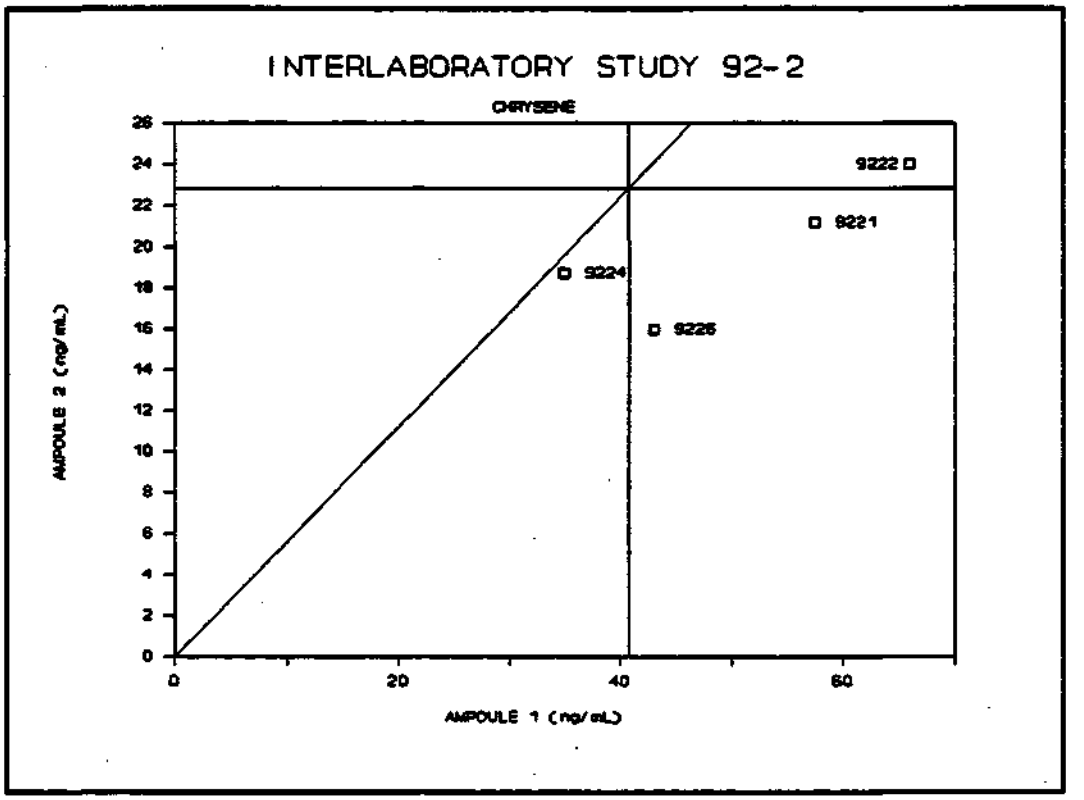

Figure 9 - Chrysene (IADN1a & IADN2a)

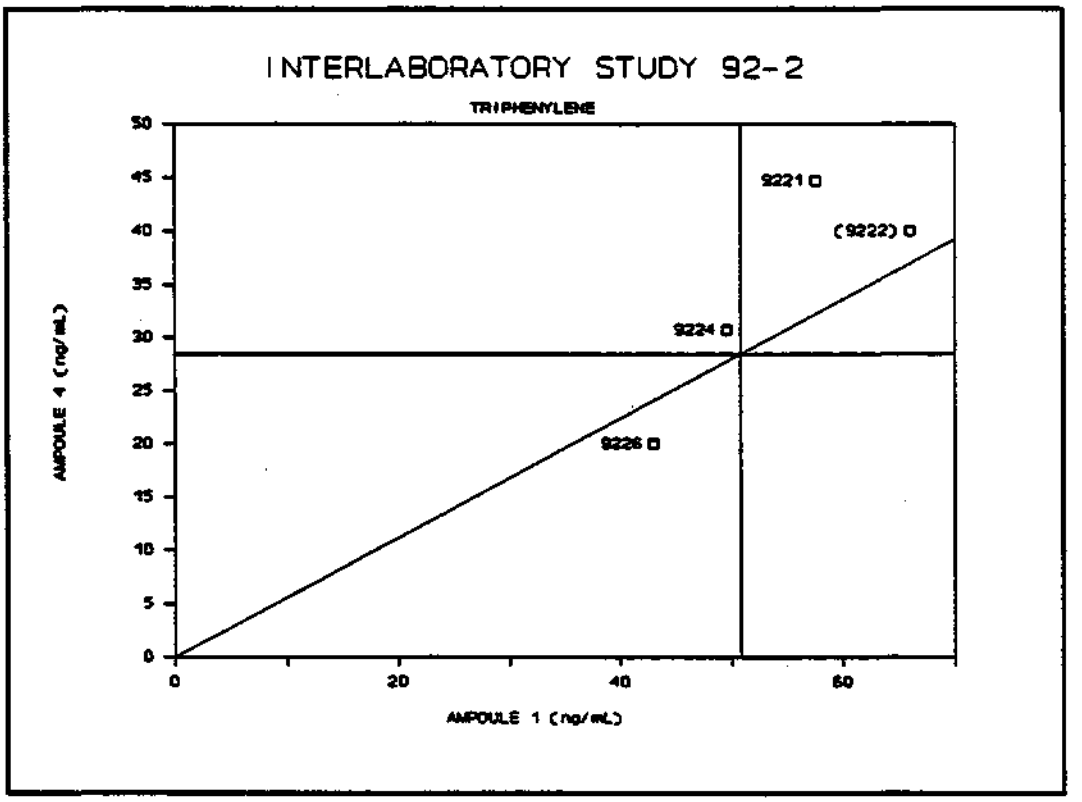

Figure 10 - Triphenylene (IADNIa & IADN4a)

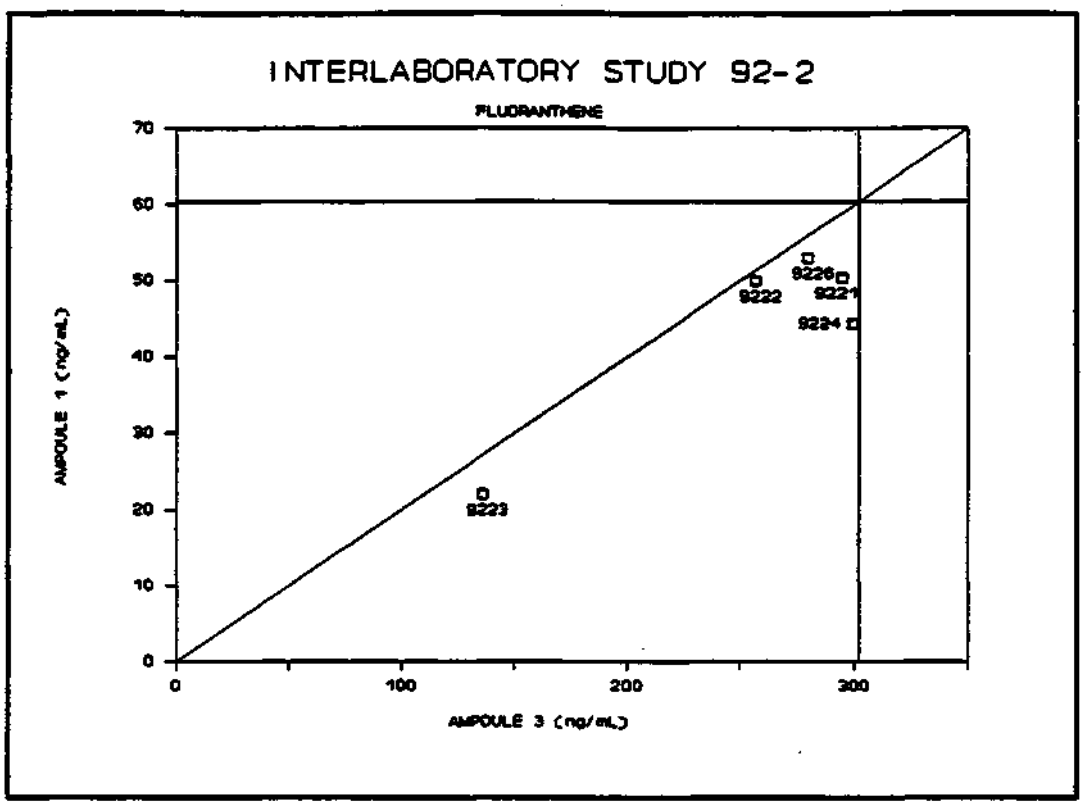

Figure 11 - Fluoranthene (IADN1a & IADN3a)

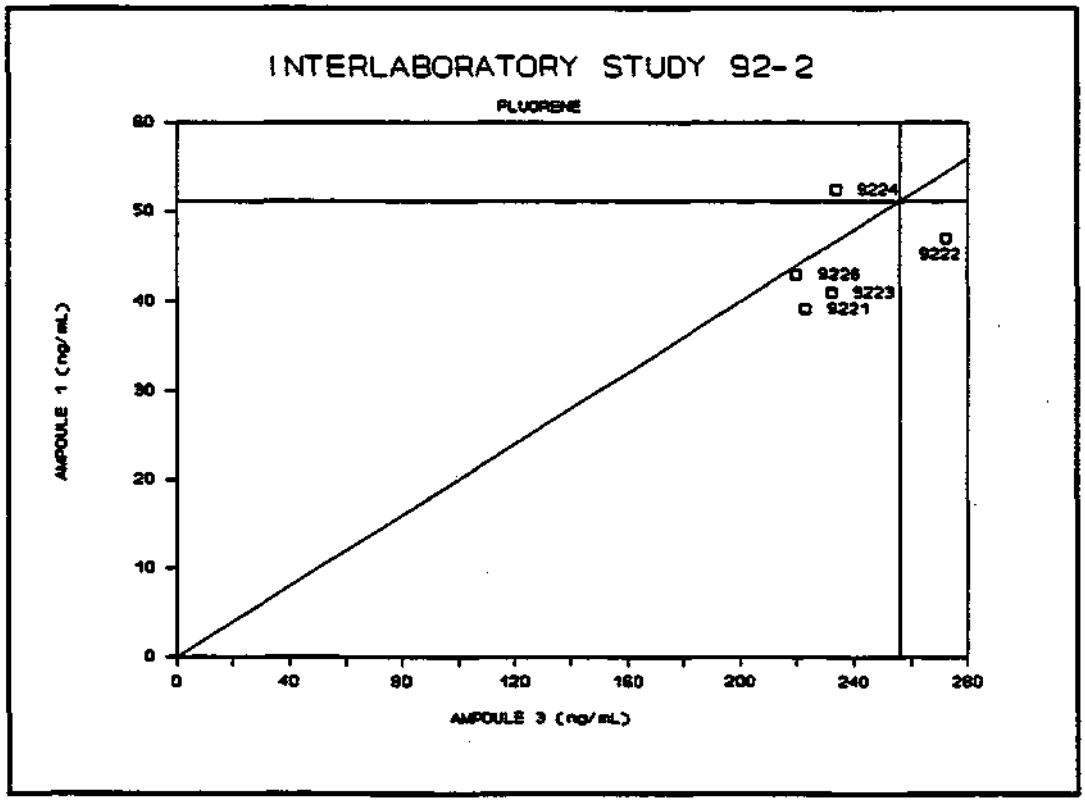

Figure 12 - Fluorene (IADN1a & IADN3a)

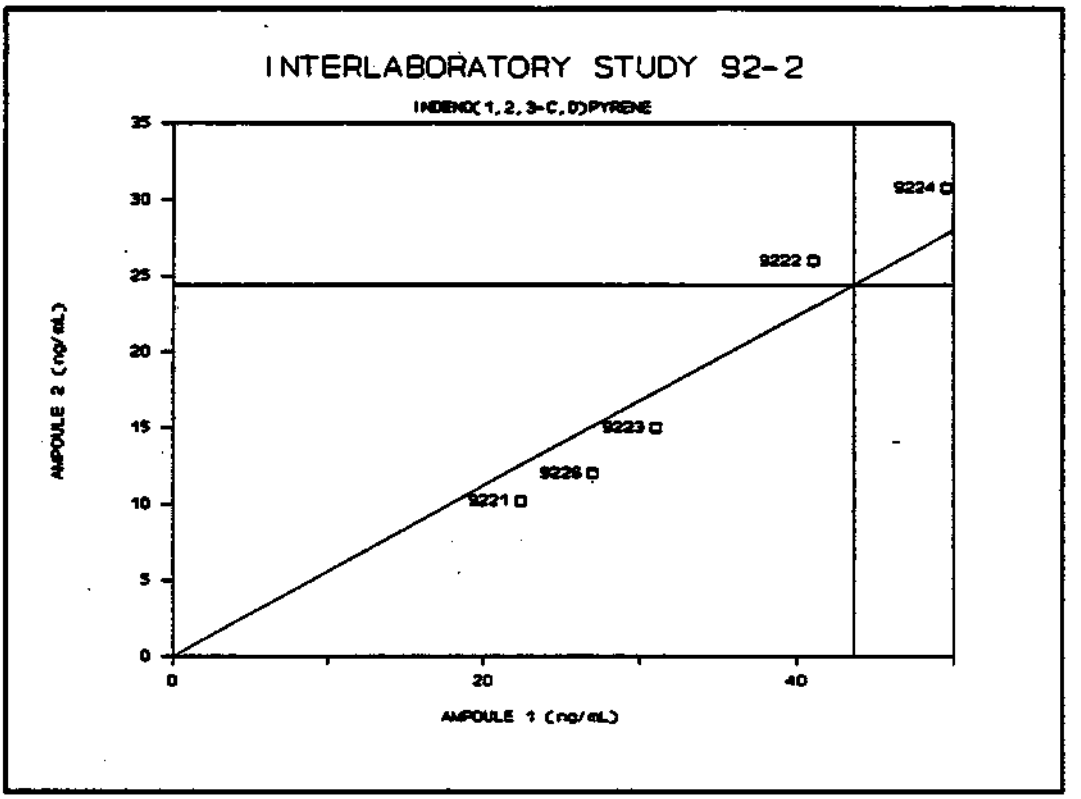

Figure 13 - Indeno(1,2,3-c,d)pyrene (IADN1a & IADN2a)

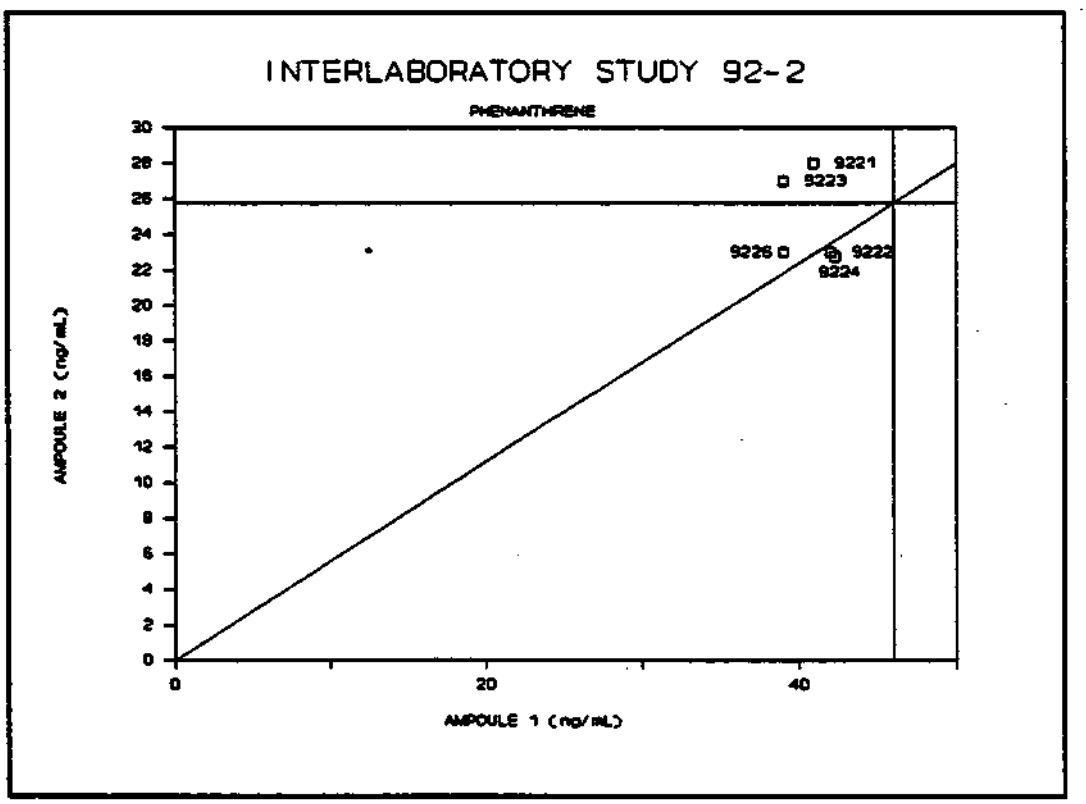

Figure 14 - Phenanthrene (IADN1a & IADN2a)

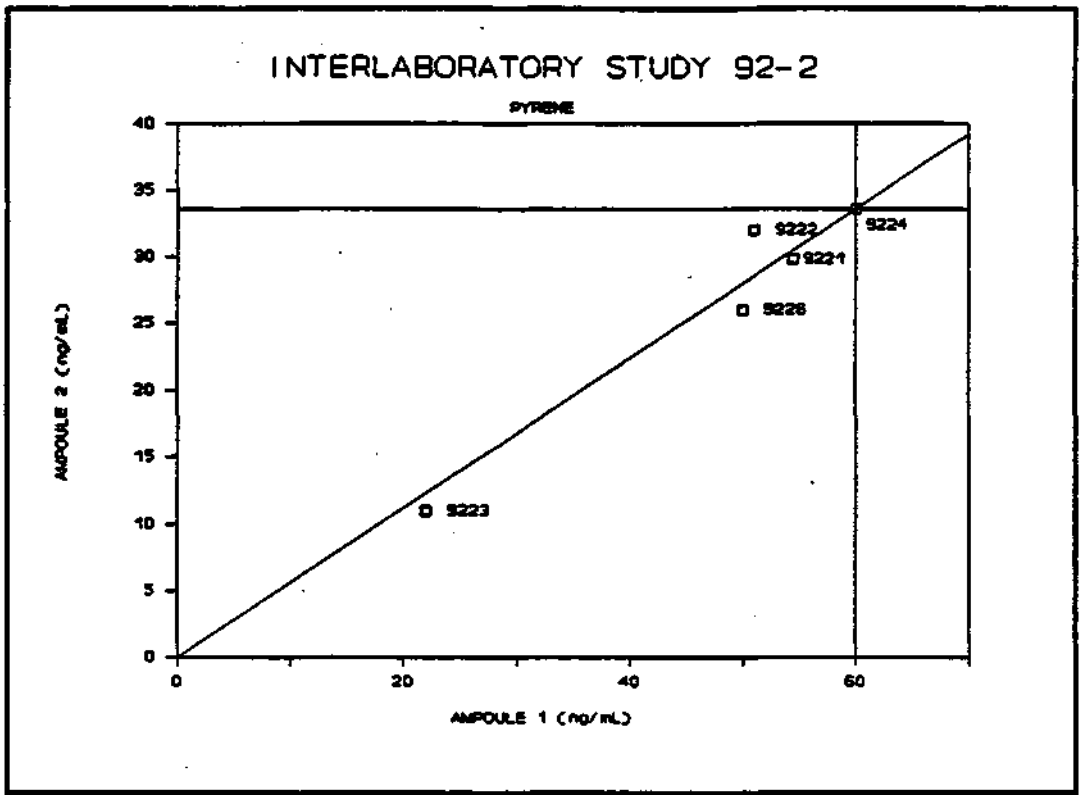

Figure 15 - Pyrene (IADN1a & IADN2a)

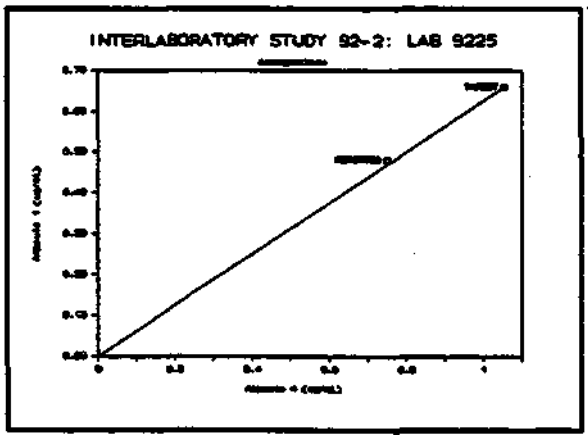

Figure 16 - Laboratory 9225: Acenaphthene

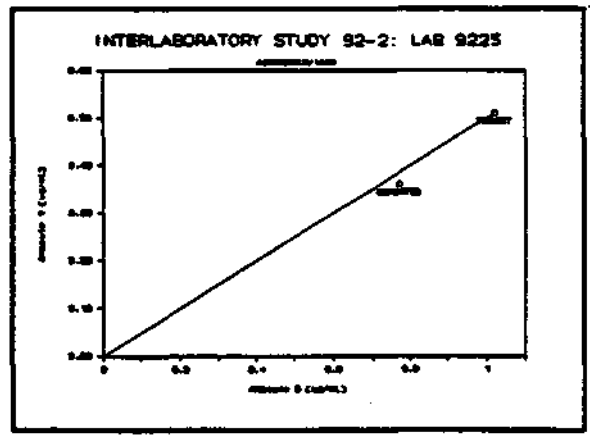

Figure 17 - Laboratory 9225: Acenaphthylene

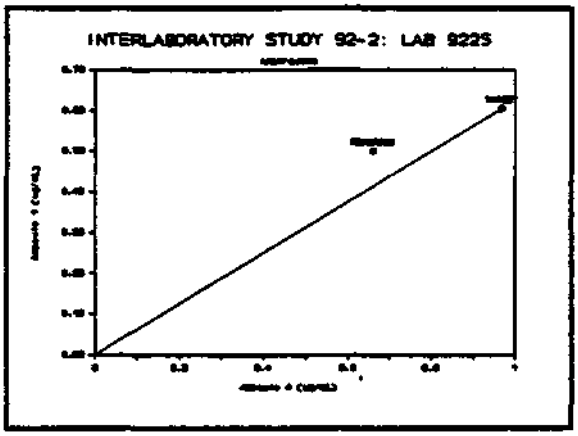

Figure 18 - Laboratory 9225: Anthracene

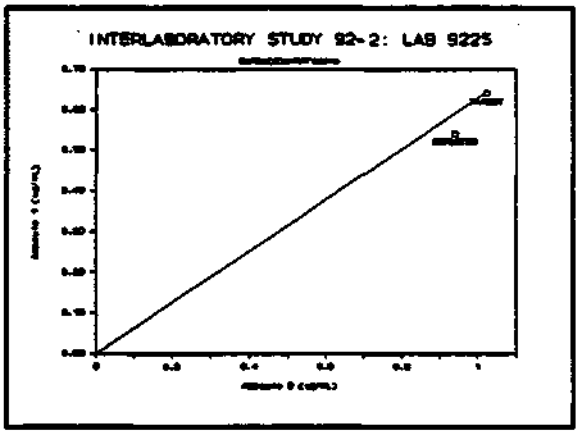

Figure 19 - Laboratory 9225: Benzo(a)Anthracene

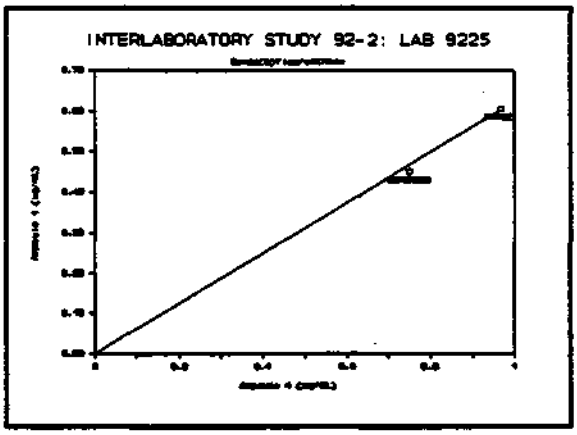

Figure 20 - Laboratory 9225: Benzo(b)Fluoranthene

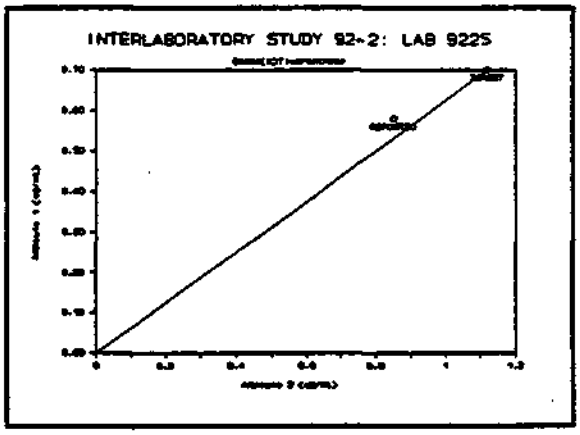

Figure 21 - Laboratory 9225: Benzo(k)Fluoranthene

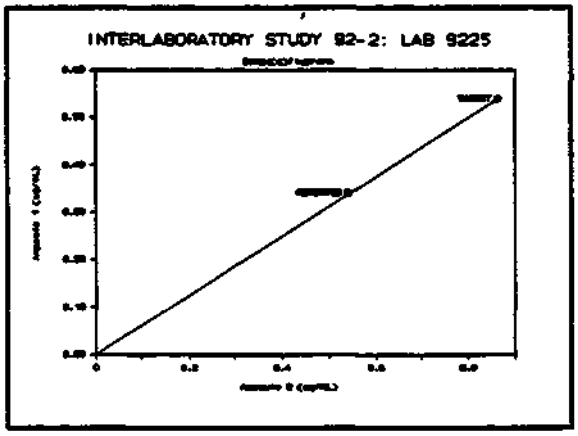

Figure 22 - Laboratory 9225: Benzo(a)Fluorene

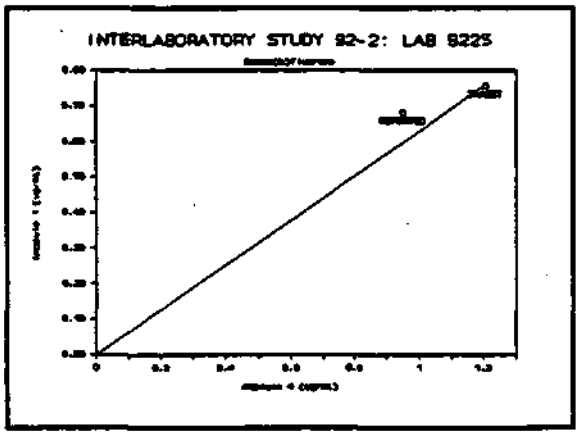

Figure 23 - Laboratory 9225: Benzo(b)Fluorene

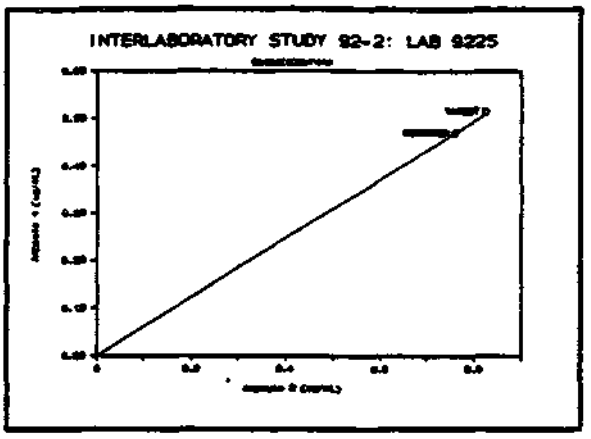

Figure 24 - Laboratory 9225: Benzo(a)Pyrene

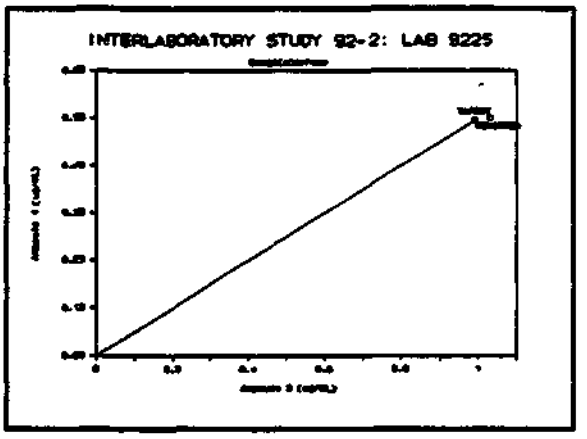

Figure 25 - Laboratory 9225: Benzo(e)Pyrene

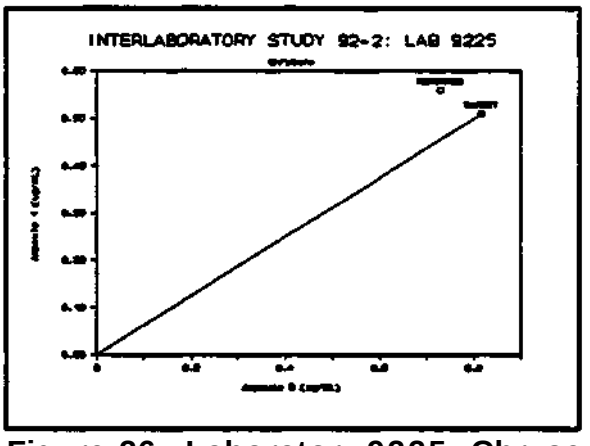

Figure 26 - Laboratory 9225: Chrysene

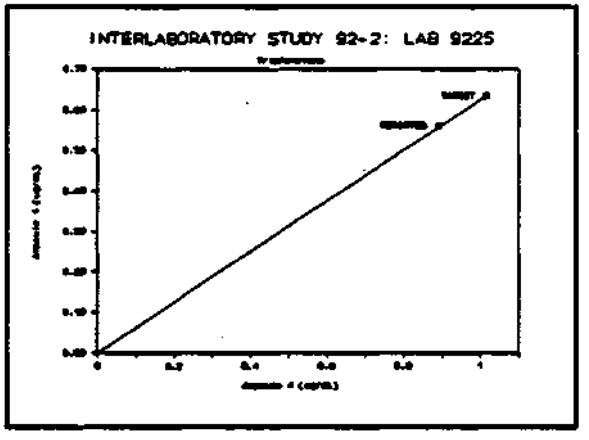

Figure 27 - Laboratory 9225: Triphenyiene

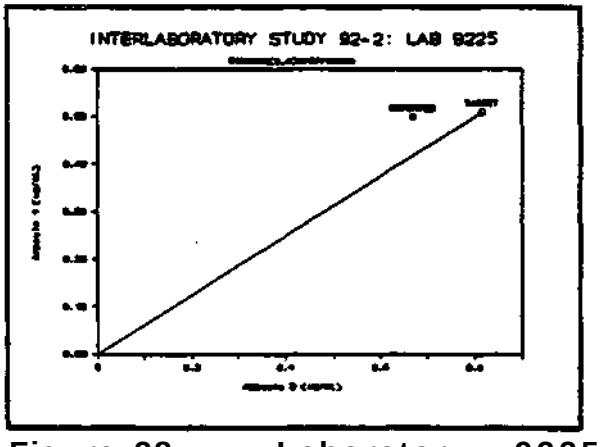

Figure 28 - Laboratory 9225: Dibenzo(a,c)Anthracene

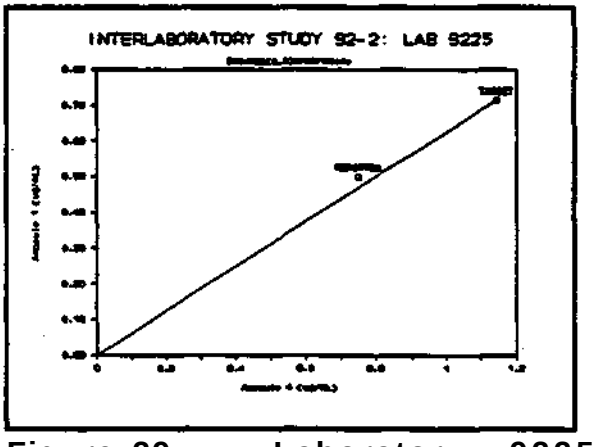

Figure 29 - Laboratory 9225: Dibenzo(a,h)Anthracene

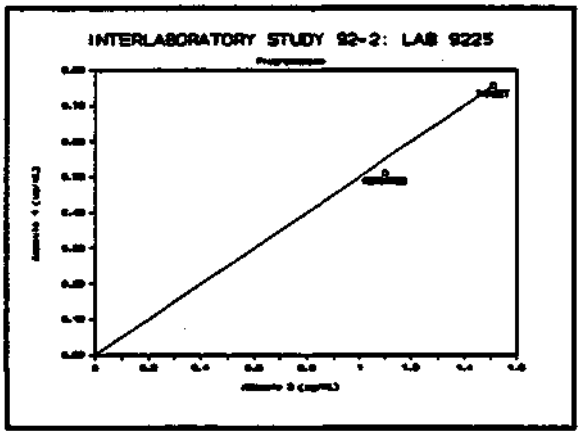

Figure 30 - Laboratory 9225: Fluoranthene

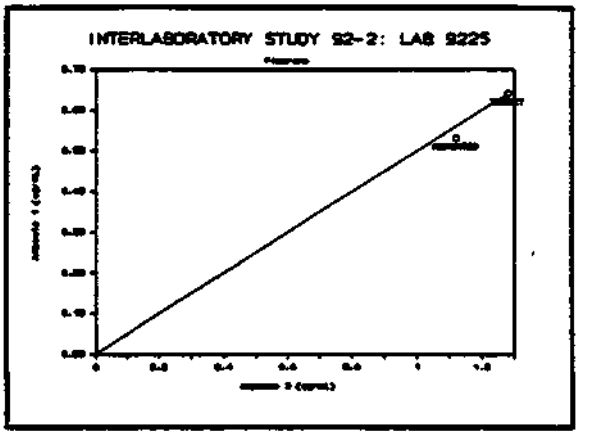

Figure 31 - Laboratory 9225: Fluorene

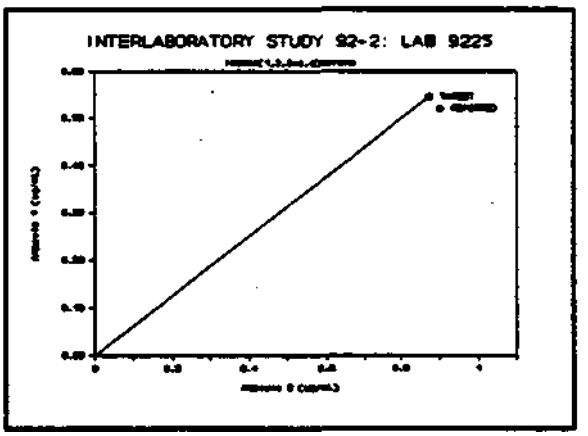

Figure 32 - Laboratory 9225: Indeno(1,2,3-c,d)Pyrene

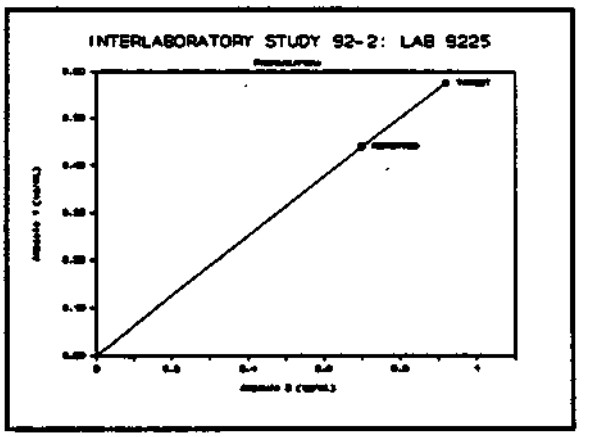

Figure 33 - Laboratory 9225: Phenanthrene

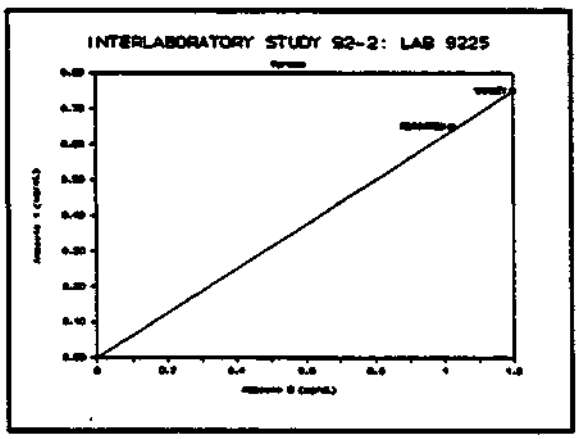

Figure 34 - Laboratory 9225: Pyrene

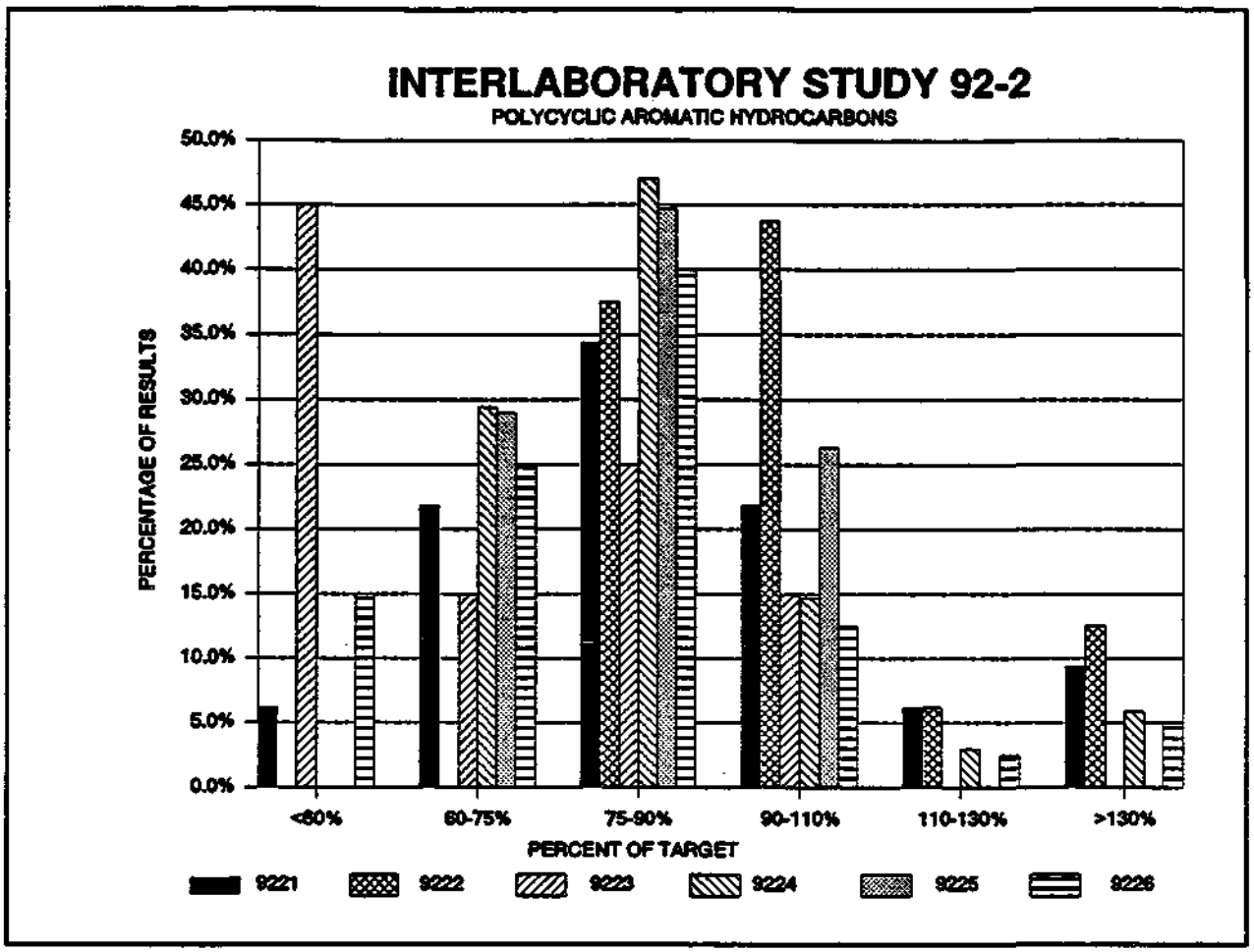

Figure 35 Distribution of Participants' Results Relative to Target

8 APPENDIX 2 - PARTICIPANTS AND CORRESPONDENCE

List of Participants

Bev Genest-Conway/Dave Warry
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(416)739-4601

Chung Chiu
Environment Canada
Environmental Technology Centre
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Gloucester, Ontario
K1G 3N3
(613)990-8560

Quality Management Office

September 21, 1992

Dear Interlaboratory Study 92-2 Participant,

Please find enclosed four 5 mL ampoules for the analysis of Polynuclear Aromatic Hydrocarbons (PAH's). The ampoules are labelled IADN1, IADN2, IADN3, and IADN4 and indicate the solvent. If you are missing any of the ampoules or they have broken in transit, please contact me at (416) 235-5842 immediately for replacement.

The ampoules are ready for direct instrumental analysis. Break open the ampoule on the scored mark and transfer the contents to the appropriate sample container for your analytical system. No dilutions should be required, but if you do so, please mark the dilution factor used on the accompanying report form. The parameters present are indicated on the form.

Please report all results on the accompanying form by October 9. 1992.

Thank you for your participation in this study.

Your identification code is:

Sylvia Cussion
Laboratory Quality Audit Scientist
(416) 235-5842
FAX (416) 235-6110

IIMTERLABORATORY STUDY 92-2

PAH's FOR THE INTEGRATED ATMOSPHERIC DEPOSITION NETWORK

Identification Code:

Units:

PARAMETER	IADN1	IADN2	IADN3	IADN4
ACENAPHTHENE				
ACENAPHTHYLENE				
ANTHANTHRENE				
ANTHRACENE				
BENZO(A)ANTHRACENE				
BENZO(B)FLUORANTHENE				
BENZO(K)FLUORANTHENE				
BENZO(A)FLUORENE				
BENZO(B)FLUORENE				
BENZO(A)PYRENE				
BENZO(E)PYRENE				
CHRYSENE				
DIBENZO(A,C)ANTHRACENE				-
DIBENZO(A,H)ANTHRACENE				
FLUORANTHENE				
FLUORENE				
INDENO(1,2,3-C,D)PYRENE				
PHENANTHRENE				
PYRENE				
TRIPHENYLENE				

INSTRUMENT AND DETECTOR USED FOR ANALYSIS:

125 Resources Rd.
Etobicoke, Ontario, M9P 3V6
Phone: (416) 235-5842
FAX: (416) 235-6110

January 4, 1993

TO: PARTICIPANTS OF INTERLABORATORY STUDY 92-2

Thank you for your participation in Interlaboratory Study 92-2 for the analysis of Polynuclear Aromatic Hydrocarbons (PAH's) in ampouied standards. This study was in support of the Integrated Atmospheric Deposition Network (IADN) program. I apologize for the delay in reporting results, but one participant did not report their final results until last week.

The results are provided in the attached tables. Target values are provided. Please inform me of any transcription errors by January 15, 1993.

Due to the variation in analytical methods among the participants, the following procedure was used to prepare the ampoules standards. A concentrated stock solution of each individual PAH was prepared in toluene. A combined solution was prepared in toluene, sealed into ampoules and labelled IADN 1-4. Due to their analytical working range, a set of these ampoules were provided to laboratory 9225. For the remaining participants, a further dilution was made in the specified solvent. The dilute solutions were ampouied and labelled IADN 1a - 4a. Each remaining participant received a set of the "a" series of ampoules in the solvent specified by them.

The Quality Assurance Working Group of the Canada-Ontario Agreement (COA) has been the directing force for these interlaboratory studies. They wish to know the identities of the participating laboratories for the purposes of data comparison for IADN. The Program Managers and Principle Investigators (U.S. and Canadian) for IADN also wish to have the laboratories identified. As the original invitation for this study indicated that laboratory codes were confidential, I am asking each participant to give me permission to reveal their identities to these groups of data users. Please notify me in writing with your permission to reveal your study code.

A date has not yet been set for the next set of ampouied standards in this series of IADN studies, but hopefully will take place in late February or in March. A letter will be sent out giving several weeks notice.

Your identification code is:

Sylvia Cussion
Laboratory Quality Audit Scientist

125 Resources Rd.
Etobicoke, Ontario, M9P 3V6
Phone: (416) 235-5842
FAX: (416) 235-6107

January 15, 1993

TO: PARTICIPANTS OF INTERLABORATORY STUDY 92-2

Please find enclosed an updated Table 1 for Interlaboratory Study 92-2 (PAH's). Laboratory 9224 provided an updated result for Fluorene in this ampoule before the table of results went out to all of the participants. I apologize for the error and any inconvenience this may have caused.

Sylvia Cussion
Laboratory Quality Audit Scientist

ISBN 0-7778-2244-X

INTERLABORATORY STUDY 92-3

ORGANOCHLORINE PESTICIDE (OC's) STANDARD SOLUTIONS

IN SUPPORT OF

THE INTEGRATED ATMOSPHERIC DEPOSITION NETWORK (IADN)

Interlaboratory Study 92-3, OCs, Standard Solutions *ISWS Lab Code: 9236*

OCTOBER 1992

Report Prepared by

Sylvia Cussion

for

Quality Management Unit
Laboratory Services Branch
Ontario Ministry of Environment and Energy

and

Air Quality Research Branch
Atmospheric Environment Service
Environment Canada
ARD Report: 93-13

The author gratefully acknowledges and thanks Lloyd Winfield for the preparation of materials, Patrick Crozier, Angelo Alfieri and Gerry Ladwig for the confirmation of concentrations, and Don King, Sathi Selliah, Renata Baily, Syed Iqbal, and Robert Vet for their help in reviewing the results.

TABLE OF CONTENTS

1 SUMMARY OF INTERLABORATORY STUDY 92-3

Interlaboratory Study 92-3 was initiated in support of the Integrated Atmospheric Deposition Network (IADN) to provide an initial assessment of laboratory variability for the analysis of Organochlorine Pesticides (OC's). Participation was limited to laboratories which contribute to the IADN database or related programs. This study was sponsored by the Canada-Ontario Agreement (COA) Air Toxics Workgroup, and conducted as a joint project between the Atmospheric Environment Service (AES) of Environment Canada and the Quality Management Unit (QMU), Laboratory Services Branch (LSB) of the Ontario Ministry of Environment and Energy (MOEE).

Six participating laboratories received a set of four ampouled standards that were ready for direct instrumental analysis. The parameter list consisted of 18 different OC's. All 18 compounds were present in each ampoule at four different concentrations.

The results of this intertaboratory study indicate that the participants have an agreement of ±20% to the target for most parameters. The within-laboratory performance tends to be consistent across the concentration range, though some participants were erratic for some parameters. Slope problems are the most common source of between-laboratory variability. As between-participant bias may be as high as 30-40%, the use of a common reference standard could help reduce this bias range to < 10-15%. This would reduce the potential bias from the contributing laboratories to the central IADN database.

2 INTRODUCTION

Interlaboratory performance studies are conducted to assess the comparability and accuracy of data among different laboratories. These studies are useful for the identification of biases, precision and accuracy problems. Participation in such studies can serve as a guide for improving individual laboratory performance and maintaining performance standards.

This study was designed to assess the analytical variability among laboratories contributing to the Integrated Atmospheric Deposition Network (IADN). IADN was established as a joint venture between Canada and the United States under the direction of the International Joint Commission[1]. The intent of IADN is to identify toxic airborne substances in the Great Lakes Basin, and by means of the network, quantify the total and net atmospheric loadings of these contaminants, and define spatial and temporal trends in the atmospheric deposition of these substances. Data from several participating agencies is to be merged into a central database. Comparability of these contributing data sets is an important component of the IADN Quality Assurance Implementation Plan[3]. This interiaboratory study provides information on the laboratory component of between agency differences, and can be used to help establish the comparability of the data sets. Sponsorship of this interiaboratory study was through the Canada-Ontario Agreement (COA) Air Toxics Workgroup. Funding for the purchase of materials came from the Atmospheric Environment Service (AES) of Environment Canada. Co-ordination and implementation of the study was done by the Quality Management Unit (QMU) of Laboratory Services Branch (LSB) of the Ontario Ministry of Environment and Energy (MOEE).

Interiaboratory Study 92-3 targets laboratories analyzing for Organochlorine Pesticides (OC's) in precipitation and/or ambient air. A target list of 18 OC's was chosen for this study, comprising target lists from several contributing agencies. The aim of this study was to establish the comparability of instrumental calibration among the participating laboratories. Each participant received a set of ampouled standards ready for direct instrumental analysis. Each ampoule contained ail of the parameters in the target list.

A list of participants is given in Appendix 2. Each participant was assigned a unique identification code for ease in data manipulation.

Section 3 describes sample preparation, sample distribution, analytical methodology, and data evaluation procedures. Pinal results are tabled in Appendix 1 and discussed in Section 4.

3 PROCEDURE

3.1 Preparation of Ampouled Standards

Neat OC's of 99% + purity were purchased from Ultra Scientific and Supelco by AES. All subsequent work was done by the QMU of LSB, MOEE. Three concentrated stock solutions containing six compounds each were prepared in 2% toluene/iso-octane, and sealed into 5 mL amber ampoules. The stock concentrations were between 10 to 15 mg/L and verified using gas chromatography/electron capture detector (GC/ECD) analysis by an analytical unit at LSB not involved in analysis of ambient air or precipitation. Ampouled solutions were stored in a freezer at -20°C.

Solutions for the interlaboretory study were prepared from the concentrated stock solutions by diluting appropriate aliquots into a combined solution in iso-octane. Concentrations were chosen to span the routine instrumental calibration range of the participants. The solutions were sealed in 5 mL amber ampoules and labelled IADN OC1, IADN OC2, IADN OC3, and IADN OC4. (Further reference to these ampoules eliminates "IADN".) All ampoules were stored in a freezer at -20°C until shipped to the participants.

3.2 Sample Distribution

Samples were packed into styrofoam shipping containers and shipped by Purolator Courier to the participating laboratories. A list of the laboratories receiving sample sets is given in Appendix 2. Samples were shipped on October 5, 1992. A copy of all correspondence is also included in Appendix 2.

3.3 Analytical Methodology

Participating laboratories were requested to analyze the solutions using their routine in-house methods used to analyze ambient air or precipitation samples for the IADN program: The solutions were ready for direct instrumental injection and participants were asked not to do any sample preparation steps. Participants were requested on the report form provided (Appendix 2) to summarize their Instrument and Detector used for the analysis. Information regarding the gas chromatograph column was requested at a later date. All participants were assigned a unique identification code that does not correspond to the order the participants are listed in Appendix 2.

3.4 Data Reporting

Results were submitted to the QMU, LSB in written form. All data were manually entered by laboratory code into an electronic spreadsheet.

The participating laboratories were mailed a copy of the tables of results on January 15, 1993. Three participants submitted revisions to some of their results. For all of these participants, both sets of results are included in the tables. Their comments are noted as foot-notes to the tables and discussed in the individual laboratory review.

The interlaboratory mean, median, standard deviation (SD), and relative standard deviation (%RSD) were calculated for each parameter in each of the ampoules for which there were 2 or more results reported, and are included in Tables 1-4, Appendix 1. For p,p-DDD in Ampoule OC2, Laboratory 9236's result was excluded from the calculation of the interlaboratory mean, median, SD and %RSD. The explanation for this is given in the individual review of this participant's results in section 4.

The results for each participant were also plotted to facilitate interpretation of the interlaboratory performance. The results for each parameter are plotted as a difference from the target versus concentration, both as an absolute value (ng/mL) and as a percentage difference from the target. These figures are all included in Appendix 1.

4 DISCUSSION

OVERVIEW OF INTERLABORATORY PERFORMANCE

Results were received from all of the participants who received the ampouled solutions. Qualifying remarks from the participants are provided in the individual laboratory review below. A description of the principles upon which the following discussion is based is provided in Appendix 3.

The results for *a*-Hexachlorocyclohexane (*a*-HCH) in Figure 1 demonstrate a negative slope bias among the participants. Only Laboratory 9236 had a positive slope. Ail of the participants except Laboratory 9236 agreed with each other within ±10% at the higher concentrations (Figure 2). However they are biased low relative to the target, except for Laboratory 9236's result for OC2.

The *y*-Hexachlorocyclohexane (*y*-HCH) results (Figure 3) indicate a negative slope bias. All of the participants agreed with each other within a range of 1-2.5 ng/mL across the concentration range, but were low relative to the target. At the higher concentrations, this range of agreement is within 15% (Figure 4).

The majority of participants have good agreement with the target and each other for p.p-DDT (Figures 5 and 6). Laboratory 9232 was erratic and Laboratory 9236 has a negative slope bias.

The results for o,p-DDT (Figure 7) demonstrate very good agreement with the target and among the participants. Laboratory 9234 appears to have a slight negative slope problem. There may be a slight degree of curvature at the highest concentration, as many of the participants have a positive difference from the target for samples OC3 and 0C4, but then have a slight negative difference from the target for OC2. The overall between laboratory variability is 20%, except for Laboratory 9232 in Ampoule OC1.

All of the participants' results for p,p-000 are plotted in Figures 9 and 10, but a second set of graphs with Laboratory 9236 excluded are also presented in Figures 11 and 12. See individual discussion below for an explanation of Laboratory 9236's results for p,p-DDD. The majority of the other participants demonstrate good agreement with the target and with each other for p,p-DDD (Figure 11). Laboratory 9234 has a negative slope problem. The range of results between the participants is approximately 20% (Figure 12).

The p.p-DDE results (Figure 13) demonstrate consistent performance across the concentration range for most participants, with generally good agreement with the target. Laboratory 9233-V was biased high. Laboratories 9234 and 9236 have a negative slope problem. Excluding Laboratory 9233-V, and Laboratory 9236 for Ampoules OC1 and OC2, the between laboratory variability is approximately 20% (Figure 14).

The majority of the participants reported results for *a*-Chlordane that differed from the target by approximately - 10%. This was consistent across the analytical range (Figure 15). Agreement among the participants was within a range of approximately 10%, except for Laboratory 9234 in Ampoules 0C4 and OC1 (Figure 16). Laboratory 9234 has a negative slope problem.

The results for *y*-Chldrdane (Figure 17) demonstrate consistent performance by all of the participants across the analytical range, except for Laboratory 9234. The consensus among the participants suggests a -5% difference from the target, with a range of 10% among the majority of participants, except for Laboratory 9234 (Figure 18). For most programs, this degree of variability is better than expected.

Laboratories 9233-V and 9234 did not report a positive response for the lowest concentration of Heptachlor Epoxide (Ampoule OC1, Table 1). This may have been below these participants' detection limit for this parameter. Agreement was very good among the participants and with the target value for Heptachior Epoxide (Figure 19). Laboratory 9234 was erratic for this parameter. Excluding Laboratory 9234, the between laboratory variability was 10-15% (Figure 20).

Most participants demonstrated consistent performance across the concentration range for Methoxychlor (Figure 21). Laboratory 9234 was biased high. Laboratory 9232 was erratic and may have a curvature problem at the higher concentration level. Excluding Laboratory 9234, and Laboratory 9232 for Ampoule 0C3, the between laboratory variability was approximately 25% (Figure 22).

The Dieldrin results (Figures 23 and 24) demonstrate consistent performance across the concentration range by most participants. There is a between-laboratory range of approximately 30%. Laboratory 9231 was biased slightly high compared to the other participants. Laboratory 9236 has a slight negative slope problem.

For Hexachlorobenzene (HCB), Laboratory 9236 has a high positive slope bias and Laboratory 9234 has a large negative slope bias. The other participants demonstrate consistent performance across the analytical range and acceptable agreement with the target (Figure 25). The overall results demonstrate a between-laboratory range of 40% (Figure 26).

Most participants demonstrated consistent performance across the concentration range for Endosulfan I (Figure 27). Laboratory 9233-HP may have a curvature problem at the highest concentration level. Laboratory 9234 is biased high and may also have an intercept problem. The between-laboratory range is approximately 20% (Figure 28), excluding Laboratory 9234 for OC2 and OC1, and Laboratory 9233-HP for 0C4.

The Endosulfan II results show consistent performance across the concentration range (Figure 29) except for Laboratory 9231. There is a slight drop at the higher concentration levels (0C4 and OC2) which may indicate some curvature. Laboratory 9231 has a positive slope bias. The between-laboratory range, excluding Laboratory 9231, is approximately 10-15% (Figure 30).

Graphs were not plotted for those parameters with less than five sets of results. Only Laboratory 9234 reported results for o,p-DDE. They were low relative to the target with a possible negative slope (Tables 1-4).

Only three participants reported results for o,p-DDD. Agreement with the target and each other was good at the lower concentrations (Tables 2-4), but all three laboratories were biased low at the highest concentration (Table 1), suggesting a slope problem.

Four laboratories reported results for Endrin. Two laboratories were high and two were low (Tables 1,2 and 4), indicating no consensus among the participants or agreement with the target. Endrin is part of the secondary list of target parameters for the IADN program[2]. These results indicate that the use of a reference standard to validate the

accuracy of calibration standards is particularly important for the laboratories contributing Endrin data to the central IADN database.

Four laboratories reported results for Oxychlordane. All the results were low relative to the target value (Tables 1-4). Laboratory 9234 was erratic, as they had a positive result for the lowest concentration sample (OC3) but reported "ND" for the second concentration level (OC2).

The main source of between-laboratory variability appears to be slope bias. This may be corrected with the use of a reference standard by all participants contributing to the central IAON database, as mentioned above for Endrin. Temperature programming conditions, gas flow rates, detector differences, and software integration differences are some of the other possible sources of variation between the participants. While all the participants used a DB-5 capillary column as one of their analytical columns (Table 5), there were differences in column length (30 m or 60 m) that may also contribute to variability among the participants, due to the presence of co-eluters or poor resolution between analytical peaks.

INDIVIDUAL LABORATORY PERFORMANCE

Laboratory 9231

Laboratory 9231 noted with their results that they routinely analyze samples for OC's using a DB-5 column. A second injection was done using a DB-17 column for confirmation for those parameters that had non-optimal resolution on the DB-5 column. Those parameters were o,p-DDD, Heptachlor Epoxide, Dieldrin, and Oxychlordane. They did not indicate whether this was a routine procedure that would be used for samples.

They had very good agreement with the target for most parameters. They were biased low for *a*-HCH and *y-HCH.* They had a high slope bias for Dieldrin and Endosulfan II, though they were within 10-15% of the target.

Laboratory 9232

Laboratory 9232 demonstrated erratic performance for p,p-DDT, o,p-DDT, and Methoxychlor. They should investigate their instrumental conditions with respect to these three parameters. Performance was consistent for the other parameters in this study. They generally had good agreement with the target, with some slight high or low slope biases for a few parameters.

Laboratory 9233

Laboratory 9233 analyzed the solutions using two different instruments. Their results are marked "-HP" and "-V" in Tables 1-4 to correspond with the two systems listed in Table 5. When they received the original table of results, they questioned their own results for Heptachlor Epoxide, Hexachlorobenzene, and Oxychlordane, particularly in regards to the age of their own calibration standard. A new calibration standard was immediately prepared, and when compared to their old standard, they noted the differences for the above three parameters. They re-analyzed the interlaboratory study solutions and submitted revised results for the above three compounds, though the same values were obtained for Heptachlor Epoxide using the Vartan system. The

original results are enclosed in brackets in the tables of results, with the revised results being used for the statistical calculations and the graphs.

The results using the HP system demonstrated consistent performance across the concentration range for all parameters except Endosulfan I. They may have a curvature problem at the highest concentration level in this study, as they reported a much lower result for ampoule 0C4 than the target (Figure 27).

The results using the Varian system also demonstrated consistent performance across the concentration range except for p,p-DDE and Heptachlor Epoxide. The results for p.p-DDE (Figure 13) indicate a high slope bias. Using the Varian system. Laboratory 9233 did not report a positive response for Heptachlor Epoxide in OC1, This suggests that this analytical system is not as sensitive for Heptachlor Epoxide but the Varian system had only a 5% difference from target at higher concentrations (Figure 20).

The results from the HP system were 10% lower than the results from the Varian system for the majority of parameters. As seen in Table 6 and Figure 31, there was a greater percentage of results from the Varian in the range 90-110% and 110-130% of target than for the HP system. Laboratory 9233 used the same calibration standard and the same type of capillary columns on both instrumental systems, it appears that the differences in the two sets of results are instrument related. Temperature programming conditions, gas flow rates, detector differences, and software integration differences are some of the possible sources of variation between the two data sets. Laboratory 9233 should do further investigations to resolve these differences so that they can report a consistent data set using either analytical system.

Laboratory 9234

Laboratory 9234 originally analyzed the solutions using a new Varian 3400 with a Septum Programmable Injector (SPI). When they received the original table of results, they investigated the possible sources of their discrepancies from the target and determined that the SPI was the source of their differences. They reanalysed the solutions using their older Vista 6000 with a split/splitless injector, and submitted a revised data set, requesting that the original data set be withdrawn. The original data set is included in Tables 1-4 and is marked with an asterisk. The revised data set was used for the statistical calculations and the graphs.

Laboratory 9234 had a negative slope problem and was biased low for most parameters. Their performance for Heptachlor Epoxide and Oxychlordane was erratic. For Heptachlor Epoxide at the low concentration (OC1) they reported "ND", while at the higher concentrations both positive and negative differences from the target were observed. For Oxychlordane, a "NO" was reported for a target value of 7.30 ng/mL (OC2), but a value of 2.54 ng/mL was reported for 0C3 that had a target value of 3.65. They had a high positive slope problem for Methoxychlor and Endosulfan I. Only for p,p-DDT did they demonstrate good performance across the concentration range with no slope problems and good agreement with the target. Verification of their standards with a common reference standard should improve Laboratory 9234's agreement with the other participants and the target.

Laboratory 9235

Laboratory 9235's results were the most consistent with the target and the most consistent in the centre of the range among the participants (Table 6 and displayed in

Figure 31). Only for Endosulfan II did they report the lowest results among the participants, but they differed from the target by only -10%.

Laboratory 9236 - ISWS

Laboratory 9236 provided revisions to their results after receiving the original tables of results. They reviewed their quantitation of o-HCH and found an error. They requantitated the chromatograph and provided revised results. The revised *a*-HCH results were used in the statistical calculations and graphs, with the original results included in Tables 1-4 in brackets.

They also noted that in their analytical system, p,p-DDD (on their target list) co-elutes with o.p-DDT (not on their target list). As their results were high for p,p-DDD, they attributed their bias to the co-elution of o.p-DDT. They subtracted the target value of o.p-DDT from their reported p,p-DDD value and submitted revised results. The original p,p-DDD results are retained as part of the data set, with the "corrected" results in square brackets. In a sample, this laboratory would not know that a peak identified as p,p-DDD could also include o.p-DDT unless they had a separate calibration standard. For unknown samples, they would be unable to subtract a "target value" of a co-eluting compound, so it would be inappropriate to do so for the interlaboratory study solutions. As seen in Table 2, their result for p.p-DDD in Ampoule OC2 was particularly biased high by this co-elution effect. Laboratory 9236's OC2 value has been excluded from the statistical calculations for p.p-DDD results as it is an obvious outlier.

Laboratory 9236 had a negative slope problem and were biased low for p,p-DDT, p,p-DDE and Dieldrin. They had the reverse problem for Hexachlorobenzene and o-HCH, for which they had a positive slope problem. They demonstrated consistent performance for *y*-HCH and Dieldrin.

5 CONCLUSION

The results of this interlaboratory study indicate that the participants have an agreement of ±20% to the target for most parameters. The within-laboratory performance tends to be consistent across the concentration range, though some participants were erratic for some parameters. Slope problems are the most common source of between-laboratory variability. As between-participant bias may be as high as 30-40%, the use of a common reference standard could help improve this bias to 10-15%. This would reduce the potential bias from the contributing laboratories to the central IADN database.

6 REFERENCES

1. International Joint Commission, United States and Canada; January 1988. *Revised Great Lakes Water Quality Agreement of 1978 as amended by Protocol signed November 18, 1987.*

2. Canada/U.S. Coordinating Committee on Annex 15; March 1990. *Integrated Atmospheric Deposition Network Implementation Plan.*

3. *Integrated Atmospheric Deposition Network 'STRAW MAN' Quality Assurance Program Plan* (DRAFT); November 1992.

7 APPENDIX 1 - RESULTS AND GRAPHS

TABLE 1 - Results for IADN 0C1 In ng/mL

PARAMETER	TARGET	9231	9232	9233-HP	9233-V	9234	9235	9236	MEAN	MEDIAN	SD	n	%RSD	9234 *
a-HCH	2.58	1.32	2.86	1.6	2.2	2.46	2.1	2.26 (0.537)	2.11	2.2	0.516	7	24.42%	2.35
g-HCH	15.60	13.61	12.86	12.4	14.1	12.19	13.2	13.793	13.20	13.2	0.741	7	5.62%	10.15
p,p-DDT	4.80	4.37	3.60	4.4	4.6	5.13	5.0	4.628	4.53	4.6	0.500	7	11.04%	2.94
o,p-DDT	2.40	2.36	1.90	2.4	2.6	2.53	2.2	N/A	2.33	2.36	0.253	6	10.86%	1.94
p,p-DDD	5.95	5.91	6.83	5.0	5.8	6.09	5.0	9.092 [6.68]	6.24	5.91	1.404	7	22.48%	ND
o,p-DDD	16.90	14.28	12.85	N/A	N/A	14.45	N/A	N/A	13.86	14.28	0.879	3	6.34%	11.39
p,p-DDE	2.55	2.33	2.22	2.2	3.0	3.72	2.3	3.1685	2.71	2.33	0.595	7	22.01%	ND
o,p-DDE	6.05	N/A	N/A	N/A	N/A	5.26	N/A	N/A	-	-	-	1	-	4.17
a-Chlordane	17.10	16.15	14.14	15.0	15.4	13.70	15.5	N/A	14.98	15.2	0.912	6	6.09%	10.28
g-Chlordane	5.50	5.07	5.38	4.9	5.1	5.27	5.2	N/A	5.15	5.15	0.168	6	3.26%	3.81
Heptachlor Epoxide	2.55	2.69	2.75	2.5 (ND)	ND	ND	2.5	N/A	1.74	2.5	1.352	6	77.67%	ND
p,p-Methoxychlor	14.70	15.97	10.08	11.4	14.3	19.82	12.7	N/A	14.05	13.5	3.511	6	25.00%	8.20
Dieldrin	5.40	6.11	5.01	4.7	5.4	4.82	4.6	5.675	5.19	5.01	0.580	7	10.80%	5.13
Hexachlorobenzene	2.65	2.19	2.46	2.8 (0.8)	3.1 (0.9)	2.57	2.7	2.941	2.68	2.7	0.305	7	11.40%	1.88
Endrin	16.60	26.00	13.39	N/A	N/A	20.61	13.6	N/A	18.40	17.105	6.077	4	33.03%	12.97
Endosulfan I	5.80	4.83	5.55	5.7	6.5	7.74	5.1	N/A	5.90	5.625	1.067	6	18.08%	7.53
Endosulfan II	2.53	2.81	2.48	2.4	2.7	N/A	2.3	N/A	2.54	2.48	0.212	5	8.34%	N/A
Oxychlordane	21.90	19.42	N/A	18.0 (ND)	19.6 (45.3)	21.13	N/A	N/A	19.54	19.51	1.280	4	6.55%	20.00

TABLE 2 - Results for IADN 0C2 in ng/mL

PARAMETER	TARGET	9231	9232	9233-HP	9233-V	9234	9235	9236	MEAN	MEDIAN	SD	n	%RSD	9234 *
a-HCH	15.11	12.52	13.70	11.4	13.0	12.17	12.9	16.67 (3.9585)	13.19	12.9	1.692	7	12.83%	13.25
g-HCH	5.20	3.33	5.04	3.8	4.7	4.37	4.5	4.5785	4.33	4.5	0.579	7	13.38%	3.74
p,p-DDT	2.40	2.17	2.77	2.3	2.4	2.92	2.6	1.942	2.44	2.4	0.343	7	14.05%	1.54
o,p-DDT	14.40	13.78	13.31	13.7	14.0	11.80	14.5	N/A	13.52	13.74	0.927	6	6.86%	7.87
p,p-DDD	2.98	3.06	3.51	2.7	3.0	3.55	2.5	17.829 # [3.43]	3.50	3.06	0.422	6	13.81%	2.20
o,p-DDD	6.30	5.52	7.12	N/A	N/A	5.55	N/A	N/A	6.06	5.55	0.915	3	15.09%	4.51
p,p-DDE	15.30	14.87	14.06	14.4	16.6	12.19	13.5	15.041	14.67	14.4	1.983	7	13.52%	9.33
o,p-DDE	3.03	N/A	N/A	N/A	N/A	2.62	N/A	N/A	-	-	-	1	-	2.13
a-Chlordane	5.70	5.01	5.31	5.0	5.3	5.19	5.2	N/A	5.17	5.195	0.136	6	2.63%	3.65
g-Chlordane	2.75	2.51	3.00	2.6	2.6	2.80	2.7	N/A	2.70	2.65	0.177	6	6.54%	1.98
Heptachlor Epoxide	15.30	15.19	14.85	14.8 (14.9)	15.6	16.85	15.2	N/A	15.42	15.195	0.760	6	4.93%	13.61
p,p-Methoxychlor	4.90	5.09	5.32	4.6	4.6	7.36	5.1	N/A	5.35	5.095	1.029	6	19.25%	3.86
Dieldrin	2.70	3.03	2.39	2.5	2.5	2.49	2.5	2.9565	2.62	2.5	0.256	7	9.77%	2.13
Hexachlorobenzene	15.90	14.59	13.06	17.1 (5.0)	17.7 (5.2)	11.62	16.2	20.22	15.78	16.2	2.928	7	18.55%	10.76
Endrin	5.60	8.23	5.44	N/A	N/A	7.65	4.6	N/A	6.48	6.545	1.737	4	26.80%	5.64
Endosulfan I	2.90	2.51	3.30	3.1	3.4	4.09	2.5	N/A	3.15	3.2	0.601	6	19.06%	4.03
Endosulfan II	15.15	16.86	13.80	13.7	14.8	N/A	13.5	N/A	14.53	13.80	1.395	5	9.60%	N/A
Oxychlordane	7.30	6.26	N/A	5.8 (13.5)	6.1 (14.1)	ND	N/A	N/A	4.54	5.95	3.033	4	66.80%	ND

* Original results submitted by Laboratory 9234 using Septum Programmable Injector (SPI). See individual lab review for detailed explanation.

( ) Results in brackets were original values reported by Laboratories 9233 and 9236. See individual lab reviews for detailed explanation.

[ ], # "Corrected" results for Laboratory 9236. See individual lab review for explanation. # result excluded from statistical calculations

TABLE 3 - Results for IADN OC3 in ng/mL

PARAMETER	TARGET	9231	9232	9233-HP	9233-V	9234	9235	9236	MEAN	MEDIAN	SD	n	%RSD	9234 *
a-HCH	5.04	2.98	5.17	3.3	4.3	4.46	4.4	4.54 (1.077)	4.16	4.4	0.760	7	18.25%	5.00
g-HCH	2.60	1.59	2.74	1.9	2.4	2.17	2.3	2.2095	2.19	2.2095	0.366	7	16.73%	1.88
p,p-DDT	11.52	11.81	14.46	10.8	11.2	9.96	11.3	9.431	11.28	11.2	1.622	7	14.38%	6.50
o,p-DDT	4.80	5.06	5.24	4.7	5.2	4.52	4.7	N/A	4.90	4.88	0.302	6	6.16%	4.03
p,p-DDD	14.28	15.09	13.91	12.3	13.7	11.55	13.6	18.406 (13.81)	14.08	13.7	2.225	7	15.80%	9.60
o,p-DDD	3.15	2.81	3.32	N/A	N/A	2.79	N/A	N/A	2.97	2.81	0.300	3	10.10%	2.29
p,p-DDE	5.10	4.90	4.64	4.5	6.2	5.55	4.8	6.411	5.29	4.90	0.774	7	14.64%	2.11
o,p-DDE	14.52	N/A	N/A	N/A	N/A	10.14	N/A	N/A	-	-	-	1	-	9.52
a-Chlordane	2.85	2.59	2.90	2.6	2.8	2.86	2.7	N/A	2.71	2.85	0.139	6	5.15%	2.16
g-Chlordane	13.20	13.09	12.74	11.8	11.9	10.01	12.7	N/A	12.04	12.3	1.116	6	9.27%	8.46
Heptachlor Epoxide	5.10	5.06	5.24	4.9 (3.8)	5.3	5.02	5.1	N/A	5.05	5.08	0.247	6	4.88%	3.63
p,p-Methoxychlor	2.45	2.84	3.32	2.5	2.3	3.32	2.8	N/A	2.81	2.72	0.429	6	15.26%	ND
Dieldrin	12.96	13.97	12.33	11.5	12.5	9.46	11.4	13.028	12.03	12.33	1.435	7	11.93%	8.79
Hexachlorobenzene	5.30	4.73	4.69	5.6 (1.6)	6.0 (1.8)	4.25	5.4	6.017	5.24	5.4	0.693	7	13.22%	3.83
Endrin	2.80	4.97	3.03	N/A	N/A	4.05	2.4	N/A	3.61	3.54	1.132	4	31.33%	2.40
Endosulfan I	13.92	13.96	13.12	14.3	15.2	15.24	14.6	N/A	14.40	14.45	0.803	6	5.58%	16.56
Endosulfan II	5.05	5.87	5.34	4.8	5.2	N/A	4.7	N/A	5.18	5.2	0.466	5	9.04%	N/A
Oxychlordane	3.65	3.33	N/A	2.8 (5.4)	3.2 (7.4)	2.54	N/A	N/A	2.97	3.0	0.363	4	12.25%	3.48

TABLE 4 • Results for IADN 0C4 in ng/mL

PARAMETER	TARGET	9231	9232	9233-HP	9233-V	9234	9235	9236	MEAN	MEDIAN	SD	n	%RSD	9234 *
a-HCH	12.08	9.38	11.69	9.1	10.4	9.88	10.2	12.11 (2.9365)	10.39	10.2	1.128	7	10.85%	11.00
g-HCH	10.40	8.16	9.68	8.3	9.5	7.75	9.2	8.5015	8.73	8.5015	0.735	7	8.42%	7.03
p,p-DDT	16.32	16.99	20.06	16.1	16.1	15.12	13.5	10.05	15.42	16.1	3.097	7	20.09%	9.37
o,p-DDT	11.52	11.96	12.30	11.7	12.1	10.09	10.5	N/A	11.44	11.83	0.919	6	8.03%	8.76
p,p-DDD	20.23	20.87	20.37	18.5	19.5	17.01	19.7	28.0335 (16.514)	20.57	19.7	3.528	7	17.15%	12.81
o,p-DDD	12.60	11.46	11.30	N/A	N/A	9.52	N/A	N/A	10.76	11.30	1.077	3	10.01%	8.38
p,p-DDE	12.24	12.21	11.49	10.9	15.0	10.88	11.7	13.52	12.24	11.7	1.514	7	12.37%	5.79
o,p-DDE	20.57	N/A	N/A	N/A	N/A	15.07	N/A	N/A	-	-	-	1	-	13.13
a-Chlordane	11.40	10.66	10.65	10.4	10.8	9.22	10.5	N/A	10.37	10.575	0.581	6	5.60%	7.38
g-Chlordane	18.70	18.38	18.12	17.2	16.8	14.72	17.7	N/A	17.15	17.45	1.326	6	7.73%	11.60
Heptachlor Epoxide	12.24	12.32	11.04	11.5 (11.6)	12.2	9.87	12.4	N/A	11.56	11.85	0.982	6	8.50%	7.32
p,p-Methoxychlor	9.80	11.71	12.64	10.3	9.6	14.79	10.2	N/A	11.54	11.005	1.944	6	16.85%	5.55
Dieldrin	18.36	20.57	17.39	16.8	17.9	13.88	15.8	18.525	17.25	17.39	2.107	7	12.21%	12.36
Hexachlorobenzene	12.72	11.84	10.08	13.6 (4.0)	14.5 (4.2)	9.43	13.2	16.015	12.67	13.2	2.366	7	18.68%	8.80
Endrin	11.20	16.28	11.05	N/A	N/A	14.04	9.3	N/A	13.17	12.545	3.930	4	29.85%	9.24
Endosulfan I	19.72	19.74	18.67	13.8	21.2	22.44	20.5	N/A	19.39	20.12	3.023	6	15.59%	22.65
Endosulfan II	12.12	14.14	11.98	11.6	12.1	N/A	11.0	N/A	12.16	11.98	1.185	5	9.74%	N/A
Oxychlordane	14.60	12.73	N/A	13.0 (27.0)	12.8 (29.1)	11.85	N/A	N/A	12.60	12.765	0.510	4	4.05%	12.80

* Original results submitted by Laboratory 9234 using Septum Programmable Injector (SPI). See individual lab review for detailed explanation.

( ) Results in brackets were original values reported by Laboratories 9233 and 9236. See individual lab reviews for detailed explanation.

[ ], # "Corrected" results for Laboratory 9236. See individual lab review for explanation. # result excluded from statistical calculations.

TABLE 5 - Instruments and GC Columns

Lab Code	9231	9232	9233-HP	9233-V	9234	9235	9236
Instrument	GC/ECD: HP5890	GC/ECD: HP5890	GC/ECD: HP5890	GC/ECD: Varian 3400	GC/ECD: Vista 6000 *	GC/ECD: HP5890	GC/ECD: HP5890
Column	DB-5, 60 m DB-17	DB-1, 30 m DB-5, 30 m	DB-5, 60 m DB1701, 60 m	DB-5, 60 m DB1701, 60 m	DB-5, 60 m	DB-1, 30 m DB-5, 30 m	DB-5, 30 m

All participants received a set of ampoules prepared in iso-octane.

* This participant originally analyzed the ampoules using a Varian Star 3400 GC/ECD, a DB-5 60 m column, and a new SPI (Septum Programmable Injector). It was subsequently discovered that the SPI was not suitable for pesticide analysis. The ampoules were re-analyzed using the above analytical system.

TABLE 6 - Distribution of Participants Results

LAB ID CODE	9231		9232		9233-HP		9233-V		9234		9235		9236	
Target Range	n	%	n	%	n	%	n	%	n	%	n	%	n	%
<60%	2	2.9%	0	0.0%	0	0.0%	1	1.7%	2	2.9%	0	0.0%	0	0.0%
60-75%	2	2.9%	3	4.7%	5	8.3%	0	0.0%	7	10.3%	0	0.0%	1	3.6%
75-90%	15	22.1%	10	15.6%	20	33.3%	9	15.0%	28	41.2%	23	38.3%	7	25.0%
90-110%	36	52.9%	41	64.1%	35	58.3%	40	66.7%	16	23.5%	37	61.7%	8	28.6%
110-130%	9	13.2%	9	14.1%	0	0.0%	10	16.7%	6	8.8%	0	0.0%	10	35.7%
>130%	4	5.9%	1	1.6%	0	0.0%	0	0.0%	9	13.2%	0	0.0%	2	7.1%

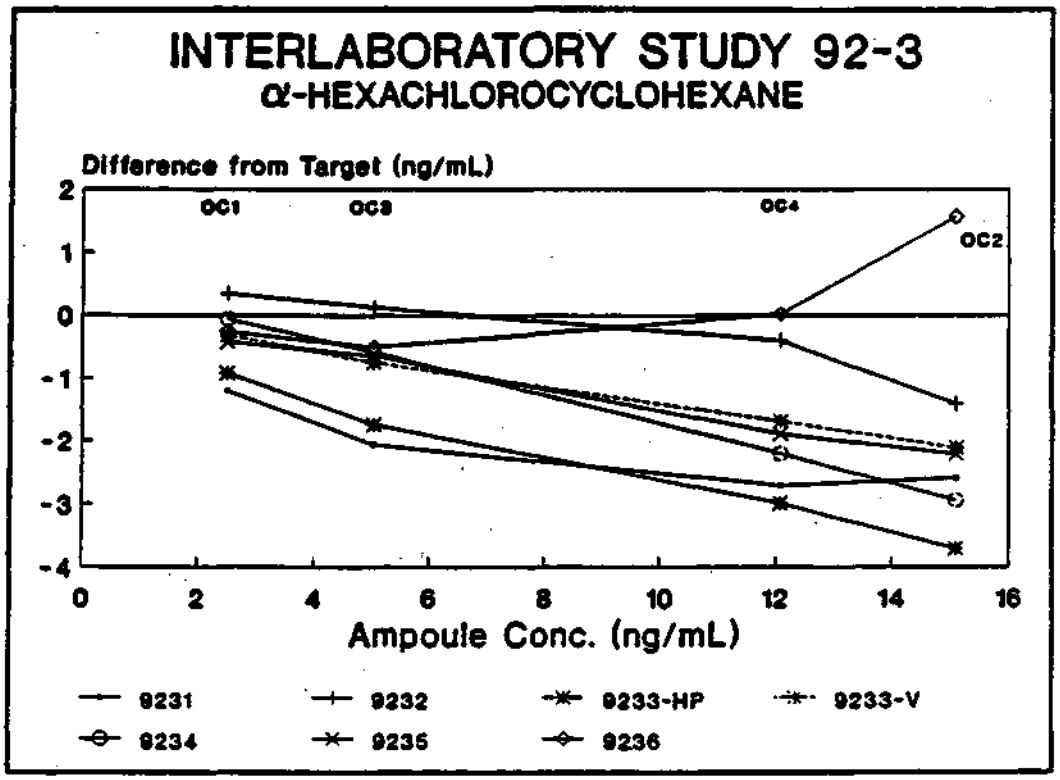

Figure 1 - Absolute Difference from Target

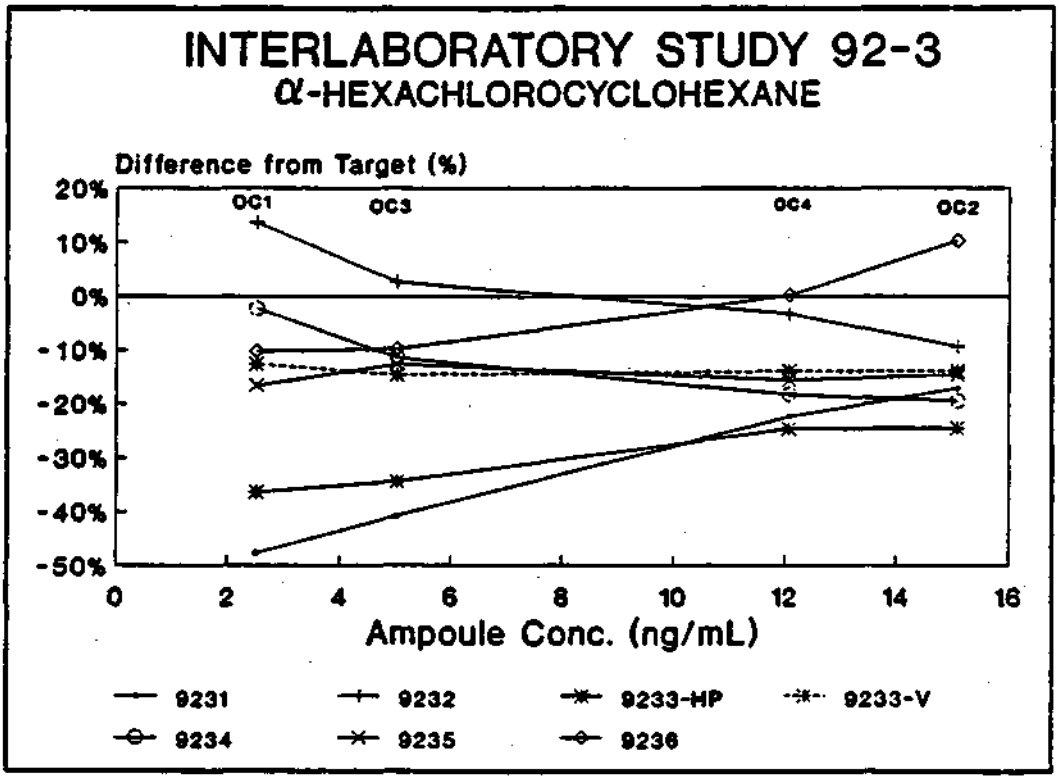

Figure 2 - Percent Difference from Target

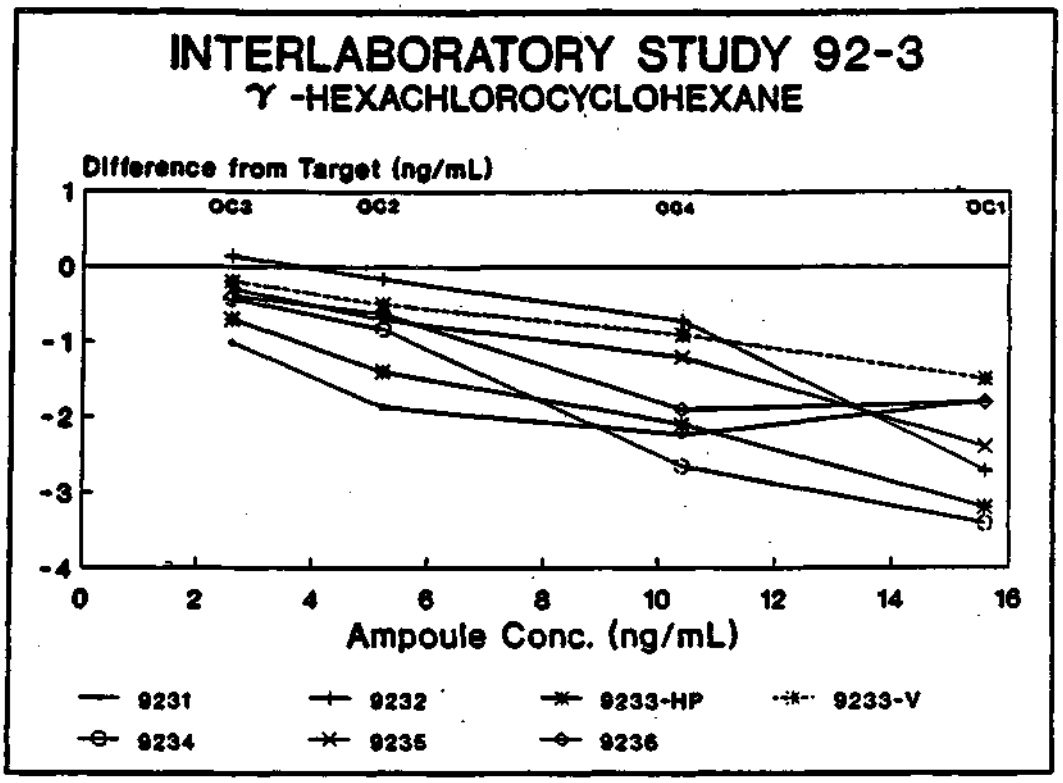

Figure 3 • Absolute Difference from Target

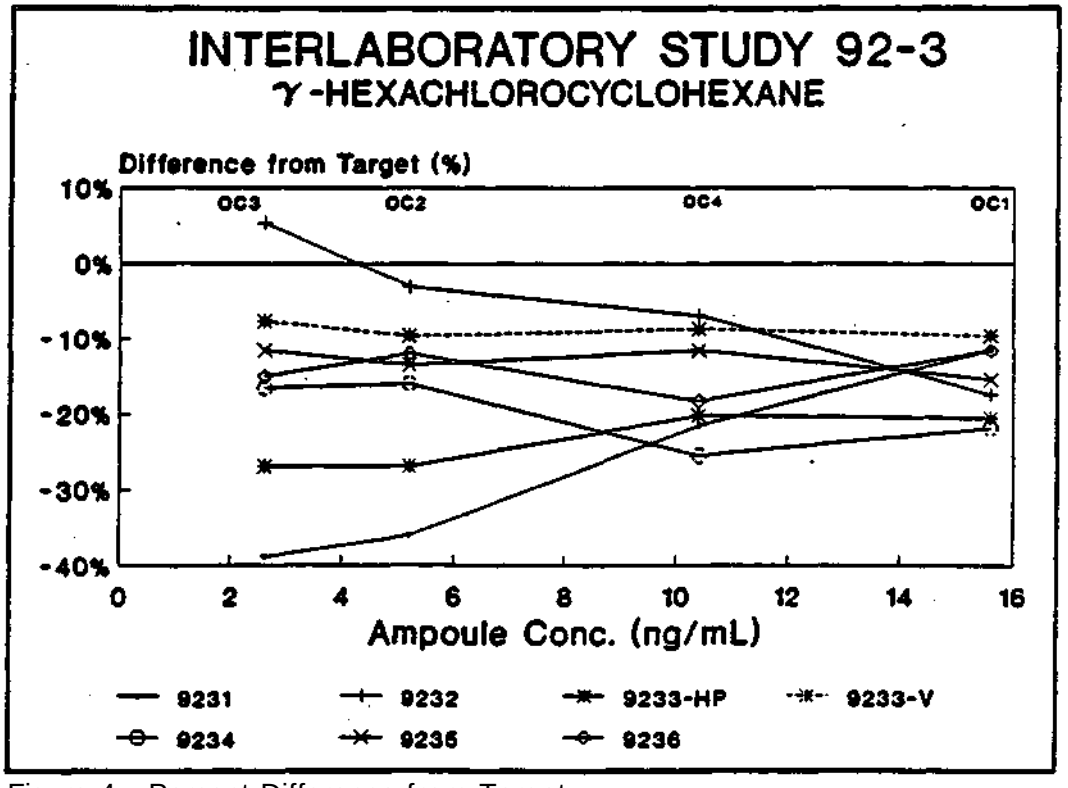

Figure 4 - Percent Difference from Target

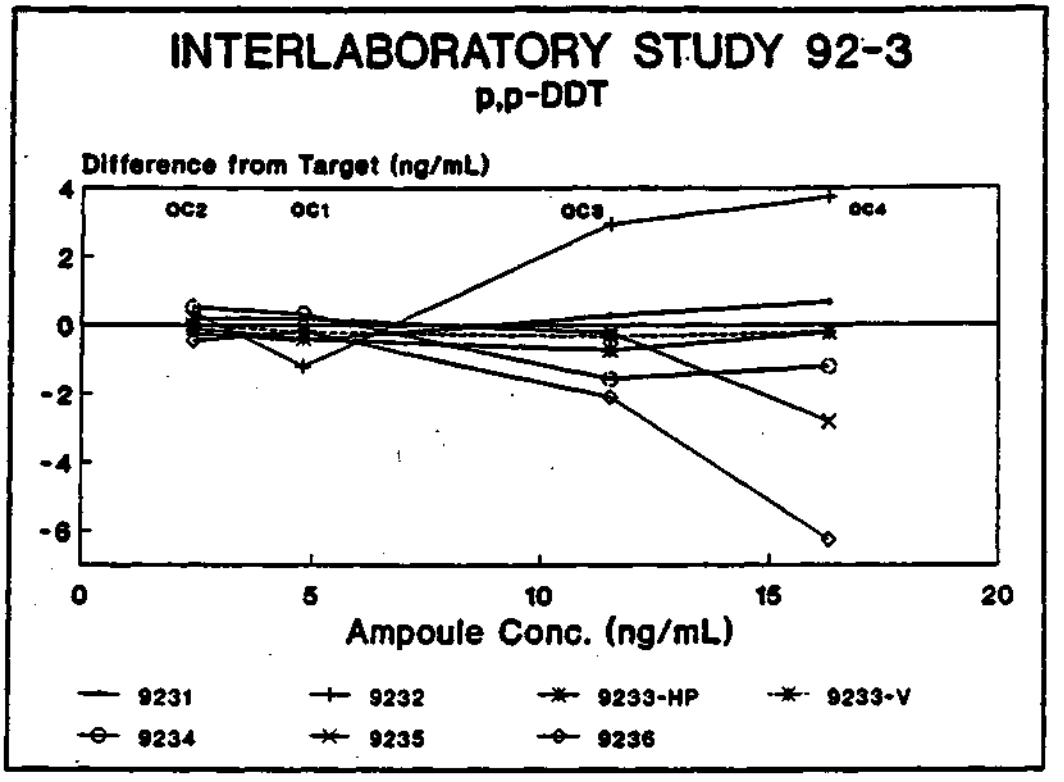

Figure 5 - Absolute Difference from Target

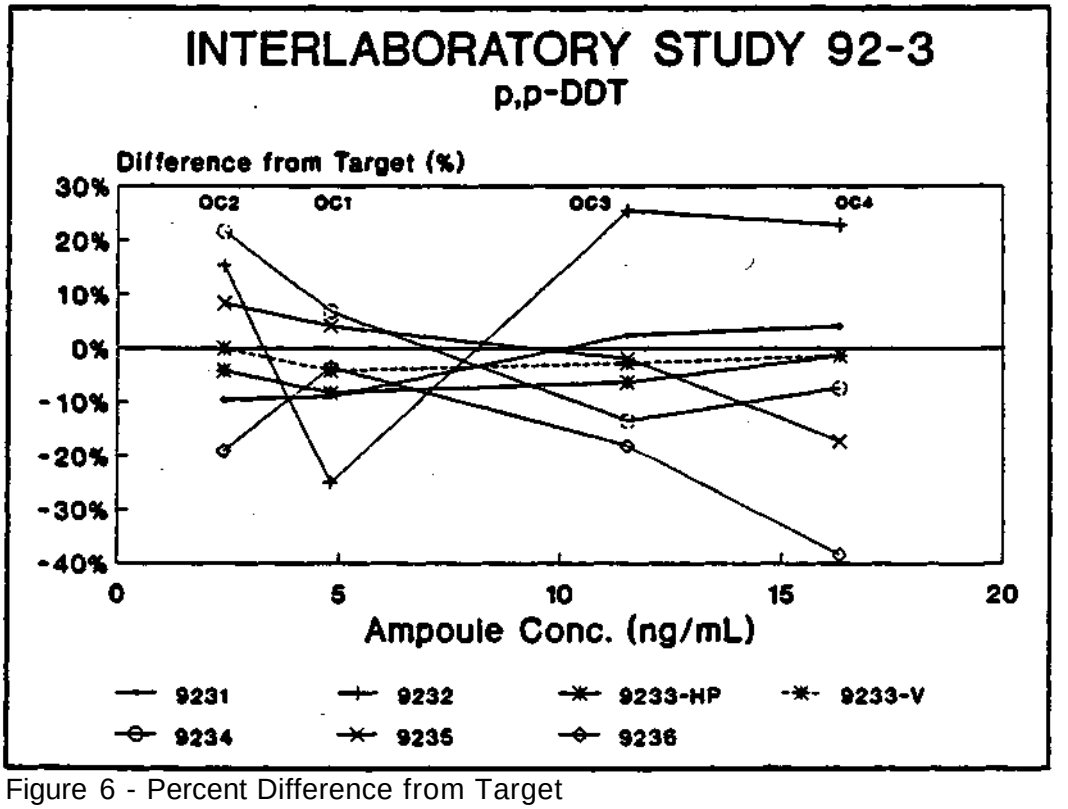

Figure 6 - Percent Difference from Target

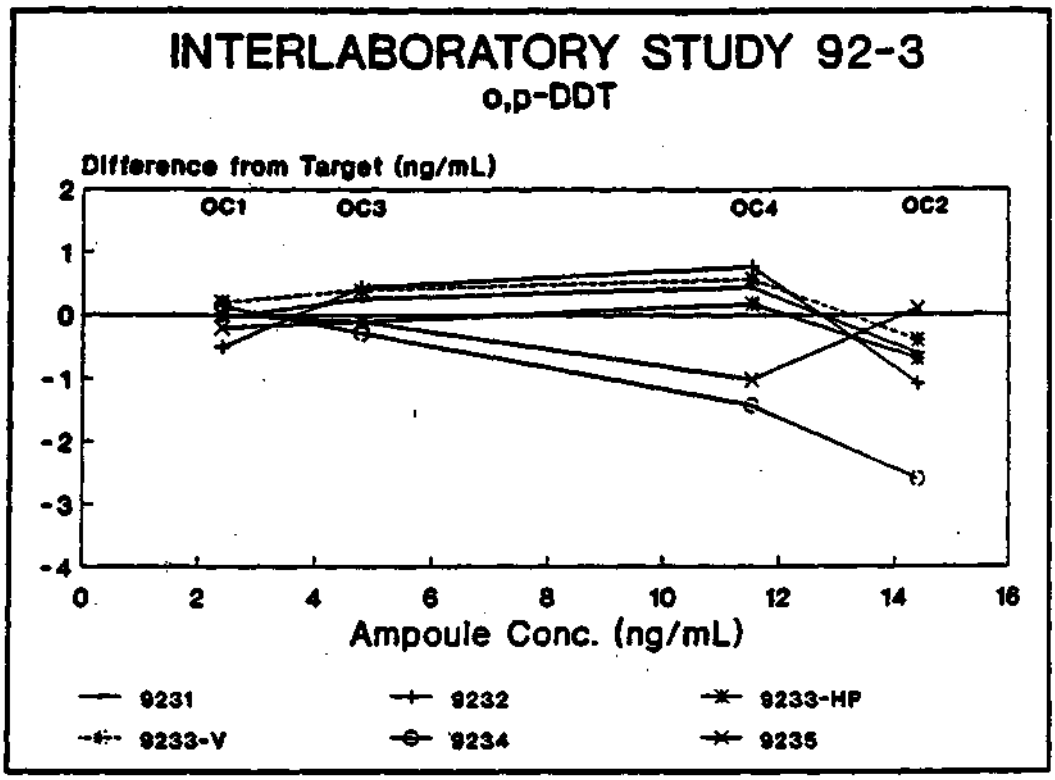

Figure 7 • Absolute Difference from Target

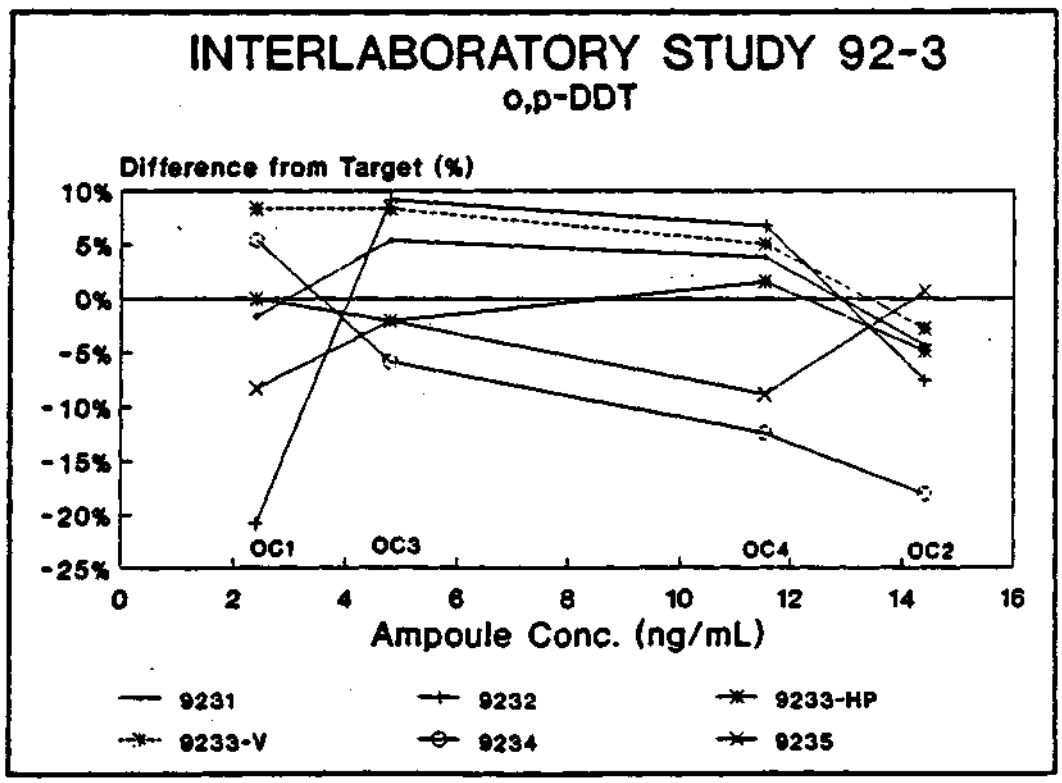

Figure 8 - Percent Difference from Target

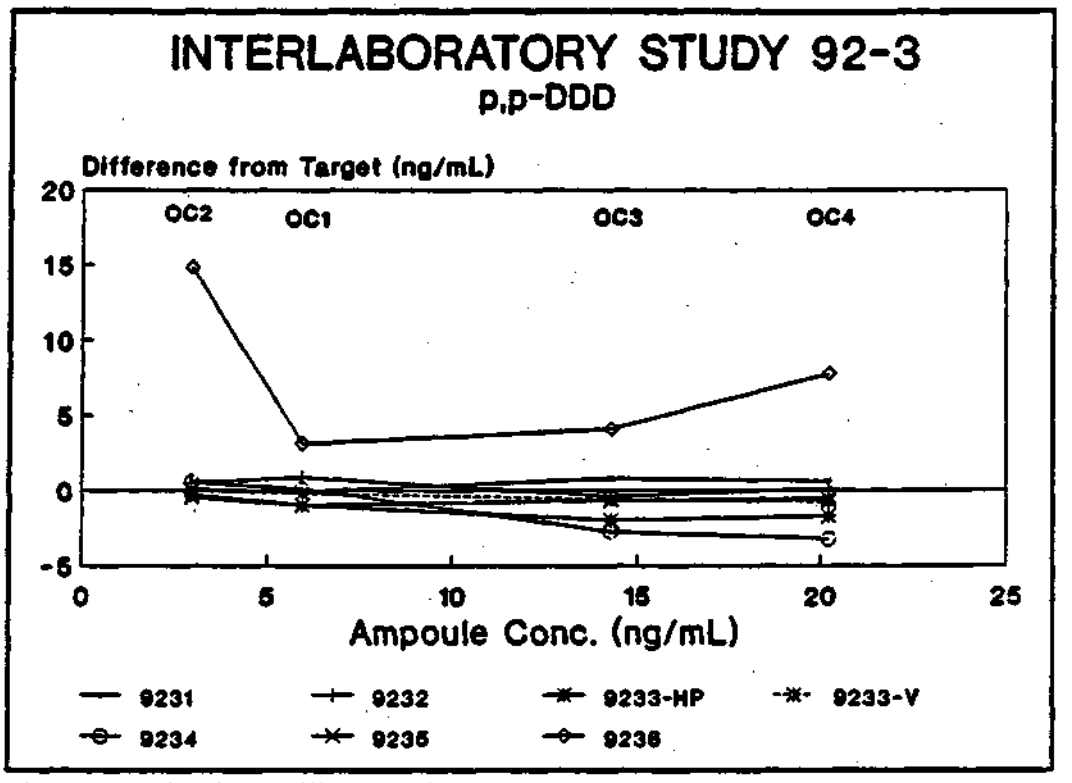

Figure 9 - Absolute Difference from Target

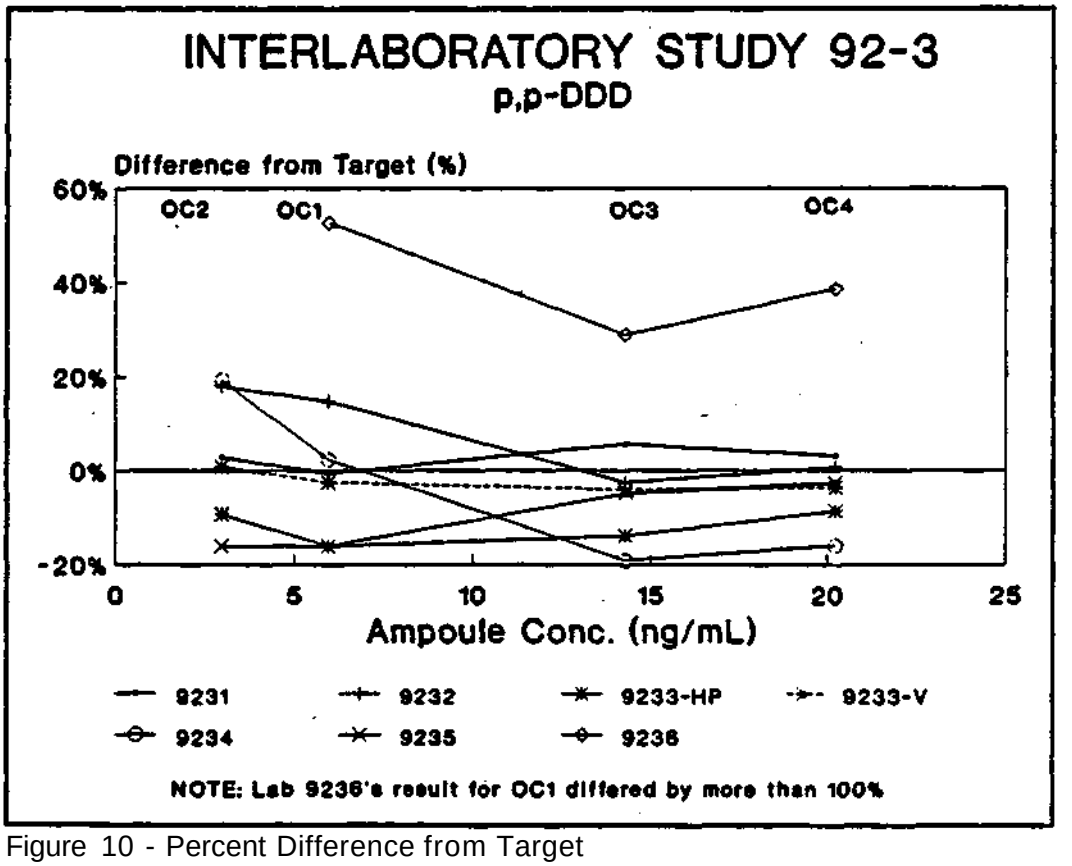

Figure 10 - Percent Difference from Target

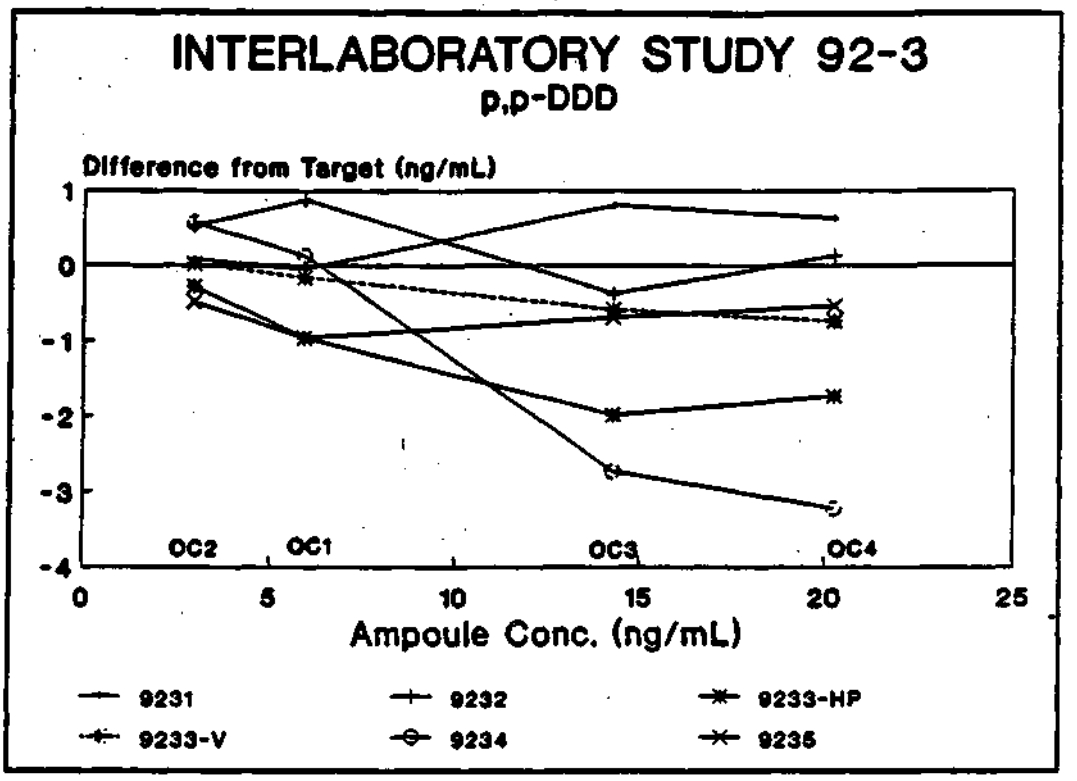

Figure 11 - Absolute Difference from Target

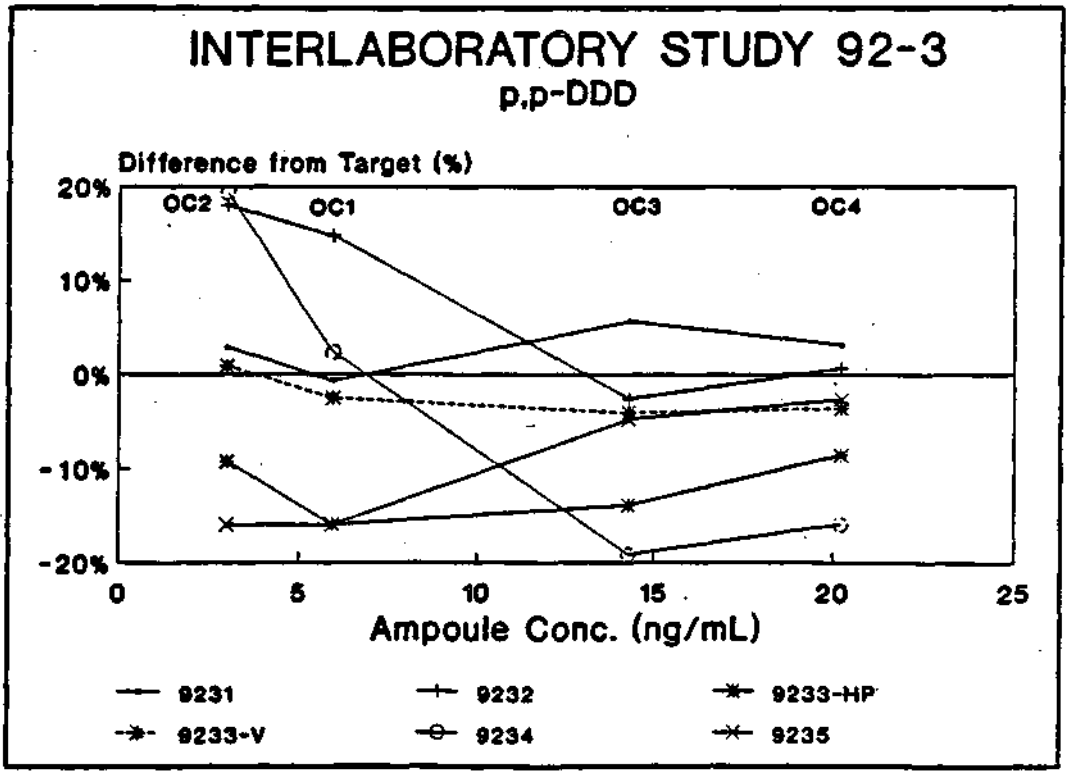

Figure 12 - Percent Difference from Target

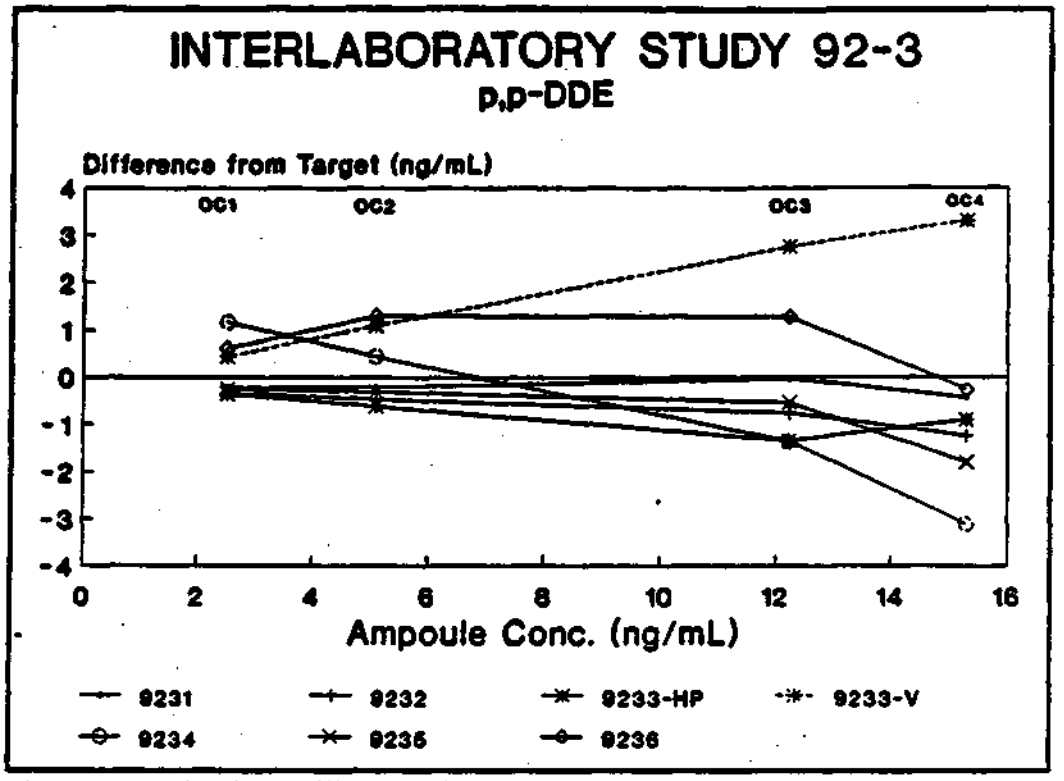

Figure 13 - Absolute Difference from Target

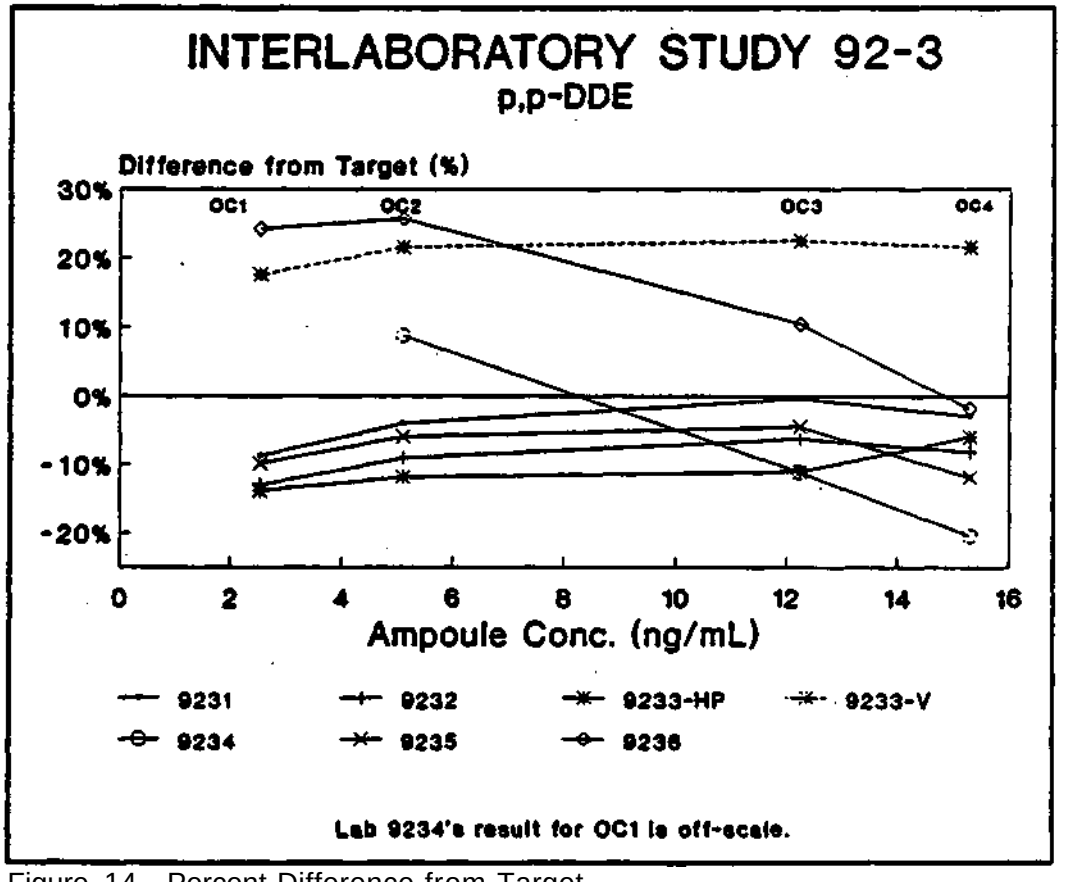

Figure 14 - Percent Difference from Target

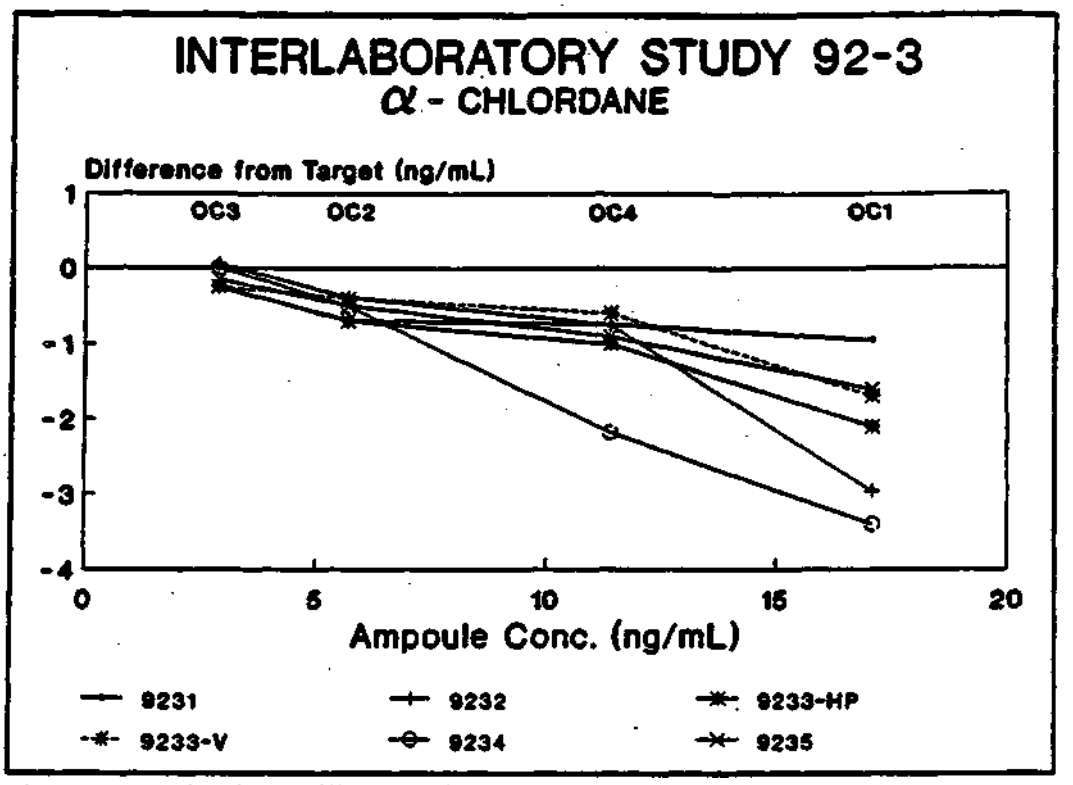

Figure 15 - Absolute Difference from Target

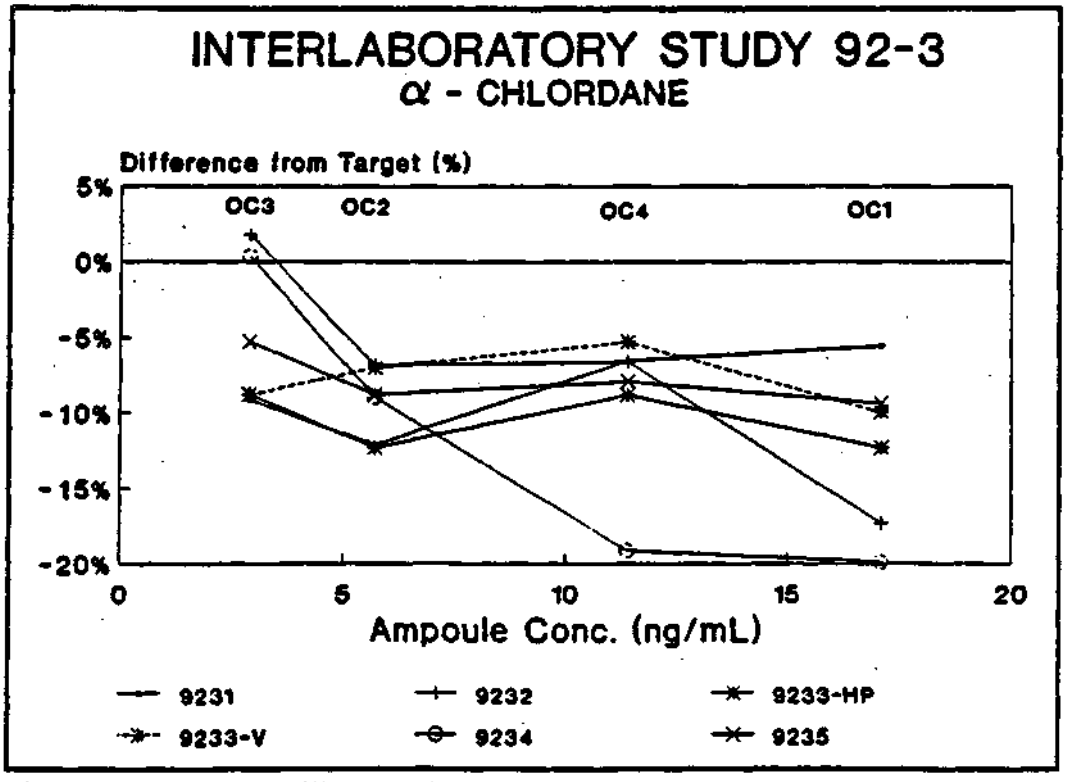

Figure 16 - Percent Difference from Target

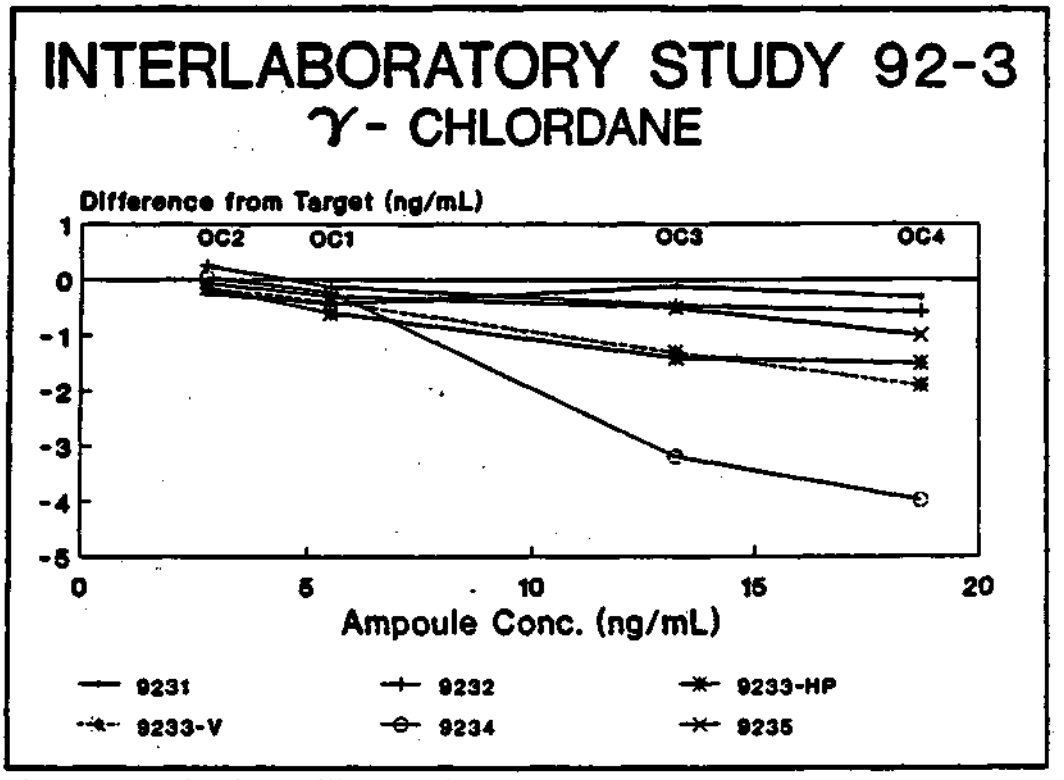

Figure 17 - Absolute Difference from Target

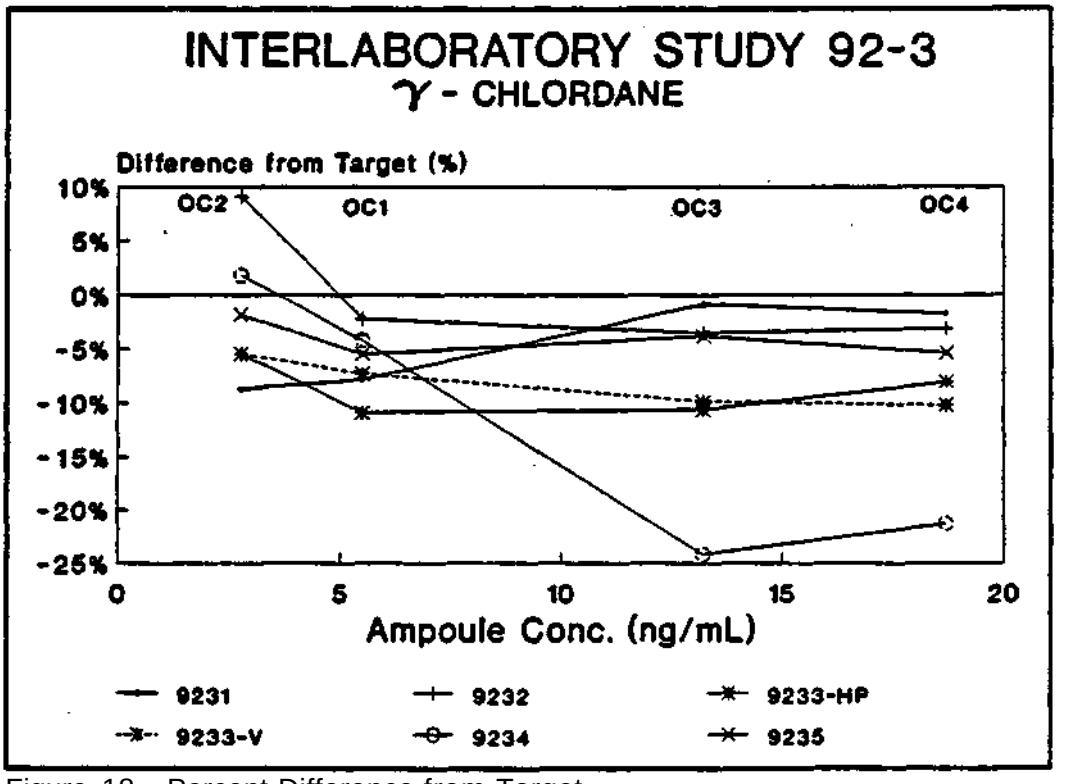

Figure 18 - Percent Difference from Target

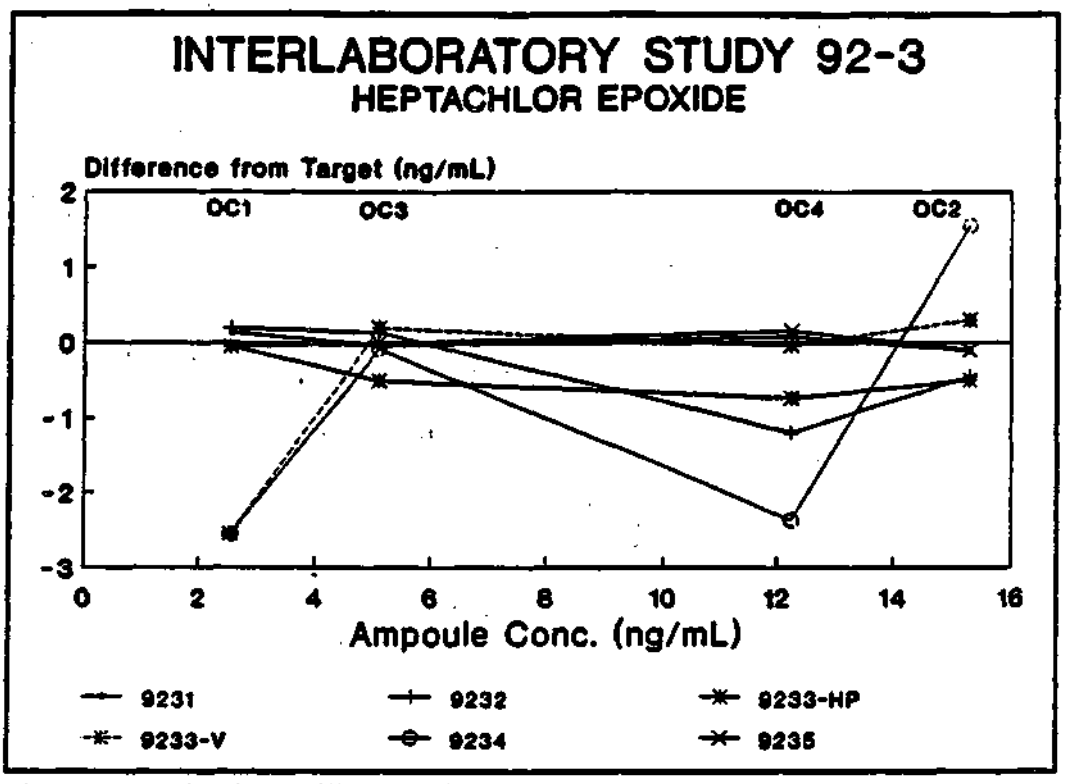

Figure 19 - Absolute Difference from Target

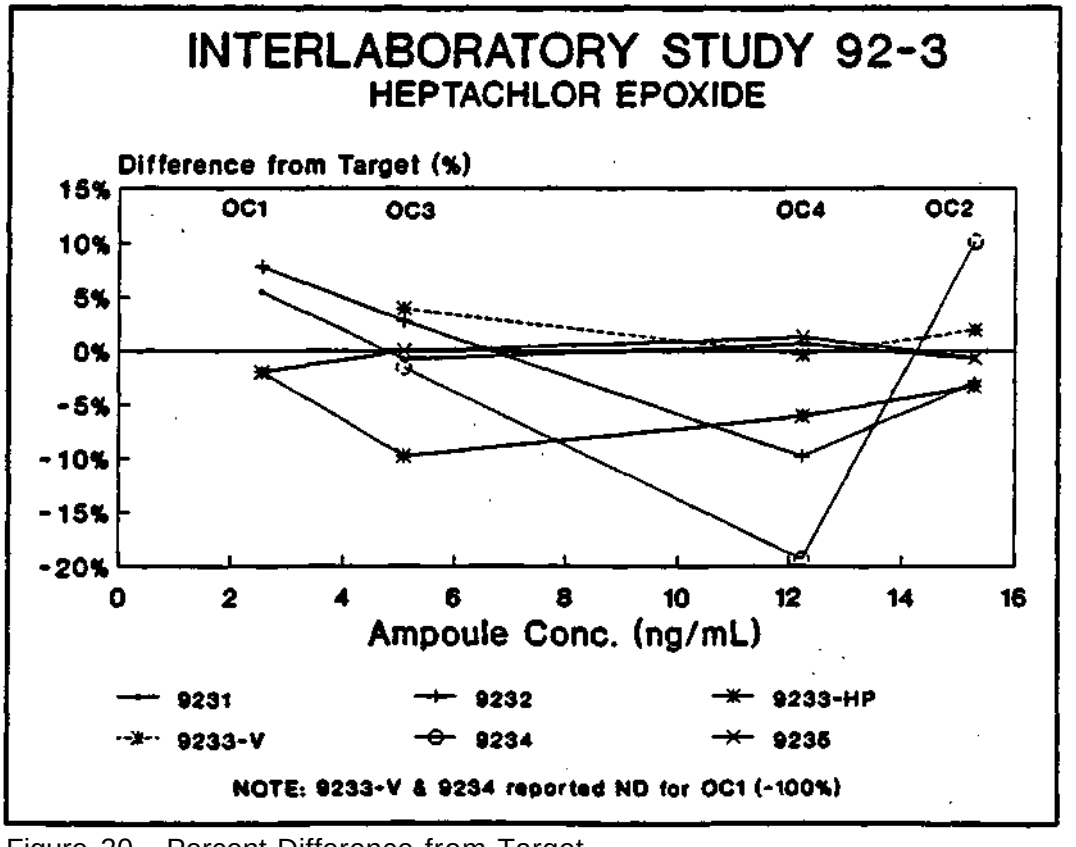

Figure 20 - Percent Difference from Target

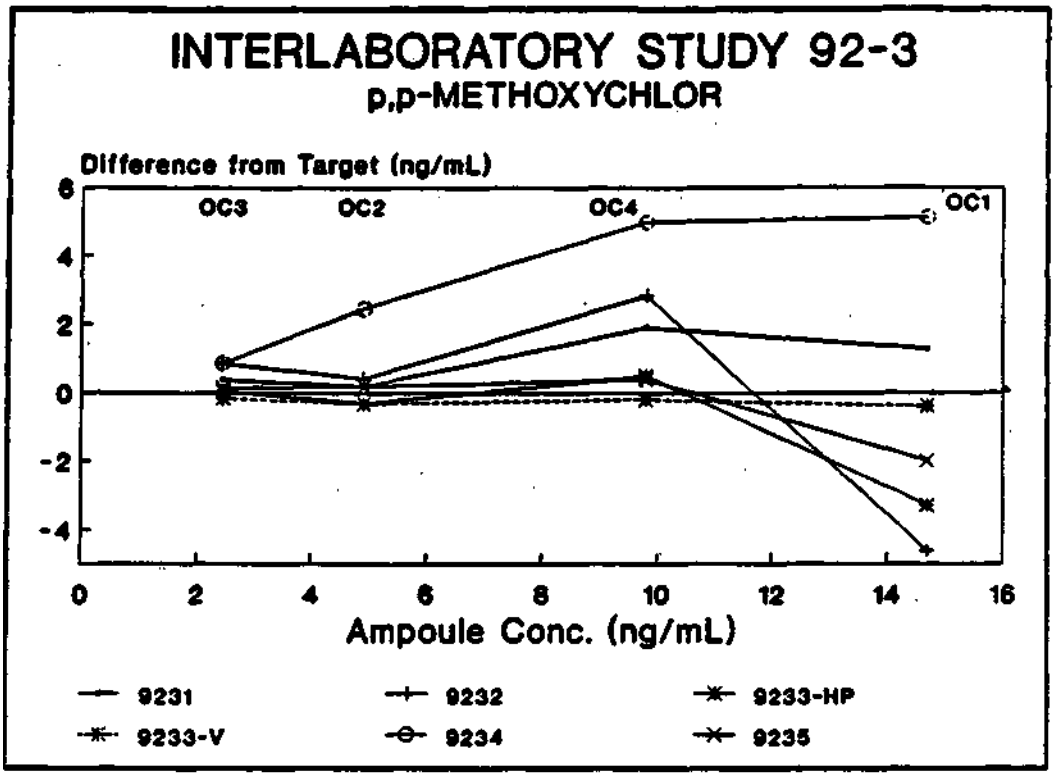

Figure 21 - Absolute Difference from Target

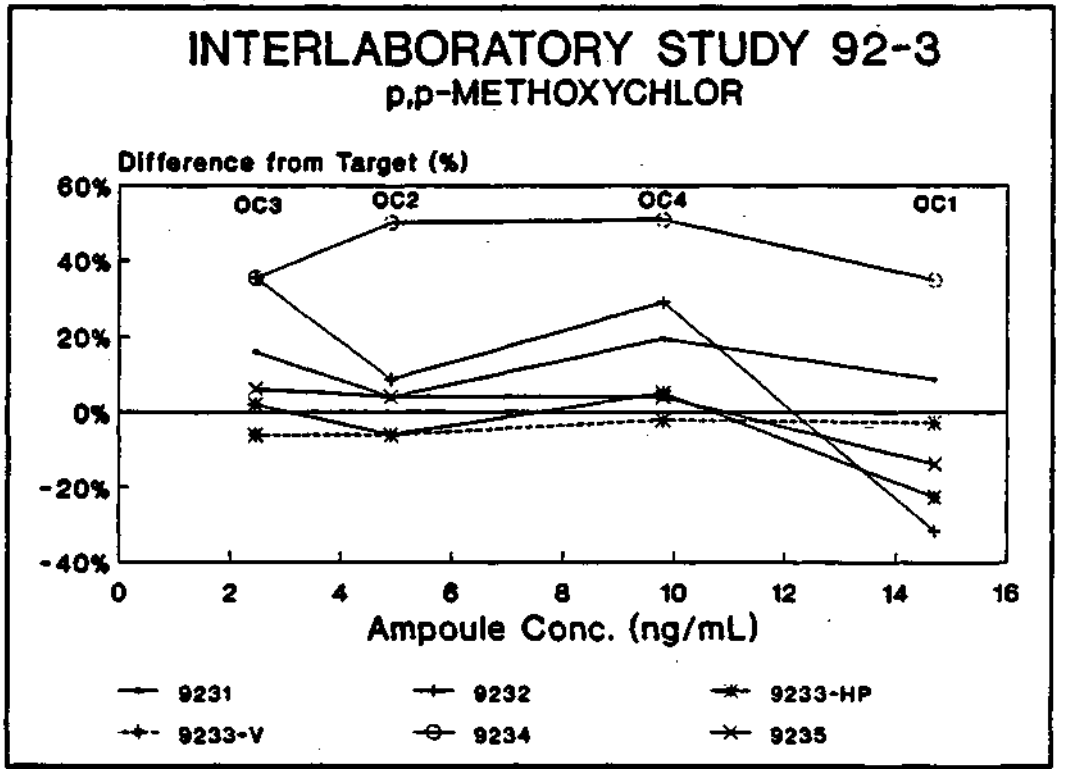

Figure 22 - Percent Difference from Target

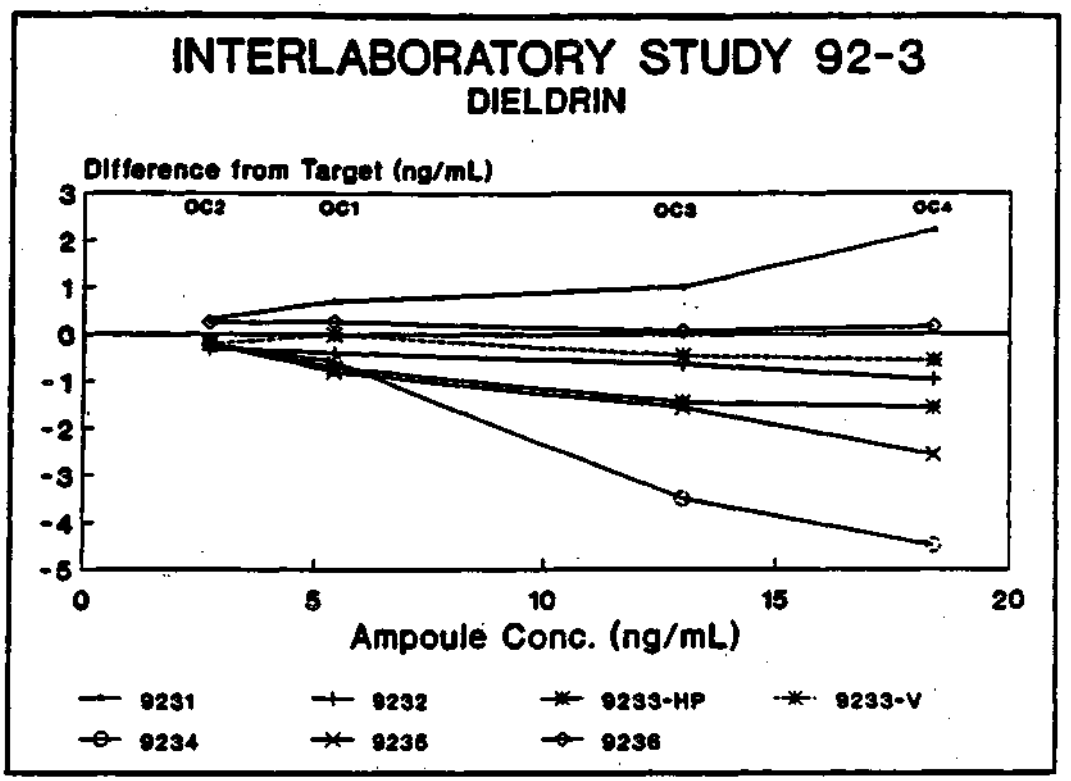

Figure 23 - Absolute Difference from Target

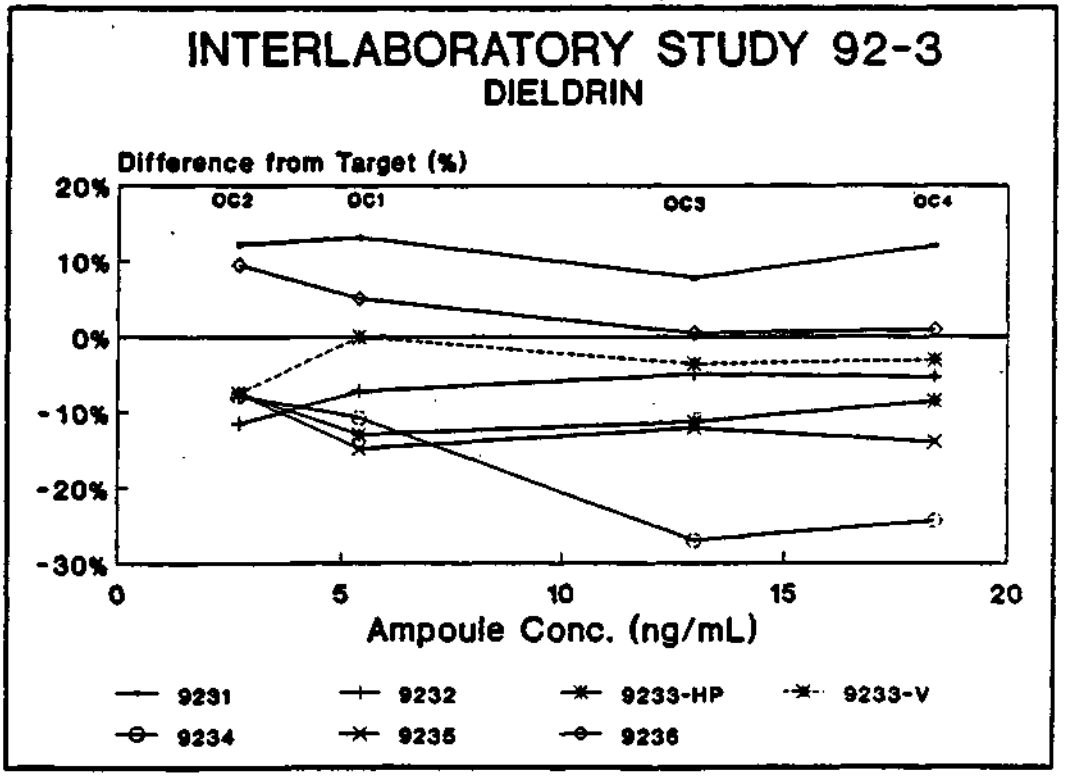

Figure 24 - Percent Difference from Target

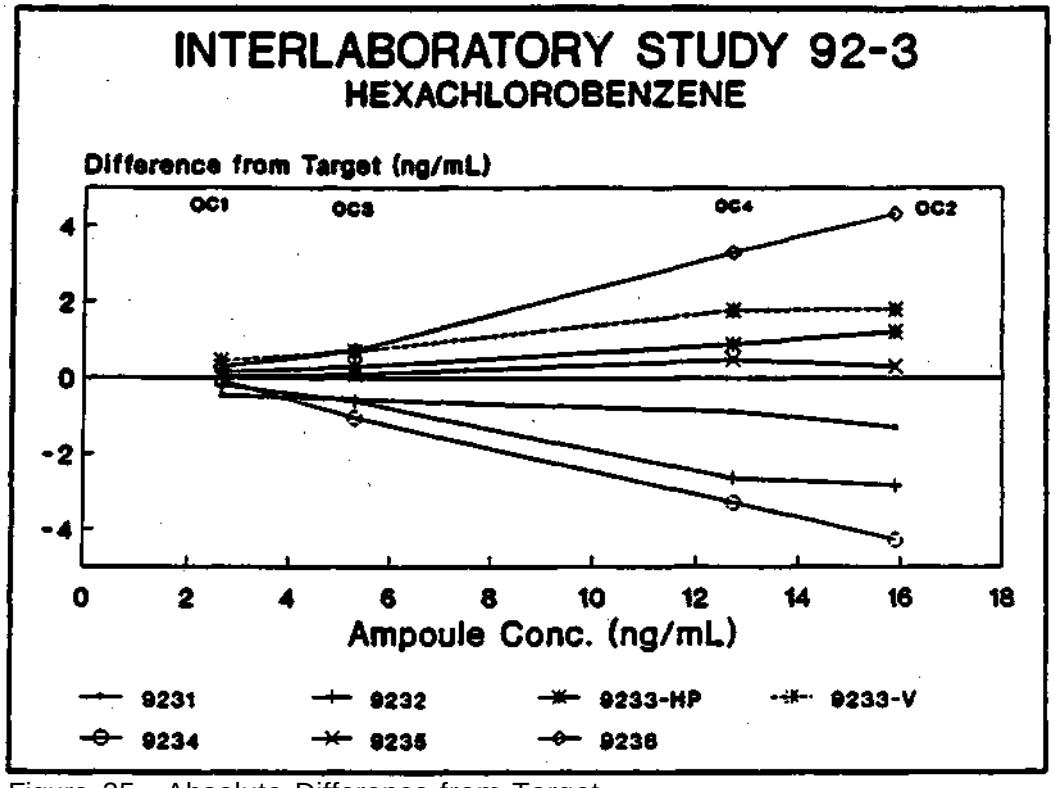

Figure 25 - Absolute Difference from Target

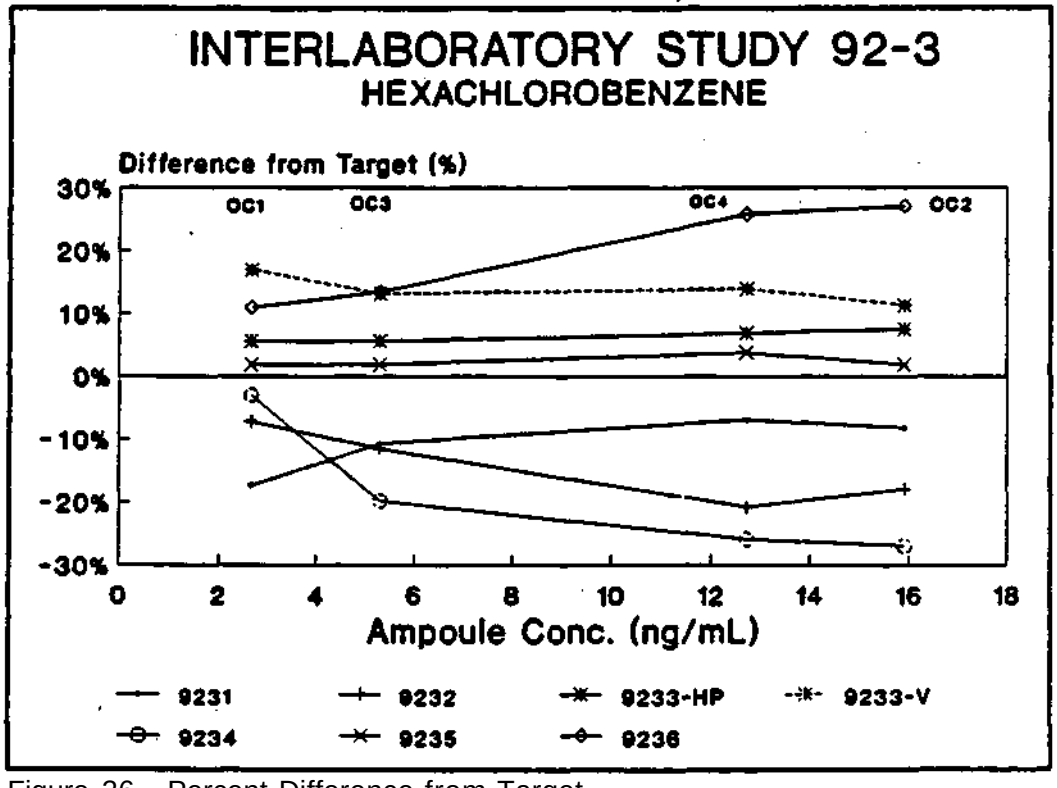

Figure 26 - Percent Difference from Target

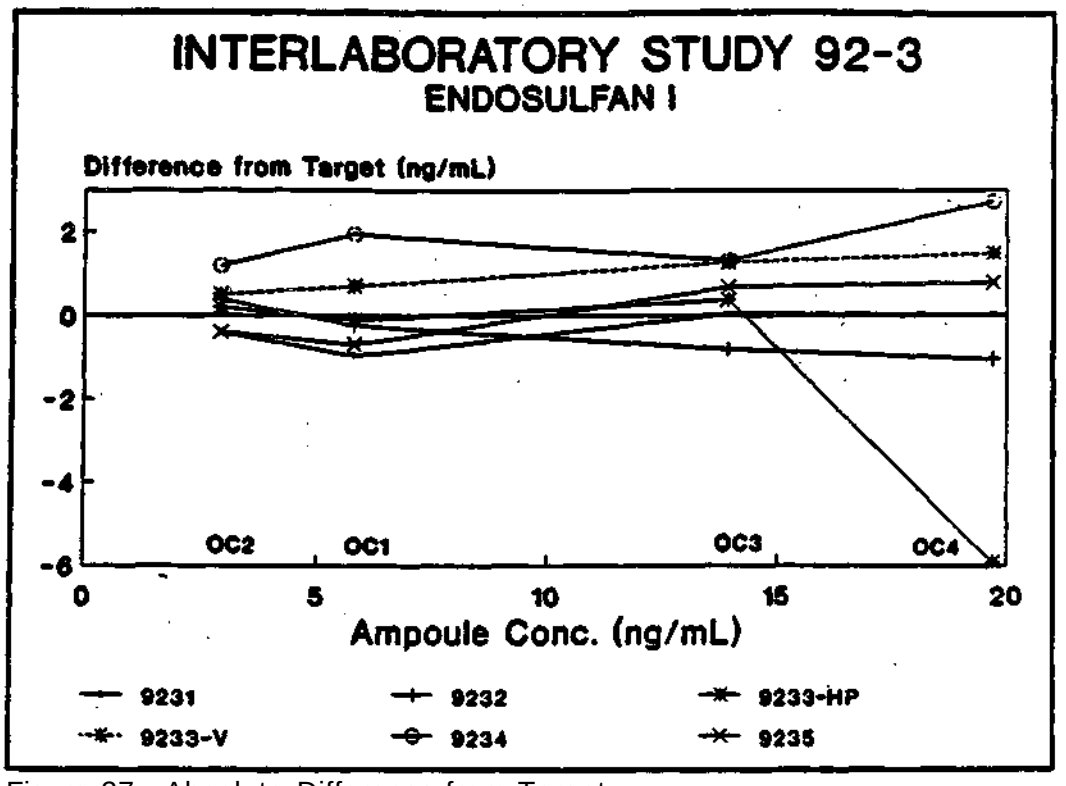

Figure 27 - Absolute Difference from Target

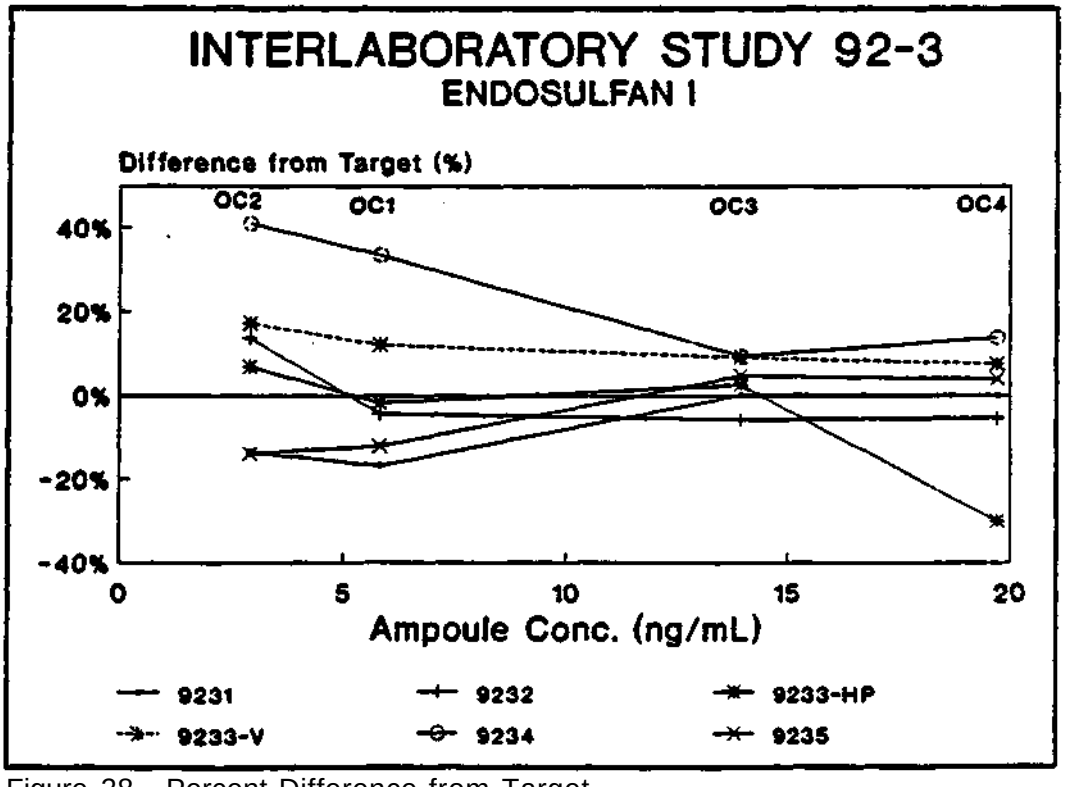

Figure 28 - Percent Difference from Target

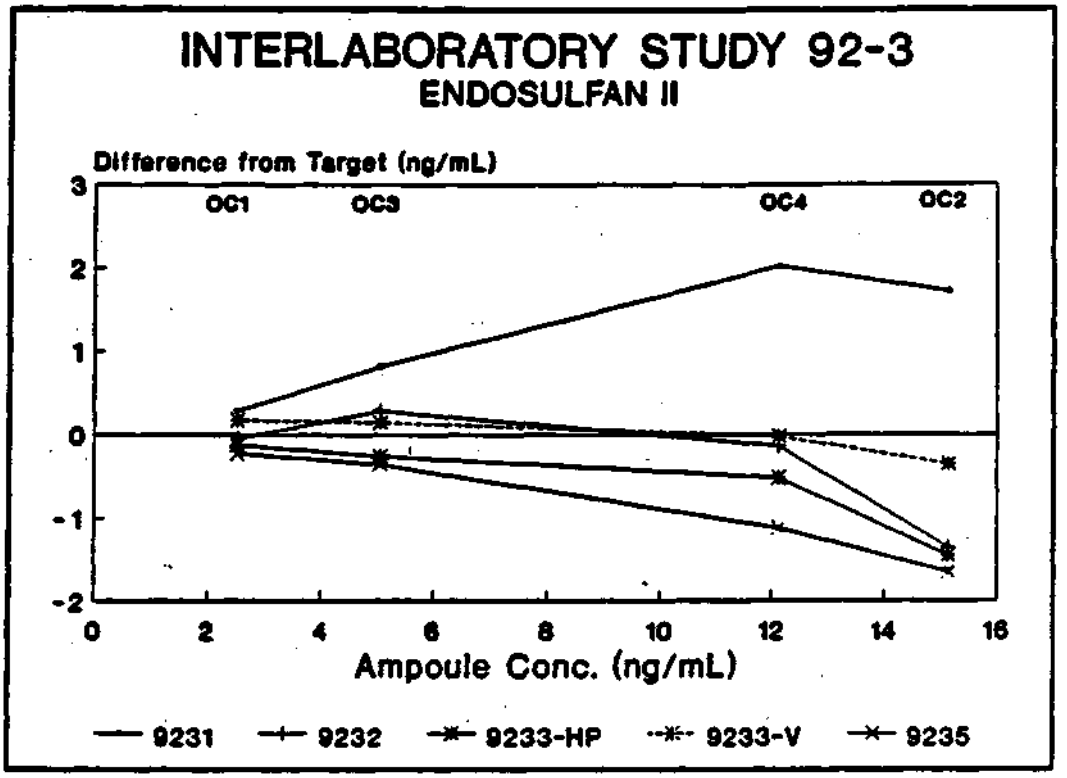

Figure 29 - Absolute Difference from Target

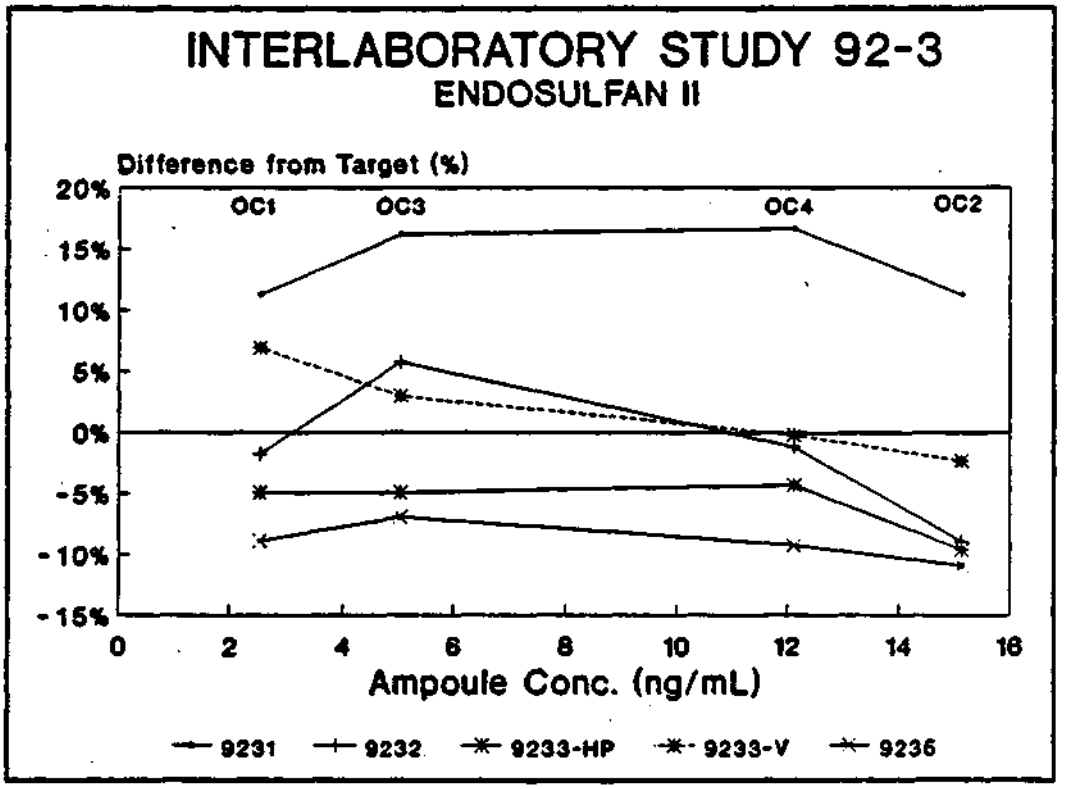

Figure 30 - Percent Difference from Target

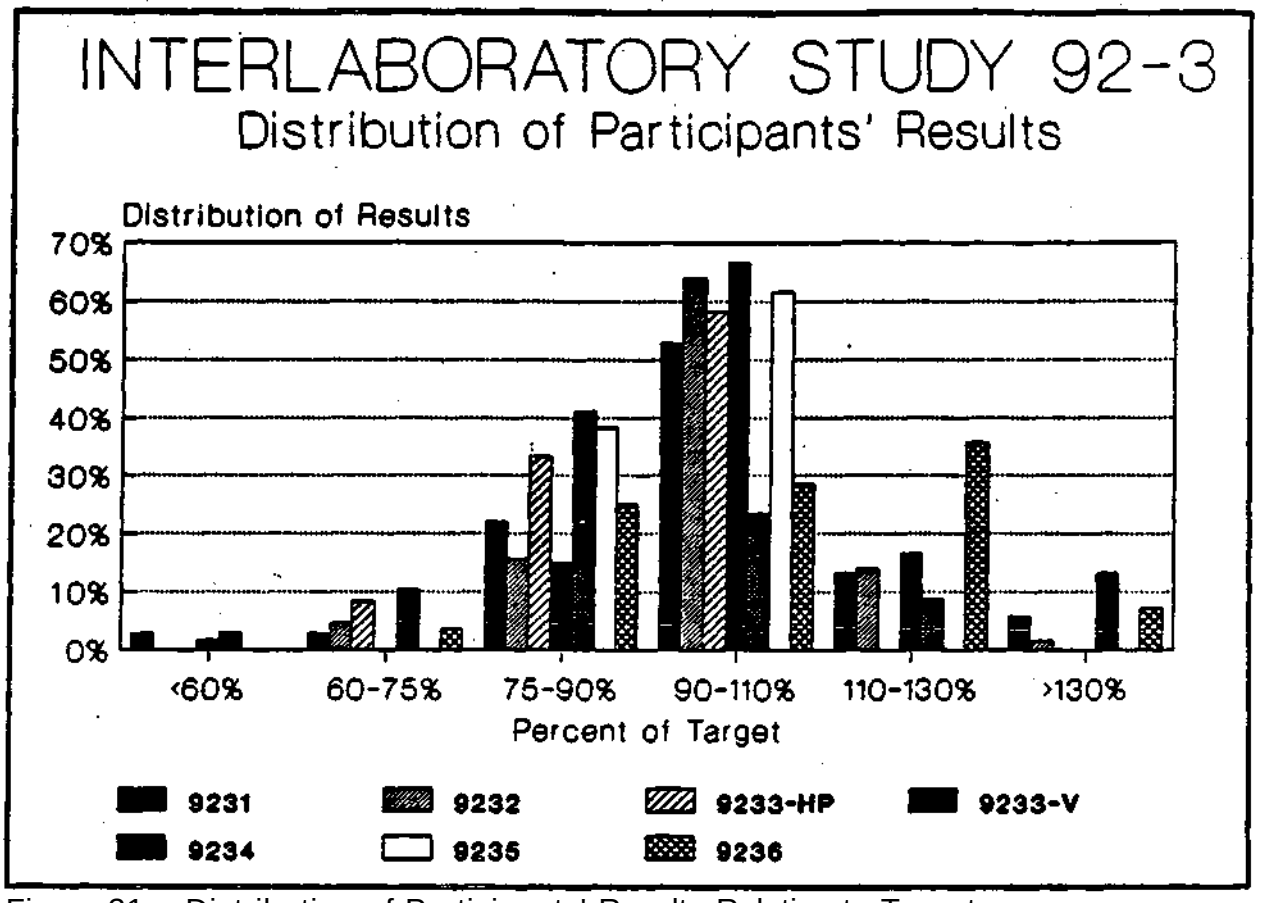

Figure 31 - Distribution of Participants' Results Relative to Target

8 APPENDIX 2 - PARTICIPANTS AND CORRESPONDENCE

List of Participants

Bev Genest-Conway/Dave Warry
National Laboratory for Environmental Tasting
867 Lakeshore Rd., P.O. Box 5050
Burlington, Ontario
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Laboratory Services Branch
Atmospheric & Biomaterials Analyses Section
125 Resources Rd.
Etobicoke, Ontario
M9P 3V6
(416)235-5755/6004

Bert Grift
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Freshwater Institute
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Winnipeg, Manitoba
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Chemistry Division
Illinois Department of Energy and Natural Resources
2204 Griffith Drive
Champaign, Illinois, U.S.A.
61820-7495
(217) 244-6413/333-9321

Ken Brice
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Air Quality Process Research Division
4905 Dufferin St.
Downsview, Ontario
M3H 5T4
(416) 739-4601

William Strachan/Debbie Burniston
Lakes Research Branch
National Water Research Institute
867 Lakeshore Rd., P.O. Box 5050
Burlington, Ontario
L7R 4A6
(905) 336-4775/6025

Quality Management Unit

October 5,1992

Dear Interlaboratory Study 92-3 Participant,

Please find enclosed four 5 mL ampoules for the analysis of Organochlorine Pesticides (OC's). The ampoules are labelled IADN OCs 1. IADN OCs 2, IADN OCs 3, and IADN OCs 4. If you are missing any of the ampoules or they have broken in transit, please contact me at (416) 235-5842 immediately for replacement. .

The ampoules are ready for direct instrumental analysis. Break open the ampoule on the scored mark and transfer the contents to the eppropriate sample container for your analytical system. No dilutions should be required, but if you do so, please mark the dilution factor used on the accompanying report form. The parameters present are indicated on the form.

Please report all results on the accompanying form by October 23. 1992.

Thank you for your participation in this study.

Your identification code is:

Sylvia Cussion
Laboratory Quality Audit Scientist
(416)235-5842
FAX (416) 235-6110

INTERLABORATORY STUDY 92-3

OC's FOR THE INTEGRATED ATMOSPHERIC DEPOSITION NETWORK

Identification Code:

Units:

PARAMETER	IADN OCs 1	IADN OCs 2	IADN OCs 3	IADN OCs 4
a-Hexachlorocyclohexane (*a*-HCH)				
y-Hexachlorocyclohexane (*y*-HCH)				
p.p-DDT				
o,p-DDT				
p.p-DDD				
o,p-DDD				
p,p-DDE				
o,p-DDE				
a-Chlordane				
y-Chlordane				
Heptachlor Epoxide				
Methoxychlor				
Oieldrin				
Hexachlorobenzene (HCB)				
Endrin				
Endosulfan I				
Endosulfan II				
Oxychlordane				

INSTRUMENT AND DETECTOR USED FOR ANALYSIS:

125 Resources Rd.
Etobicoke, Ontario, M9P 3V6
Phone: (416) 235-5842
FAX: (416) 235-6107

January 15, 1993

TO: PARTICIPANTS OF INTERLABORATORY STUDY 92-3

Thank you for your participation in Interiaboratory Study 92-3 for the analysis of Organochlorine Pesticides (OC's) in ampouied standards. This study was in support of the Integrated Atmospheric Deposition Network (IADN) program. I apologize for the delay in reporting results, but one participant did not report their final results until this week.

The results are provided in the attached tables. Target values are provided. Please inform me of any transcription errors by January 29, 1993.

Each participant received a set of ampoules prepared from the same stock solution, prepared in iso-octane.

The Quality Assurance Working Group of the Canada-Ontario Agreement (COA) has been the directing force for these interiaboratory studies. They wish to know the identities of the participating laboratories for the purposes of data comparison for IADN. The Program Managers and Principle Investigators (U.S. and Canadian) for IADN also wish to have the laboratories identified. As the original invitation for this study indicated that laboratory codes were confidential, I am asking each participant to give me permission to reveal their identities to these groups of data users. Please notify me in writing with your permission to reveal your study code.

A date has not yet been set for the next set of ampouied standards in this series of IADN studies, but hopefully will take place in late February or in March. A letter will be sent out giving several weeks notice.

Your identification code is:

Sylvia Cussion
Laboratory Quality Audit Scientist

9 APPENDIX 3 - INTERPRETATION OF BIASES IN DIFFERENCE PLOTS

Interlaboratory study results may be evaluated by comparing the difference from target (D) to the target or consensus value (X). This may be graphically represented with the Difference (D) on the vertical axis and the Target or consensus value (X) on the horizontal axis. By joining the individual points for each participant in order of increasing concentration, imprecision (squiggle in the line) versus bias or curvature (location of line relative to its expected position) may be demonstrated.

The precision envelope for the difference plots may be described by the following equation:

$$D = B_i + B_s \circ C \pm (DL + f \circ C)$$

where:	D	Difference from target	B_i	Intercept Bias
	C	Concentration	B_s	Slope Bias
	DL	Detection Limit	f	Fluctuation factor

The fluctuation factor (f) for Organics is usually 10-20%. Data users' needs may determine how large a value for f is acceptable.

If there are no biases present (B_i and B_s = 0), the shape is symmetrical to and centred on the target line. Measurement differences among participating laboratories in an interlaboratory study should be attributable only to random fluctuation. An example using DL = 5μg/L and f = 10% is given in Figure 32.

When an intercept bias is present, the envelope shifts in the direction of the bias. If this shift exceeds the Method Detection Limit (MOD, this becomes a matter of concern for the analyst. An example with B_i = -5 μg/L is given in Figure 34.

When a slope bias is present, the envelope broadens in the direction of the bias as concentration increases. When this bias exceeds the MDL + 10% concentration, it becomes a matter of concern for the analyst. An example of B, = + 10% is given in Figure 36.

Most interlaboratory study data sets will show a combination of slope and intercept biases among the participants. The precision envelope changes according the magnitude of both effects. An example using B_i = -5 μg/L and B_s = + 10% is given in Figure 38.

The results may also plotted using the relative difference (R) on the vertical axis, the precision envelope flares dramatically as the concentration approaches zero. This type of plot tends towards an exaggerated impression of unacceptable variability at the bottom end and may mask biases at higher concentration levels. However it can be useful when describing the range of performance among a group of participants. The above examples that were presented using concentration units (absolute scale) are also presented using a relative scale (Figures 33, 35, 37 and 39).

REFERENCE

King, D.E.; July 1993; *Interpretation of Interlaboratory Comparison (Round-Robin) Data;* Internal Report, Ministry of Environment and Energy, Laboratory Services Branch; Draft.

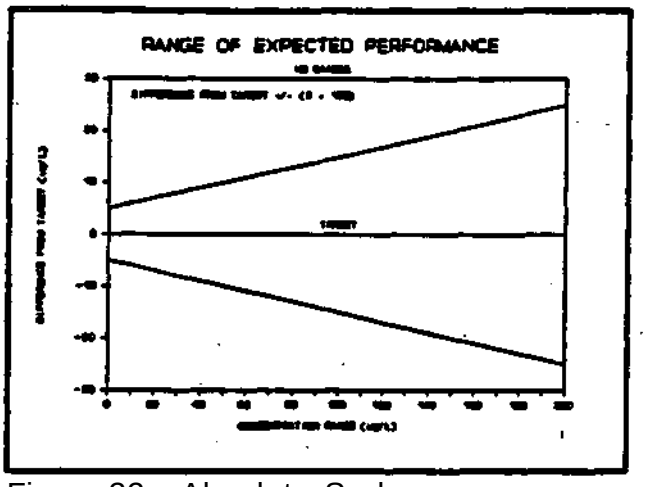

Figure 32 • Absolute Scale

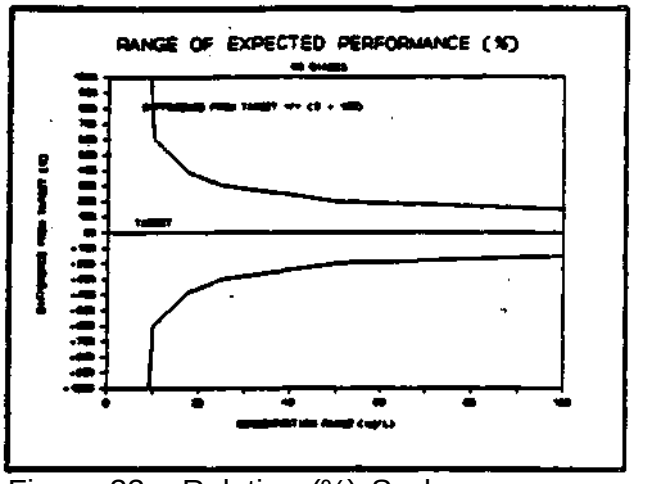

Figure 33 - Relative (%) Scale

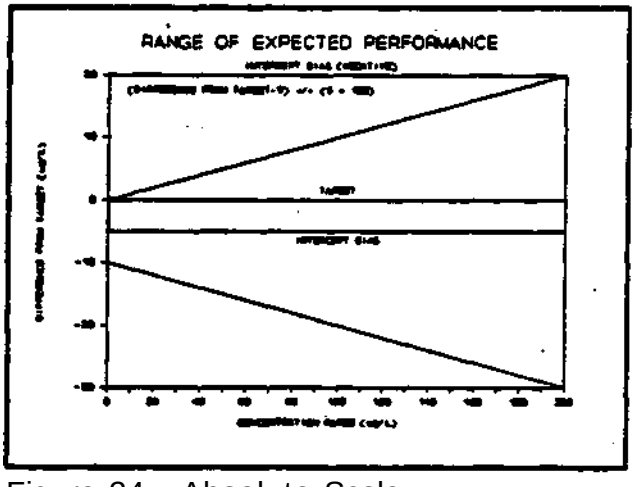

Figure 34 - Absolute Scale

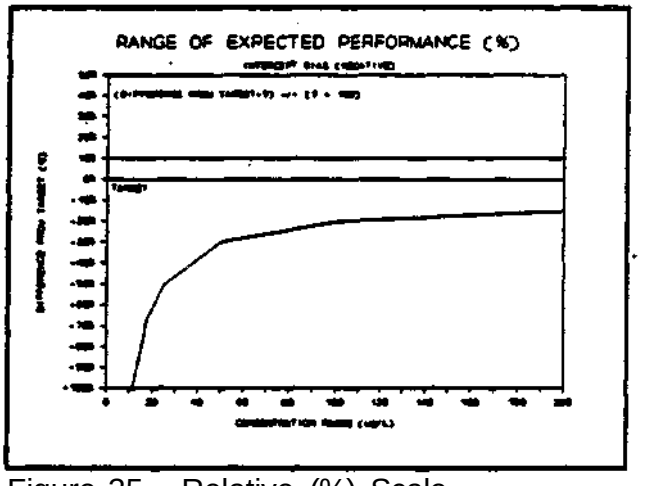

Figure 35 • Relative (%) Scale

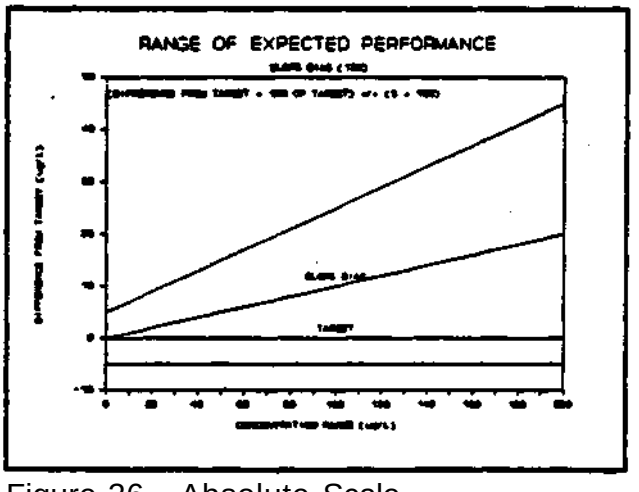

Figure 36 - Absolute Scale

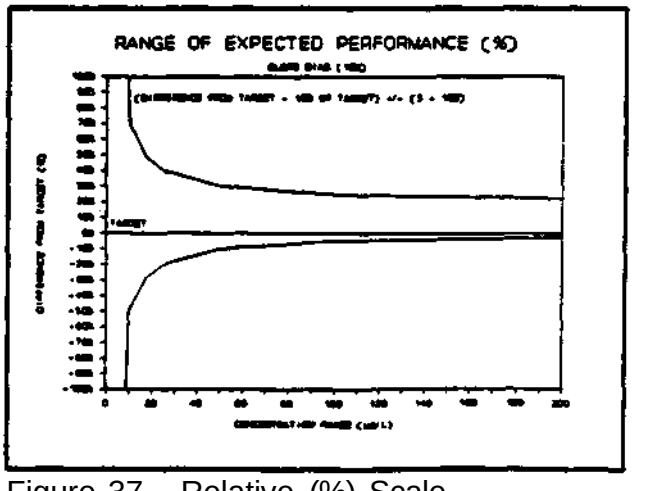

Figure 37 - Relative (%) Scale

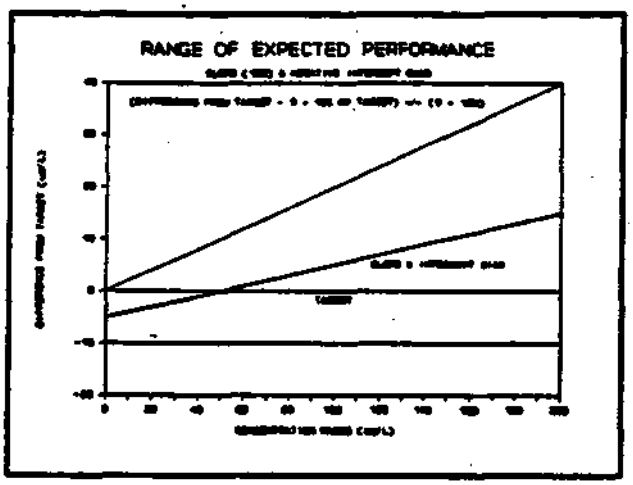

Figure 38 - Absolute Scale

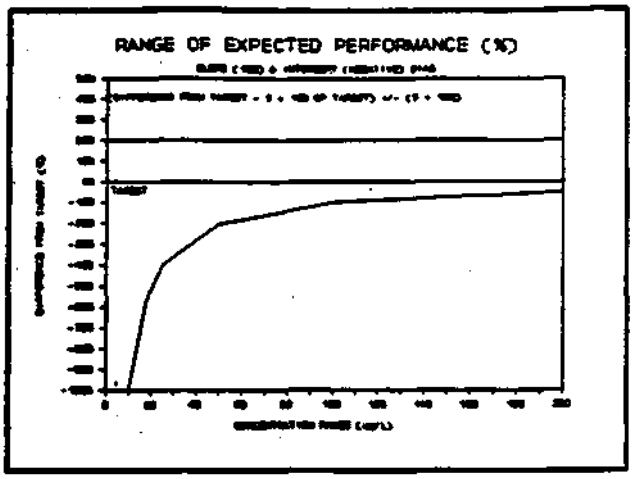

Figure 39 - Relative (%) Scale

ISBN 0-7778-2245-8

INTERLABORATORY STUDY 92-4

TRACE METAL STANDARD SOLUTIONS

IN SUPPORT OF

THE INTEGRATED ATMOSPHERIC DEPOSITION NETWORK (IADN)

Interlaboratory Study 92-4, Trace Metal. Standard Solutions ISWS Lab Code: 9241, 9241A

JULY 1992

Report Prepared by

Sylvia Cussion

for

Quality Management Unit
Laboratory Services Branch
Ontario Ministry of Environment and Energy

and

Air Quality Research Branch
Atmospheric Environment Service
Environment Canada
ARD Report: 93-14

The author gratefully acknowledges and thanks Lloyd Winfield for the preparation of materials, Russ Bennett for the confirmation of concentrations, and Don King, Sathi Selliah, Renata Baily, Syed Iqbal, and Robert Vet for their help in reviewing the results.

TABLE OF CONTENTS

1 SUMMARY OF INTERLABORATORY STUDY 92-4

Interlaboratory Study 92-4 was initiated in support of the Integrated Atmospheric Deposition Network (IADN) to provide an initial assessment of laboratory variability for the analysis of Trace Metals. Participation was limited to laboratories which contribute to the IADN database or related programs. This study was sponsored by the Canada-Ontario Agreement (COA) Air Toxics Workgroup, and conducted as a joint project between the Atmospheric Environment Service (AES) of Environment Canada and the Quality Management Unit (QMU), Laboratory Services Branch (LSB) of the Ontario Ministry of Environment and Energy (MOEE).

Eight participating laboratories received a set of four ampouled standards that were ready for direct instrumental analysis. The parameter list consisted of 8 different elements. Results were received from seven laboratories.

The results of this interlaboratory study indicate that the participants have an agreement of ±10% to the target for all elements except Aluminum. The lack of sensitivity for Aluminum analysis suggests that ±30% is the level of agreement achievable at this time. Within-laboratory performance across the concentration range was very consistent, with one or two individual problems for one or two elements. Intercept problems are the most common source of between-laboratory variability. Individual participants may be biased high or low for one or two individual Trace Metals. As between-participant bias may be as high as 20%, the use of a common reference standard could help improve this bias to 5-10%. This would reduce the potential bias from contributing laboratories to the central IADN database.

2 INTRODUCTION

Interlaboratory performance studies are conducted to assess the comparability and accuracy of data among different laboratories. These studies are useful for the identification of biases, precision and accuracy problems. Participation in such studies can serve as a guide for improving individual laboratory performance and maintaining performance standards.

This study was designed to assess the analytical variability among laboratories contributing to the Integrated Atmospheric Deposition Network (IADN). IADN was established as a joint venture between Canada and the United States under the direction of the International Joint Commission[1]. The intent of IADN is to identify toxic airborne substances in the Great Lakes Basin, and by means of the network, quantify the total and net atmospheric loadings of these contaminants, and define spatial and temporal trends in the atmospheric deposition of these substances. Data from several participating agencies is to be merged into a central database. Comparability of these contributing data sets is an important component of the IADN Quality Assurance Implementation Plan[3]. This interlaboratory study provides information to help establish the comparability of data sets and is a recommended activity of the IADN Quality Assurance Program Plan[3]. Sponsorship of this interlaboratory study was through the Canada-Ontario Agreement (COA) Air Toxics Workgroup. Funding for the purchase of materials came from the Atmospheric Environment Service (AES) of Environment Canada. Co-ordination and implementation of the study was done by the Quality Management Unit (QMU) of Laboratory Services Branch (LSB) of the Ontario Ministry of Environment and Energy (MOEE).

Interlaboratory Study 92-4 targets laboratories analyzing for Trace Metals in ambient air and/or precipitation. The aim of this study was to establish the comparability of instrumental calibration among the participating laboratories. Each participant received a set of 4 ampouled standards containing eight different elements (Trace Metals) ready for direct instrumental analysis.

A list of participants is given in Appendix 2. Each participant was assigned a unique identification code for ease in data manipulation.

Section 3 describes sample preparation, sample distribution, analytical methodology, and data evaluation procedures. Final results are tabled in Appendix 1 and discussed in Section 4.

3 PROCEDURE

3.1 Preparation of Ampouled Standards

The QMU of LSB, MOEE provided individual concentrated stock solutions of the eight trace metals to be used in this study. These solutions had been previously verified against US-EPA materials and used extensively for LSB in-house Performance Evaluation samples and MOEE interlaboratory studies. Four combined solutions were prepared by diluting aliquots of the concentrated stocks in distilled, deionized water (DDW). Target levels attempted to cover the routine analytical range of most participants. The solutions were preserved with 2% concentrated nitric acid. The solutions were sealed into 50 mL clear ampoules and verified using Inductively-Coupled Plasma/Mass Spectrometry (ICP/MS) analysis by an analyst at LSB not involved in the analysis of ambient

air or precipitation. The ampouled solutions were stored at room temperature until shipped to the participants.

3.2 Sample Distribution

Samples were packed into styrofoam shipping containers and shipped by Purolator Courier to the participating laboratories. A list of the laboratories receiving sample sets is given in Appendix 2. Samples were shipped on July 13, 1992. A copy of all correspondence is also included in Appendix 2.

3.3 Analytical Methodology

Participating laboratories were requested to analyze the samples using their routine in-house methods used to analyze ambient air or precipitation samples for the IADN program. The solutions were intended for direct instrumental analysis and participants were told not to use any digestion or pre-concentration procedures. Participants were requested on the report form provided (Appendix 2) to indicate the Instrument used. All participants were assigned a unique identification code that does not correspond to the order the participants are listed in Appendix 2.

3.4 Data Reporting

Results were submitted to the QMU, LSB in written form. All data were manually entered by laboratory code into an electronic spreadsheet. Participants were not asked to provide replicate results, though several laboratories did provide duplicate or triplicate results or results using two different techniques. For those participants that did provide more than one result using the same analytical technique, a mean value was entered into the Table of Results.

The participating laboratories were mailed a copy of the tables of results on November 4, 1992. No corrections were reported, but there was one revision to the results for Lead. Laboratory 9246 initially provided two sets of Lead and Cadmium results, using both Inductively-Coupled Plasma/Atomic Emission Spectroscopy (ICP-AES) and Graphite Furnace Atomic Absorption Spectroscopy (GFAAS), without indicating which technique was used for the IADN program. The original table of results for Lead contained the ICP-AES values, but samples for the IADN program have Lead analysis done by GFAAS. The ICP-AES Lead values were replaced by the GFAAS Lead values.

The interlaboratory mean, standard deviation (SD), and relative standard deviation (%RSD) were calculated for each Trace Metal and are included in Tables 1-4, Appendix 1.

To easily compare the performance of the participating laboratories, the difference from target for each participant versus target concentration was plotted for each individual Trace Metal. The percent difference from target for each individual Trace Metal was plotted in a similar manner. These graphs are included in Appendix 1.

4 DISCUSSION

OVERVIEW OF INTERLABORATORY PERFORMANCE

Results were received from seven of the laboratories which received the ampouled standards. Comments re difficulties with analyses reported by the participants are noted below in the individual laboratory review. A description of the principles upon which the following discussion is based is provided in Appendix 3.

The results for Aluminum (Figure 1) demonstrate an intercept range of approximately 50 µg/L, excluding Laboratory 9244 (see individual discussion below). Most laboratories demonstrate consistent performance across the analytical range targeted by ampoules IADN2, IA0N3 and IA0N4. More variable performance is observed at the lowest concentration level (Ampoule IADN1). Laboratories 9245 and 9247 are biased high. The analytical techniques used for Trace Metal analysis are less sensitive for Aluminum as compared to other elements in this study, so that it may be difficult for the participants to improve their performance at lower concentration levels. There is a between-laboratory range of ±20% (Figure 2) that should be improved upon.

The Arsenic results (Figure 3) demonstrate between-laboratory slope-dependant bias. Laboratory 9246 has a high slope bias. The participants demonstrated a between-laboratory range of 20% (Figure 4), excluding Laboratory 9246, though Laboratory 9241A was also high for Ampoule IADN1.

The results for Cadmium (Figure 5) demonstrate slope-dependant bias. Laboratories 9241A and 9248 have low slope biases. The between-laboratory range for the other participants is 15% at the lower concentrations and is very good at 10% for the highest concentration (Figure 6), despite the negative slope biases noted above.

The Chromium results (Figure 7) indicates an intercept dependant bias of approximately 2-5 µg/L. Many of the participants appear to lack sufficient sensitivity for this element at the lowest target concentration in this study. Laboratory 9242 had erratic performance for this element. The between-laboratory range is approximately 40% at the lower concentrations and improves to 20% at the highest concentration (Figure 8), excluding Laboratory 9242.

The interlaboratory performance for Copper (Figure 9) demonstrates a general intercept problem of approximately 3-5 µg/L. Laboratory 9248 also has a negative slope bias of - 10%. Excluding Laboratories 9242 and 9244 for Ampoules IADN1 and IADN2, the between-laboratory range is approximately 30% (Figure 10).

The Lead results (Figure 11) indicate an intercept bias of approximately 2 µg/L. Except for Laboratory 9241A (see individual review), the between-laboratory bias is within ±10% (Figure 12).

The results for Selenium (Figure 13) indicate some intercept problems. Laboratory 9246 had erratic performance for this element. The other laboratories demonstrate a between-laboratory range of approximately 20% (Figure 14).

The Zinc results (Figure 15) demonstrate an intercept bias of approximately 5 //g/L, excluding Laboratory 9247. Laboratory 9241 has high positive slope bias. The between-laboratory range was approximately 25% (Figure 16), excluding Laboratories 9241 and 9247 in Ampoule IADN1. Laboratory 9247 may also have had an intercept problem or some contamination in sample IADN1.

Several laboratories have intercept problems which should be investigated. Precipitation and ambient air are expected to have low concentration of Trace Metals. Intercept biases will have a noticeable effect on low level data. By improving on intercept problems, laboratories contributing to the IADN database will reduce the risk of providing biased results to the central database.

The overall performance indicates that the between-laboratory variability for most elements is within ±10% over the concentration range of this study. Several participants had a high or low slope bias on one or two elements. This should be investigated and corrected with the use of a reference standard. While one participant may differ by only + 10% from the target, and another by -10% from the target, the two participants differ by 20% with respect to each other. If the two "extreme" laboratories are contributing to the IADN database with a 20% bias between them, this could lead to greater differences in the data sets than desired. By monitoring their in-house standards with a common reference standard, the laboratories contributing to the IADN database should be able to reduce their between-laboratory variability to ±5%. This would result in only a 10% bias between the "extreme" laboratories and improve the comparability of the data being submitted to the central IADN database.

INDIVIDUAL LABORATORY PERFORMANCE

Laboratory 9241

Laboratory 9241 reported results for all parameters except Selenium using ICP-AES but noted that they routinely use GFAAS for low levels of Copper, Lead, Cadmium and Arsenic. Selenium is only done on GFAAS. However, at the time of the study, their GFAAS was broken, so they submitted the ICP-AES results to meet the study deadline of August 7, 1992. In September their GFAAS was repaired and they analyzed the solutions for Cadmium, Lead, Arsenic and Selenium, submitting these results prior to the table of interlaboratory results being submitted to all the participants. Their ICP-AES results are listed under the code 9241 and the GFAAS results are listed under the code 9241 A. The original ICP-AES results for Cadmium, Lead, and Arsenic are not included in the calculations of interlaboratory mean and standard deviation.

Laboratory 9241 had intercept problems for all of the Trace Metals except Cadmium. They had a high slope bias for Zinc.

Their performance at the higher concentrations for Lead appears erratic (IADN 3 and IADN4, Figure 11), and may also indicate a negative slope bias. Dilution factors were not reported, but it appears possible that Ampoule IADN3 was not diluted for Lead and analyzed near the top of their analytical range. Ampoule IADN4 may have been diluted for Lead and analyzed at a point in the calibration range where a slope bias was not as pronounced.

Laboratory 9242

Laboratory 9242 was unable to report results for Arsenic and Selenium as their analytical method requires unpreserved samples, and the interlaboratory study ampoules were all acidified with nitric acid.

Laboratory 9242 had intercept problems for all of the Trace Metals except Zinc.

They also noted that they diluted the solutions 1:4 with ultra pure water, to simulate

the same treatment given to precipitation samples. An aliquot of the ultrapure water was analyzed for any background levels of the metals, and the final results were corrected for background levels (uncorrected values were not reported).

Laboratory 9243

No results were received from this participant as they were unable to analyze the aqueous matrix. All Trace Metals analyses done by this laboratory is done using X-Ray Fluorescence on solid matrices.

Laboratory 9244

Laboratory 9244 was the only participant to use Neutron Activation as their analytical method. This procedure is routinely used for the analyses of solid matrices (eg. air filters) and is not easily used for the analysis of aqueous matrices, such as the ampouled solutions used in this study. They were not able to analyze all the solutions for all of the elements in this study.

Laboratory 9244 included a comment with their results indicating that they had difficulty with their analysis for Aluminum because of high blank readings. Their results for Aluminum were excluded from the calculations for the interlaboratory mean, standard deviation and relative standard deviation.

The high bias of their results suggest that the Neutron Activation technique is not appropriate for aqueous samples. They were not able to analyze the low level ampoules for Chromium, but their results for the higher concentration (IA0N3 and IA0N4) show acceptable agreement with the target. Their results for Copper show a high blank or intercept problem, suggesting that this method, when used on aqueous samples, is not sufficiently sensitive. Their result for the highest Copper concentration (IADN4) showed good agreement with the target. Their Selenium results show a high intercept or blank combined with a negative slope. This again may be a problem associated with using this analytical technique for aqueous samples. Future interlaboratory studies on spiked filters should be a more appropriate way of comparing this participant's performance with other laboratories who are contributing to the IADN database.

Laboratory 9245

Laboratory 9245 noted that the Arsenic and Selenium levels were much higher than their usual working level of 0.1 to 5.0 μg/L. The solutions were diluted 10X for Arsenic and Selenium analysis.

Laboratory 9245 had intercept problems for Arsenic, Copper, and Selenium. The above noted dilutions for Arsenic and Selenium may have magnified this problem. They had a high slope bias for Aluminum. Consistent performance across the concentration range and good agreement with the target was demonstrated for Cadmium, Chromium, Lead and Zinc.

Laboratory 9246

Laboratory 9246 analyzed the samples using two different instruments, ICP-AES and GFAAS. The ICP analysis was a full elemental scan, while the GFAAS results were for Arsenic, Cadmium and Lead only. In the preliminary table of results provided to the participants in November 1992, the ICP Lead results were reported. As samples for

the IADN program are analyzed using GFAAS, the Lead results were replaced with the GFAAS data. The statistical calculations were revised using the GFAAS results.

Laboratory 9246 had problems with their analysis for Zinc, though their accompanying QC data did not indicate a problem. Personal communication with laboratory staff indicated that they had a blank problem for Zinc that resulted in over-correction of the ampouled solutions' results. This resulted in NO values for IADN1 and IADN2, and a very low bias for ampoules IADN3 and IADN4. They requested that their results for Zinc be excluded from the evaluation and they have corrected their analytical protocol to prevent this problem from re-occurring.

Laboratory 9246 had an intercept problem for Aluminum, though they had good agreement with the target at the higher concentrations. They were biased high relative to the target and other participants for Arsenic. Erratic performance for was demonstrated for Selenium. They had generally consistent performance across the concentration range and good agreement with the target for the other four metals in this study.

Laboratory 9247

Laboratory 9247 used two different instruments for their analyses, as noted in Table 2. When reporting their results, they indicated that the solutions in the ampoules were at considerably higher levels than they routinely analyze. Several dilutions were performed (ranging from 1:4 up to 1:499) on all of the ampoules for Cadmium, Lead, and Arsenic analysis. All of the results plus a mean were provided on an accompanying report. The mean results were recorded on the interlaboratory study report form (Appendix 2) and these are the values listed in Table 1. They did not indicate if this was the same procedure that would be used for high level samples. The use of multiple dilutions may have introduced biases that would not be present on undiluted samples.

Laboratory 9247 had a high slope bias for Aluminum. They had an intercept problem for Zinc and Lead (not as severe). They were erratic at the lower concentrations for Cadmium, possibly due to dilution effects. Good performance was demonstrated for the other elements.

Laboratory 9248

Laboratory 9248 was the only participant to use ICP with Mass Spectrometry. They did not report results for Chromium and Selenium.

They demonstrated good performance across the concentration range and were within 10% of the target values for all elements. However, they were biased low relative to the other participants for all elements except Lead. As noted above in the Overall Review, this could lead to biases in the central IADN database. This is a situation where the use of a common reference material by all of the participants would indicate whether Laboratory 9248 really is biased low, or whether the other participants are all biased high.

5 CONCLUSION

The results of this interlaboratory study indicate that the participants generally agree within ± 10% of the target for all elements except Aluminum. The lack of sensitivity

for Aluminum analysis suggests that ±20% may be the best agreement achievable at the present time. Within-laboratory performance across the concentration range was very consistent, with one or two individual problems for one or two elements. Intercept problems are the most common source of between-laboratory variability. Individual participants may be biased high or low for one or two individual elements and are recommended to investigate these biases. As between-participant bias may be as high as 20%, the use of a common reference standard could help reduce this bias to 5-10%. This would reduce the potential bias from the contributing laboratories to the central IADN database.

6 REFERENCES

1. International Joint Commission, United States and Canada; January 1988. *Revised Great Lakes Water Quality Agreement of 1978 as amended by Protocol signed November 18, 1987.*

2. Canada/U.S. Coordinating Committee on Annex 15; March 1990. *Integrated Atmospheric Deposition Network Implementation Plan.*

3. *Integrated Atmospheric Deposition Network "STRAW MAN" Quality Assurance Program Plan* (DRAFT); November 1992.

7 APPENDIX 1 • RESULTS AND GRAPHS

TABLE 1: METAL RESULTS IN µg/L

CODE	IADN1	IADN2	IADN3	IADN4	CODE	IADN1	IADN2	IADN3	IADN4
Al					Cr				
TARGET	80.92	100.6	152.0	225.0	TARGET	9.996	1.999	19.99	79.97
9241	104	113	137	244	9241	8.7	6.0	16.3	82.7
9242	81.2	128.7	176.1	256.9	9242	3.6	<.2	33.2	77.3
9244 [a]	186	-	243.67	342.33	9244	-	-	25.5	88.15
9245	92	147	195	280	9245	11.5	2.5	22.3	84.6
9246	101	105	164	236	9246	9	ND	21	78
9247	102.90	141.85	196.95	285.15	9247	10.50	2.40	20.20	80.00
9248	71.22	92.24	131.96	200.07	9248	-	-	-	-
MEAN	92.05	121.3	166.8	250.4	MEAN	8.66		23.08	81.79
STD DEV	13.358	21.525	27.93	31.33	STD DEV	3.048		5.787	4.169
n	6	6	6	6	n	5		6	6
REL DEV	14.61%	17.75%	16.74%	12.51%	REL DEV	35.20%		25.07%	5.10%
Cd					Pb				
TARGET	9.885	1.977	19.77	158.2	TARGET	9.987	19.97	74.90	79.89
9241 [b]	16.4	3.2	27.3	171	9241 [b]	<60	<60	91	<60
9241A	9.49	1.84	17.44	140	9241A	10.22	17.67	60.45	79.0
9242	8.7	1.2	17.8	151.7	9242	11.4	20.5	76.0	80.0
9244	-	-	-	-	9244	-	-	-	-
9245	10.3	2.0	20.6	163	9245	11.2	21.5	81.0	83.4
9246	9.7	2.1	19.2	159	9246 [c]	10	18	69	68
9247	10.98	1.95	18.66	155.10	9247	12.56	22.78	73.38	77.72
9248	9.04	1.78	18.07	143.22	9248	11.28	20.83	72.82	77.96
MEAN	9.702	1.812	18.61	152	MEAN	11.11	20.213	72.108	77.68
STD DEV	0.834	0.321	1.151	8.953	STD DEV	0.922	2.004	6.956	5.170
n	6	6	6	6	n	6	6	6	6
REL DEV	8.60%	17.69%	6.18%	5.89%	REL DEV	8.30%	9.91%	9.65%	6.66%

---

a Laboratory 9244 reported high blanks for Aluminum. Results are excluded from the calculations of mean and standard deviation. "-" in table indicates that Laboratory 9244 did not report results for that element and/or ampoule.

b Laboratory 9241 had instrument problems during the course of this study. In an attempt to meet the deadline for reporting results, they analyzed the solutions using ICP-AES. They repeated their analysis for Cadmium, Lead, Arsenic and Selenium using Graphite Furnace-AAS (GFAAS). The second set of results are labelled 9241A. The first set of values for these four parameters were not included in the calculations of mean and standard deviation.

c Laboratory 9246 reported Lead results using both ICP-AES and GFAAS. The preliminary table of results had the ICP-AES results, but the IA0N samples are analyzed using GFAAS, therefore this table has been revised using the GFAAS results.

TABLE 1: METAL RESULTS IN µg/L

CODE	IADN1	IADN2	IADN3	IADN4	CODE	IADN1	IADN2	IADN3	IADN4
Cu					Zn				
TARGET	9.998	4.999	29.99	79.98	TARGET	10.0	25.0	100	240
9241	13.2	6.4	34.4	87.3	9241	16.8	32.5	116	273
9242	18.2	9.1	32.4	88.2	9242	11.0	30.8	106.8	255.5
9244	16	9.95	37.5	77.333	9244	-	-	-	-
9245	13.1	6.8	34.8	87.3	9245	11.0	25.7	108	248
9246	11	5	32	81	9246	ND	ND	37	171
9247	12.86	6.46	32.38	84.56	9247	17.92	27.08	102.40	244.10
9248	10.94	5.78	27.58	71.42	9248	9.61	24.4	98.9	234.4
MEAN	13.61	7.07	33.01	82.45	MEAN	13.266	28.096	94.85	237.67
STD DEV	2.637	1.792	3.071	6.252	STD DEV	3.801	3.433	28.924	35.128
n	7	7	7	7	n	5	5	6	6
REL DEV	19.37%	25.34%	9.30%	7.58%	REL DEV	28.65%	12.22%	30.49%	14.78%
					MEAN [d]			108.26	254.5
					STD DEV			6.464	14.460
					n [d]			5	5
					REL DEV			5.97%	5.68%
As					Se				
TARGET	10.08	5.04	50.4	161.3	TARGET	9.975	4.988	49.88	141.1
9241 [e]	<60	<60	<60	96	9241 [e]	-	-	-	-
9241A	12.00	4.71	54.42	168.0	9241A	9.17	4.45	45.21	148.0
9242	-	-	-	-	9242	-	-	-	-
9244	-	-	-	-	9244	9.1	7.05	45	130.3
9245	9.0	3.6	50.0	155	9245	8.7	3.6	49.5	150
9246	13	6	59	176	9246	7	4	66	143
9247	10.83	4.78	49.48	168.28	9247	-	-	-	-
9248	9.43	4.53	45.71	147.17	9248	-	-	-	-
MEAN	10.852	4.724	51.72	162.89	MEAN	8.493	4.775	51.428	142.83
STD DEV	1.687	0.856	5.108	11.580	STD DEV	1.016	1.556	9.934	8.854
n	5	5	5	5	n	4	4	4	4
REL DEV	15.55%	18.13%	9.88%	7.11%	REL DEV	11.97%	32.58%	19.32%	6.20%

[d] Mean, Standard Deviation and Relative Deviation recalculated excluding Laboratory 9246.

[e] Laboratory 9241 had instrument problems during the course of this study. In an attempt to meet the deadline for reporting results, they analyzed the solutions using ICP-AES. They repeated their analysis for Cadmium, Lead, Arsenic and Selenium using Graphite Furnace-AAS (GFAAS). The second set of results are labelled 9241 A. The first set of values for these four parameters were not included in the calculations of mean and standard deviation.

TABLE 2: INSTRUMENTATION OF PARTICIPANTS

ID Code	Instrumentation
9241	Thermo-Jarrell Ash ICP-AES, Vacuum, direct reader
9241A	Instrumentation Laboratory Video 22 AAS-GF
9242	ICP, ARL 3580
9244	Neutron Activation
9245	ICP, ARL 3580; direct aspiration for Al, Cd, Cr, Cu, Pb & Zn; hydride formation for As & Se
9246	GFAAS for As, Cd & Pb ICP-AES for Al, Cr. Cu, Se & Zn
9247	Perkin Elmer 5000 AAS for As, Cd, Cr & Pb Jarrell Ash ICP for Al, Cu & Zn
9248	ICP-MS

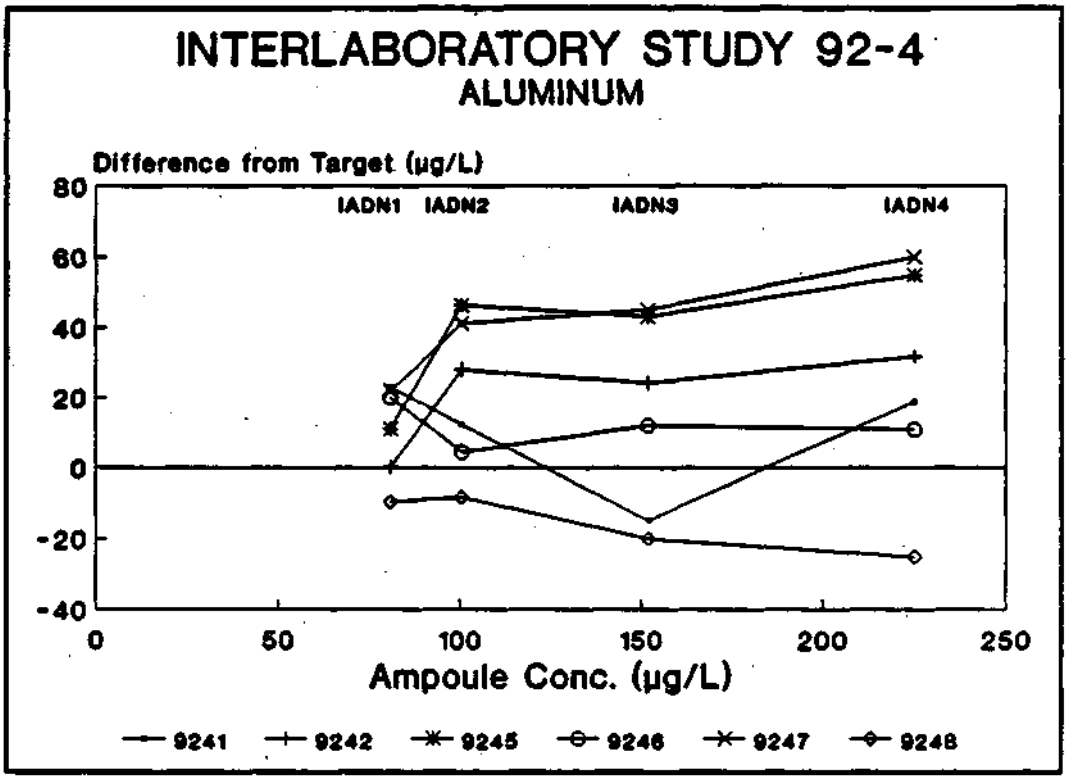

Figure 1 - Absolute Difference from Target

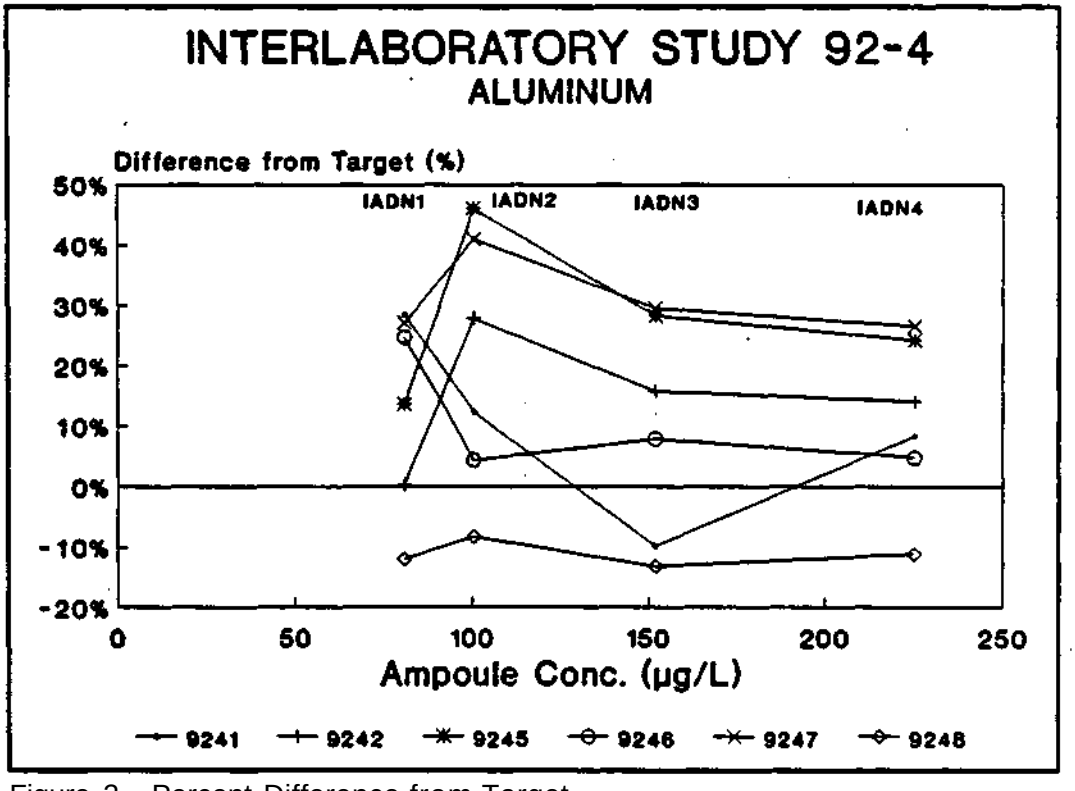

Figure 2 - Percent Difference from Target

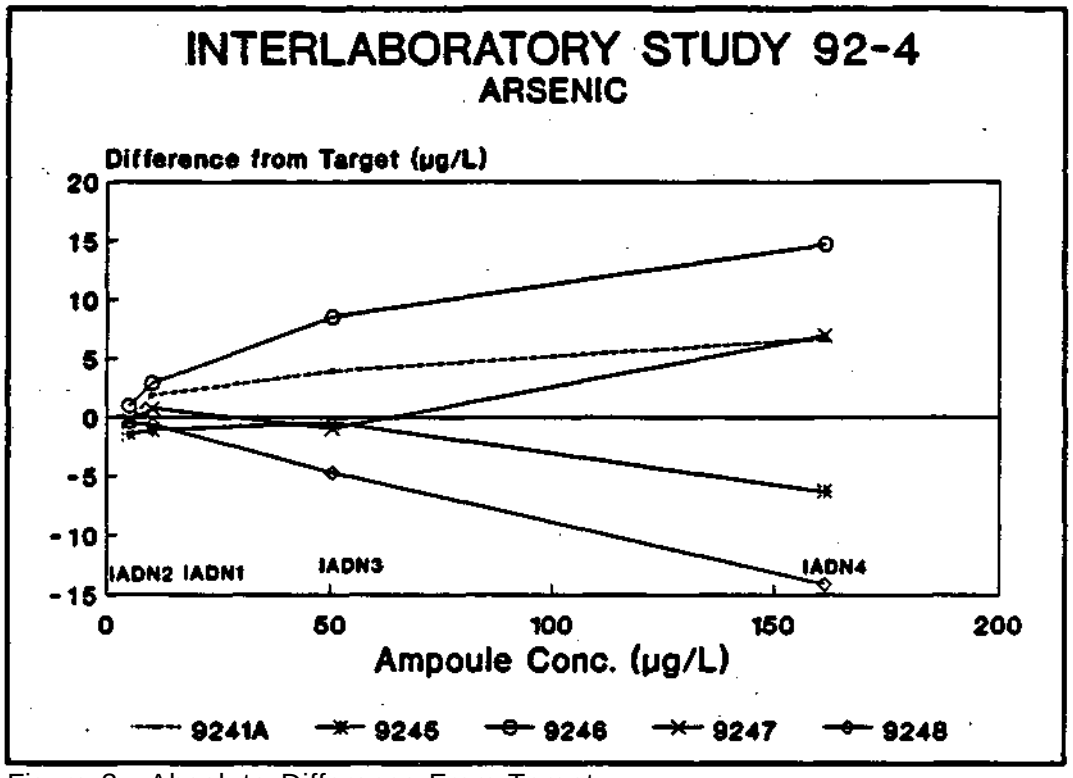

Figure 3 - Absolute Difference From Target

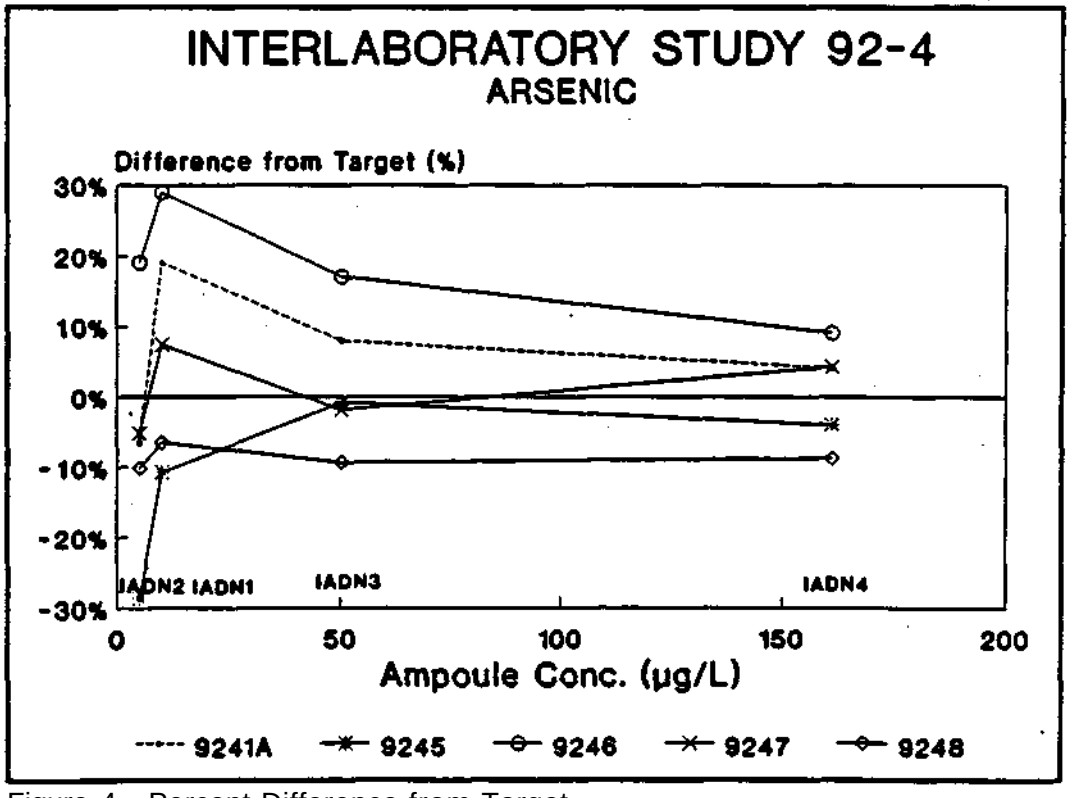

Figure 4 - Percent Difference from Target

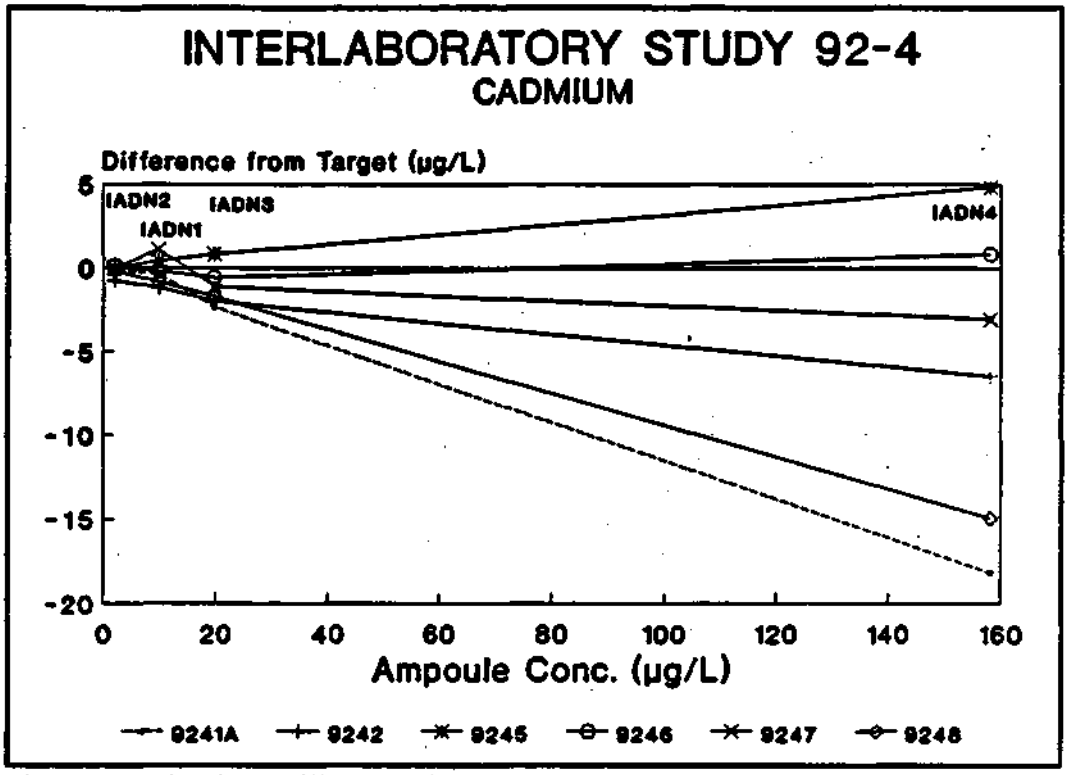

Figure 5 - Absolute Difference from Target

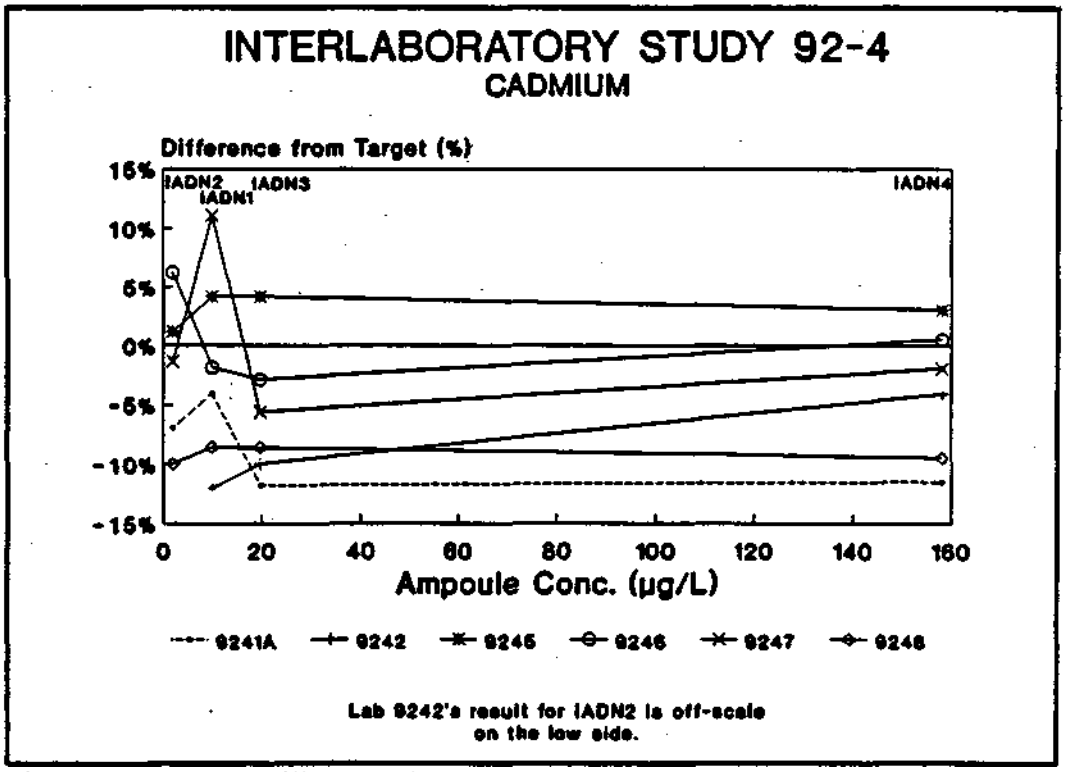

Figure 6 - Percent Difference from Target

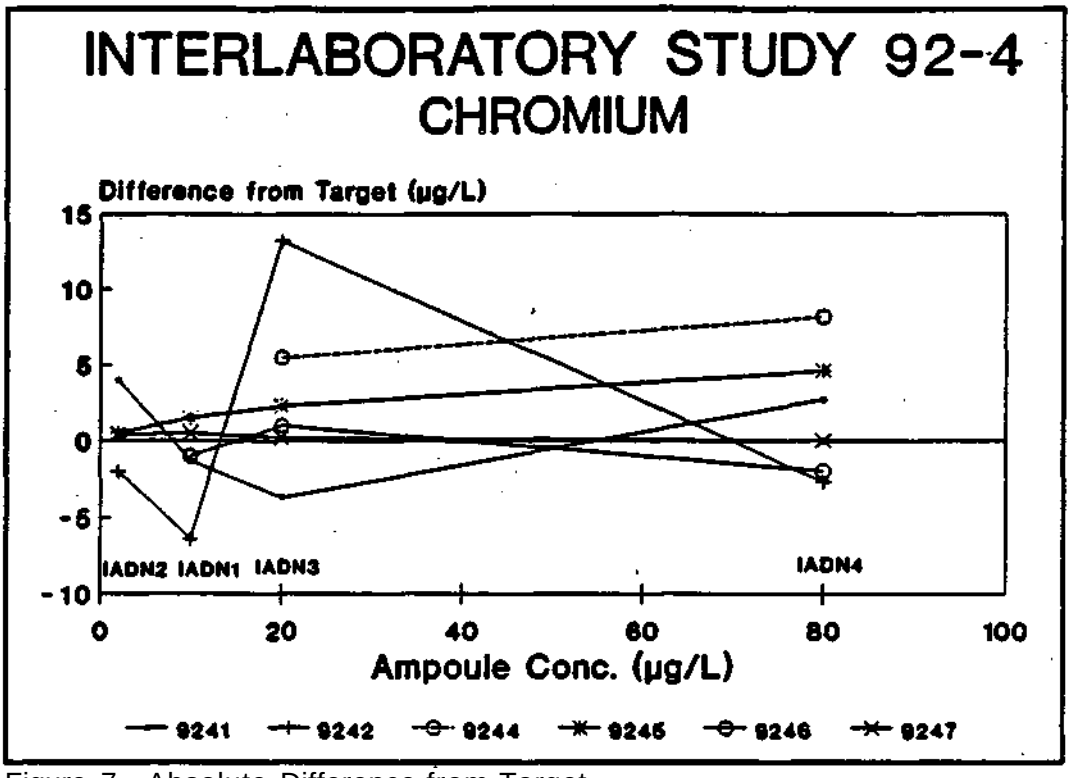

Figure 7 - Absolute Difference from Target

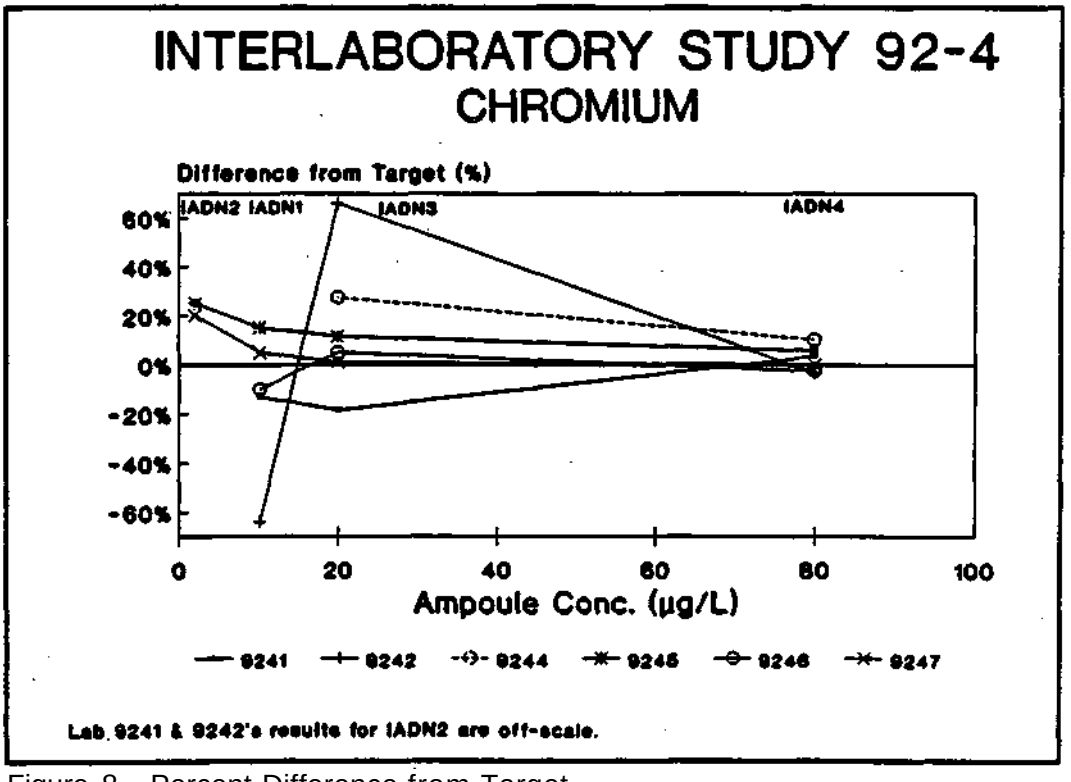

Figure 8 - Percent Difference from Target

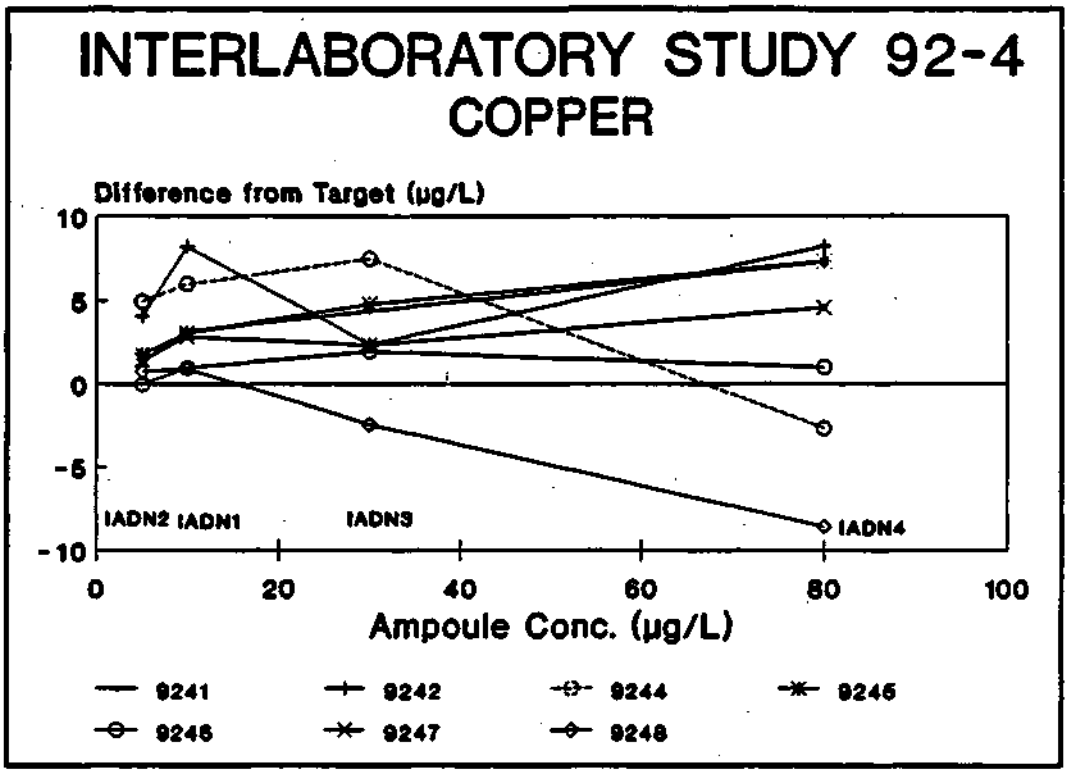

Figure 9 - Absolute Difference from Target

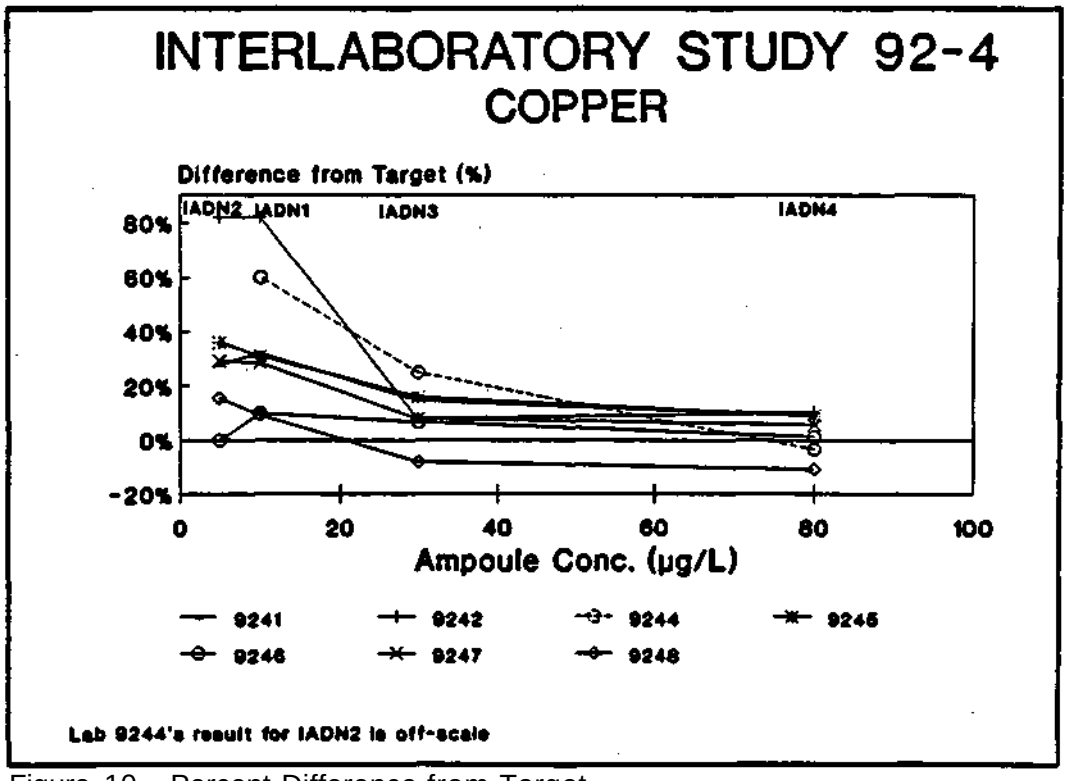

Figure 10 - Percent Difference from Target

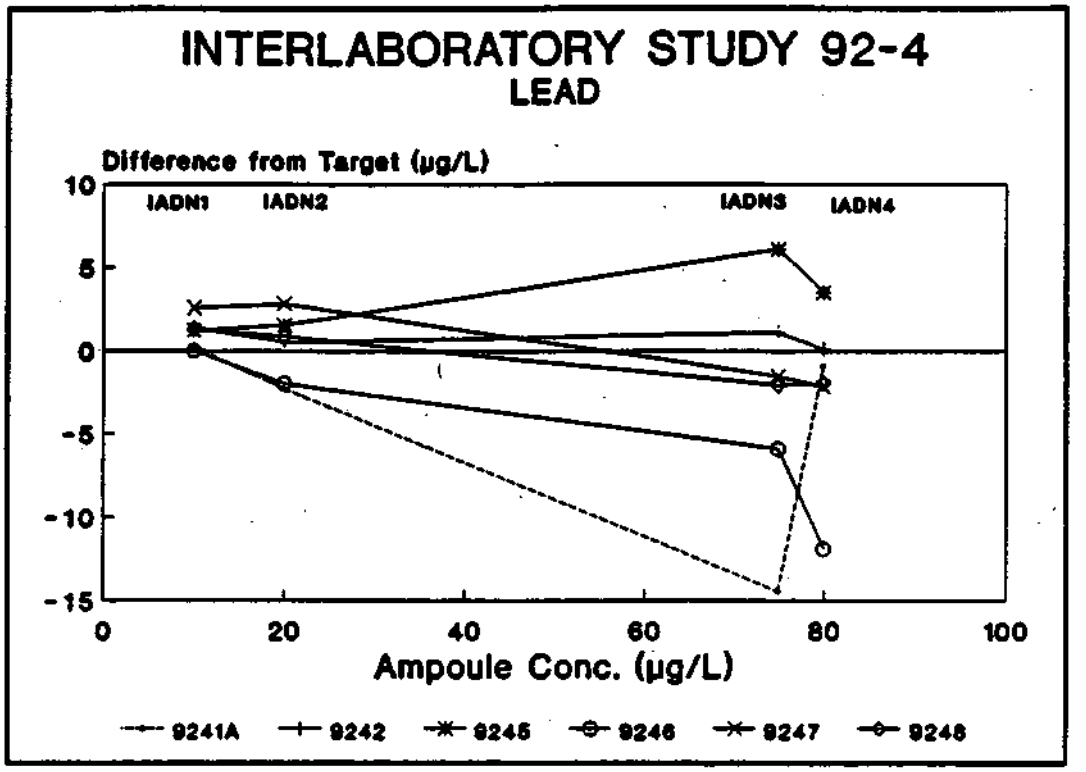

Figure 11 - Absolute Difference from Target

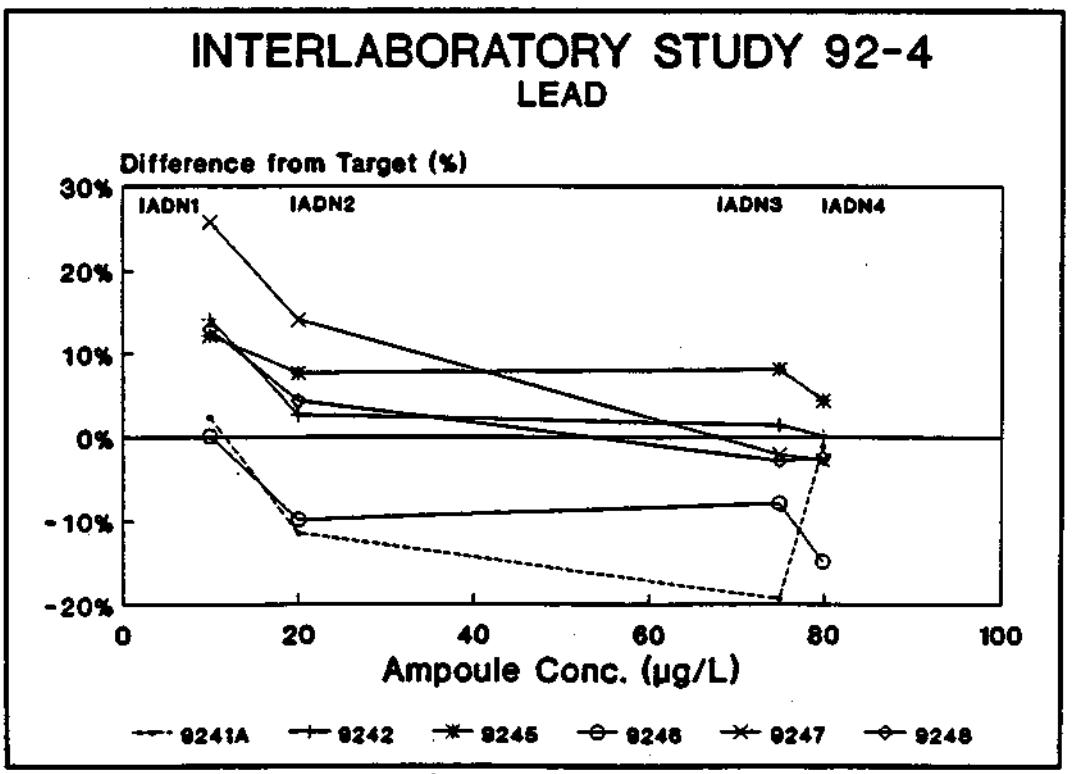

Figure 12 - Percent Difference from Target

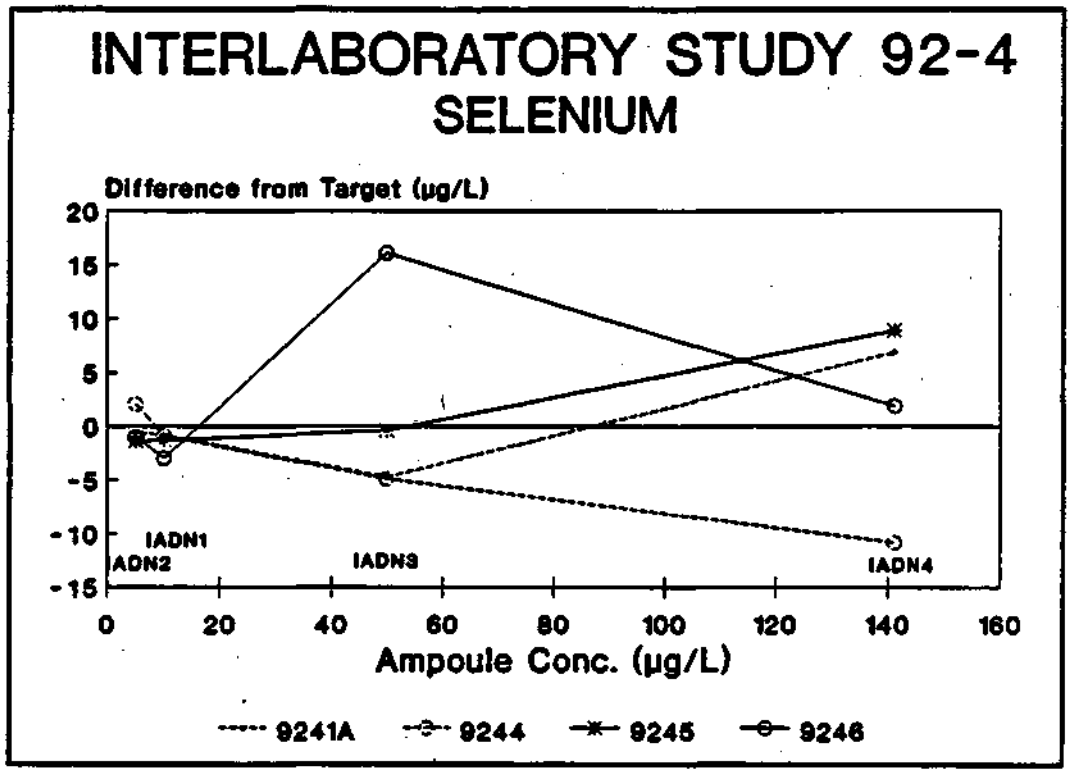

Figure 13 - Absolute Difference from Target

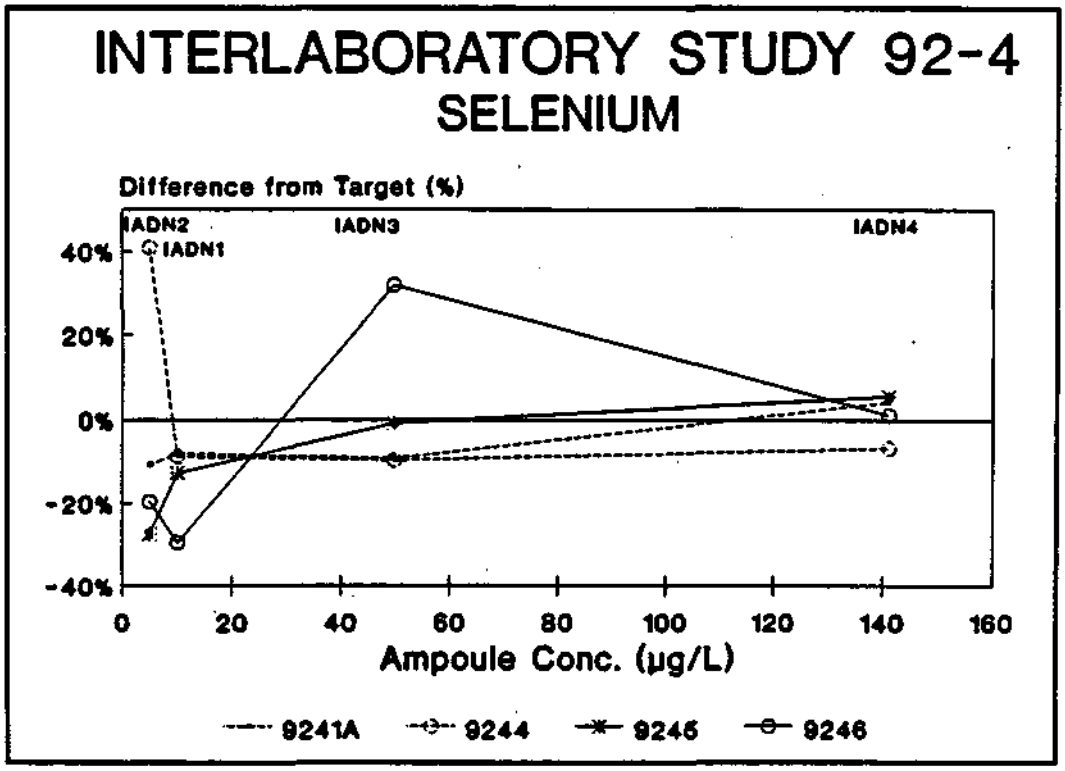

Figure 14 - Percent Difference from Target

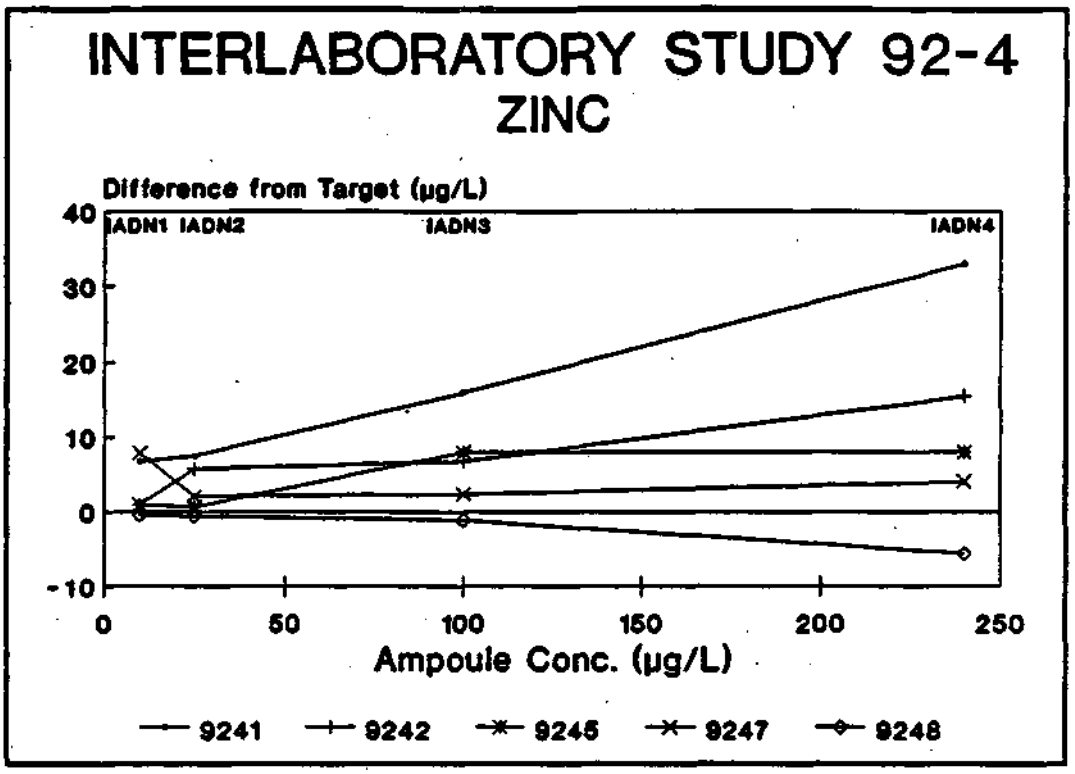

Figure 15 - Absolute Difference from Target

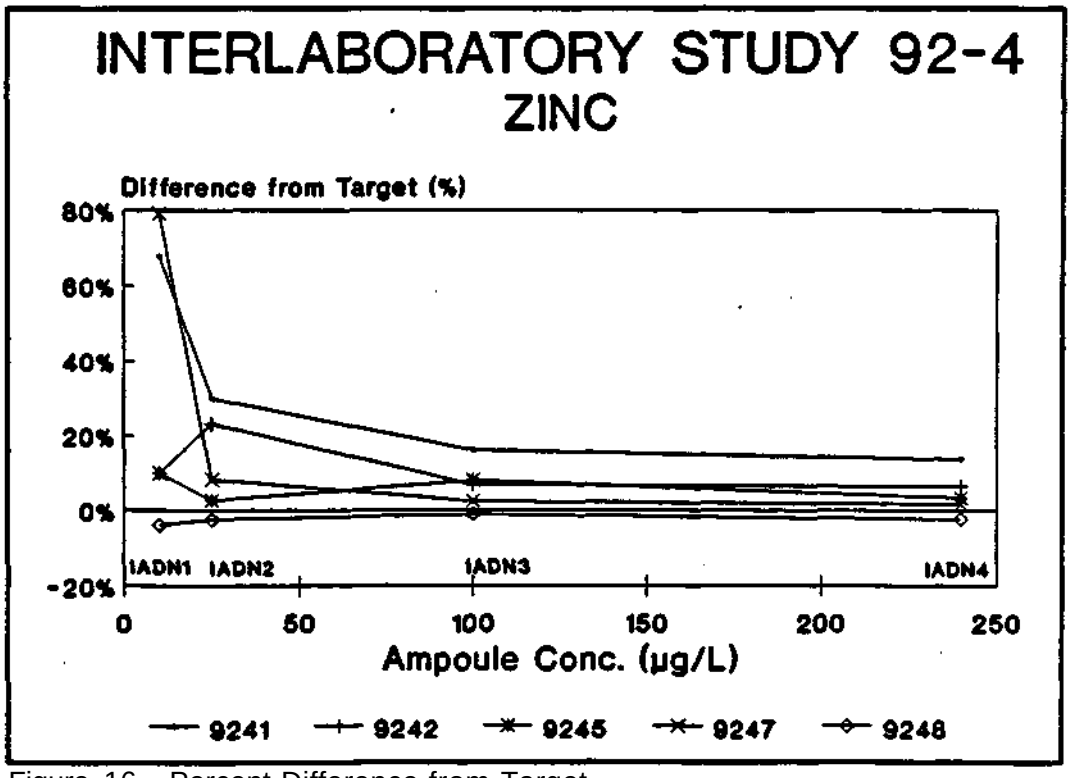

Figure 16 - Percent Difference from Target

8 APPENDIX 2 - PARTICIPANTS AND CORRESPONDENCE

List of Participants

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Quality Management Office

July 13, 1992

Dear Interlaboratory Study 92-4 Participant,

Please find enclosed four 50 mL ampoules for the analysis of metals. The ampoules are labelled IADN1, IADN2, IADN3, and IADN4. If you are missing any of the ampoules or they have broken in transit, please contact Sathi Selliah at (416) 235-5700 immediately for replacement.

The ampoules are ready for direct instrumental analysis. Break open the ampoule on the scored mark and transfer the contents to the appropriate sample container for your analytical system. No dilutions should be required, but if you do so, please mark the dilution factor used on the accompanying report form. All the ampoules contain the following metals: Aluminum, Chromium, Copper, Zinc, Arsenic, Selenium, Cadmium and Lead.

Please report all results on the accompanying form by August 7. 1992.

Thank you for your participation in this study.

Your identification code is:

Sylvia Cussion
Laboratory Quality Audit Scientist
(416) 235-5842
FAX (416) 235-6110

INTERLABORATORY STUDY 92-4

METALS FOR THE INTEGRATED ATMOSPHERIC DEPOSITION NETWORK

Identification Code:

Units:

Element	IADN1	IADN2	IADN3	IADN4
Al				
Cd				
Cr				
Cu				
Pb				
Zn				
As				
Se				

INSTRUMENT USED FOR ANALYSIS:

Quality Management Office

November 4, 1992

Dear Participant of Interlaboratory Study 92-4,

Please find enclosed the table of results from Interlaboratory Study 92-4. If there are any transcription errors, please contact me at (416) 235-5842.

As originally indicated in the initial study outline, there will be three phases for Interlaboratory Study 92-4. The target date for the submission of Phase 2 samples (ampouled solutions) is mid-January 1993. Exact details will be provided in December 1992.

Your identification code is:

Sincerely,

Sylvia Cussion
Laboratory Quality Audit Scientist
(416) 235-5842

9 APPENDIX 3 - INTERPRETATION OF BIASES IN DIFFERENCE PLOTS

Interlaboratory study results may be evaluated by comparing the difference from target (D) to the target or consensus value (X). This may be graphically represented with the Difference (D) on the vertical axis and the Target or consensus value (X) on the horizontal axis. By joining the individual points for each participant in order of increasing concentration, imprecision (squiggle in the line) versus bias or curvature (location of line relative to its expected position) may be demonstrated.

The precision envelope for the difference plots may be described by the following equation:

$$D = B_i + B_s \cdot C \pm (DL + f \cdot C)$$

where:	D	Difference from target	B_i	Intercept Bias
	C	Concentration	B_s	Slope Bias
	DL	Detection Limit	f	Fluctuation factor

The fluctuation factor (f) for Trace Metals is usually 5-10%. Data users' needs may determine how large a value for f is acceptable.

If there are no biases present (B_i and B_s = 0). the shape is symmetrical to and centred on the target line. Measurement differences among participating laboratories in an interlaboratory study should be attributable only to random fluctuation. An example using DL = 5 //g/L and f = 10% is given in Figure 17.

When an intercept bias is present, the envelope shifts in the direction of the bias. If this shift exceeds the Method Detection Limit (MDL), this becomes a matter of concern for the analyst. An example with B_i = -5 μg/L is given in Figure 19.

When a slope bias is present, the envelope broadens in the direction of the bias as concentration increases. Then this bias exceeds the MDL + 10% concentration, it becomes a matter of concern for the analyst. An example of B, = + 10% is given in Figure 21.

Most interlaboratory study data sets will show a combination of slope and intercept biases among the participants. The precision envelope changes according the magnitude of both effects. An example using B_i = -5 μg/L and B, = + 10% is given in Figure 23.

The results may also plotted using the relative difference (R) on the vertical axis, the precision envelope flares dramatically as the concentration approaches zero. This type of plot tends towards an exaggerated impression of acceptable variability at the bottom end and may mask biases at higher concentration levels. However it can be useful when describing the range of performance among a group of participants. The above examples that were presented using concentration units (absolute scale) are also presented using a relative scale (Figures 18, 20, 22 and 24).

REFERENCE

King, D.E.; July 1993; *Interpretation of Interlaboratory Comparison (Round-Robin) Data;* Internal Report. Ministry of Environment and Energy, Laboratory Services Branch; Draft.

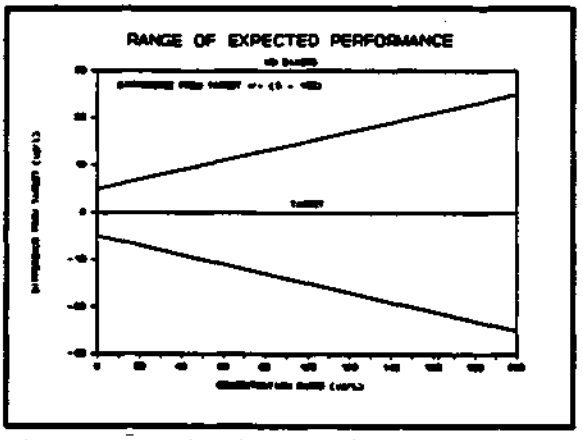


Figure 17 - Absolute Scale

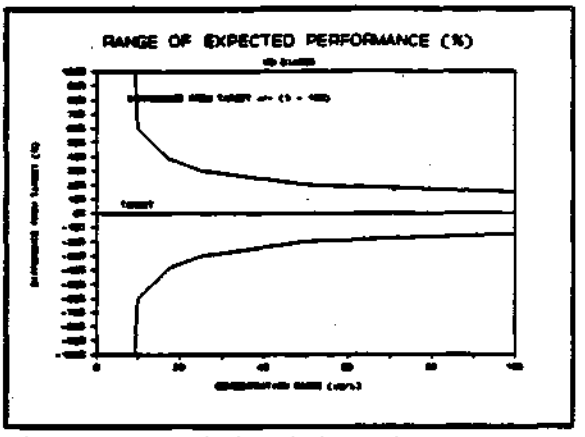


Figure 18 - Relative {%) Scale

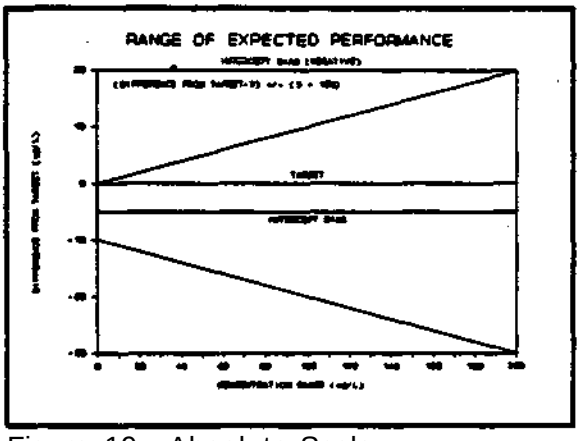


Figure 19 - Absolute Scale

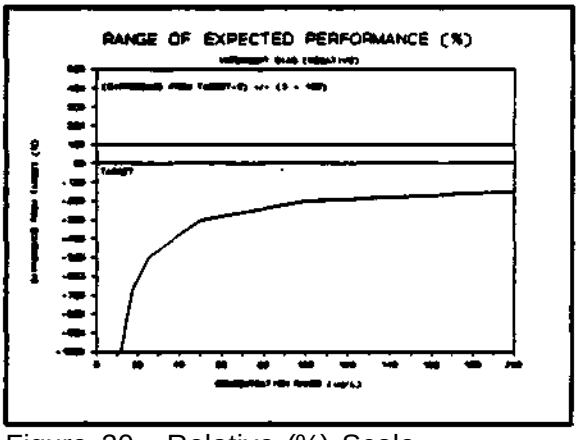


Figure 20 - Relative (%) Scale

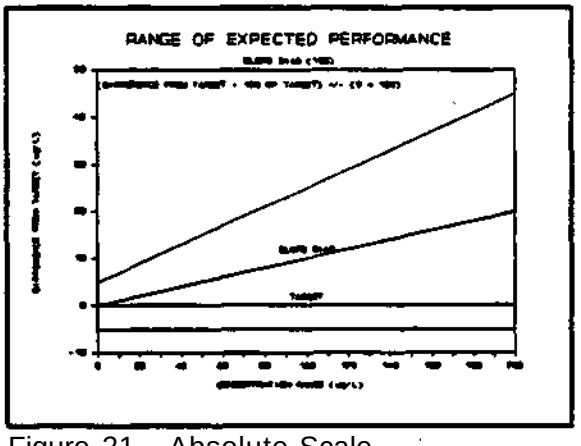


Figure 21 - Absolute Scale

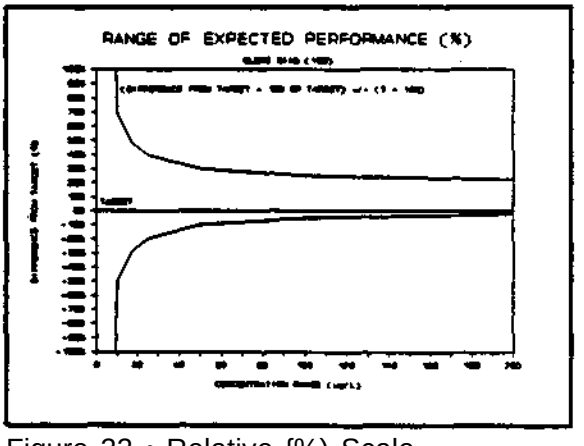


Figure 22 • Relative {%) Scale

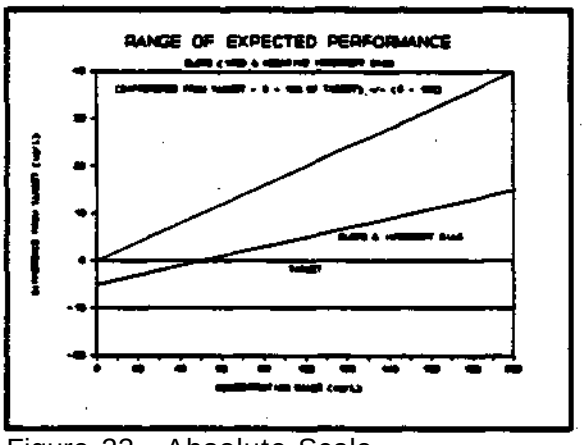


Figure 23 - Absolute Scale

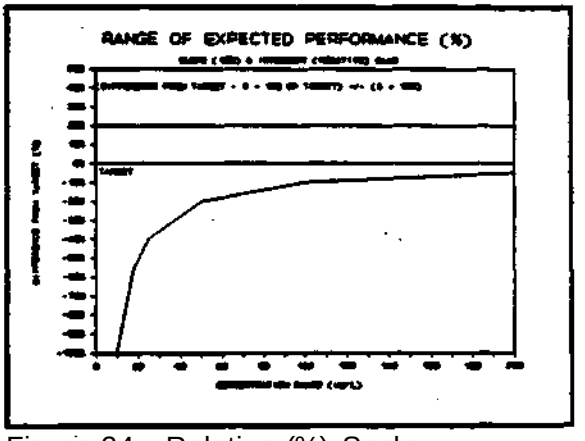
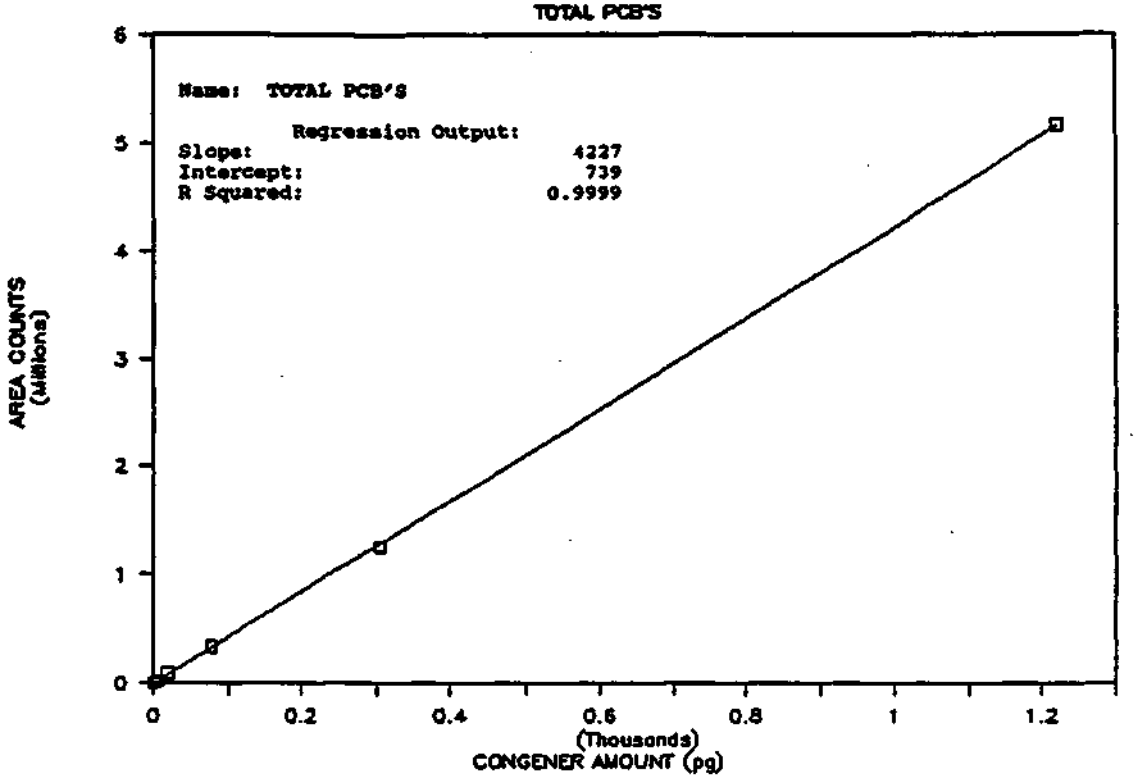


Figure 24 - Relative (%) Scale

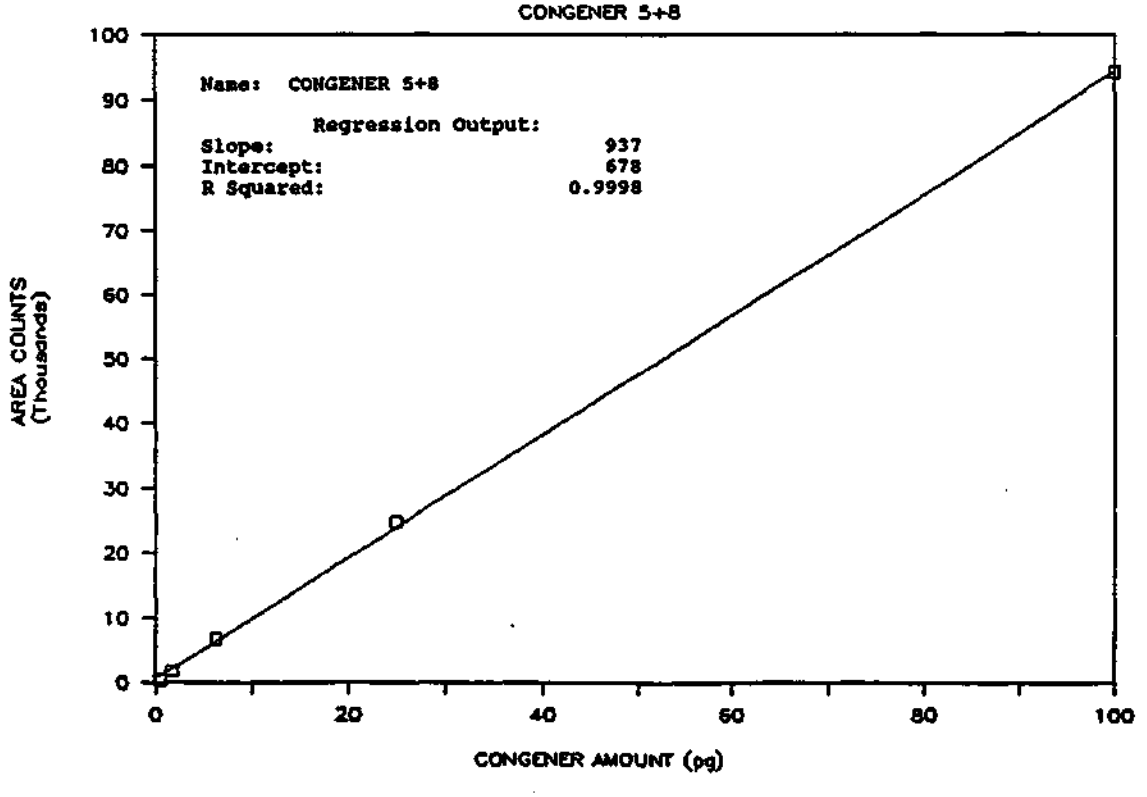
Appendix C

Instrument Linearity Data

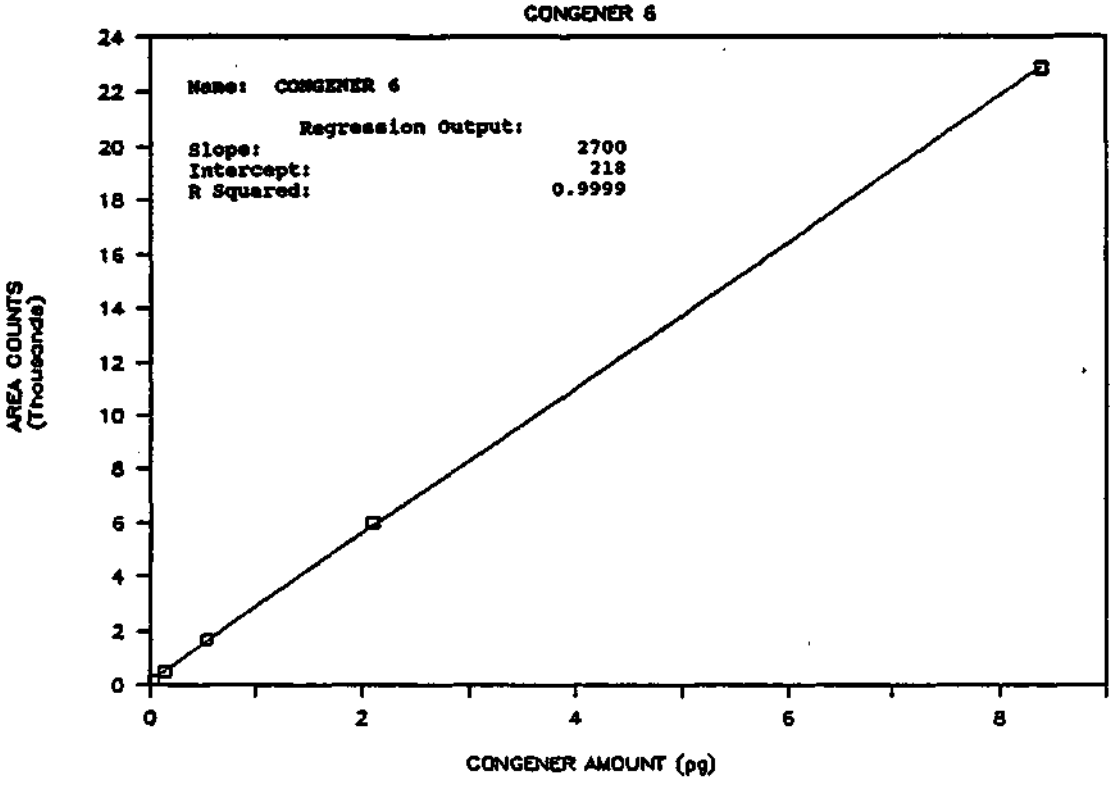
LINEARITY STUDY - PCB'S



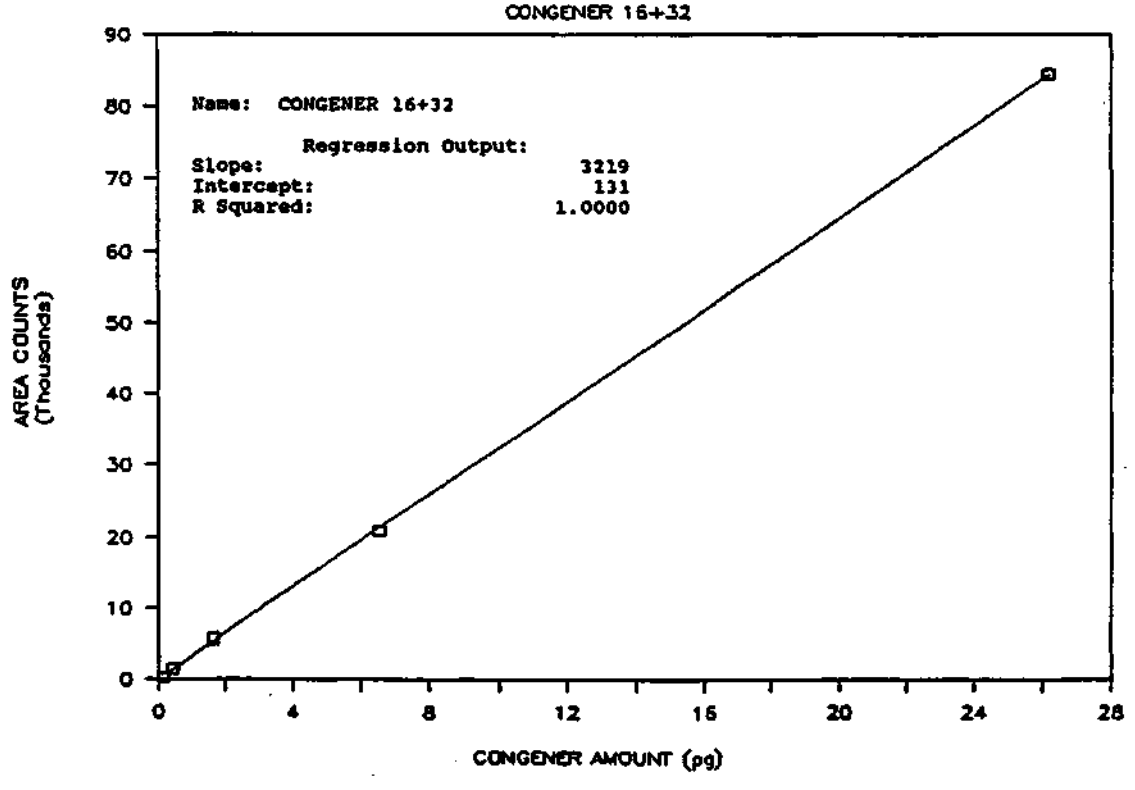
LINEARITY STUDY - PCB'S



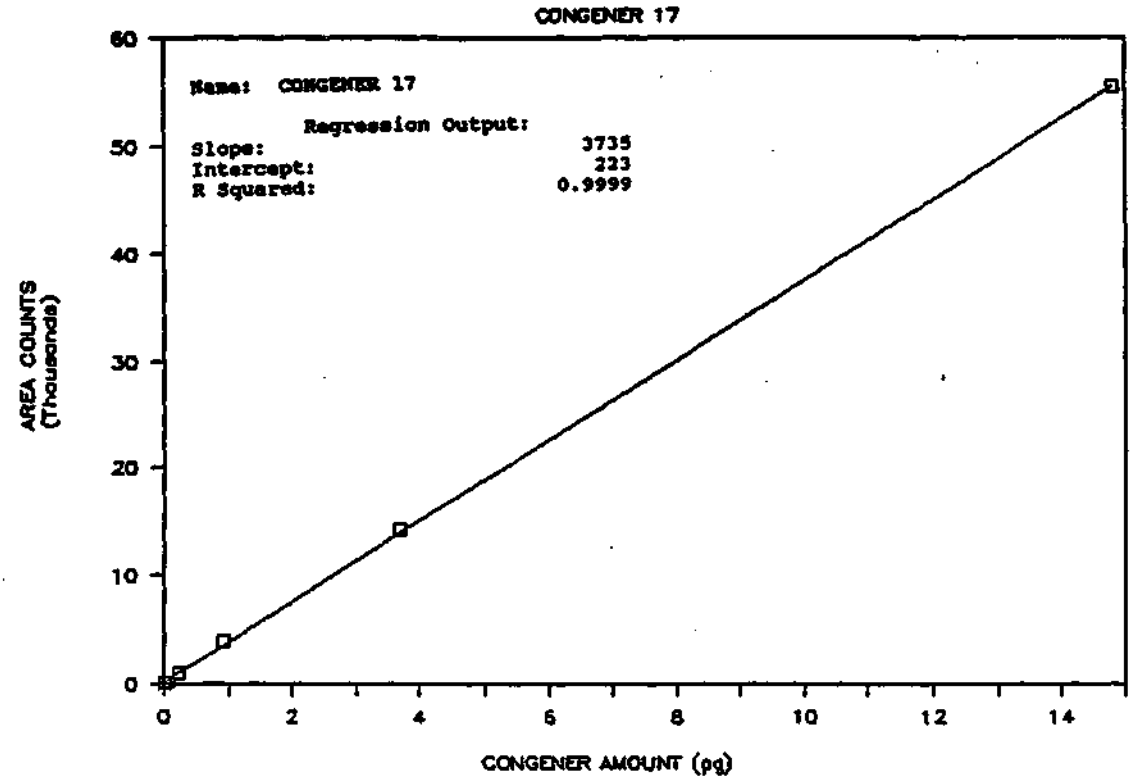
LINEARITY STUDY - PCB'S



LINEARITY STUDY - PCB'S



LINEARITY STUDY - PCB'S



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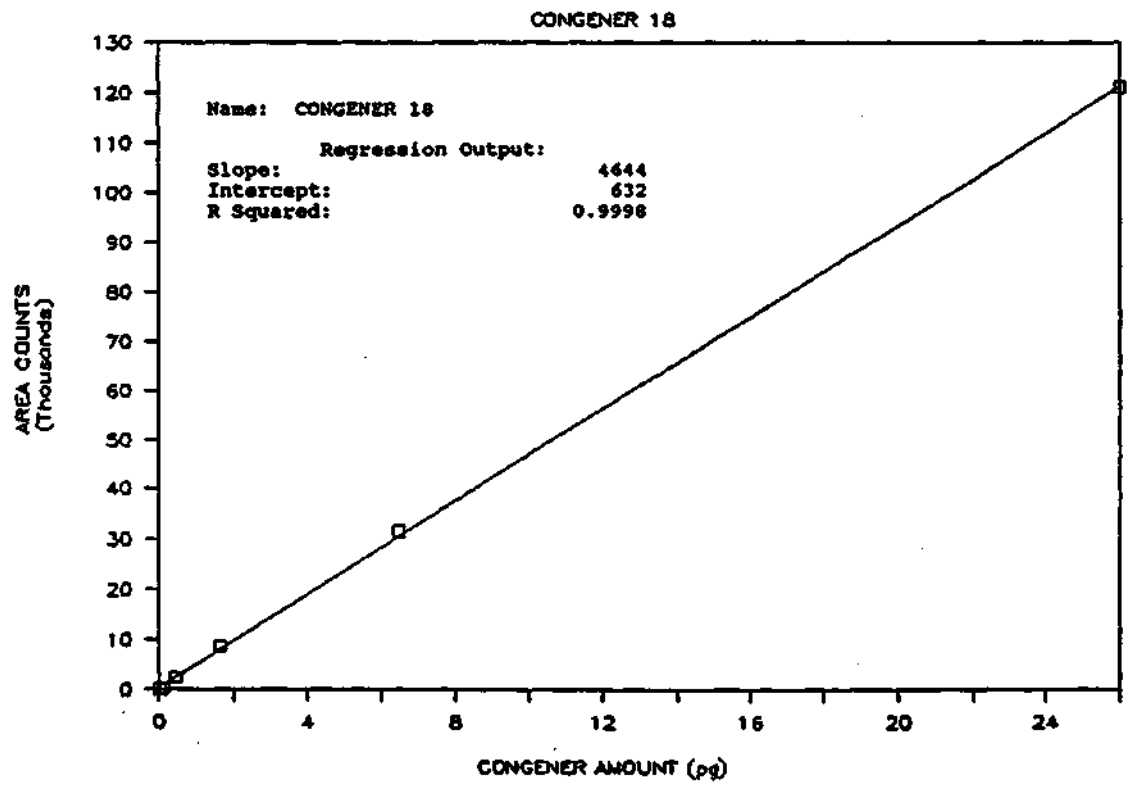
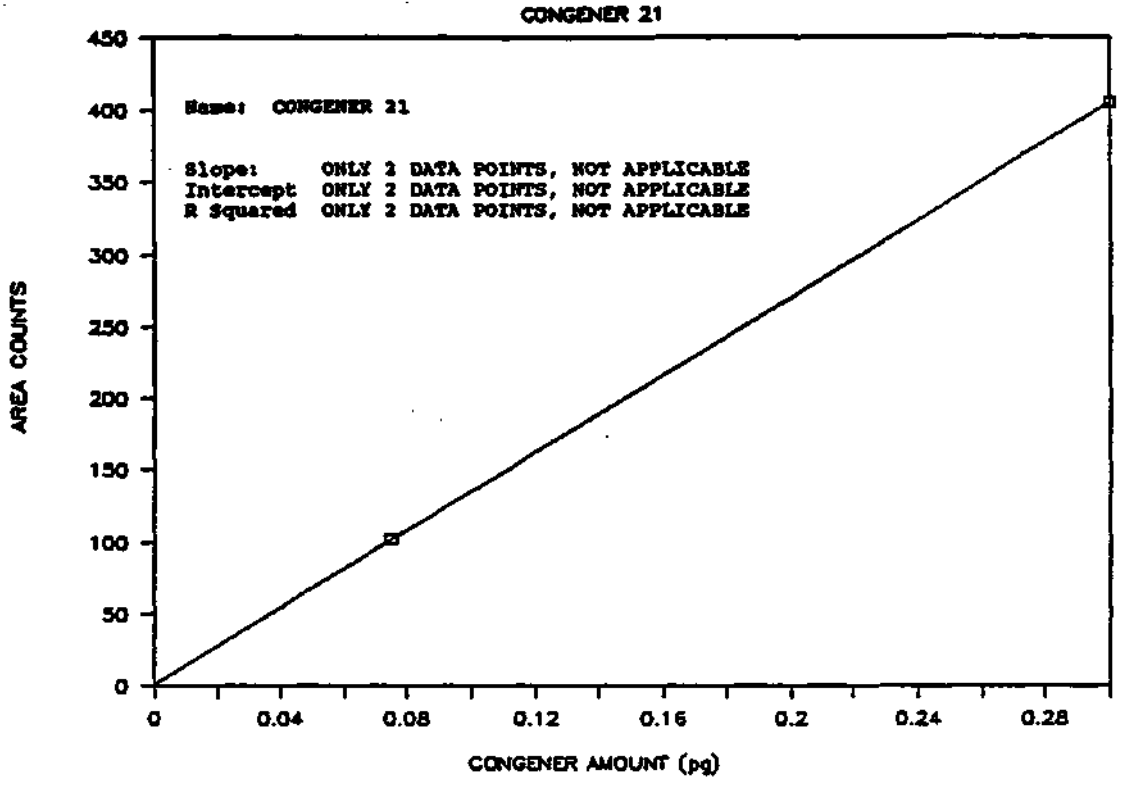


LINEARITY STUDY - PCB'S



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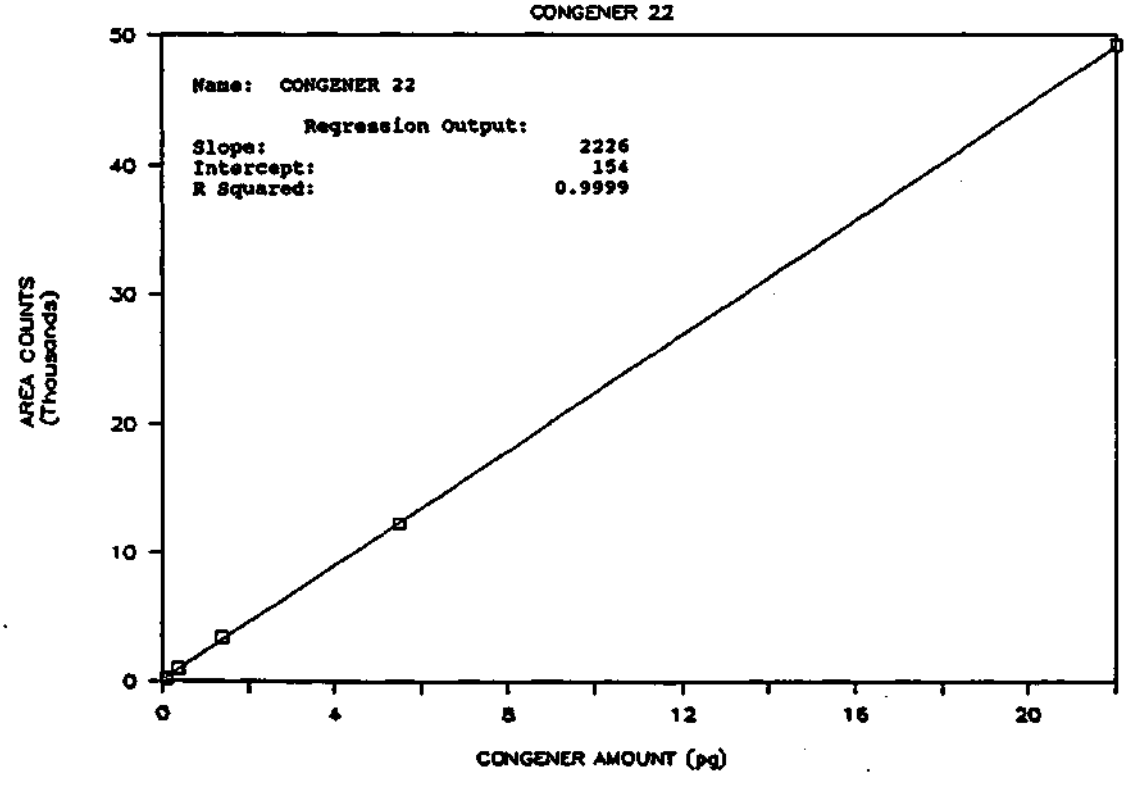

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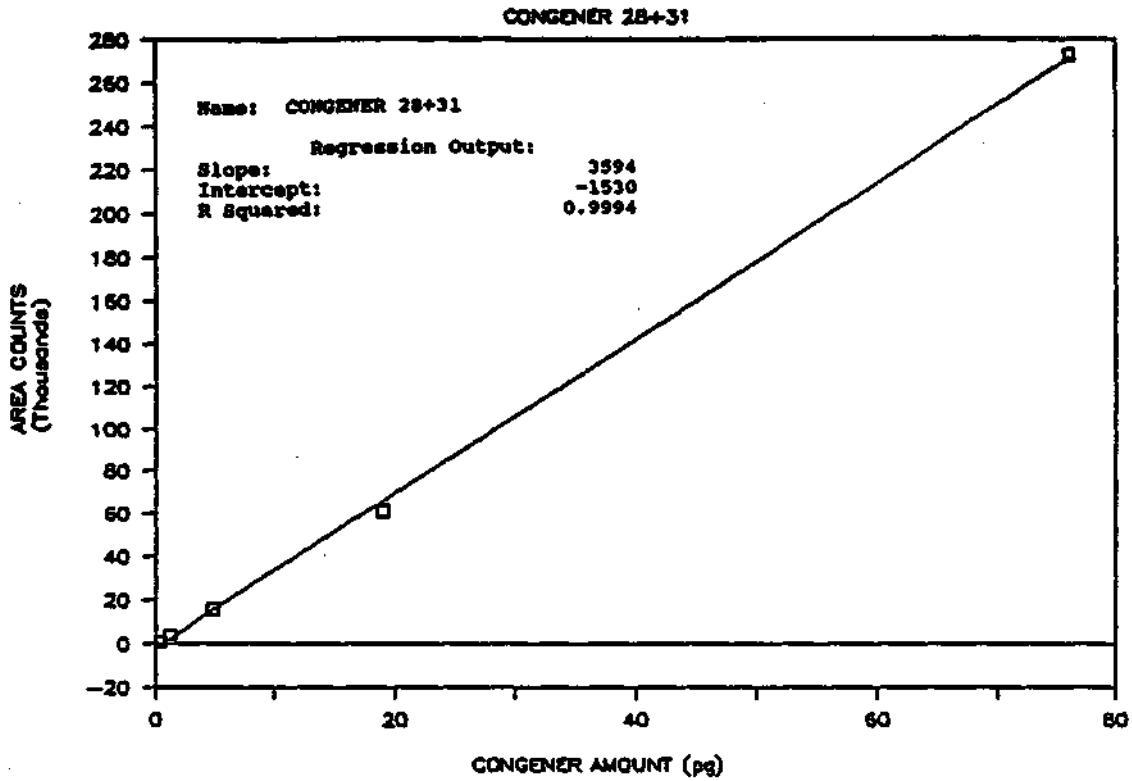

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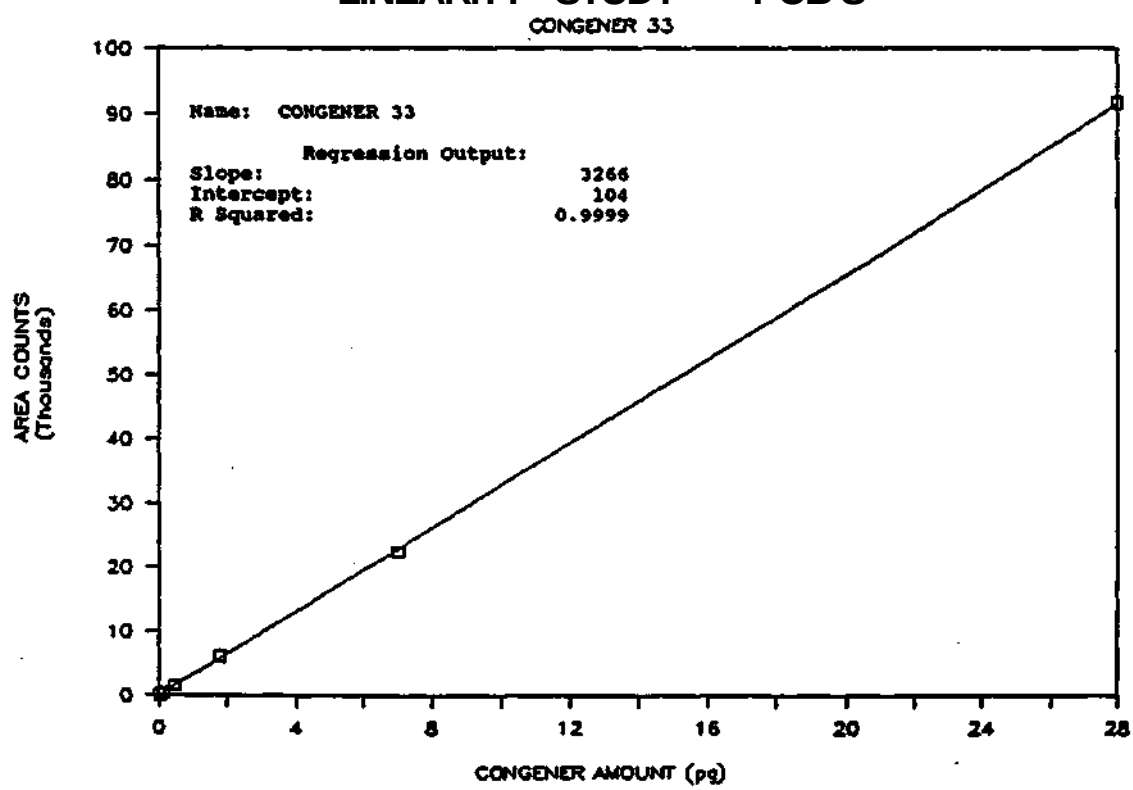

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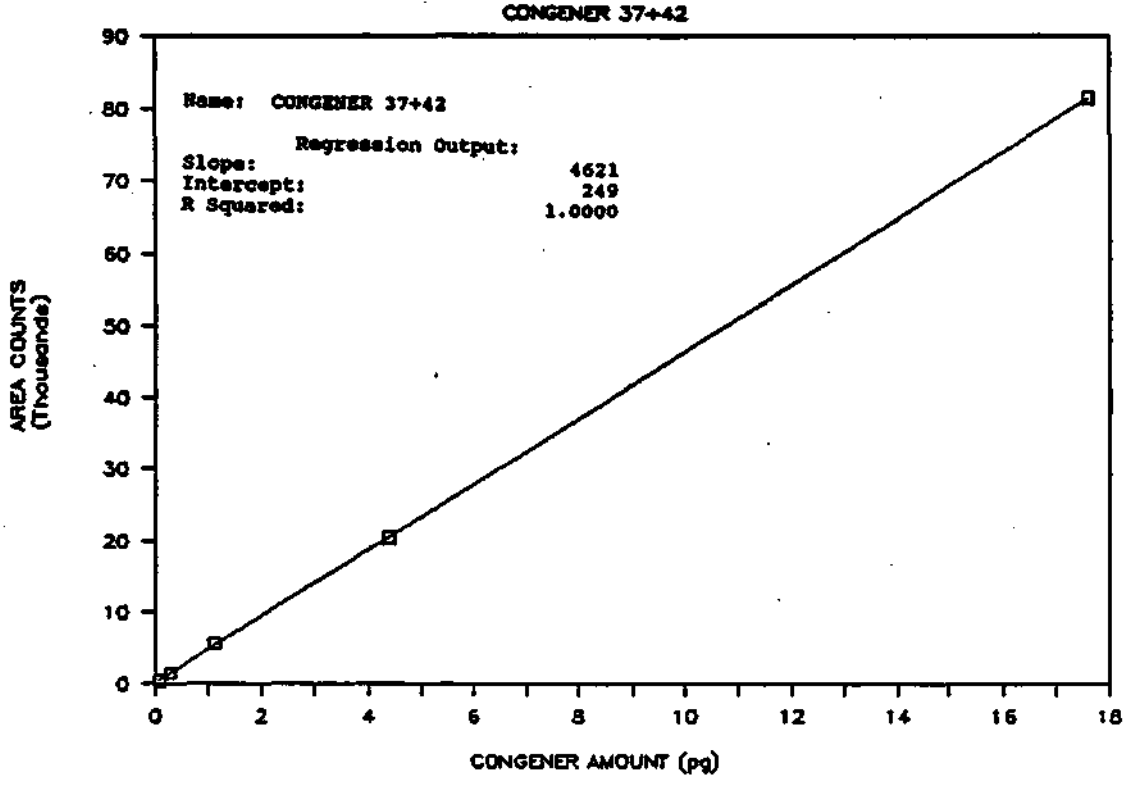
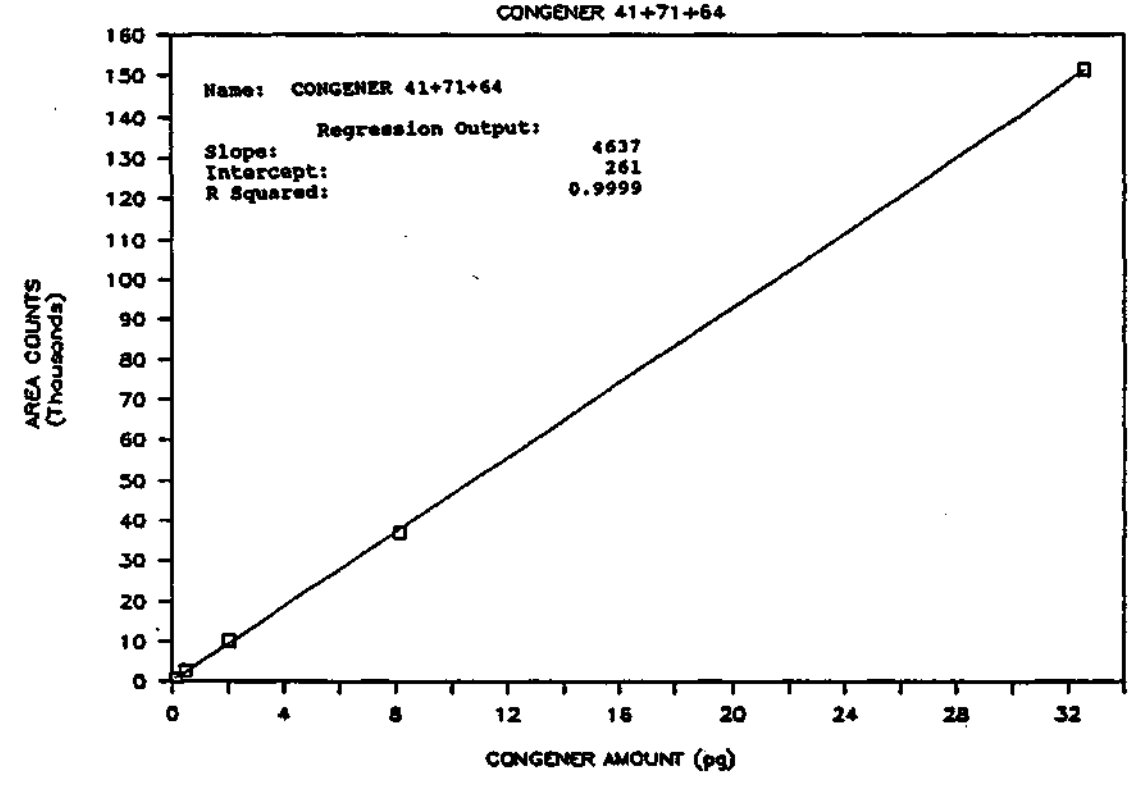
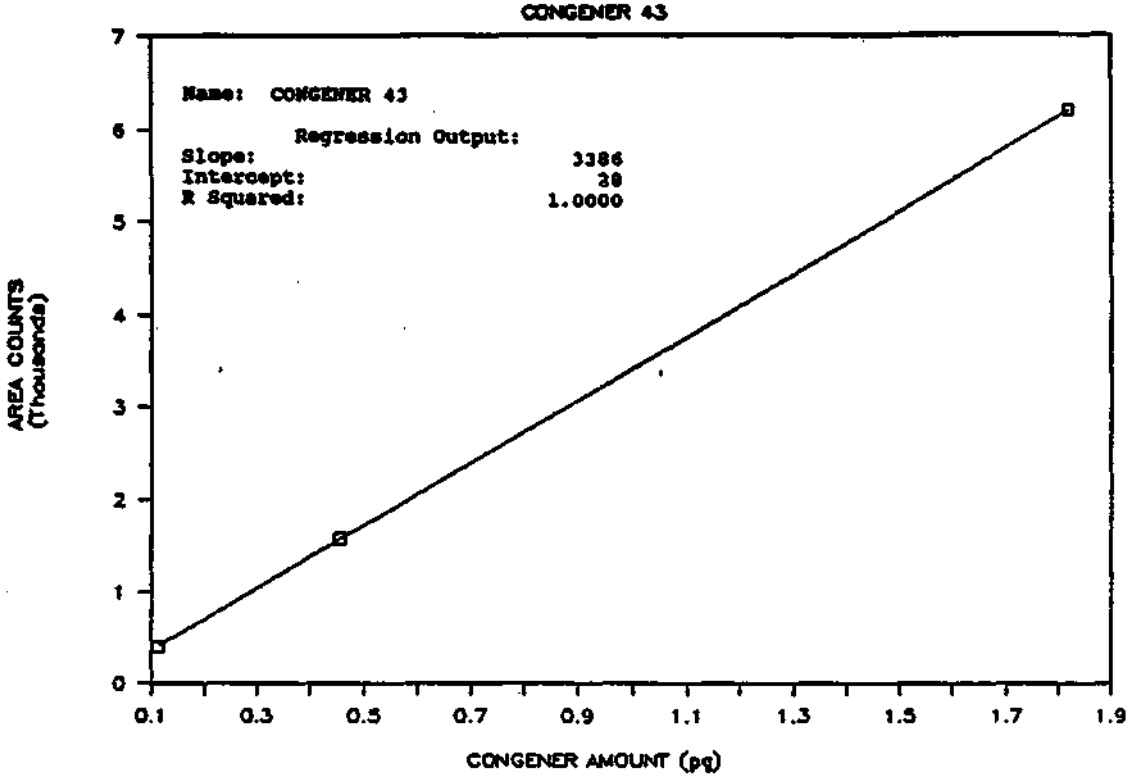


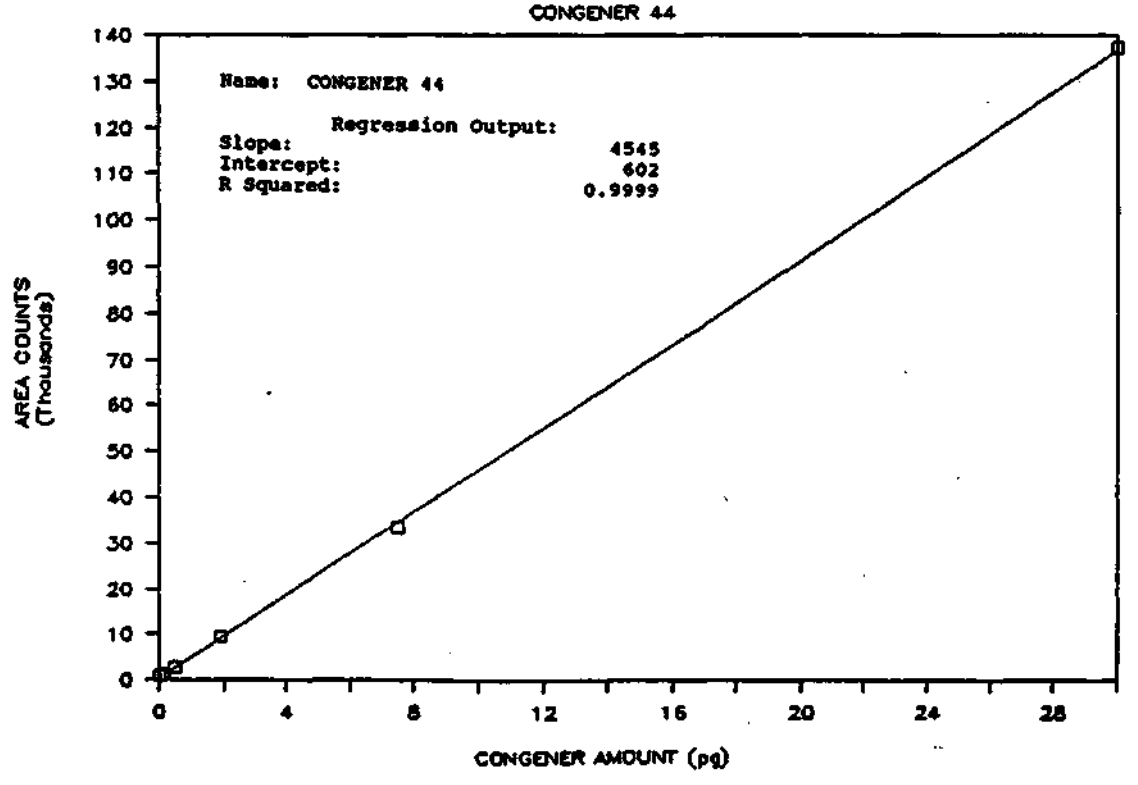
LINEARITY STUDY - PCB'S



LINEARITY STUDY - PCB'S



LINEARITY STUDY - PCB'S



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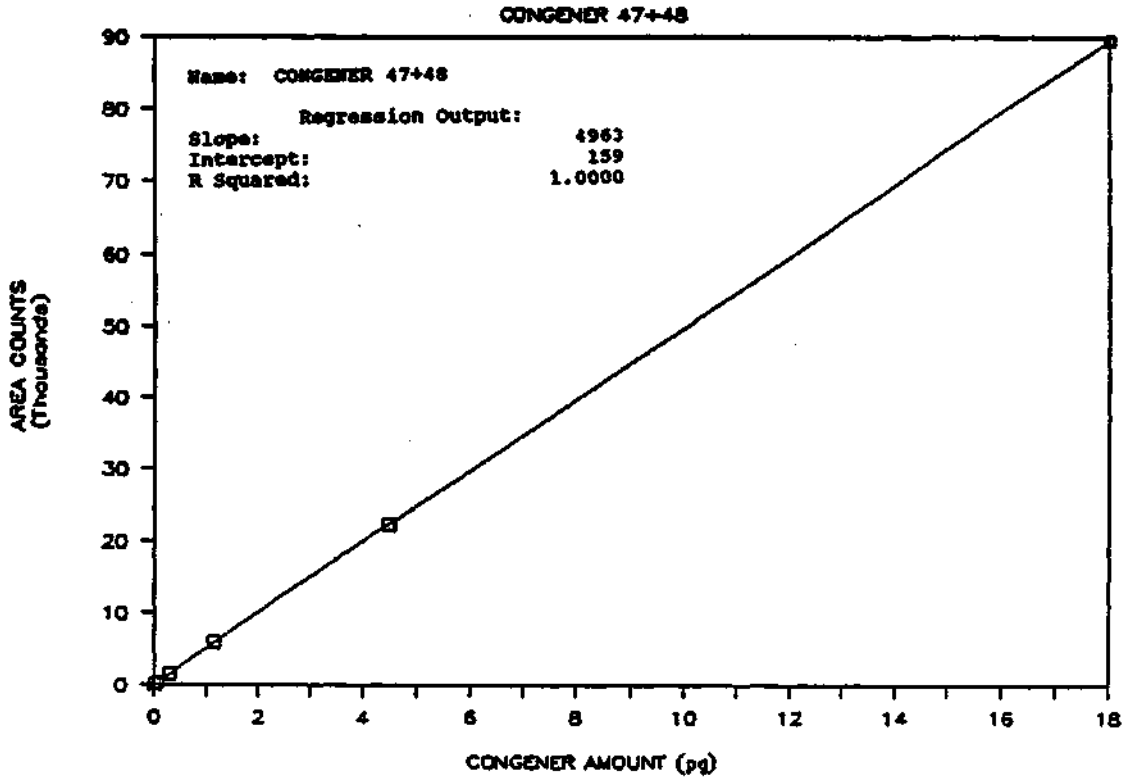

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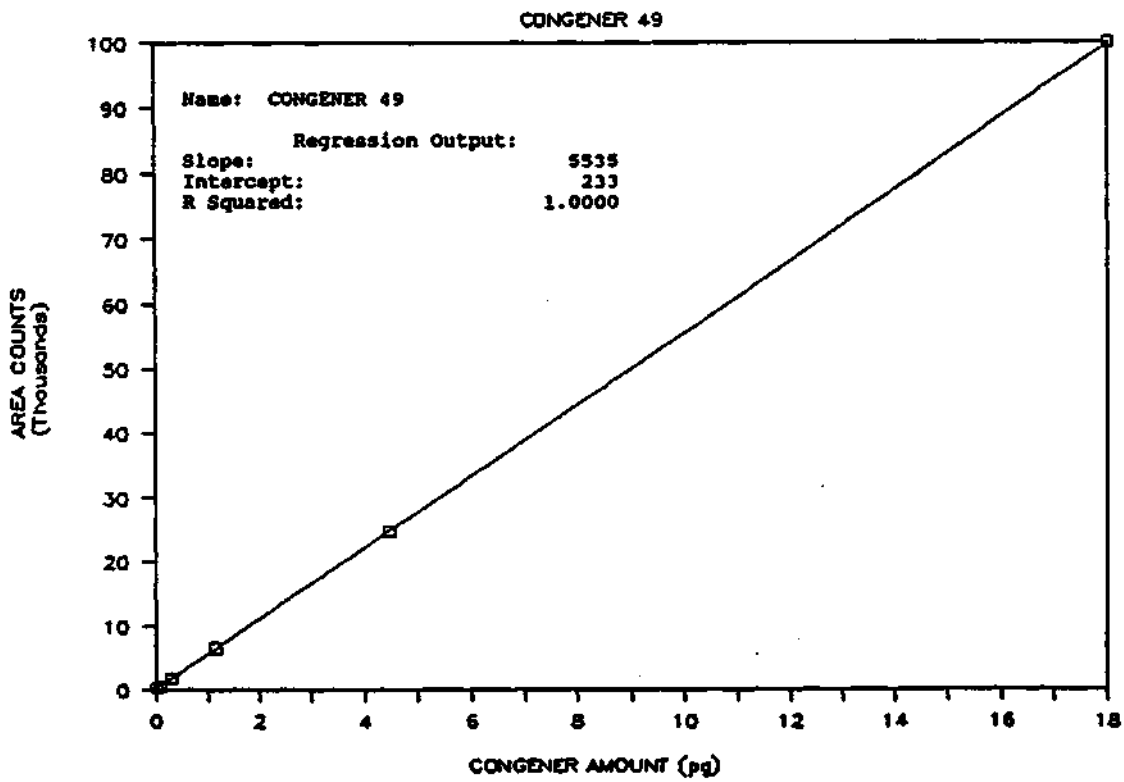
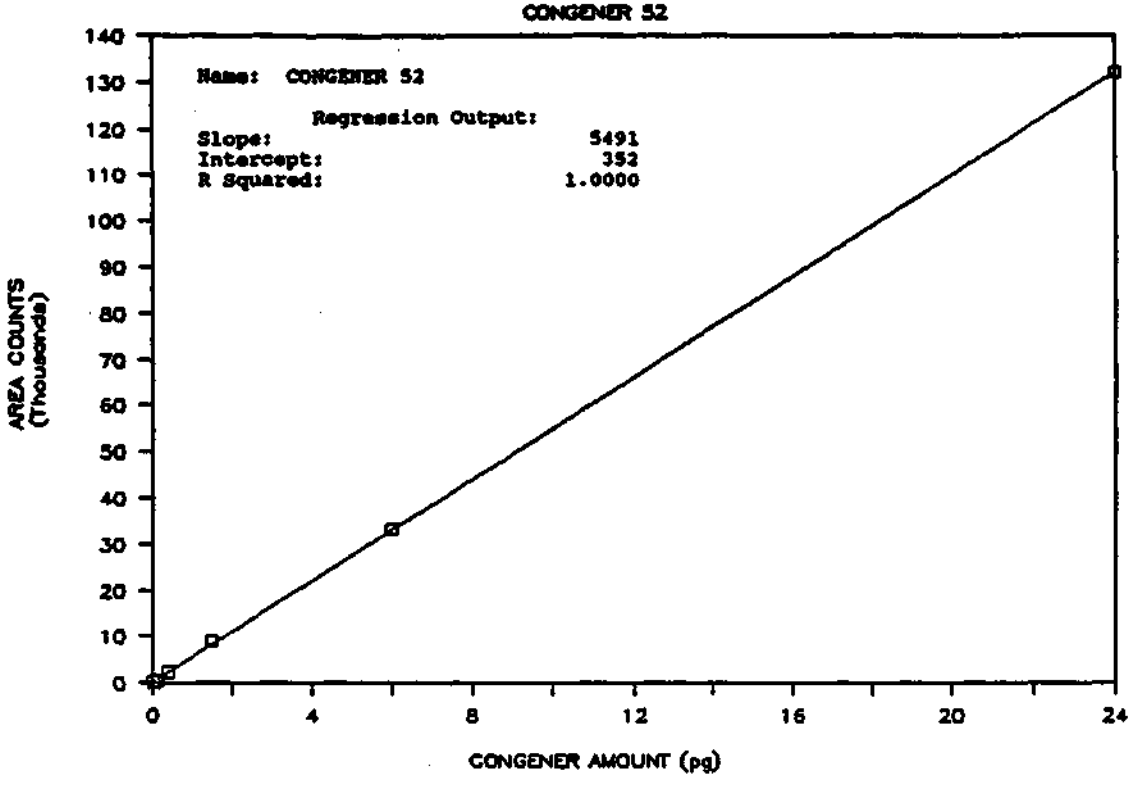
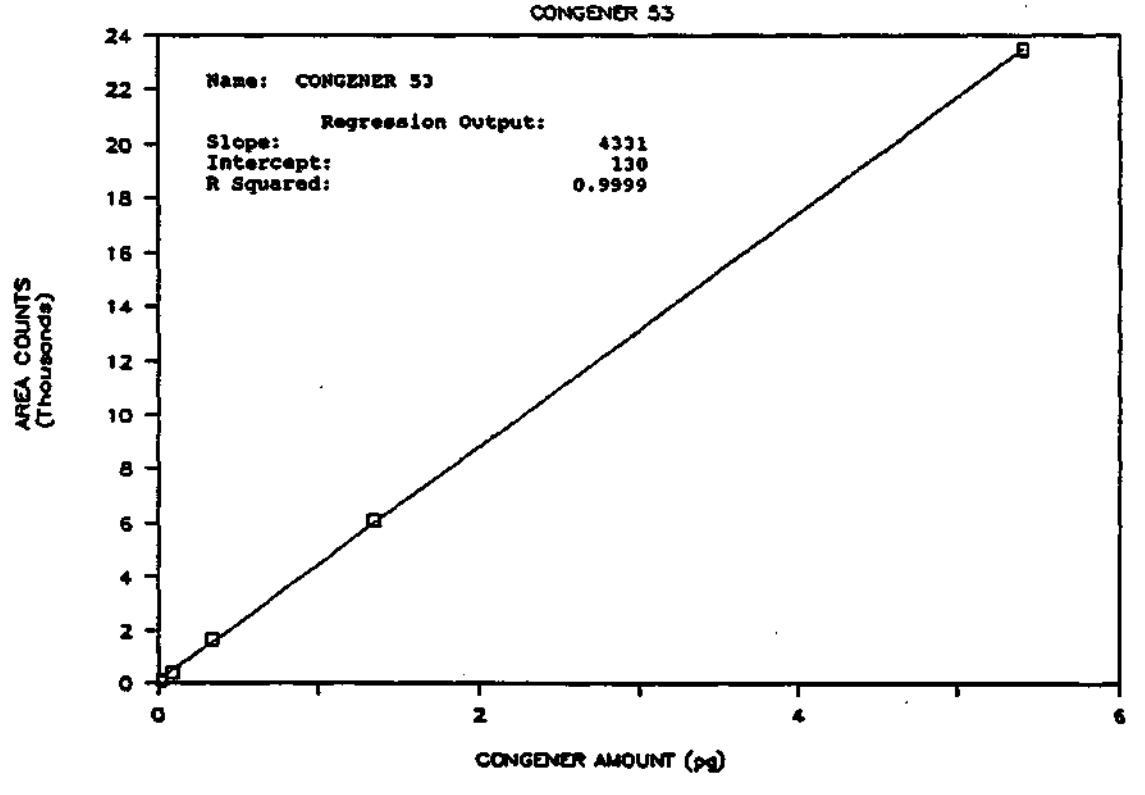


LINEARITY STUDY— PCB'S



LINEARITY STUDY - PCB'S



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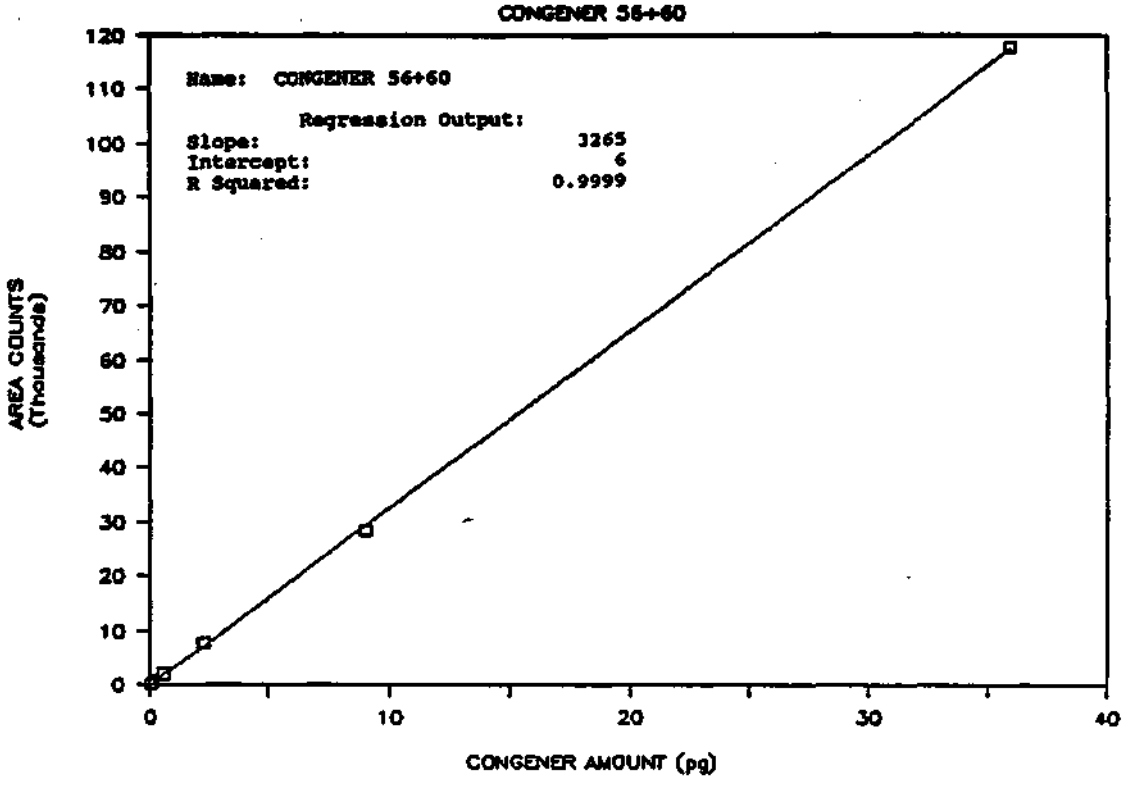
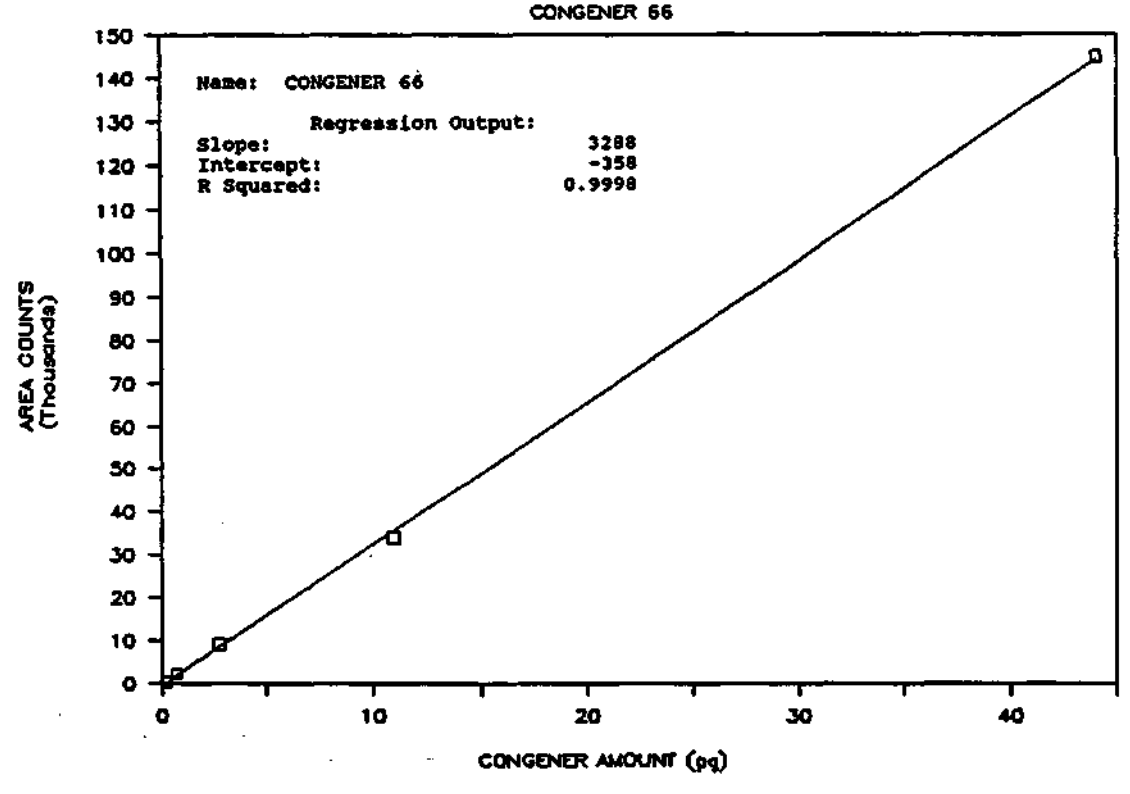


LINEARITY STUDY - PCB'S



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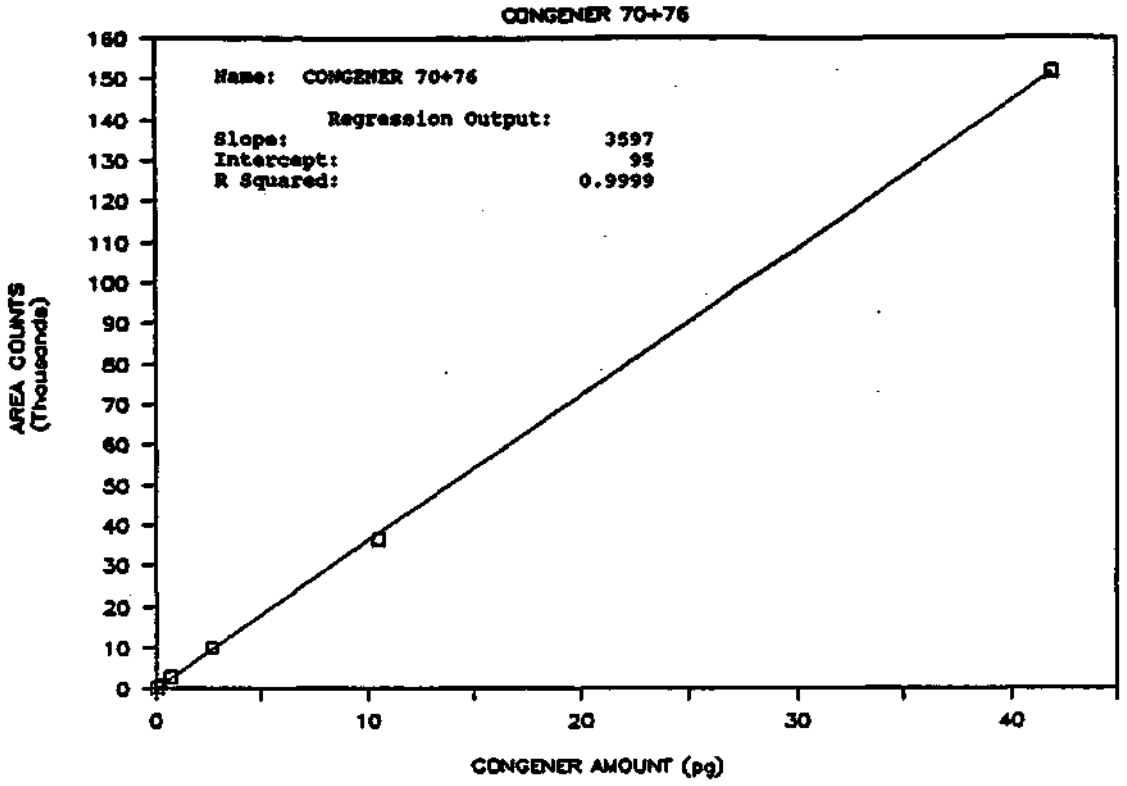

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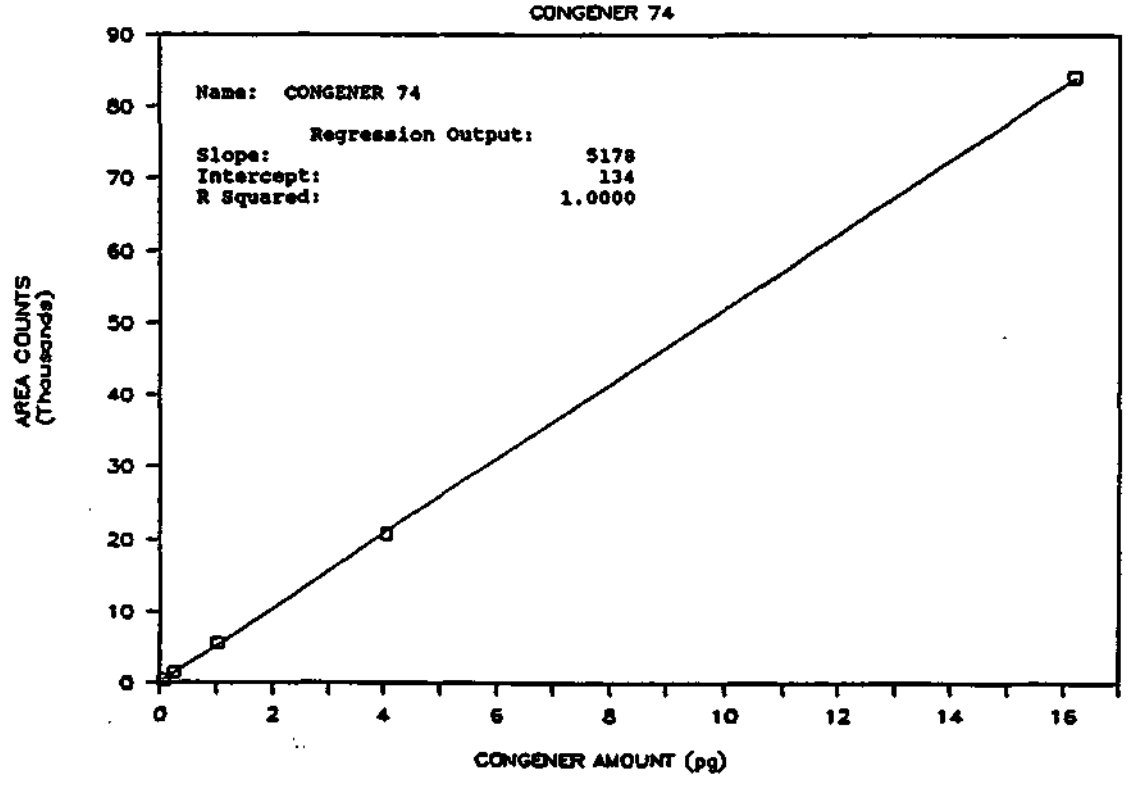

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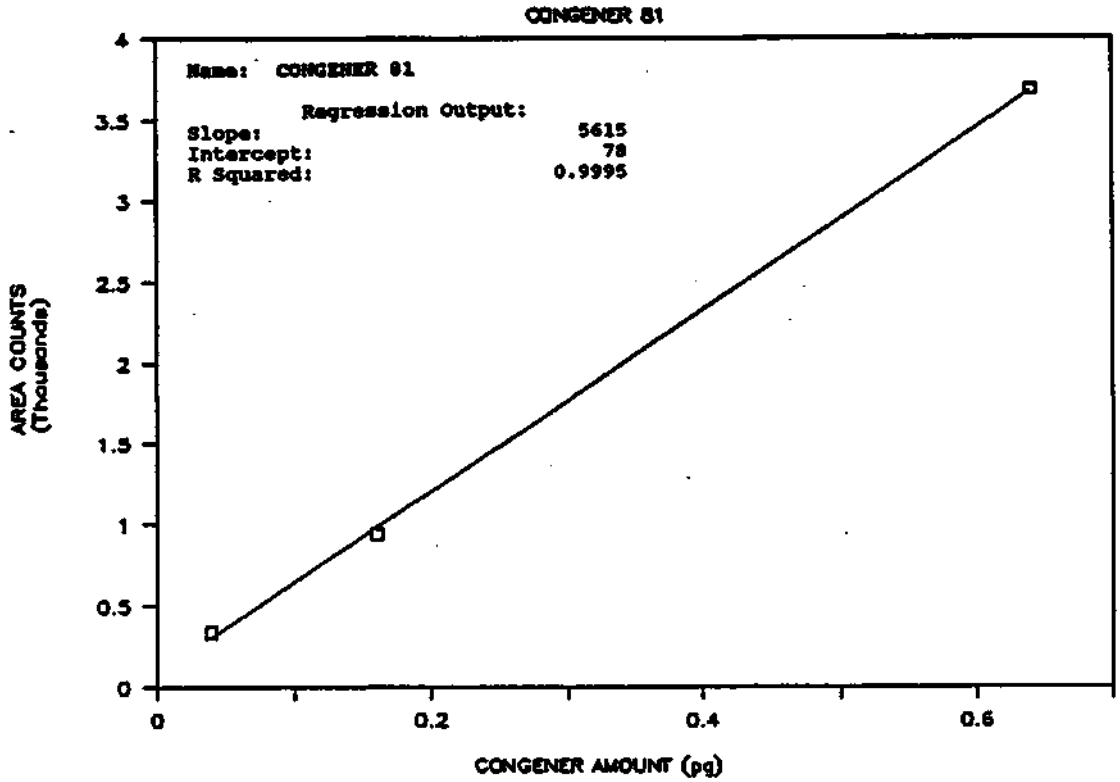

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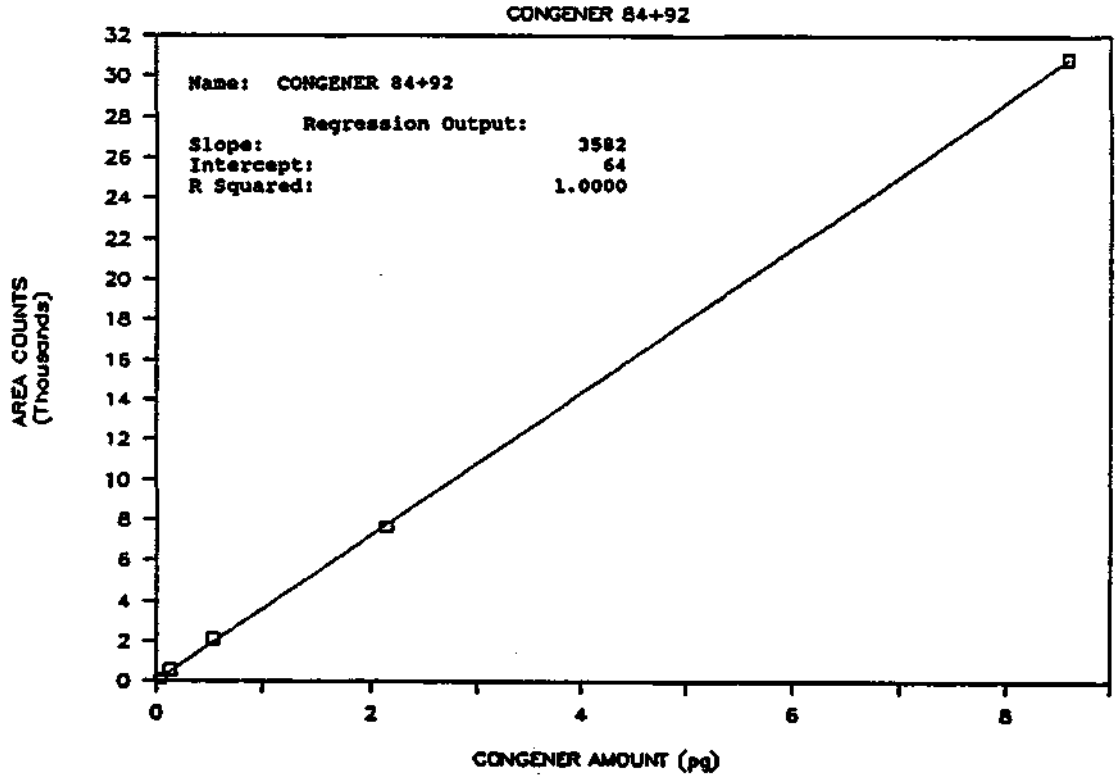

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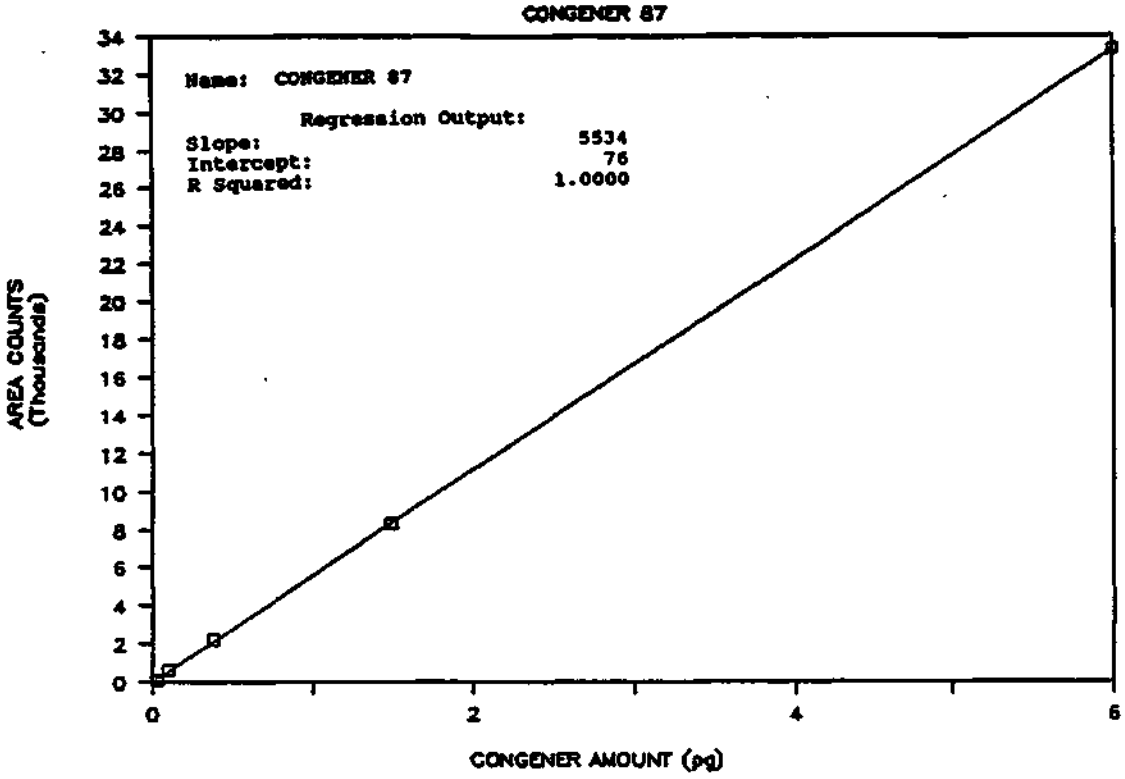

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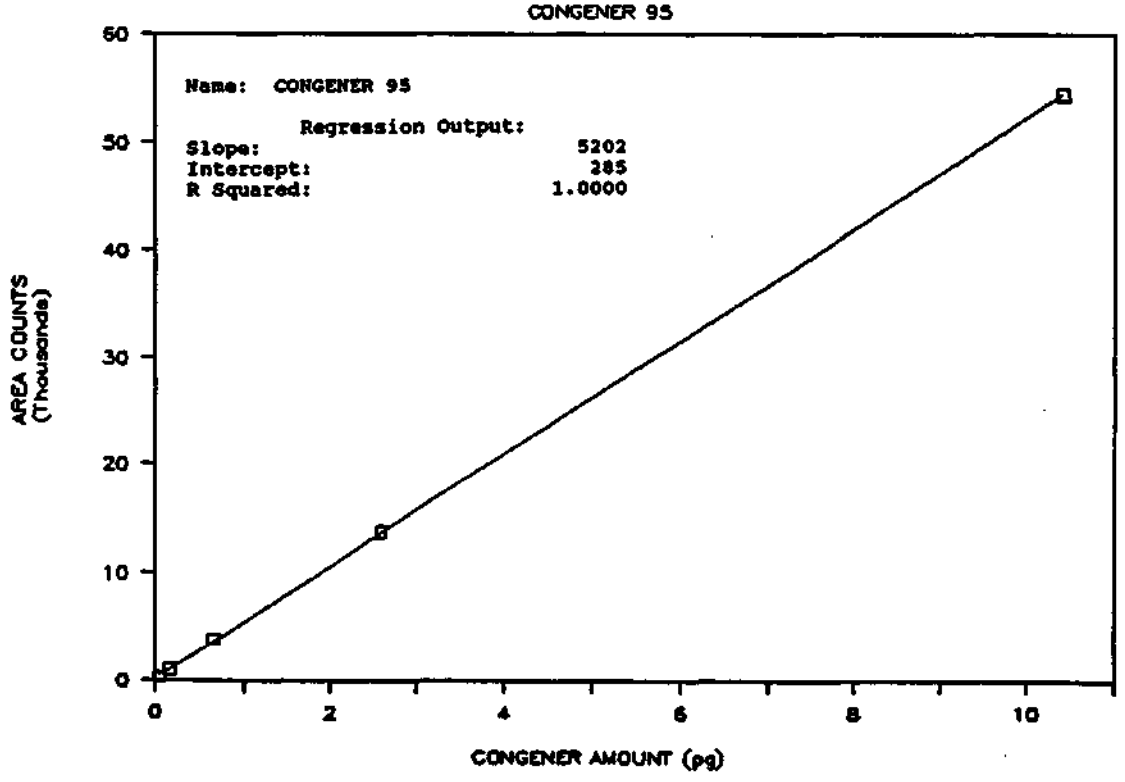

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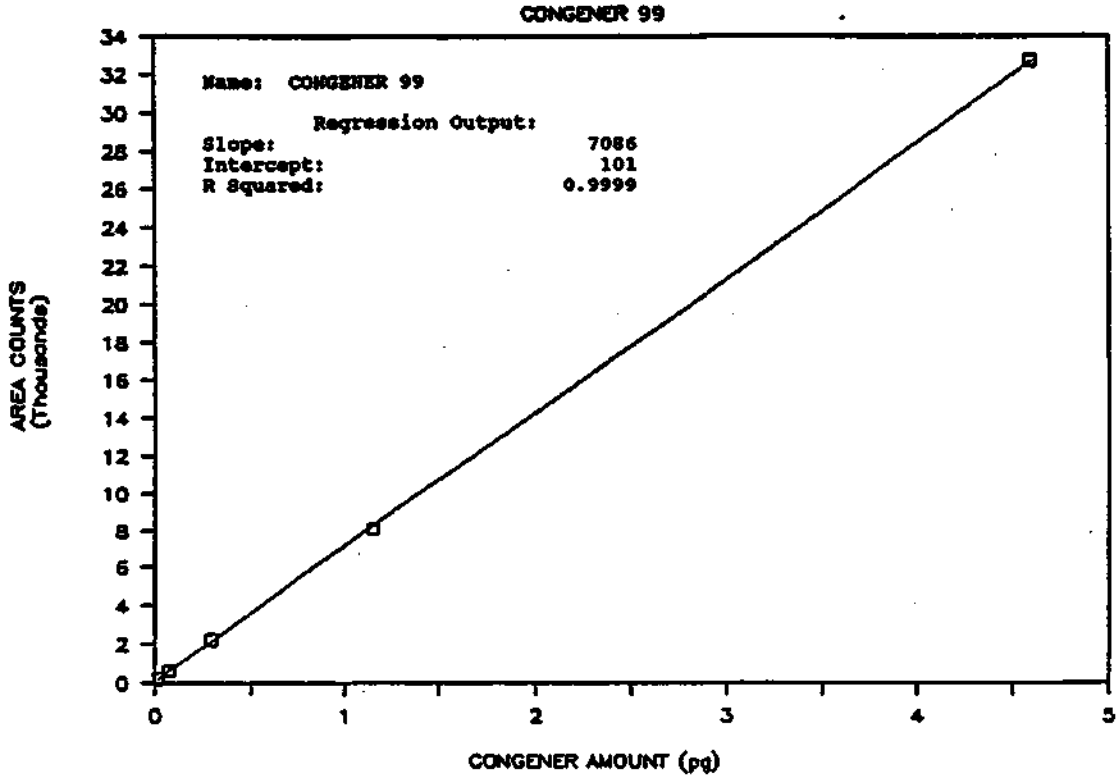

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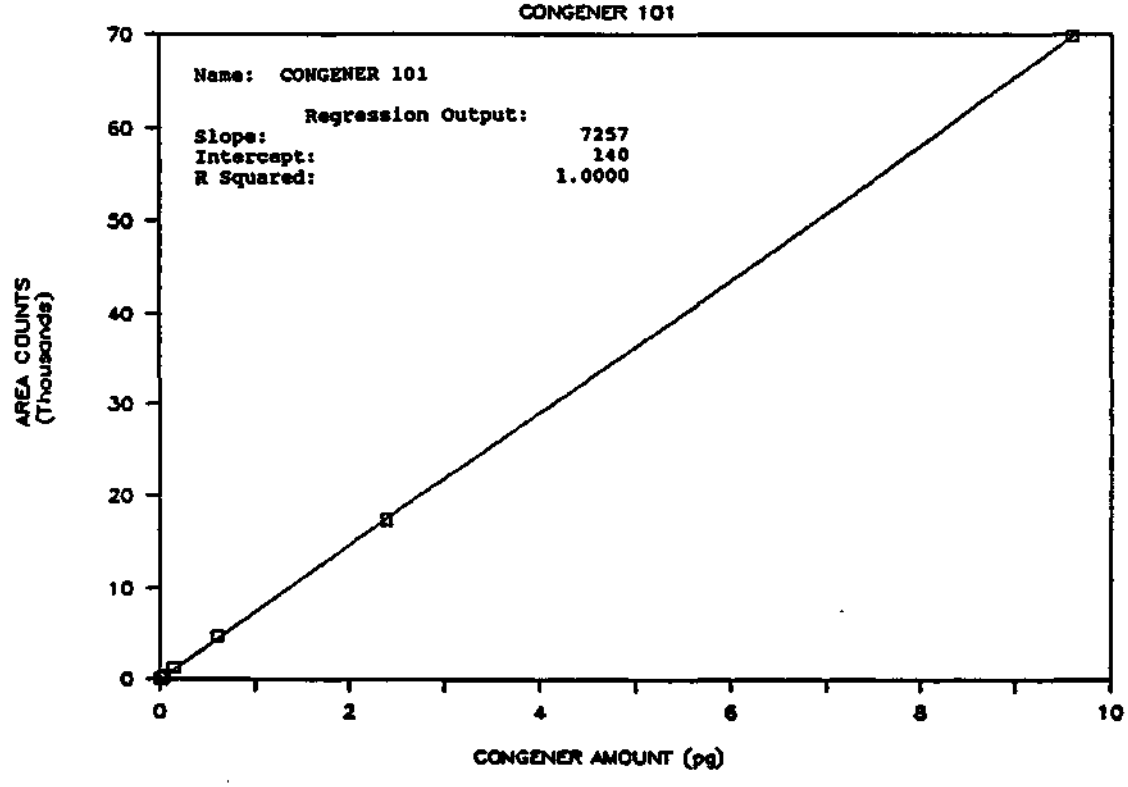
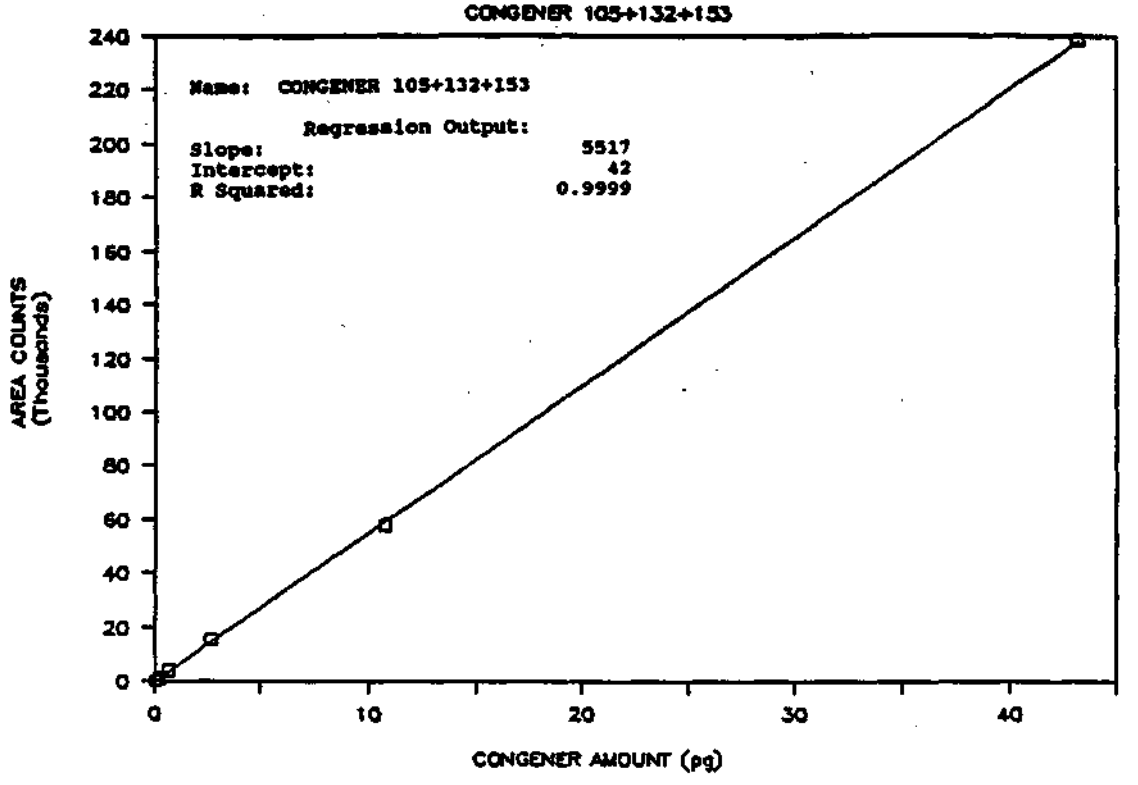


LINEARITY STUDY — PCB'S



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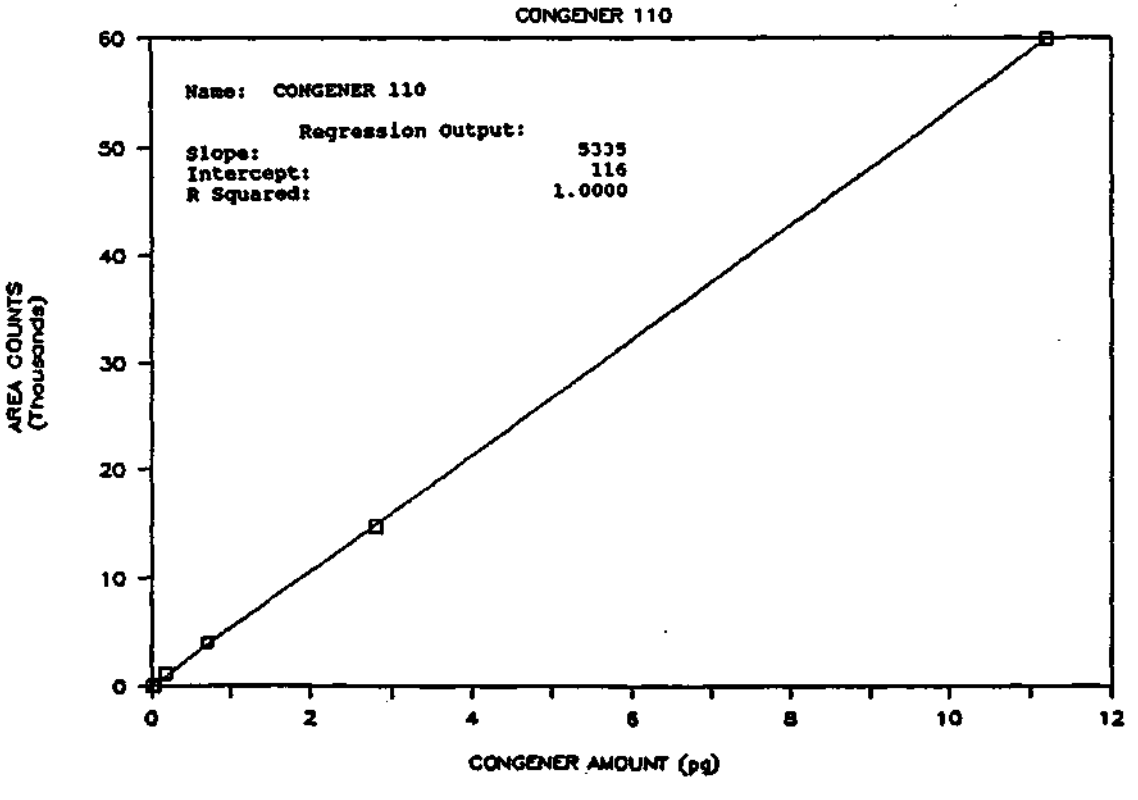

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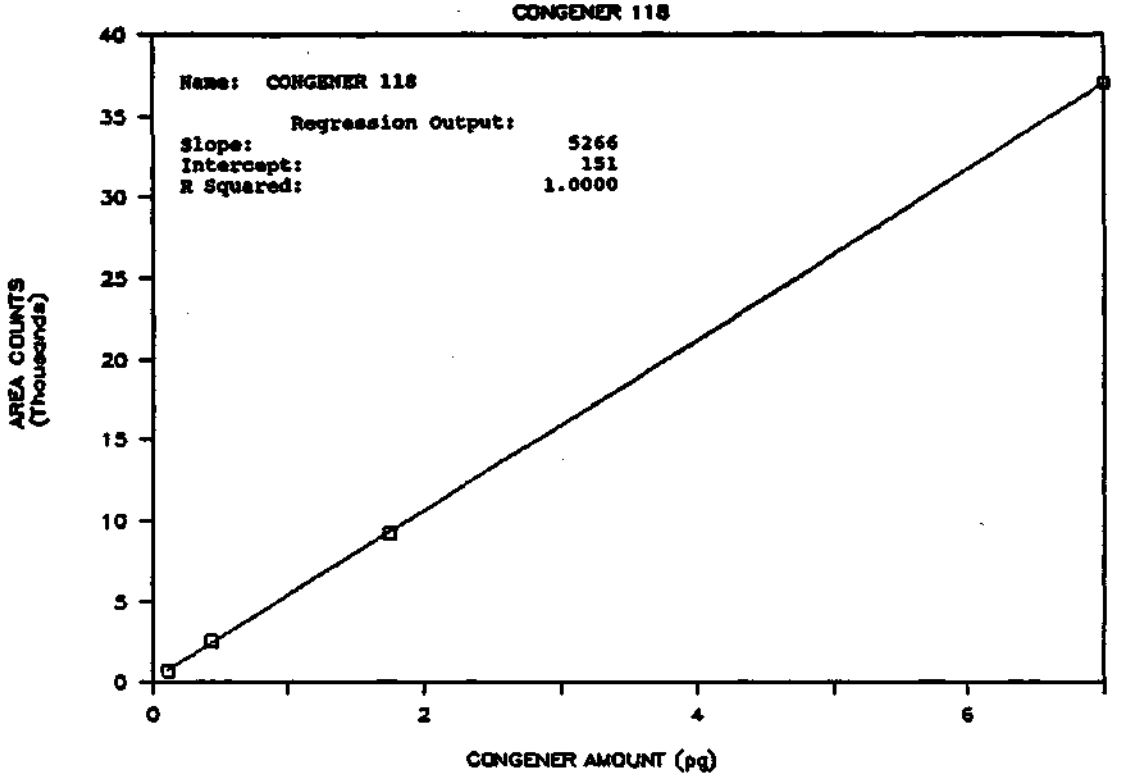
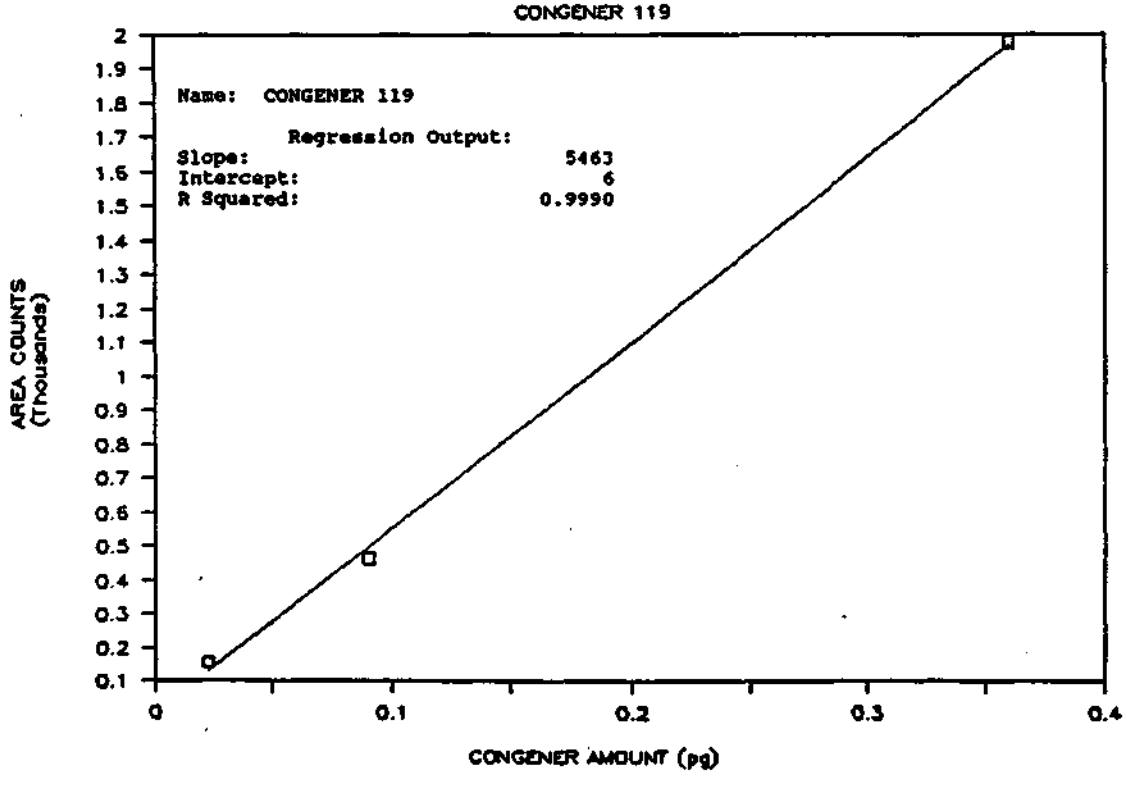
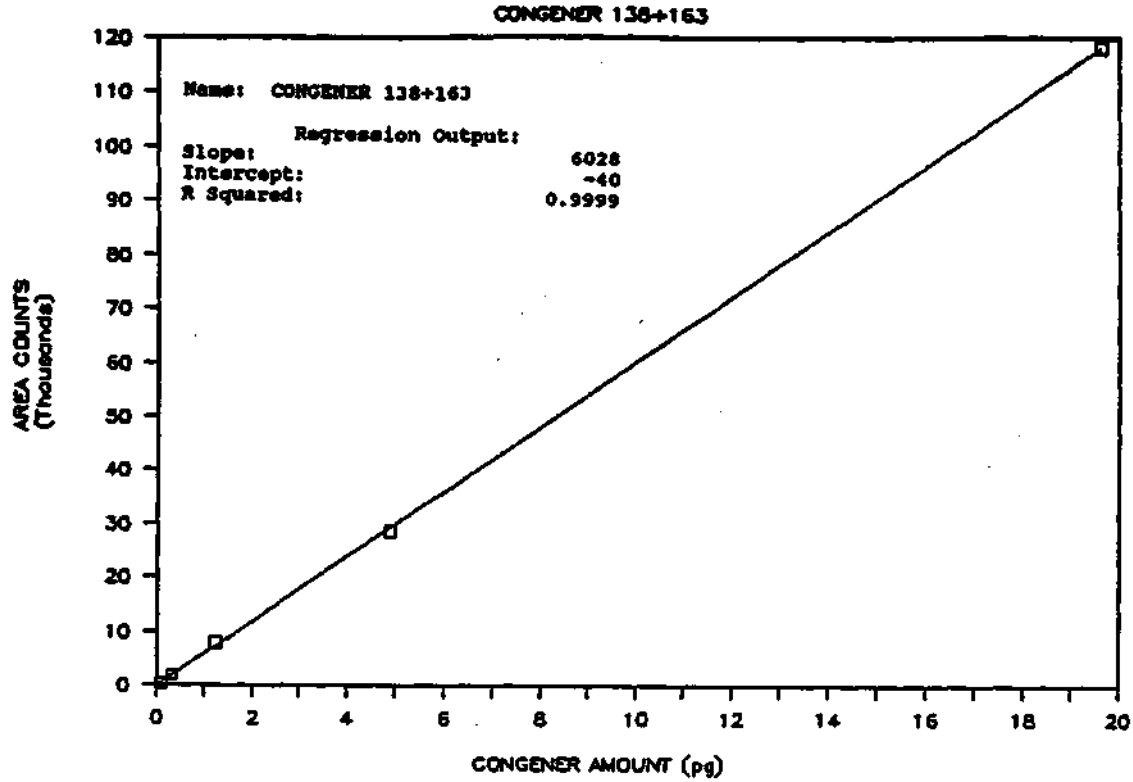


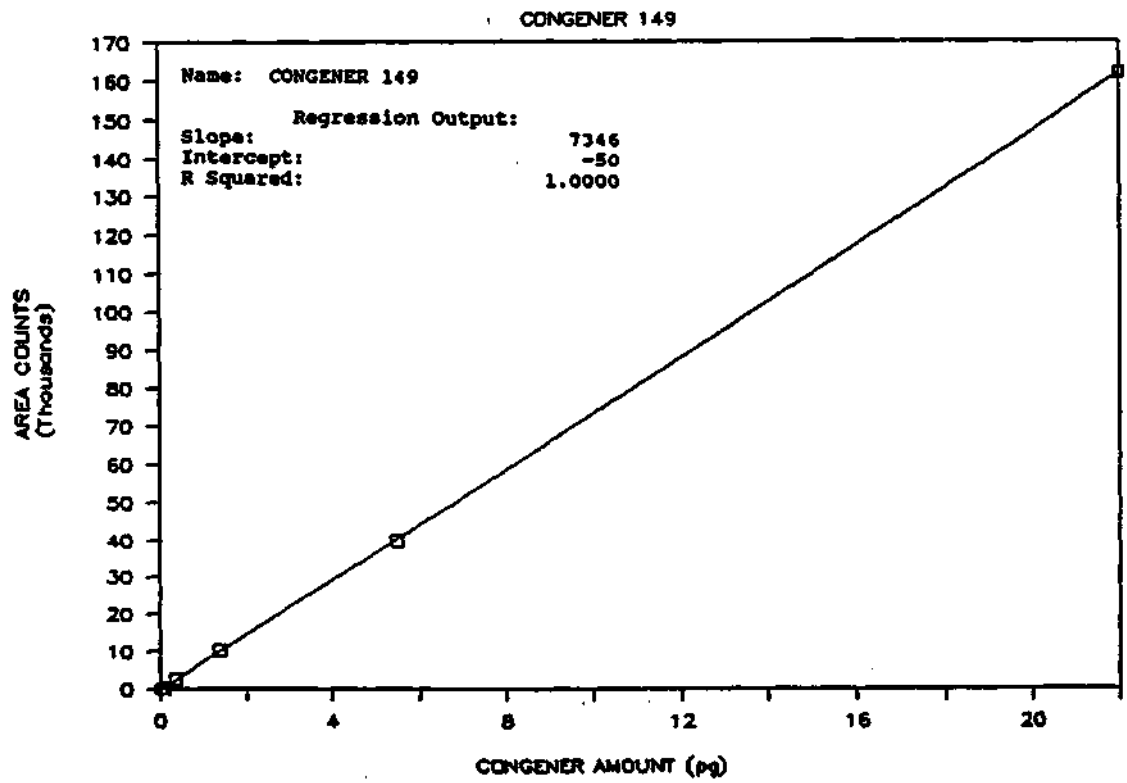
LINEARITY STUDY - PCB'S



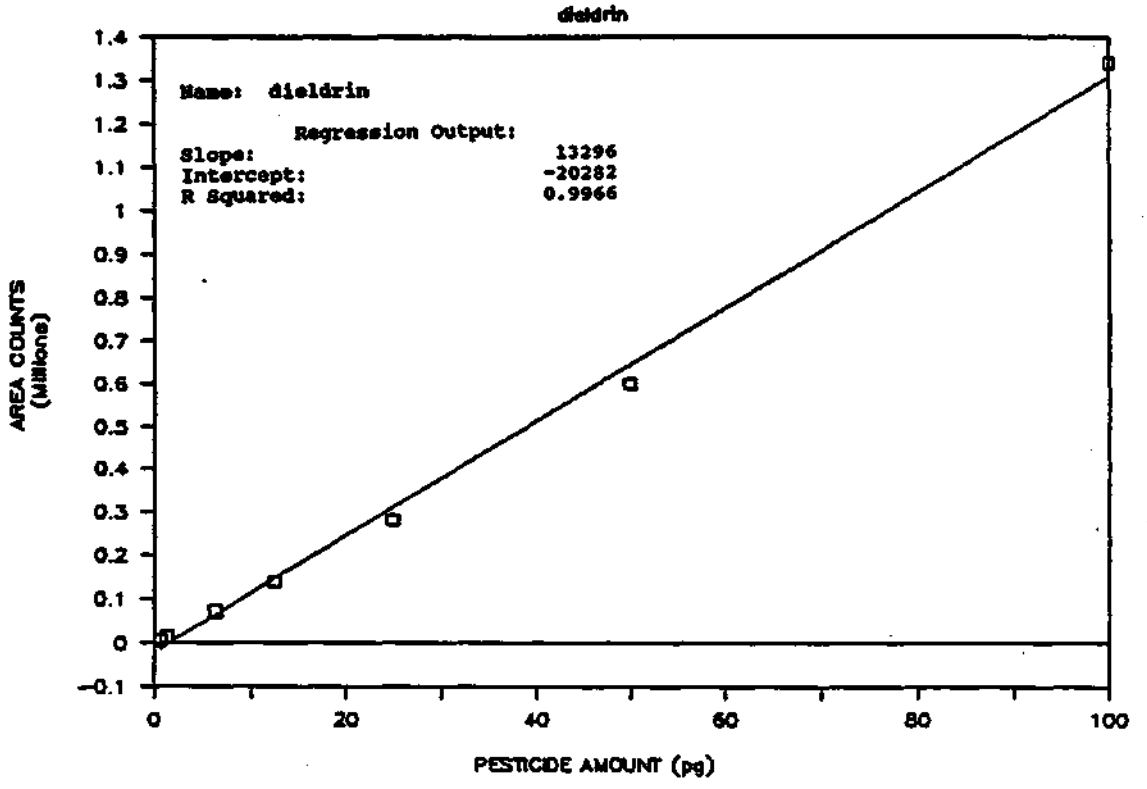
LINEARITY STUDY - PCB'S



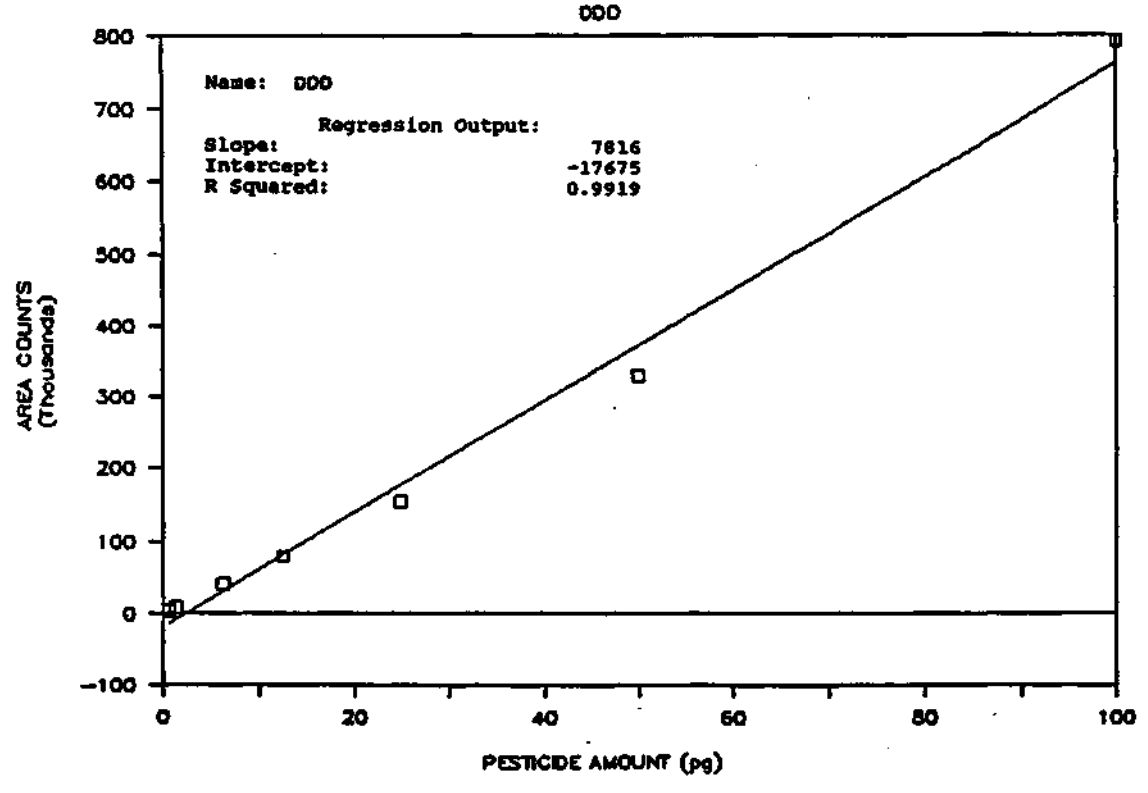
LINEARITY STUDY - PCB'S



LINEARITY STUDY — PESTICIDES



LINEARITY STUDY - PESTICIDES



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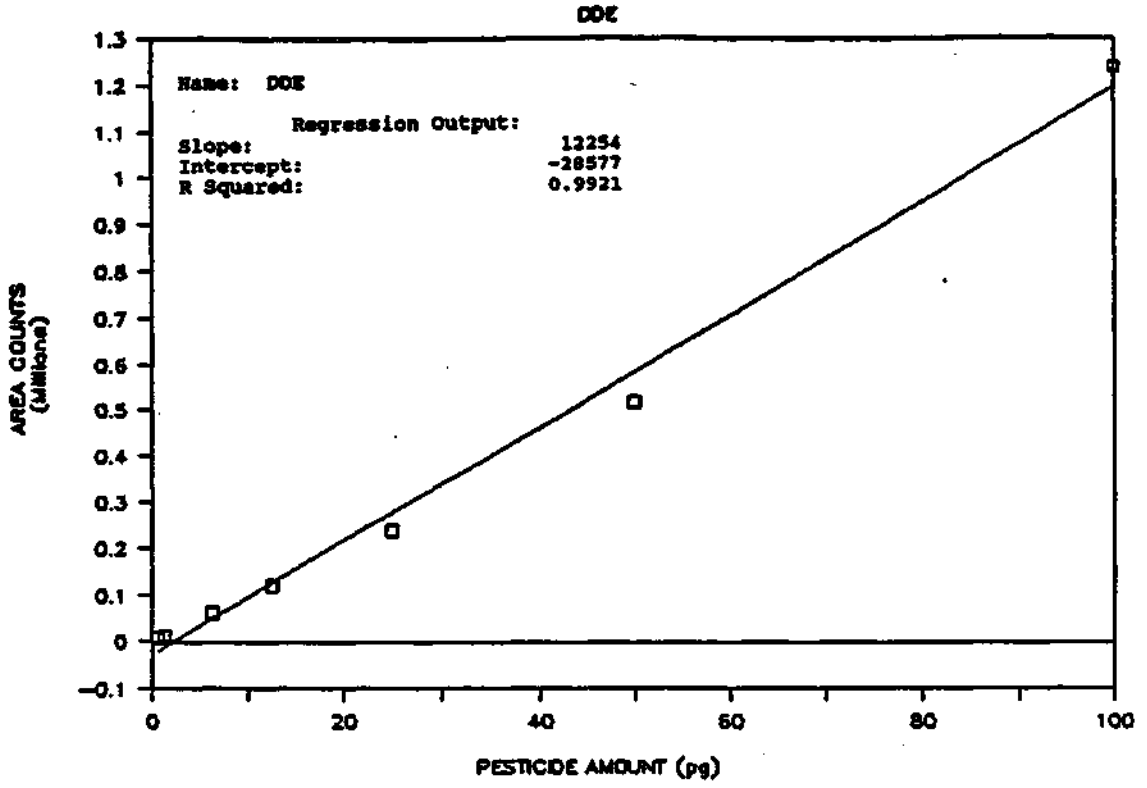

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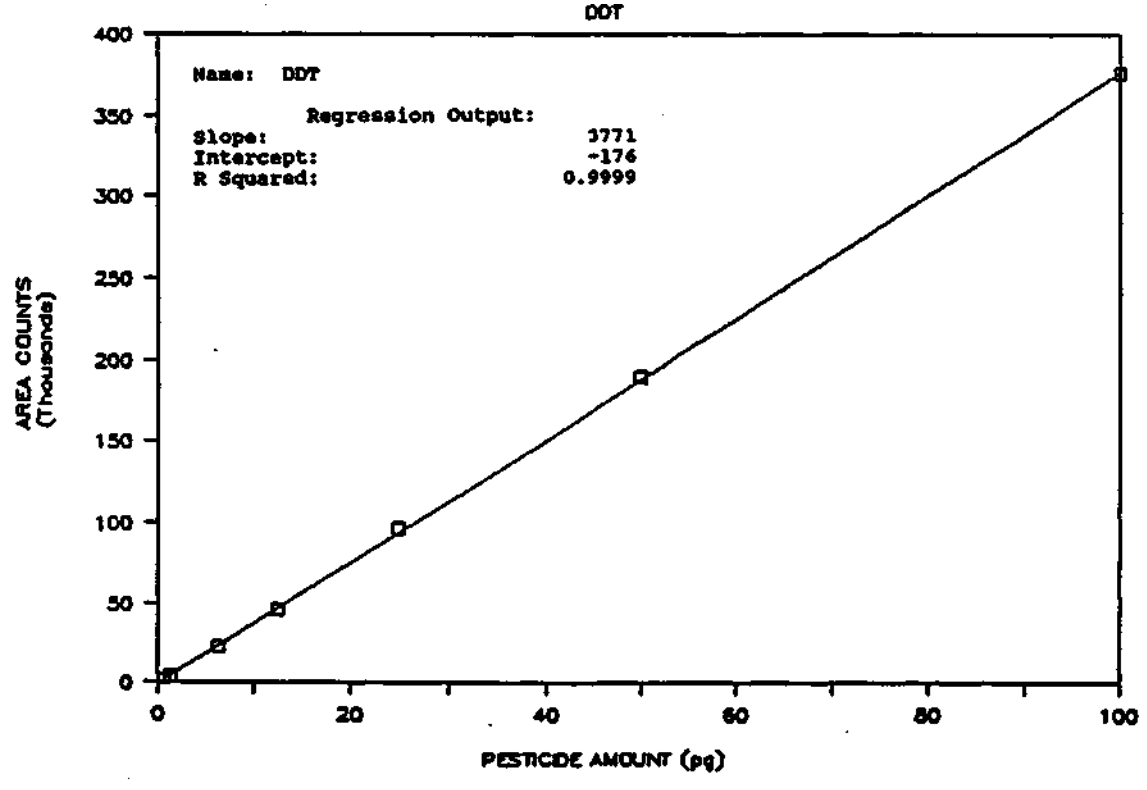
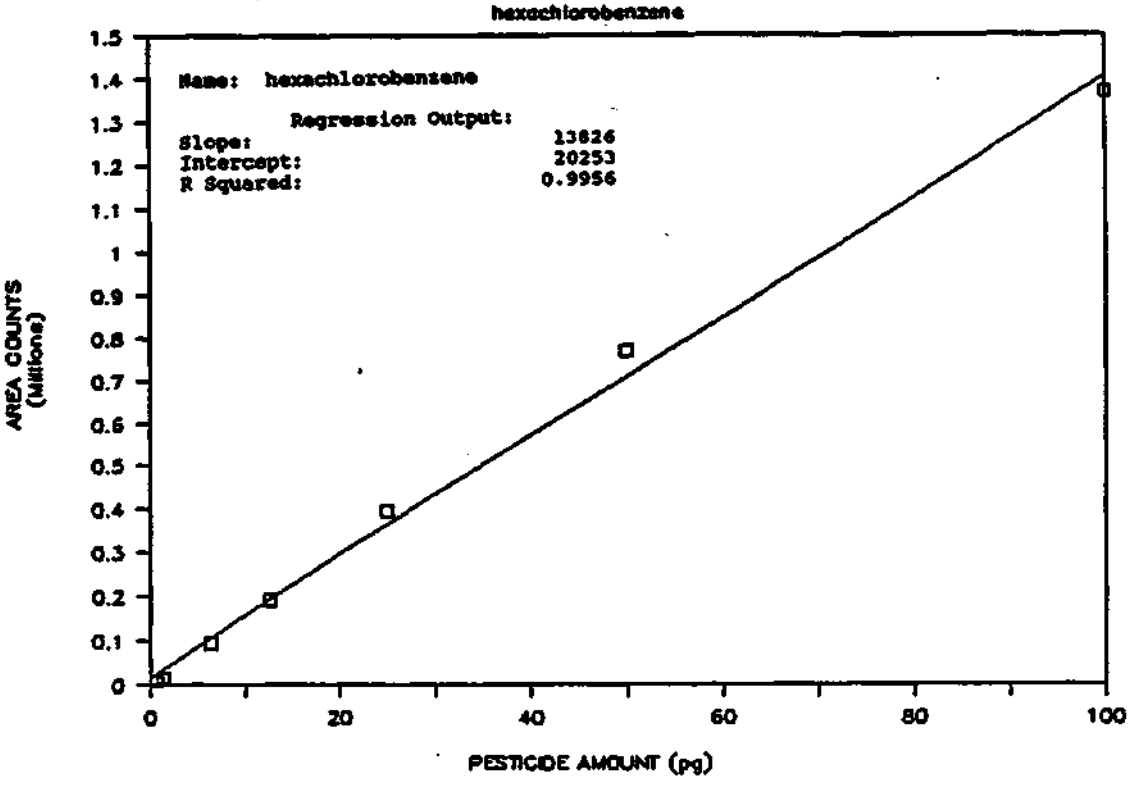


LINEARITY STUDY — PESTICIDES



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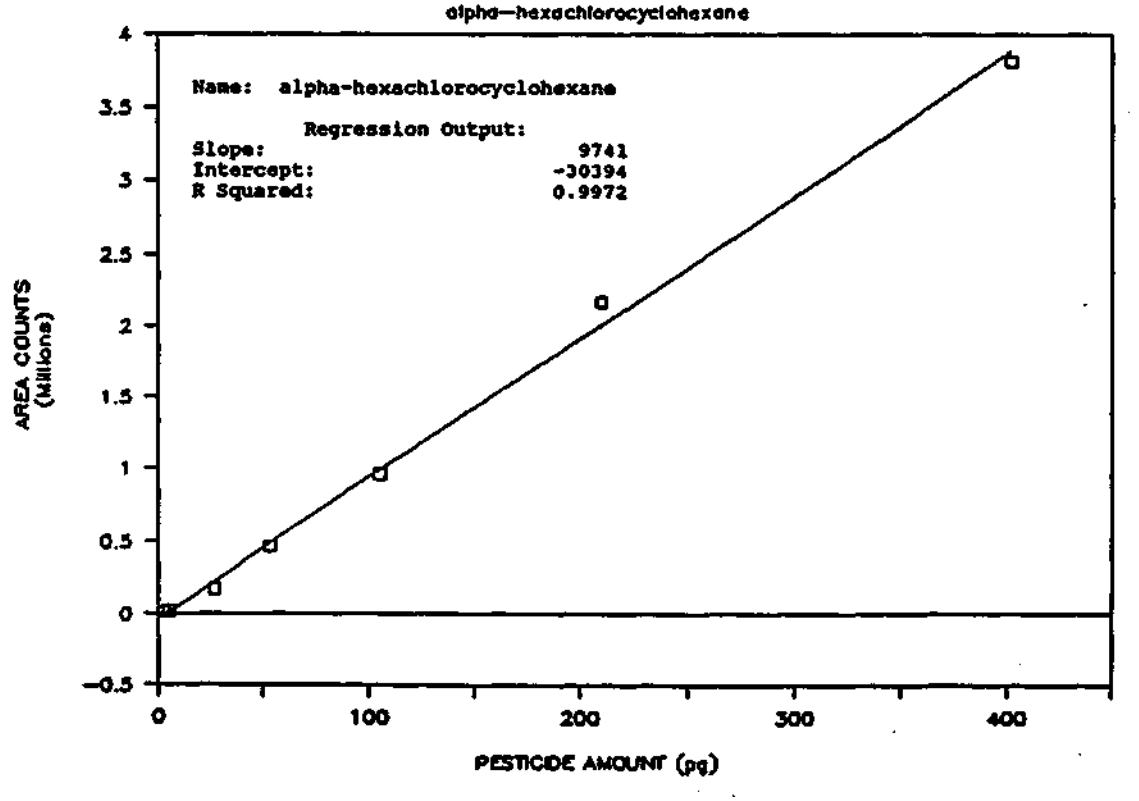

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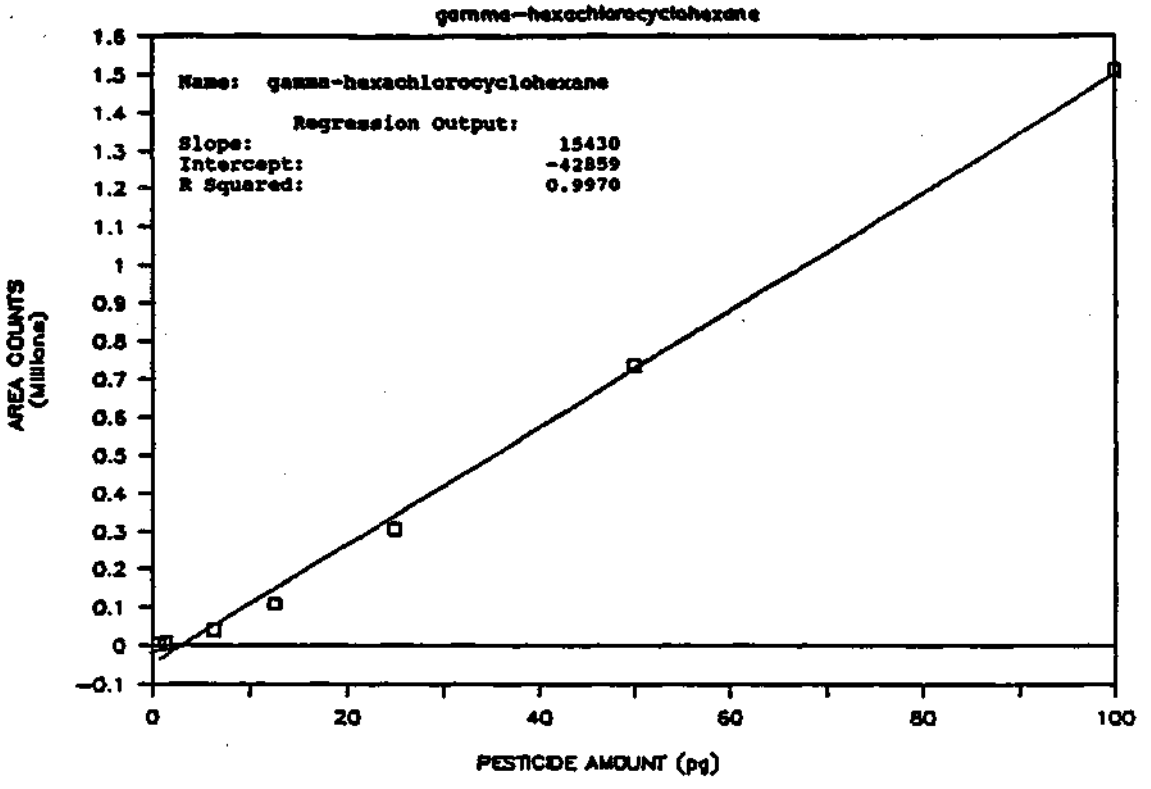

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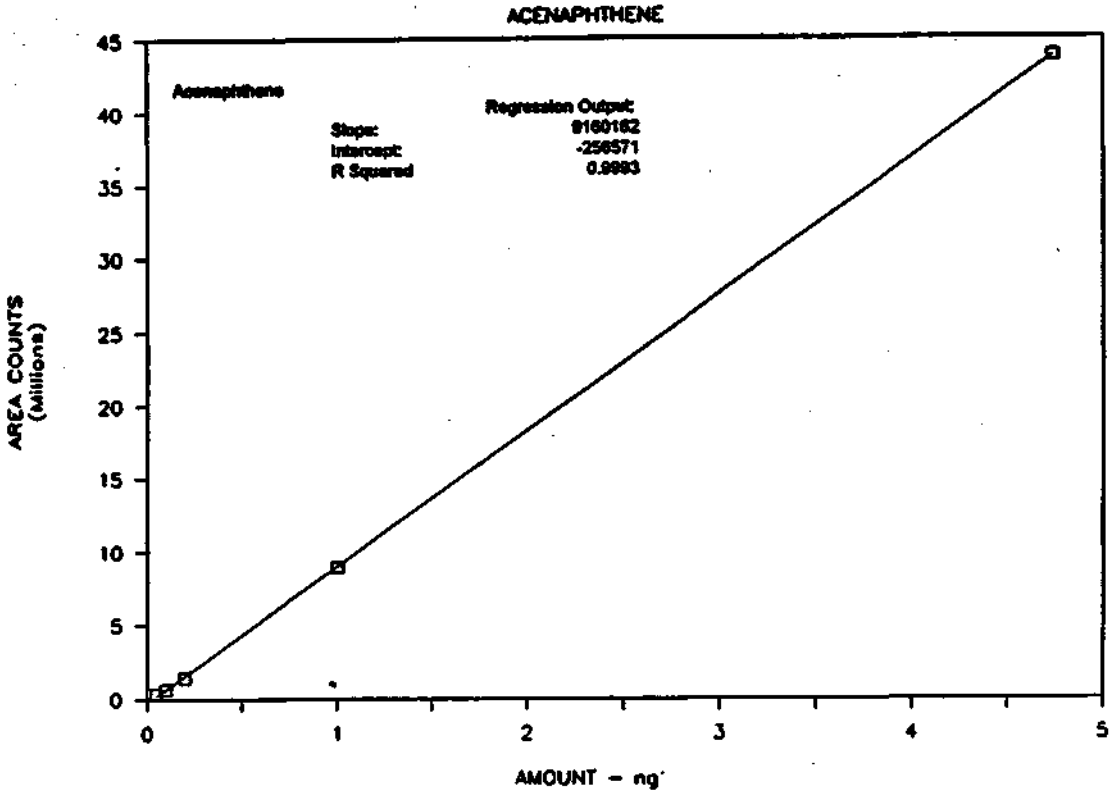

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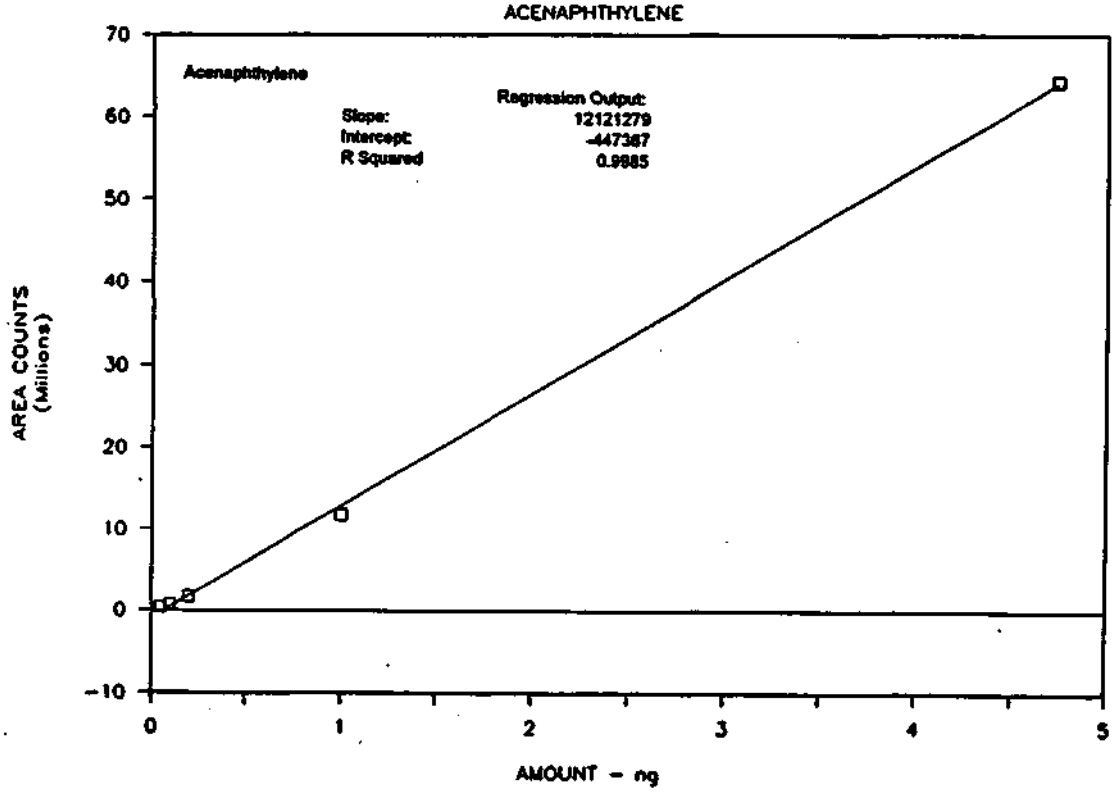

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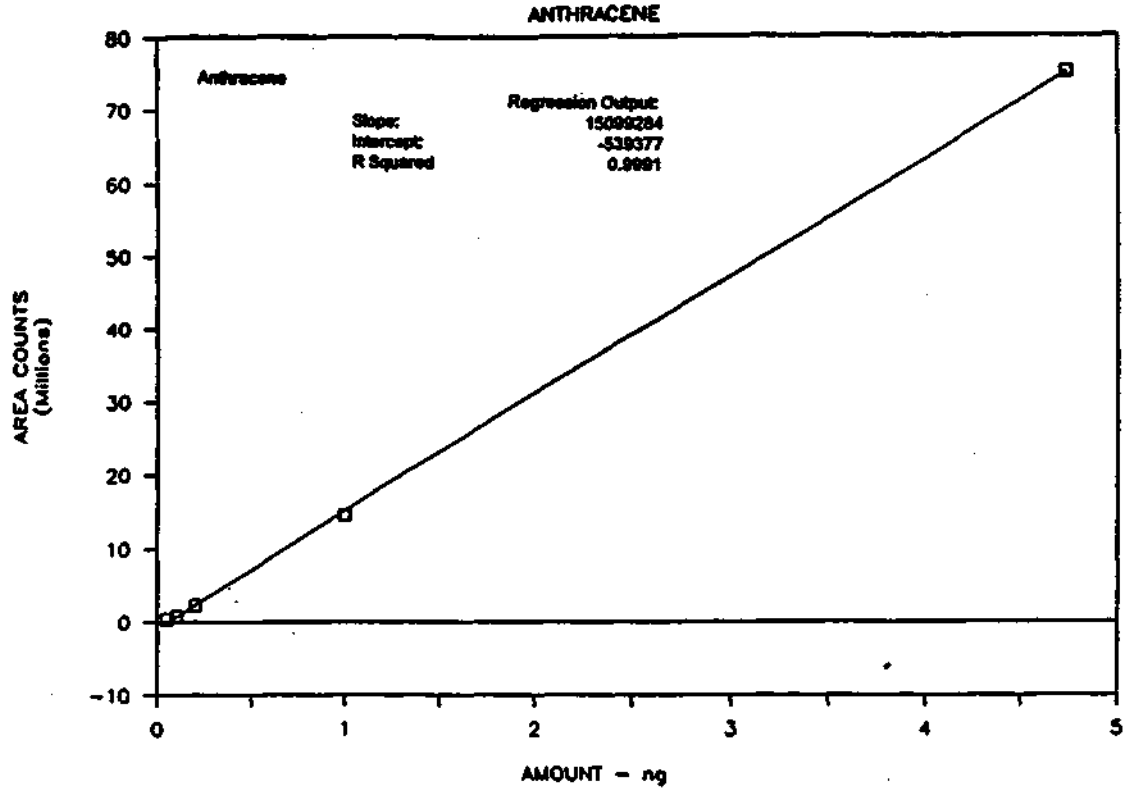

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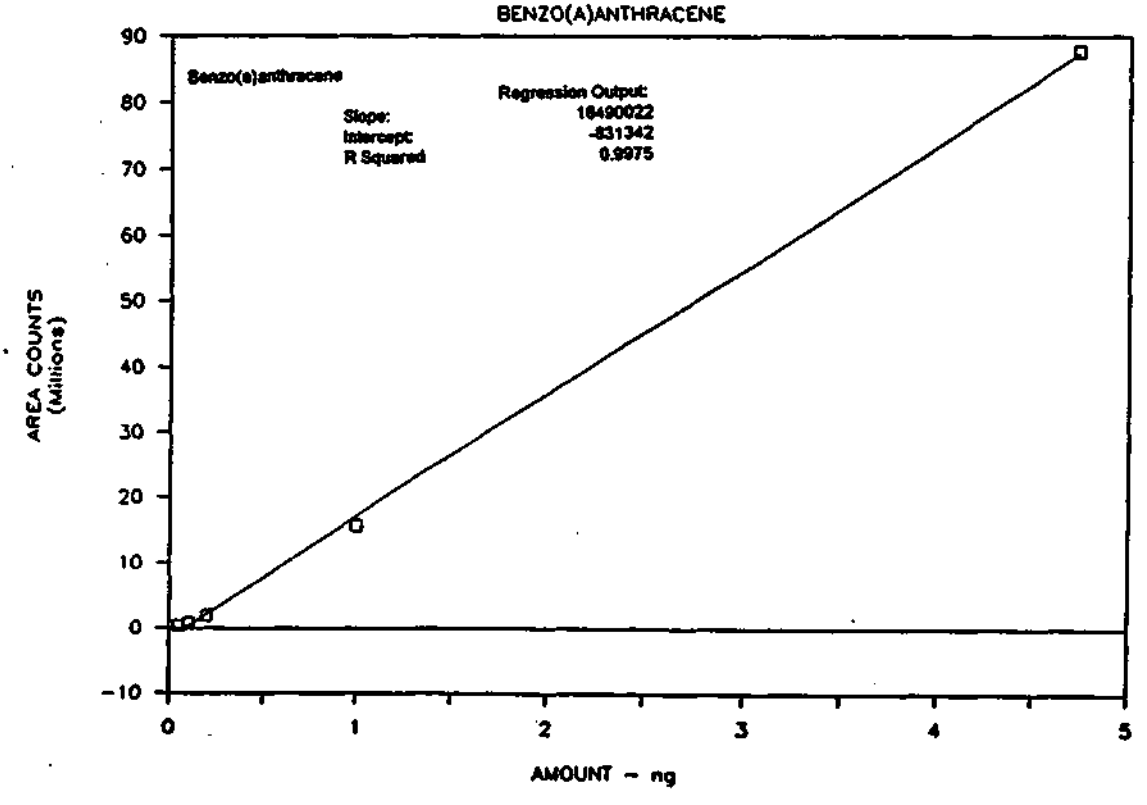

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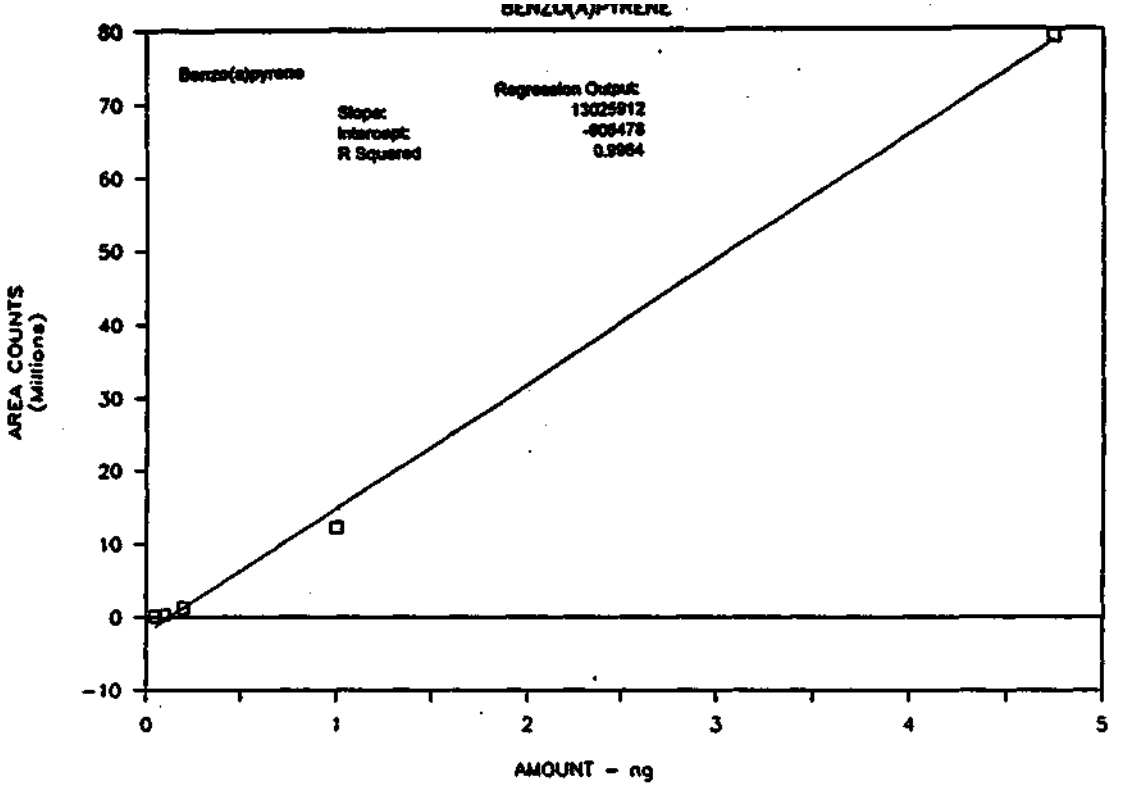

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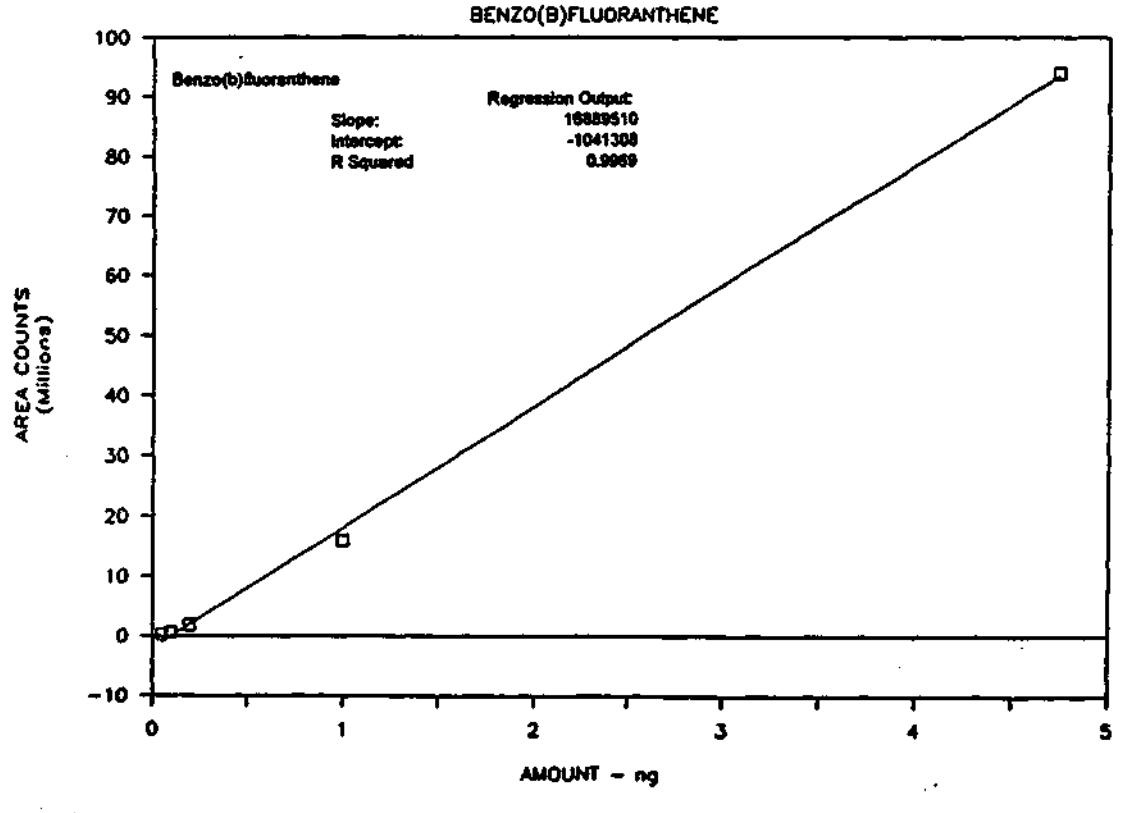

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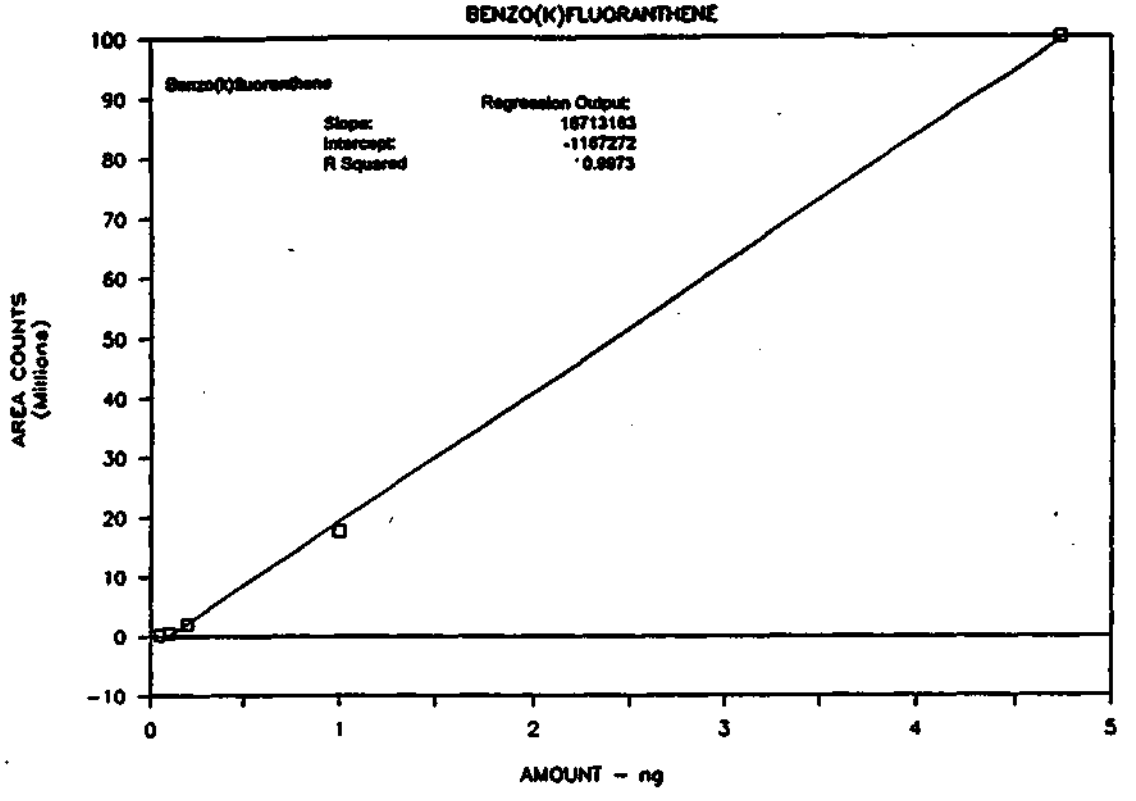

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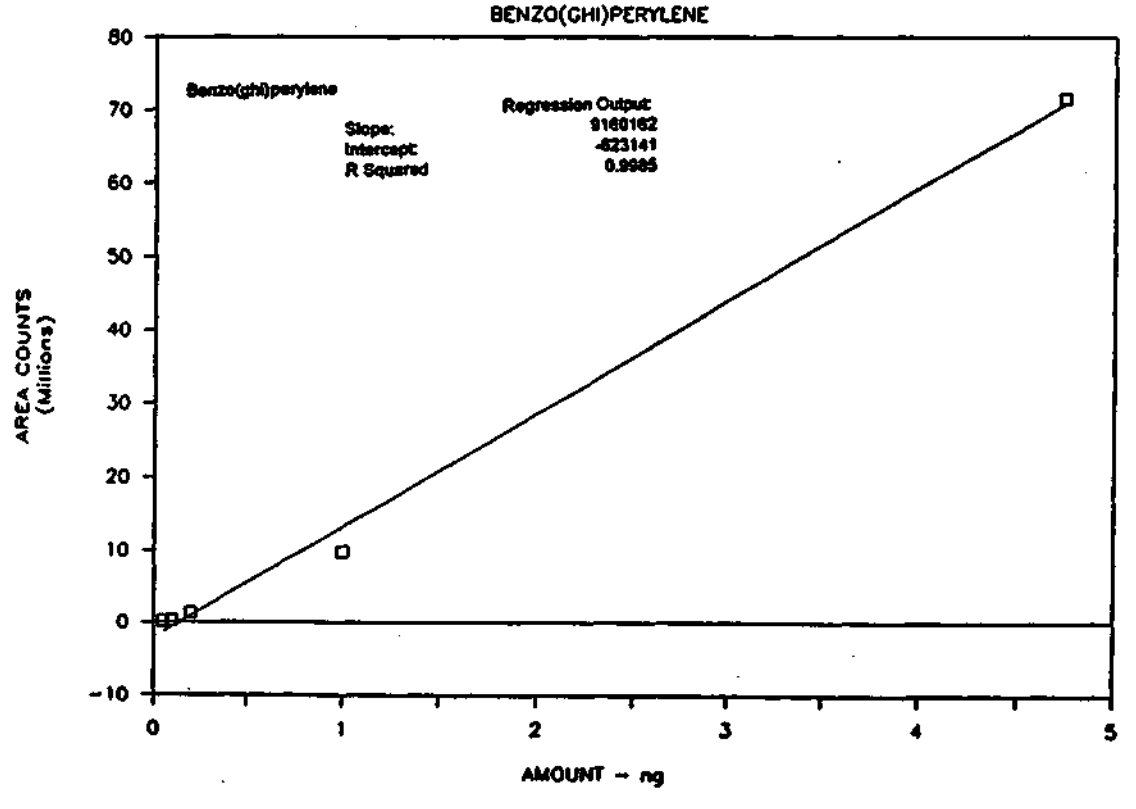

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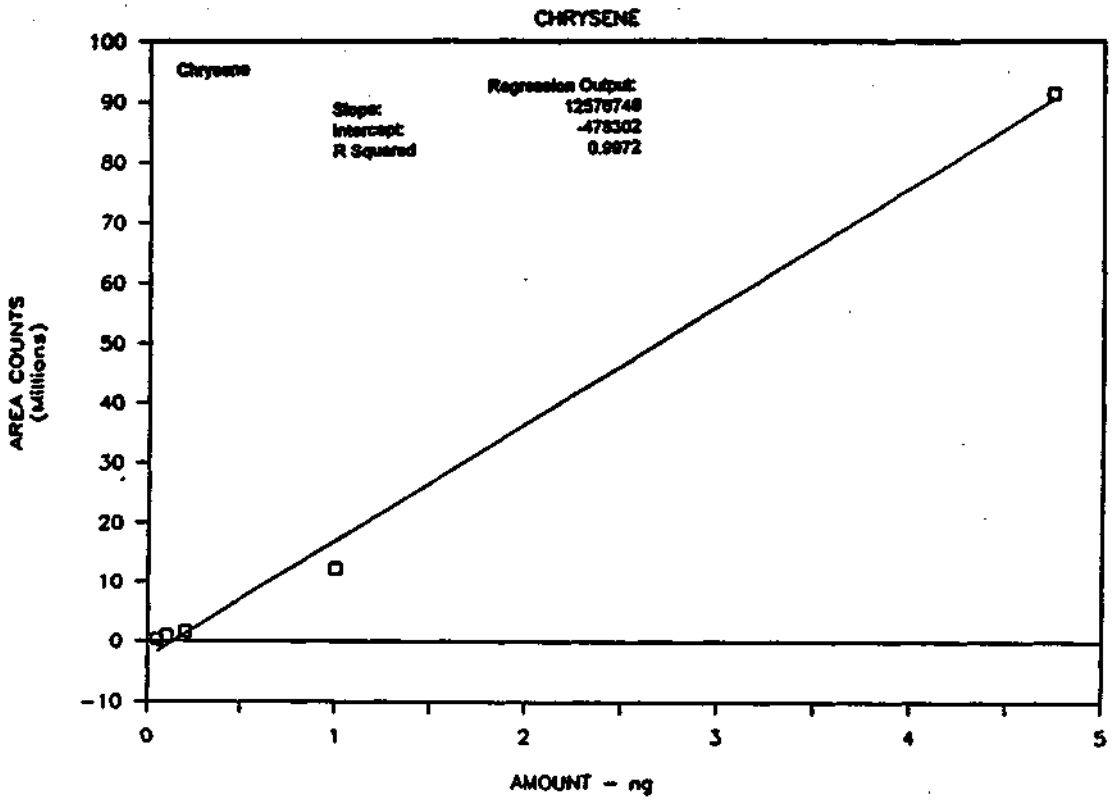
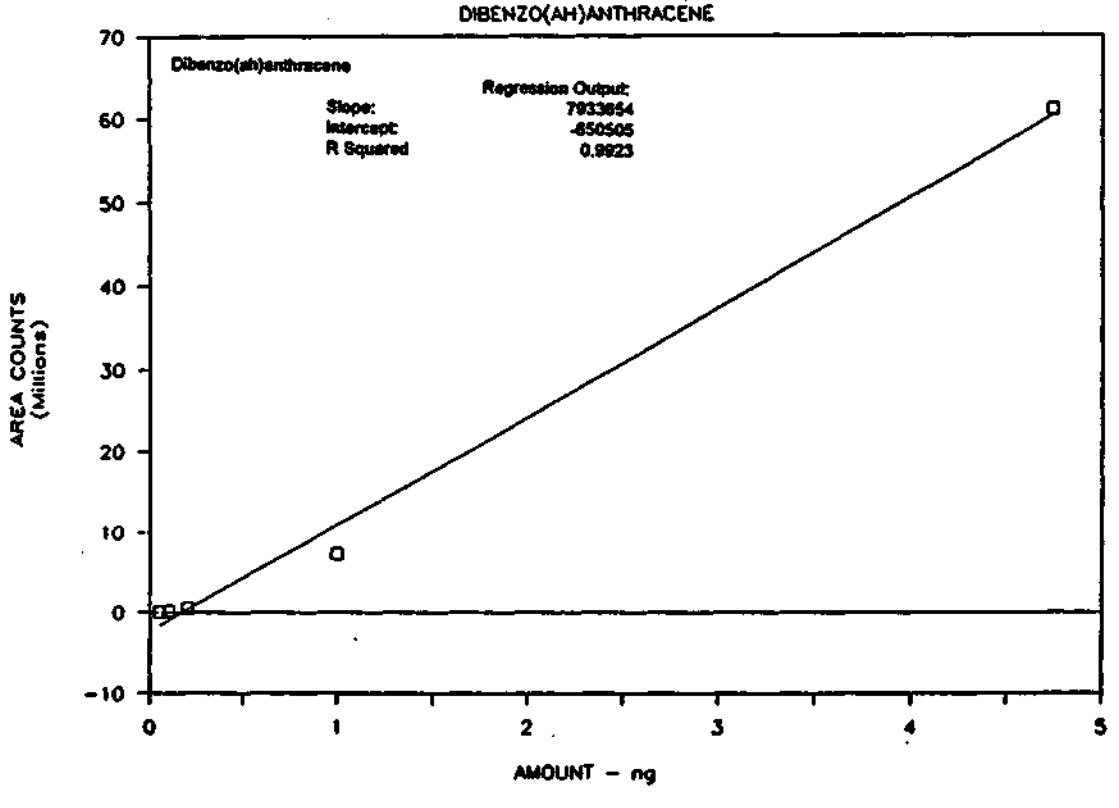


LINEARITY STUDY



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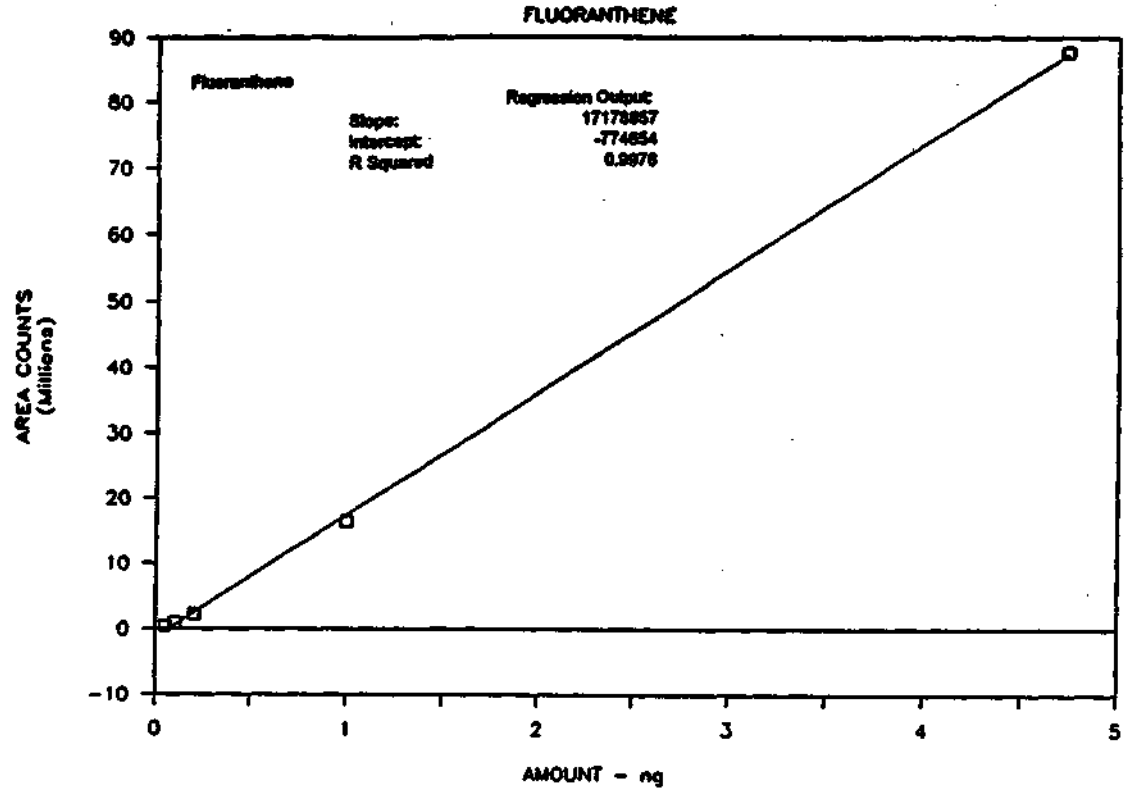

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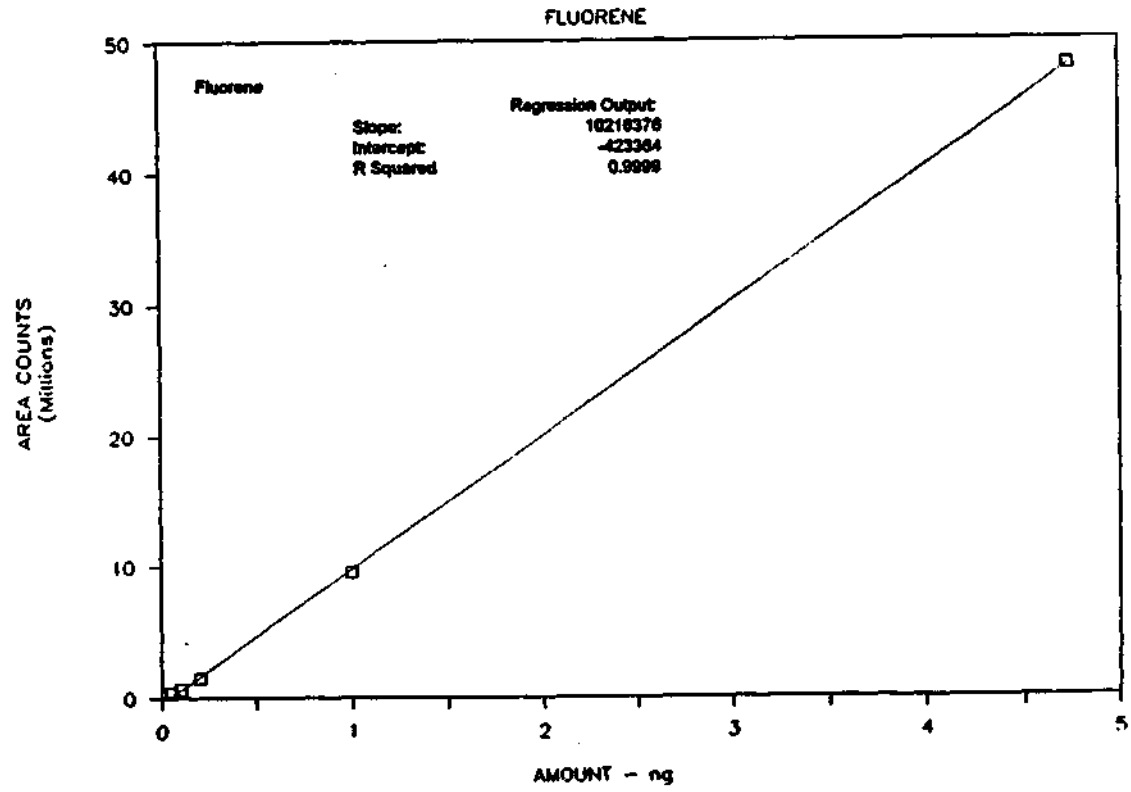

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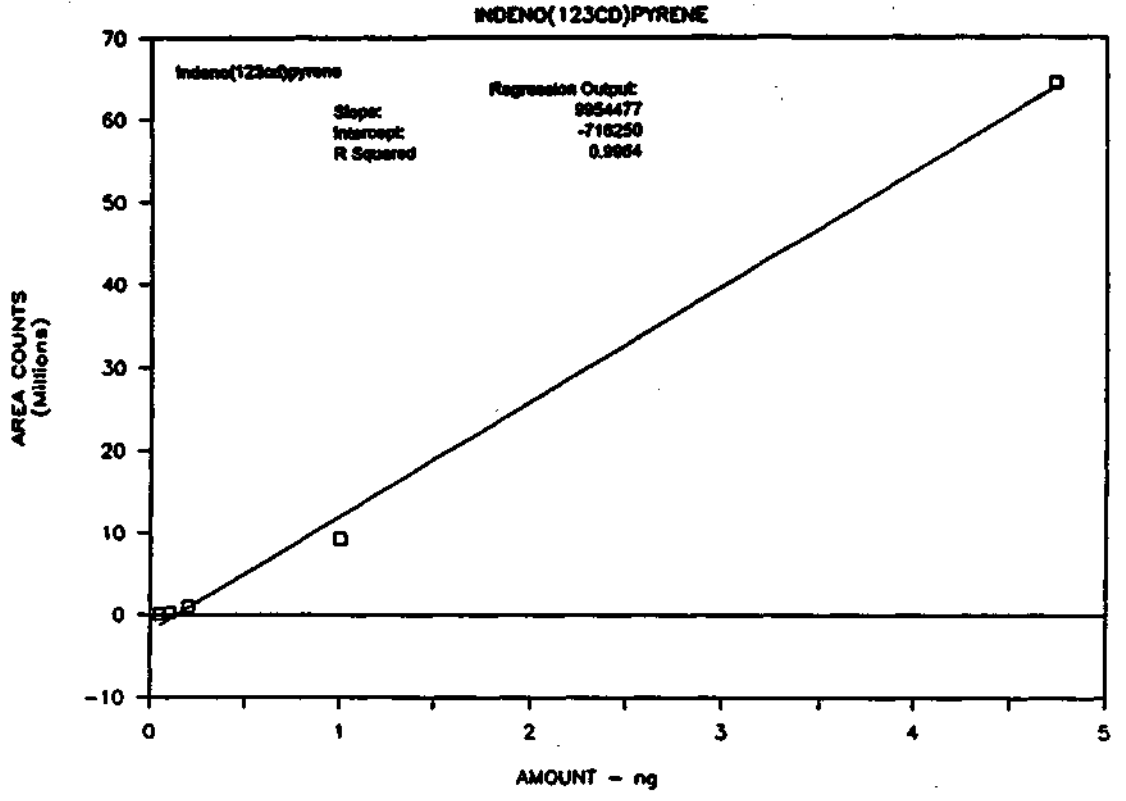

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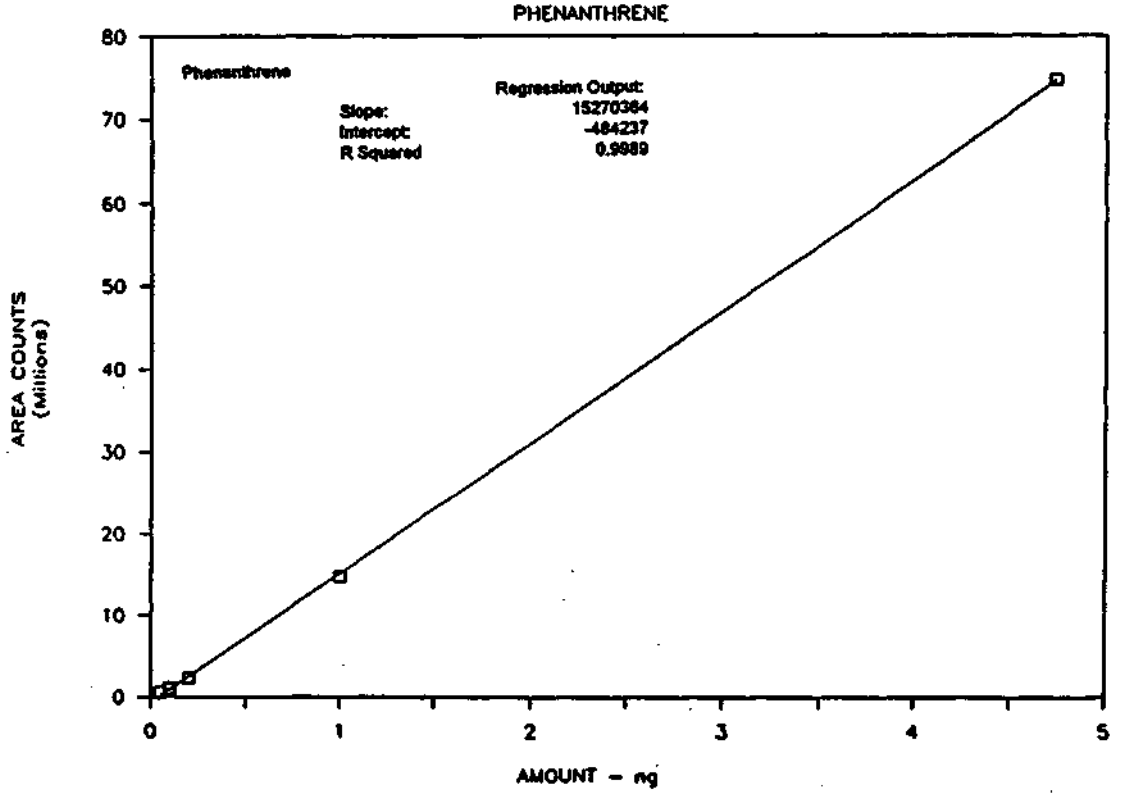

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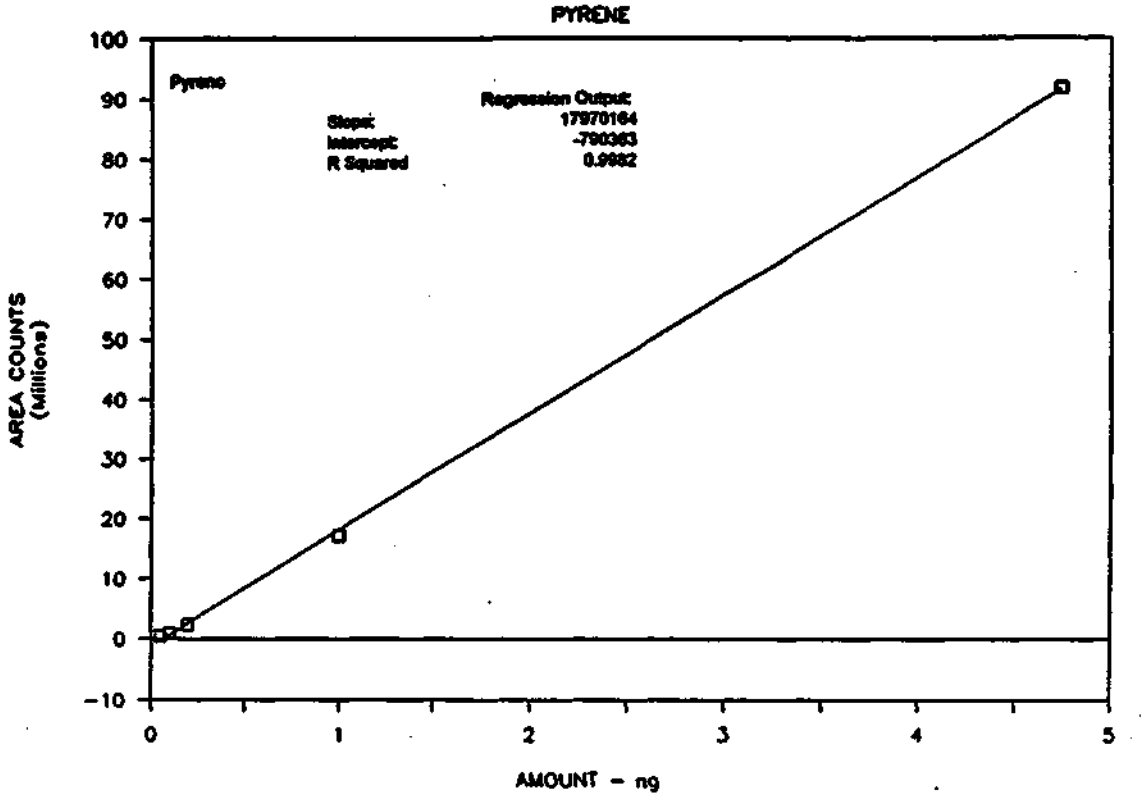

Appendix D

Quartz Fiber Filter (QFF) Field Blank and Lab Blank Data

Quartz Filters-Limit of Detection (LOD) and Field Blank Statistics

Analyte	LOD (ng/matrix)	LOD (pg/m^3)	Std Dev (ng/matrix)	N	Non zero	Average (ng/matrix)	Median (ng/matrix)	Minimum (ng/matrix)	Maximum (ng/matrix)
PCBs:									
5+8	11.7047	4.7774	2.8266	3	3	3.2246	3.876	0.661	5.137
6	0	0	0	3	0	0	0	0	0
16+32	2.9587	1.2076	0.8067	3	2	0.5386	0.343	0	1.273
17	1.7992	0.7344	0.5183	3	1	0.2443	0	0	0.733
18	2.2711	0.9270	0.578	3	2	0.537	0.725	0	0.886
21	0	0	0	3	0	0	0	0	0
22	0	0	0	3	0	0	0	0	0
28+31	5.3844	2.1977	1.2518	3	3	1.629	2.06	0.462	2.365
33	4.87	1.9878	1.4029	3	1	0.6613	0	0	1.984
37+42	1.1272	0.4601	0.3145	3	2	0.1834	0.0733	0	0.477
41+71+64	1.5881	0.6482	0.4574	3	1	0.2156	0	0	0.647
43	0.7645	0.3120	0.1945	3	2	0.181	0.246	0	0.297
44	1.2249	0.5000	0.2819	3	3	0.379	0.367	0.155	0.615
47+48	1.0725	0.4378	0.2817	3	2	0.2273	0.222	0	0.46
49	1.6354	0.6675	0.3946	3	3	0.4516	0.566	0.0878	0.701
52	1.8341	0.7486	0.4009	3	3	0.6313	0.761	0.259	0.874
53	0.9229	0.3767	0.2658	3	1	0.1253	0	0	0.376
56+60	4.2124	1.7193	0.9678	3	3	1.309	1.099	0.645	2.183
66	2.3763	0.9699	0.6227	3	2	0.508	0.507	0	1.017
70+76	2.6237	1.0709	0.5499	3	3	0.974	0.974	0.525	1.423
74	2.2437	0.9158	0.5198	3	3	0.6843	0.457	0.422	1.174
81	0	0	0	3	0	0	0	0	0
84+92	2.2785	0.9300	0.4738	3	3	0.857	0.77	0.521	1.28
87	0.8611	0.3515	0.1543	3	3	0.398	0.402	0.27	0.522
95	1.4197	0.5795	0.3129	3	3	0.481	0.626	0.186	0.631
99	0.5299	0.2163	0.1418	3	2	0.1044	0.0843	0	0.229
101	1.4635	0.5973	0.3215	3	3	0.499	0.595	0.202	0.7
105+132+153	2.2546	0.9202	0.3282	3	3	1.27	1.168	1.068	1.574
110	0.669	0.2731	0.0698	3	3	0.4593	0.472	0.397	0.509
118	1.7016	0.6945	0.4206	3	3	0.4396	0.254	0.229	0.836
119	0.7633	0.3116	0.2199	3	1	0.1036	0	0	0.311
138+163	2.371	0.9678	0.5675	3	3	0.6683	0.573	0.26	1.172
149	1.1876	0.4847	0.2174	3	3	0.5353	0.443	0.423	0.74
TOTAL PCBs	65.9903	26.9348	14.0717	3	3	23.775	29.4499	10.5522	31.323

Quartz Filters-Limit of Detection (LOD) and Field Blank Statistics (continued)

Analyte	LOD (ng/matrix)	LOD (pg/m^3)	Std Dev (ng/matrix)	N	Non zero	Average (ng/matrix)	Median (ng/matrix)	Minimum (ng/matrix)	Maximum (ng/matrix)
PESTICIDES:									
p,p' DDD	0	0	0	2	0	0	0	0	0
p,p' DDE	0.6717	0.2742	0.1286	3	3	0.2856	0.335	0.165	0.357
p,p' DDT	27.356	11.1657	7.816	2	1	3.908	0	0	7.816
DIELDRIN	40.6735	16.6014	11.621	2	1	5.8105	0	0	11.621
HCB	1.5168	0.6191	0.3968	3	2	0.3263	0.331	0	0.648
a-HCH	11.5227	4.7031	3.2922	2	1	1.6461	0	0	3.2922
g-HCH	8.6334	3.5238	2.345	2	2	1.5985	0.426	0.426	2.771
PAHs:									
ACENAPHTHENE	1.70	0.6939	0.40	3	1	0.20	0	0	0.60
ACENAPHTHYLENE	0	0	0	3	0	0	0	0	0
ANTHRACENE	0	0	0	3	0	0	0	0	0
BENZO(a)ANTHRACENE	14.20	5.7959	4.00	3	1	1.90	0	0	5.70
BENZO(b)FLUORANTHENE	40.50	16.5306	11.60	3	1	5.50	0	0	16.50
BENZO(k)FLUORANTHENE	35.10	14.3265	10.10	3	1	4.70	0	0	14.30
BENZO(ghi)PERYLENE	38.40	15.6735	11.00	3	1	5.20	0	0	15.60
BENZO(a)PYRENE	47.60	19.4286	13.70	3	1	6.40	0	0	19.40
CHRYSENE	15.10	6.1633	4.20	3	2	2.50	1.10	0	6.40
DIBENZO(ah)ANTHRACENE	0	0	0	3	0	0	0	0	0
FLUORANTHENE	54.10	22.0816	13.70	3	3	12.90	13.20	1.60	24.00
FLUORENE	20	8.1633	5.40	3	2	3.80	2.70	0	8.60
INDENO(123,cd)PYRENE	53.90	22.00	15.50	3	1	7.30	0	0	21.90
PHENANTHRENE	87.90	35.8776	24.20	3	3	15.20	6.30	1.50	37.90
PYRENE	45.60	18.6122	13.00	3	2	6.40	0.50	0	18.70

Quartz Filter Laboratory Matrix Blanks (LB)

PCBs	n	Maximum (ng)	Minimum (ng)	Mean (ng)	Std. Dev.	% RSD
6	4	0	0	0	0	
5+8	4	5.33	0.65	2.32	2.12	0.91
18	4	2.00	0.225	1.08	0.76	0.71
17	4	0.81	0.153	0.53	0.30	0.56
16+32	4	1.21	0	0.51	0.61	1.19
28+31	4	3.78	1.824	2.58	0.88	0.34
21	4	0.80	0	0.20	0.40	2.00
33	4	2.43	0.585	1.46	0.78	0.53
53	4	0.20	0.031	0.14	0.08	0.55
22	4	0.50	0	0.12	0.25	2.00
52	4	1.30	0.528	0.77	0.36	0.46
43	4	0.28	0	0.10	0.13	1.39
49	4	1.22	0.393	0.64	0.39	0.60
47+48	4	0.77	0	0.19	0.39	2.00
44	4	1.51	0	0.62	0.75	1.21
37+42	4	1.50	0	0.73	0.62	0.84
41+64+71	4	1.34	0	0.44	0.63	1.43
74	4	1.73	0.376	1.00	0.60	0.60
70+76	4	2.63	0.619	1.26	0.93	0.74
66	4	1.46	0.359	0.73	0.51	0.70
95	4	1.41	0.187	0.61	0.55	0.90
56+60	4	1.67	0	0.66	0.81	1.23
84+92	4	1.63	0	0.89	0.73	0.82
101	4	0.85	0.49	0.65	0.18	0.27
99	4	0.34	0.0475	0.19	0.12	0.64
119	4	0.04	0	0.01	0.02	2.00
81	4	0	0	0	0	
87	4	0.21	0	0.05	0.10	2.00
110	4	0.99	0.18	0.51	0.35	0.69
149	4	1.30	0.717	0.99	0.26	0.26
118	4	0.32	0	0.08	0.16	2.00
105+132+153	4	2.79	0.944	1.65	0.80	0.48
138+163	4	1.17	0	0.42	0.55	1.32
Total PCBs	4	52.27	18.26	30.01	15.49	0.52

Quartz Filter Laboratory Matrix Blanks (LB) (continued)

PESTICIDES	*N*	*Maximum (ng)*	*Minimum (ng)*	*Mean (ng)*	*Std. Dev.*	*% RSD*
a-HEXACHLOROCYCLOHEXANE	3	4.25	2.80	3.32	0.81	0.25
g-HEXACHLOROCYCLOHEXANE	3	3.45	3.17	3.34	0.15	0.05
DIELDRIN	3	21.76	0	13.76	11.97	0.87
p,p' DDT	3	15.89	0	5.30	9.18	1.73
p,p' DDD	3	0	0	0	0	
p,p' DDE	1	0.819	0.819	0.819		
HEXACHLOROBENZENE	1	0.772	0.772	0.772		
PAHs						
ACENAPHTHYLENE	4	2.41	0	1.20	1.14	200
ACENAPHTHENE	4	2.68	0	0.67	1.34	200
FLUORENE	4	10.89	7.151	8.67	1.59	18.31
PHENANTHRENE	4	39.16	14.67	24.44	10.42	42.63
ANTHRACENE	4	13.51	0	4.65	6.38	137.22
FLUORANTHENE	4	165.80	17.02	91.97	83.95	91.28
PYRENE	4	123.60	11.66	71.20	60.20	84.56
BENZO(A)ANTHRACENE	4	12.05	6.794	9.35	2.17	23.21
CHRYSENE	4	19.36	9.637	14.90	4.17	27.98
BENZO(B)FLUORANTHENE	4	19.69	12.71	14.83	3.26	22.00
BENZO(K)FLUORANTHENE	4	0	0	0	0	
BENZO(A)PYRENE	4	0	0	0	0	
INDENO(123CD)PYRENE	4	0	0	0	0	
DIBENZO(AH)ANTHRACENE	4	0	0	0	0	
BENZO(GHI)PERYLENE	4	0	0	0	0	