

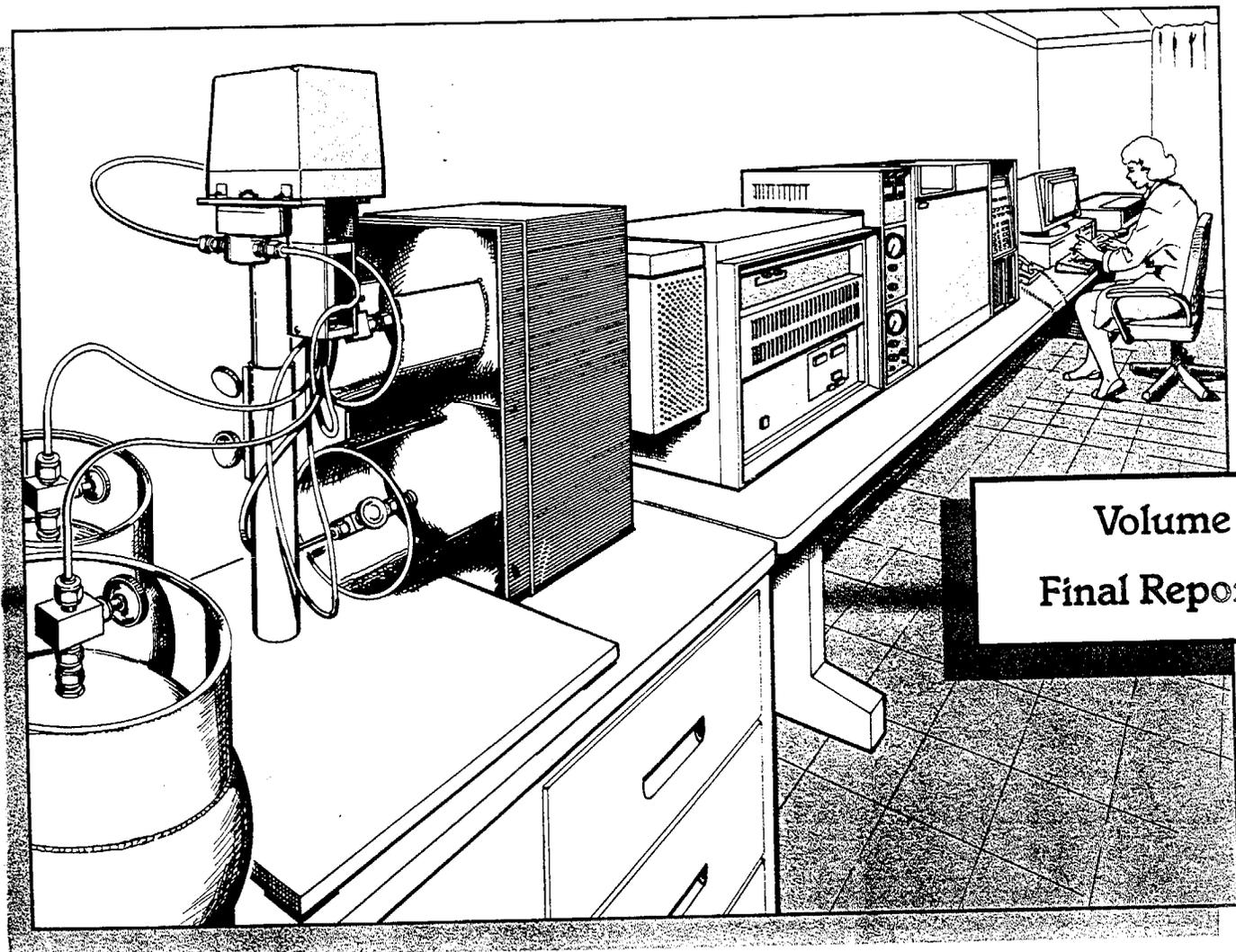
# Evaluation and Improvement of Methods for the Sampling and Analysis of Selected Toxic Air Contaminants

LIBRARY - AIR RESOURCES BOARD

to  
California Air Resources Board

April 1989

 **Battelle**  
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Volume 1  
Final Report



FINAL REPORT

(VOLUME 1)

on

EVALUATION AND IMPROVEMENT OF METHODS FOR THE  
SAMPLING AND ANALYSIS OF SELECTED  
TOXIC AIR CONTAMINANTS

to

CALIFORNIA AIR RESOURCES BOARD

April 1989

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## PROJECT SUMMARY

Assembly Bill 1807 (Tanner) directs the California Air Resources Board (ARB) to identify and monitor the concentrations of selected toxic air contaminants (TACs) present in the ambient atmosphere. For most of these TACs, the ambient concentrations are generally less than one part-per-billion per compound (24-hour time integrated samples). The use and improvement of current sampling and analysis methods for determining these contaminants are being carried out by the ARB, the U.S. Environmental Protection Agency, local districts and independent contractors.

## PROJECT OBJECTIVES

The objective of this project is to examine the materials and methods presently being used by the ARB to sample and analyze TACs. The advantages and disadvantages of the present methods are to be documented by field and laboratory analyses. Alternative materials and methods are to be recommended in those cases where serious disadvantages can be corrected. Experimental data must be obtained to demonstrate superiority of alternative approaches.

The specific TACs to be studied include the following:

chloroethene	1,2-dibromoethane
1,1-dichloroethene	tetrachloroethene
dichloromethane	benzene
trichloromethane	toluene
1,2-dichloroethane	m-xylene
1,1,1-trichloroethane	o-xylene
tetrachloromethane	p-xylene
trichloroethene	

Two additional halogenated organic compounds, dichlorodifluoromethane (freon-12) and trichlorotrifluoroethane (freon-113) are also to be included because they are good indicators of urban pollutant build-up.

## BATTELLE'S APPROACH

Battelle's examination and evaluation of existing and alternative sampling and analysis methodologies involved laboratory studies conducted at Battelle, statistical analyses of ARB's field and laboratory data, and a field study in Bakersfield, California. Our project results are presented in two volumes. Volume 1 contains five chapters as follows:

- Chapter I - Storage and Transportation Effects on TAC Concentrations in Tedlar Bags and Stainless Steel Canisters
- Chapter II - Evaluation of Selected Whole Air Sampling Devices

- Chapter III - Evaluation of ARB's Analytical Method-ADDL002
- Chapter IV - Alternative Analytical Approaches
- Chapter V - Evaluation of ARB Quality Control Procedures

Volume 2 contains Battelle's laboratory studies and statistical analyses of ARB data. The laboratory studies include the Tedlar bag permeation studies and bag/can storage studies at zero and 0.5 ppb TAC concentrations. Statistical analysis of ARB data includes the bag swap and bag/can collocated sample studies that were conducted by ARB in 1987. The results presented in Volume 2 are summarized and compared with the Bakersfield field study results in Chapter I of Volume 1. They provide complementary information on storage and transportation effects on TAC concentrations in Tedlar bags and stainless steel canisters.

### CONCLUSIONS AND RECOMMENDATIONS

Major conclusions and recommendations as they relate to the five chapter topics are given below.

#### Chapter I - Storage and Transportation Effects

Storage and transportation effects on pollutant concentrations in Tedlar bags and stainless steel canisters were evaluated under both laboratory and field conditions. Bags show appreciable effects for almost all chemicals. The specific contaminants and level of contamination depended upon the storage conditions. Based on these results, we conclude that ARB's reported ambient concentrations from bag samples have been biased. For example, in the field study the average concentration of dichloromethane as reported by the automated gas chromatographic (AGC) system was 0.28 ppb. The initial bag concentration gave a similar value of 0.36 ppb. However, the final bag concentration after storage for several days was 3.36 ppb. This compares with the average ambient concentration of 2.3 ppb reported in ARB's 1985 Toxic Air Quality Data Summary. For illustrative purposes concentrations (ppb) of toluene and 1,1,1-trichloroethane are also shown:

	<u>AGC</u>	<u>Bag Initial</u>	<u>Bag Final</u>	<u>ARB 1985 Ambient Data</u>
toluene	5.52	5.18	17.18	7.9
1,1,1-trichloroethane	0.45	0.49	3.18	2.0

Three mechanisms of contamination were found to exist: permeation into bags, contamination from residual materials used in bag processing, and memory effects from previously filled bags.

In our laboratory studies no statistically significant storage and transportation effects were observed for canisters. However, the Bakersfield field study demonstrated statistically significant effects for several compounds. The canister effects were much smaller than for the bags, and except for freon-12 (23 percent increase) the effect was minimal (i.e. <10 percent). We also found that several of the "cleaned" canisters used for the field study were initially contaminated with several chlorinated hydrocarbons.

We recommend that ARB replace Tedlar bags with stainless steel canisters as soon as possible. In the mean time ARB should minimize the storage time of air samples collected with the Tedlar bags. We recommend that storage times not exceed 48 hours. Before converting to the canisters, the procedures for cleaning the canisters should be closely reviewed and documented.

## Chapter II - Evaluation of Whole Air Sampling Devices

The commercial syringe and canister based sampling devices of interest to ARB were examined and shown to deliver reliable and valid samples to the analytical system. A certification process was developed to ensure that canister samplers are free of contamination. This process involves challenging the units with humidified zero air and humidified zero air spiked with known amounts of TACs. We recommend that this certification process be employed as an integral part of ARB's sampling and analysis program.

## Chapter III - Evaluation of ARB's Analytical Method-ADDL002

Method ADDL002 provides a very suitable technique for determining ambient concentrations of most of the 17 target compounds. Freon-12, vinyl chloride, and freon-113 are not determined quantitatively by the method. A multi-adsorbent trap such as a Tenax/carbosieve S-II material is needed to obtain acceptable collection/recovery efficiencies of these three compounds.

Specified operating parameters for the gas chromatograph of flow rate, oven temperature programming rate and detector temperatures appeared to be set optimally for peak resolution. Precision levels were reproduced. No "carry-over" effects from previous samples or standards were observed.

The use of a 30 meter, OV-1, megabore, capillary column offered much improved resolution of the 17 target compounds compared to the packed column specified in Method ADDL002.

Oxygen doping of the carrier gas to the electron capture detector provided significantly enhanced peak area responses (100 to 200 fold) for the compounds, dichloromethane and 1,2-dichloroethane.

#### Chapter IV - Alternative Analytical Approaches

Modifications to the current analytical method were prioritized. We recommend that oxygen doping and multi-adsorbent trapping be incorporated into ARB's current methodology in the near future in order to improve present deficiencies of the method (i.e. low sensitivity and recovery of some species). The automation of the analytical system for bag/canister introduction and processing should also be actively pursued.

If ARB anticipates that their list of target compounds will expand, we recommend that they employ capillary columns for better peak resolving capability. We also recommend that ARB eventually switch to a mass spectrometric detector (selective ion monitoring mode) for their primary detection system.

#### Chapter V - Evaluation of ARB Quality Control Procedures

The broad range of quality control (QC) activities documented in ARB's QA manual, SOPs, and monthly QC reports demonstrate ARB's strong commitment to ensuring quality in the TAC sampling and measurement processes. In addition to the routine activities (such as duplicate analyses, daily control samples, multipoint calibrations, performance audits) ARB has conducted numerous special studies such as the "bag swap" and "bag/canister" studies to address additional quality issues.

Our investigation of ARB's QC program focussed primarily on the daily calibration activities and the quantitative techniques used to characterize the performance of the analytical methods. We also performed statistical analyses of selected ARB QC data to evaluate the accuracy, precision, and sensitivity of ARB's Method ADDL002.

Our conclusions and recommendations are:

- ARB's current method of linear regression and descriptive statistics on the multipoint calibration data to characterize the accuracy precision and sensitivity of their method is straightforward and gives good results. However, we recommend a more general statistical approach that will result in more realistic estimates of precision and will permit ARB to better characterize the performance of the analytical system.
- ARB's protocol for updating daily response factors is difficult to follow and may not cover all possible outcomes of the daily calibration and control samples analyses. Our statistical analysis of ARB supplied data demonstrated that

precision may be improved by simply updating the daily response factor each day. We recommend that ARB closely monitor the daily calibration and control sample data.

- ARB's selection of calibration and control sample concentrations is appropriate for most of the TACs being monitored. The only exceptions are the control sample concentrations for four of the target chemicals. Their concentrations are much higher than typical ambient levels.
- ARB's documentation of laboratory and field procedures contained in the QA manual, SOPs and monthly QC reports is quite detailed. However, the QA manual and the SOPs need to be updated to reflect changes that have been implemented in practice.
- We recommend that ARB develop a data management system to improve tracking the great volume of data.
- ARB should consider developing a set of data quality objectives (DQOs) as recommended by EPA's Quality Assurance Management Staff. DQOs are statements of the quality of data that must be achieved in various segments of a monitoring program. Only after the objectives are defined can the required amount and type of QC data be decided, and also what type of statistical procedures will be used to determine if the objectives are being met.

## ACKNOWLEDGMENTS

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## VOLUME 1

### CHAPTER I. STORAGE AND TRANSPORTATION EFFECTS ON TAC CONCENTRATIONS IN TEDLAR BAGS AND STAINLESS STEEL CANISTERS

#### 1.0 Introduction

One of the major objectives of this program was to evaluate the sampling procedures and equipment used by ARB for monitoring toxic air contaminants (TACs) throughout the state. Currently, TAC sampling is performed by collecting 24-hour air samples in Tedlar bags at approximately 20 sampling locations around the state. The bag samples are then transported to the laboratory by common carrier and analyzed for approximately 10 TACs.

ARB has experienced some problems with contamination of samples in Tedlar bags during transportation and storage. However, the extent of the problem has never been fully documented. Furthermore, before implementing an alternative sampling methodology it must be demonstrated that the alternative method will perform satisfactorily.

Battelle's evaluation of existing and alternative sampling methodologies involved three types of studies: Laboratory studies and a field study conducted by Battelle, and two earlier field studies performed by ARB. Some of these studies were performed only with Tedlar bags, and others were performed with both Tedlar bags and stainless steel canisters. Each study had specific objectives. However, the common goal was to evaluate the performance of existing and alternative sampling methodologies under simulated or actual transportation and storage conditions.

When our contract began in late 1987 ARB was conducting the monitoring program for TACs out of two separate laboratories: The southern laboratory (SLB) in El Monte and the northern laboratory (NLB) in Sacramento. In late 1988 the TAC monitoring program was consolidated at the northern laboratory. Thus, some of our earlier laboratory studies focused on comparing the sampling methodologies of the two laboratories. However, by the time our field study in Bakersfield was conducted in October of 1988, the comparison of sampling methodologies between laboratories was no longer a concern.

Section 2.0 contains a brief summary of the results of several laboratory studies conducted by Battelle and two field studies previously conducted by ARB. The 1988 Bakersfield field study is detailed in Section 3.0, and our conclusions and recommendations are presented in Section 4.0

## 2.0 Summary of Results from Laboratory and ARB Studies

This section of the report focuses on results from 4 studies aimed at identifying storage and transportation effects on the measured concentrations of toxic air contaminants (TACs) in Tedlar bags and stainless steel canisters. Two of these studies were conducted in the field by ARB, and two were laboratory studies performed by Battelle. The data collected from these studies were statistically analyzed to determine if there are significant effects on TAC concentrations that can be attributed to the collection method or transportation and storage of air samples in Tedlar bags or stainless steel canisters.

### 2.1 Description of Studies

The studies that are summarized in this part of the report are:

- (1) ARB Bag Swap Study (field samples),
- (2) ARB Bag/Canister Collocated Sample Study (field samples),
- (3) Tedlar Bag Storage Study (zero air), and
- (4) Bag/Canister Storage Studies (zero air and 0.5 ppb concentrations).

The ARB "Bag Swap" study and the ARB "Bag/Canister Collocated Sample" studies were completed in 1987. The Bag Swap study was originally designed to compare the analytical systems of the SLB and NLB laboratories. Randomly selected field samples from each laboratory were shipped to the other laboratory following routine analyses. Next the second laboratory analyzed the samples and returned them to the first laboratory for a third analysis. However, because all samples originating at each laboratory were reanalyzed following the round trip, the data provided useful information about possible transportation and storage effects at ambient concentration

levels. The "Bag/Can" study provided useful data by comparing the analyses of Tedlar bag and canister samples that were collocated at the El Monte sampling station.

Battelle performed laboratory studies to collect additional data on potential storage effects. The Tedlar bag storage studies involved the storage of known levels of TACs and of zero air (Aadco, Inc.) under a variety of temperature and bag cleaning conditions. We also evaluated the effects on chemical concentrations of selected TACs stored in Tedlar bags and two brands of canisters in the bag/canister storage studies. In these studies the bags and canisters were filled with zero air and near ambient levels (0.5 ppb) of TACs and then stored for 7 days at 50°C.

Combining the results from all four studies provides useful and complementary information on the possible causes of the observed storage effects. The conditions under which these studies were conducted are quite different. However, in each case we have either measured TAC concentrations from before and after a storage period, or measured differences in concentrations between Tedlar bag and canister samples. The combined results from all 4 studies are summarized and discussed in Section 2.2. More detailed analyses of the individual studies are presented in Volume 2 of this report.

## 2.2 Summary of Results

A summary of the results from 2 laboratory studies at Battelle and 2 field studies conducted by ARB are presented in Table I-2.1. The table contains the median increase in TAC concentrations caused by sample contamination or leakage from Tedlar bags. Only those medians that were found to be significantly different from zero are reported in Table I-2.1. As discussed in Volume 2, our analysis of the bag/can storage study results did not reveal a statistically significant effect on canister sample concentrations due to storage conditions. Therefore, Table I-2.1 only contains results for Tedlar bag samples. Also, because the comparison of northern and southern laboratory results is no longer of primary interest, the only results from the southern laboratory that are presented in this summary are the results from the southern lab's bag/can collocated sample study.

TABLE I-2.1. MEDIAN OR AVERAGE TAC CONCENTRATION CHANGES IN TEDLAR BAGS DUE TO STORAGE OR TRANSPORTATION EFFECTS

#	Compound Name	Typical Ambient Conc (ppb) (1)	Median Concentration Increase (ppb)						
			ARB Bag Swap (2)	ARB Bag/Can (3)	0.5 ppb Bag/Can Storage (4)	Bag Storage Study (5)	Zero Air Bag/Can Storage (4)		
1	Dichlorodifluoromethane		---	---	NS	ND	NS	ND	
4	Vinyl Chloride		---	---	NS	ND	NS	ND	
8	1,1-Dichloroethene		---	---	NS	ND	NS	ND	
9	Dichloromethane	2.3	0.40	0.40	0.52	1.19		0.67	
11	1,1,2-Trichloro-1,2,2-Trifluoroethane		---	---	NS	ND	NS	NS	
14	Trichloromethane	0.08	NS	NS	NS	0.16	NS	NS	
15	1,2-Dichloroethane		NS	NS	-0.11	INT	NS	NS	
16	1,1,1-Trichloroethane	2.0	0.09	NS	0.10	ND	NS	0.13	
17	Benzene	2.8	NS	-0.30	84.54	ND	NS	13.92	
18	Tetrachloromethane	0.13	NS	NS	NS	ND	NS	ND	
20	Trichloroethene	0.36	0.03	0.08	NS	ND	NS	0.08	
24	Toluene	7.9	---	---	1.07	7.10	NS	0.42	
25	1,2-Dibromoethane	0.006	NS	---	-0.23	ND	NS	ND	
26	Tetrachloroethene	0.67	0.03	NS	NS	0.73	NS	0.06	
29	m-p-Xylene	2.8	---	---	0.45	ND	NS	0.46	
30	Styrene		---	---	0.37	---	---	0.85	
32	o-Xylene	1.3	---	---	0.25	ND	NS	0.18	
37	m-Dichlorobenzene		---	---	-0.25	---	---	0.02	
38	p-Dichlorobenzene		---	---	-0.18	---	---	0.09	
39	o-Dichlorobenzene		---	---	-0.26	---	---	0.03	

NS - Indicates that the estimated change was not significantly different from zero at 0.05 level.  
 ND - Not detected.  
 INT - Interference  
 (1) - Based on 1985 Toxic Air Quality Data Summary.  
 (2) - Median increase between initial and replicate analysis at the same lab.  
 (3) - Median difference between analyses of bag and collocated canister samples.  
 (4) - Median (average) increase over the 7 day test.  
 (5) - Median increase among samples from several experiments in which bags were stored at 50°C.

For the bag swap study, medians were calculated from the differences between the initial and final analyses of field samples originating from the northern laboratory (NLB). Significant differences can be attributed to the effect of a 5 to 7 day round trip between laboratories. The medians for the SLB's bag/can collocated sample study were calculated from the pairwise differences in the sample analyses. The medians for bag/canister storage studies (0.5 ppb and zero air) conducted at Battelle were calculated by averaging the changes observed for the 2 Tedlar bag samples stored at 50°C for 7 days. Bags and cans were filled simultaneously with zero air or with TACs at approximately 0.5 ppb concentrations. As mentioned earlier, no significant changes in TAC concentrations were observed in the canister samples. Finally, the values presented in Table I-2.1 for the bag storage studies represent the median concentration changes determined from 4 laboratory tests in which Tedlar bags containing zero air were exposed to a temperature of 50 degrees C during storage for more than 6 days.

The field studies contained information on 8 or 9 TAC compounds while the laboratory studies provided information on all 41 compounds contained in Battelle's gas mixture. Table I-2.1 presents only the results obtained for the compounds of interest to ARB. Average ambient concentrations in California are presented for reference. These average concentrations were reported in the 1985 Toxic Air Quality Data Summary.

The results reported in Table I-2.1 give cause for concern over the integrity of samples stored in Tedlar bags. The storage experiments have been conducted under a wide variety of conditions ranging from very typical storage and transport to extreme conditions of temperature and storage time. There are inconsistencies among the various experiments regarding specific contaminants and levels of contamination, but all four sets of experiments showed contamination of Tedlar bag samples during storage. In most cases, the level of contamination represents a significant fraction of average ambient air concentrations in California. The details provided in Volume 2 suggest that the prior history of a Tedlar bag can have a major effect on subsequent contamination of samples stored in the bag. This memory effect could account for some of the inconsistency among the sets of experiments.

The contamination levels reported in Table I-2.1 must be used with caution, because many of the experiments were carried out under extreme conditions of storage time or temperature. Nevertheless, the data indicate that samples of TACs stored in Tedlar bags may be susceptible to significant contamination during storage.

### 3.0 Bakersfield Field Study

#### 3.1 Objectives

The purpose of the field study was to evaluate ARB's Tedlar bag sampling system for monitoring TAC concentrations and to compare this system with alternatives involving the use of stainless steel canisters or Battelle's automated gas chromatograph (AGC). The primary objectives were to

1. Determine if there are significant differences between TAC concentrations in samples collected by Tedlar bags, canisters, and AGC.
2. Determine if there are significant changes in TAC concentrations in bag and canister samples following transportation between the sampling site and the analytical laboratory.
3. Compare the performance of bags and canisters for collecting samples under typical preparation, sampling, and transportation conditions.

#### 3.2 Approach

3.2.1 Study Design. Sixteen sets of samples were collected at ARB's Bakersfield, California, sampling site. Each set consisted of three collocated samples collected by different methods: (1) ARB supplied Tedlar bags, (2) ARB supplied canisters, and (3) Battelle's automated gas chromatograph (AGC). During a period of 10 days, 1/2-hour collocated samples were collected in the bags and canisters while a time-integrated sample was analyzed simultaneously by the AGC. The bag and canister samples were analyzed in sequence by the same AGC and then sent by common carrier to ARB's northern laboratory in Sacramento. Within 24 hrs of receipt of

shipment ARB personnel returned the samples to the field sampling site for reanalysis by Battelle. Therefore, each set of samples required five analyses. Our schedule of field activities is outlined below.

<u>Date</u>	<u>Activity</u>
Oct. 3	Mobile lab operational with sampling manifold and ARB sampling devices
Oct. 5	GC/MS equipment shipped
Oct. 6	Delivery of liquid nitrogen and compressed gases
Oct. 7	Battelle staff and equipment arrive
Oct. 7-10	Set-up of GC/MS equipment
Oct. 10-20	Sampling and analysis
Oct. 21	Shutdown
Oct. 22	Return to Battelle

Table I-3.1 contains the sampling/analysis schedule in which one to three sets of collocated samples were collected on each day during a 7-day sample collection period. The first priority on each day was to obtain the required field samples and perform the initial analyses of the bag and canister samples. Next, samples returned from NLB were analyzed in the order they were received. The plan required up to twelve sample analyses plus two calibration samples on each day of the study.

3.2.2 Field Instrumentation and Apparatus. ARB personnel provided a 20-ft mobile laboratory to house Battelle's AGC system along with the bag and canister sampling devices. The laboratory was equipped with an air sampling manifold to accommodate the three sampling devices. The laboratory was located in a vacant lot next to the 225 Chester Avenue monitoring station.

All bags, canisters, and their shipping containers were furnished by ARB. The bags and canisters were cleaned by ARB using established procedures and then delivered to the site just prior to field sampling.

TABLE I-3.1. SAMPLING/ANALYSIS SCHEDULE FOR THE FIELD STUDY

Day	Number of Sample Sets Collected (a)	Initial Analyses (b)	Repeat Analyses (c)	Calibration Samples
1	3	9	0	2
2	3	9	0	2
3	3	9	0	2
4	3	9	0	2
5	2	6	2	2
6	1 (d)	3	0	0 (d)
7	1	3	4	2
8	0	0	6	2
9	0	0	10	2
10	0	0	10	2
Total	16	48	32	18

- (a) Each set included bag, canister, and automated samples.
- (b) All samples were analyzed on the day collected.
- (c) Bag and canister samples were reanalyzed after return from NLB.
- (d) AGC failed on day 6, affecting QC analyses on day 6 and AGC analyses on days 6 and 7.

Bag and canister sampling devices were prototype units designed and constructed at Battelle. These units are functionally similar to commercial units currently in use in ARB's sampling network. The basic difference between the prototype and commercial units is the maximum sample flow that can be achieved with each unit. The commercial units operate over a flow range of 0 to 50 cm<sup>3</sup>/min. The prototype units can achieve flow rates as high as 500 cm<sup>3</sup>/min. Because air sampling was designed around the 1/2-hour, time-integrated collection period of the automated GC system, the prototype samplers were needed so that sufficient air would be collected in the bags and canisters. A thirty minute sampling period at 500 cm<sup>3</sup>/min. resulted in collected air volumes of 15 liters.

Battelle's AGC system was used for all analyses. The AGC system was equipped with a flame ionization detector (FID) and a mass selective detector (MSD) in parallel. The MSD was used for identifying and quantifying the target compounds, and the FID was used for monitoring over-all instrument performance. A cryogenic trap provided sample preconcentration. A modified Nutech Model 320 controller regulated the temperature of the cryogenic trap. A Perma Pure dryer was placed ahead of the trap to remove water vapor selectively. A 50 meter by 0.31 mm i.d., OV-1 fused silica column was used to resolve the target compounds. Optimal analytical results were achieved by temperature programming the GC oven from -50°C to 200°C at 8°/minute. The column exit flow was split to direct one-third of the flow to the mass spectrometric detector; the remaining flow passed through the flame ionization detector. During this study, the mass spectrometer was operated in the selective ion monitoring (SIM) mode. In the SIM mode the mass spectrometer monitored only preselected ions, rather than scanning all masses continuously between two mass limits. As a result increased sensitivity and improved quantitative analysis was achieved. The compounds and characteristic ions monitored during SIM operation are shown in Table I-3.2. SIM chromatograms of a 1 ppb calibration mixture and a blank analysis are shown in Figure I-3.1.

To calibrate the AGC, we used a primary calibration cylinder in conjunction with a gas phase dilution system to generate low ppb levels of 41 target compounds. Ultra-zero air (Linde) was used as the diluent gas. The primary calibration cylinder was initially made up by injecting the 41 compounds into a cleaned evacuated cylinder via a heated injection port.

TABLE I-3.2. COMPOUNDS AND CHARACTERISTIC IONS MONITORED  
DURING SELECTIVE ION MODE OF OPERATION

Compound	Characteristic Ions
1. dichlorodifluoromethane (Freon-12)	85, 87
2. methyl chloride	50, 52
3. 1,2-dichloro-1,1,2,2-tetrafluoroethane (Freon-114)	85, 87
4. vinyl chloride	62, 64
5. methyl bromide	94, 96
6. ethyl chloride	64, 66
7. trichlorofluoromethane (Freon-11)	101, 103
8. 1,1-dichloroethene	61, 96
9. dichloromethane	84, 86
10. 3-chloropropene	41, 76
11. 1,1,2-trichloro-1,2,2-trifluoroethane (Freon-113)	101, 103
12. 1,1-dichloroethane	63, 65
13. cis-1,2-dichloroethene	96, 98
14. trichloromethane	83, 85
15. 1,2-dichloroethane	62, 98
16. 1,1,1-trichloroethane	97, 99
17. benzene	78
18. carbon tetrachloride	117, 119
19. 1,2-dichloropropane	63, 112
20. trichloroethene	130, 95
21. cis-1,3-dichloropropene	75, 77
22. trans-1,3-dichloropropene	75, 77
23. 1,1,2-trichloroethane	97, 99
24. toluene	91, 92
25. 1,2-dibromoethane	107, 109
26. tetrachloroethene	166, 164
27. chlorobenzene	112, 114
28. ethylbenzene	91, 106
29. m&p-xylene	91, 106
30. styrene	104, 103
31. 1,1,2,2-tetrachloroethane	83, 168
32. o-xylene	91, 106
33. 4-ethyl toluene	105, 120
34. 1,3,5-trimethylbenzene	105, 120
35. 1,2,4-trimethylbenzene	105, 120
36. benzyl chloride	91, 126
37. m-dichlorobenzene	146, 148
38. p-dichlorobenzene	146, 148
39. o-dichlorobenzene	146, 148
40. 1,2,4-trichlorobenzene	180, 182
41. hexachlorobutadiene	225, 227

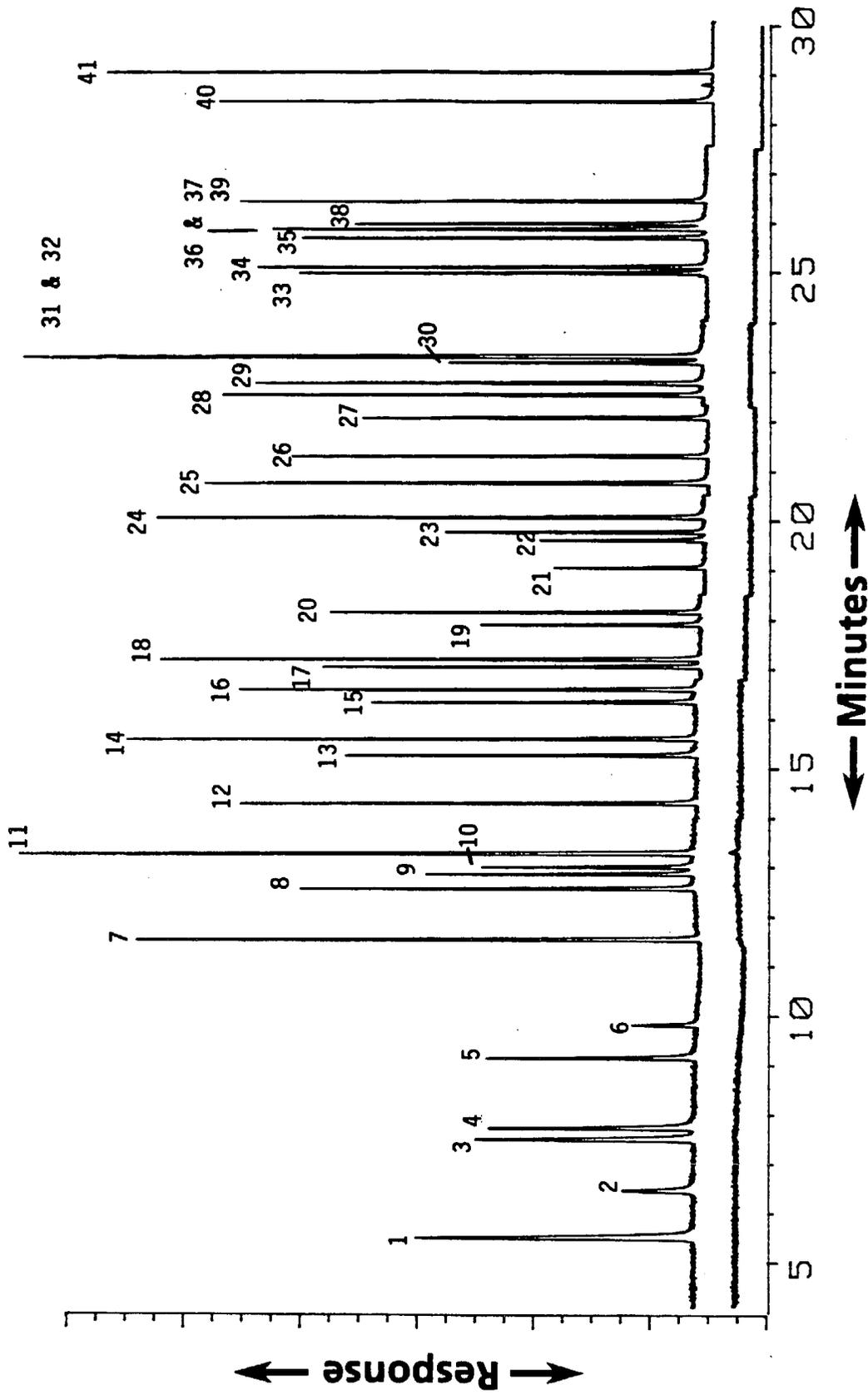


FIGURE I-3.1. SIM CHROMATOGRAMS OF A 1 ppb MIXTURE AND BLANK

Ultra-zero air was directed through the injection port to aid in the evaporation of the liquids. After all compounds were injected, the injection port was removed and the tank was pressurized to 1,000 psig. Compound concentrations in the cylinder were targeted for approximately 200 ppb.

The primary calibration cylinder was initially referenced against standard cylinders from the National Institute of Standards and Technology (NIST) and against in-house standards generated by static dilution of neat materials (>98 percent purity) into our 17.3 m<sup>3</sup>, Teflon-lined environmental chamber. This cross-checking procedure continued on a quarterly basis.

### 3.3 Results

During the ten-day field study a total of 80 chemical analyses were performed on 16 sets of field samples. Data were collected on all 41 chemicals contained in Battelle's calibration mixture. However, the statistical analysis was performed only on the data for 21 chemicals. These include the original 17 ARB target chemicals and 4 additional chemicals (styrene and p-, m-, and o-dichlorobenzene) requested by ARB.

Each of the 16 sample sets consisted of a time integrated sample analyzed by the AGC and collocated bag and canister samples. Each bag and canister sample was analyzed immediately after the sample was collected and again following the round trip between the field site in Bakersfield and the ARB laboratory in Sacramento. Table I-3.3 shows the days on which the individual samples were collected, initially analyzed, and reanalyzed following transport. The time between the initial and final analyses of the bag and canister samples ranged from three to nine days with an average of 5.5 days. Because the time in transport and storage for these samples is greater than the 24 to 48 hours normally required by ARB, the estimated effects on sample integrity may be somewhat larger than those realized by ARB.

The complete set of data from the field study is contained in Appendix I-A. The data consist of measured concentrations (ppb) for 21 chemicals from 5 separate analyses of 16 sample sets. Appendix I-A also contains some summary statistics such as the differences between measured concentrations of bag (canister) and AGC samples or between initial and

TABLE I-3.3. SAMPLING AND ANALYSIS DAYS<sup>(a)</sup>

Sample ID	Container ID	Day Sampled	Initial Anal. Day	Final Anal. Day
1A	-	1	1	-
1B	bag 1	1	1	5
1C	9144	1	1	5
2A	-	1	1	-
2B	bag 2	1	1	7
2C	9142	1	1	10
3A	-	1	1	-
3B	bag 3	1	1	7
3C	9153	1	1	10
4A	-	2	2	-
4B	bag 4	2	2	8
4C	9179	2	2	10
5A	-	2	2	-
5B	bag 5	2	2	10
5C	9195	2	2	10
6A	-	2	2	-
6B	bag 6	2	2	9
6C	9184	2	2	10
7A	-	3	3	-
7B	bag 7	3	3	9
7C	9143	3	3	10
8A	-	3	3	-
8B	bag 8	3	3	8
8C	9162	3	3	8
9A	-	3	3	-
9B	bag 9	3	3	8
9C	9192	3	3	8
10A	-	4	4	-
10B	bag 10	4	4	10
10C	9180	4	4	8
11A	-	4	4	-
11B	bag 11	4	4	9
11C	9152	4	4	9

TABLE I-3.3. (Continued)

Sample ID	Container ID	Day Sampled	Initial Anal. Day	Final Anal. Day
12A	-	4	4	-
12B	bag 12	4	4	9
12C	9186	4	4	9
13A	-	5	5	-
13B	bag 13	5	5	9
13C	9188	5	5	9
14A	-	5	5	-
14B	bag 14	5	5	9
14C	9190	5	5	9
15A	-	6	6	-
15B	bag 15	6	6	10
15C	9187	6	6	10
16A	-	7	7	-
16B	bag 16	7	7	10
16C	9185	7	7	10

(a) Days 1 through 10 correspond to the period October 11 through October 20, 1988.

final bag (canister) samples. The data are also presented graphically in Appendices I-B and I-C.

In Section 3.3.1 we present a brief summary of the field study results and discuss our major findings. The results are presented graphically in Section 3.3.2 and a statistical analysis is presented in Section 3.3.3

3.3.1 Summary of Results. Results of the field study are summarized in Table I-3.4. For each of the target chemicals the table contains the estimated mean concentration and percent detected from each of five separate analyses performed on the sixteen sets of samples. Also presented for reference are the 1985 statewide and Bakersfield mean concentrations and percents detected for selected chemicals.

To ensure consistency between these summary results and the statistical analyses presented in Section 3.3.3, the estimated concentrations were calculated using maximum likelihood estimators for a lognormal model. Except as indicated in the table, the model-based estimates differ only slightly from the simple arithmetic averages. Also, to provide a more accurate comparison among the five analyses, the estimates are adjusted to represent the average concentrations from sample sets in which all five analyses were performed. We had a temporary problem with the AGC sample in sample sets 15 and 16. Coincidentally, the concentrations in the bag and canister samples for these sets were relatively high. Therefore, the estimates in Table I-3.4 reflect the expected concentrations for the first 14 sets.

Even before applying statistical methods to the data there are some obvious and significant effects that are evident in Table I-3.4. The most notable effect involves the transportation and storage of TAC samples in Tedlar bags. Unusually high concentrations were measured for nearly all of the target chemicals in the bag samples following the transport to and from the ARB laboratory. Also, in some cases the 1985 statewide and Bakersfield estimates, which are based on transported bag samples, agree quite well with the repeat analyses of the bag samples. But as in the case of dichloromethane, for example, the automated sample results and the results from the initial analyses of the bag and canister samples (before transport) are much lower. In fact, the highest sample concentration of

TABLE I-3.4. ESTIMATED MEAN CONCENTRATIONS AND PERCENT DETECTED FOR SELECTED TOXIC AIR CONTAMINANTS, 1985 ARB SUMMARY VS FIELD STUDY<sup>(a)</sup>

Chemical Name	1985	1985		AUTO-GC Mean (% Det)	Initial Bag Mean (% Det)	Repeat Bag Mean (% Det)	Initial Can Mean (% Det)	Repeat Can Mean (% Det)
	State Mean (% Det)	Bakersfield Mean (% Det)	Bakersfield Mean (% Det)					
Dichlorodifluoromethane				1.14 (100)	1.11 (100)	1.99 (100)	1.17 (100)	1.44 (100)
Vinyl Chloride				ND (0)	ND (0)	ND (0)	ND (0)	ND (0)
1,1-dichloroethene				ND (0)	ND (0)	ND (0)	ND (0)	ND (0)
Dichloromethane	2.28 (88)	1.53 (46)		0.28 (100)	0.36 (100)	3.35 (100)	0.39 (100)	0.39 (100)
1,1,2-trichloro- 1,2,2-trifluoroethane				0.13 (100)	0.13 (100)	0.17 (100)	0.56 (100)	0.61 (100)
Trichloromethane (b)	0.08 (84)	0.28 (73)		0.01 (21)	0.01 (25)	0.03 (50)	0.01 (25)	0.01 (19)
1,2-dichloroethane (b)				0.00 (7)	0.00 (13)	0.25 (36)	0.00 (13)	0.00 (13)
1,1,1-trichloroethane	2.00 (100)			0.45 (100)	0.49 (100)	3.22 (100)	1.72 (100)	1.71 (100)
Benzene	2.84 (99)	2.74 (100)		2.35 (100)	2.10 (100)	3.83 (100)	2.27 (100)	2.30 (100)
Carbon Tetrachloride	0.13 (100)			0.13 (100)	0.12 (100)	0.13 (100)	0.13 (100)	0.14 (100)
Trichloroethene (b)	0.38 (100)			ND (0)	ND (0)	0.10 (36)	0.00 (6)	0.00 (6)
Toluene (b)	7.94 (100)	11.32 (100)		5.52 (100)	5.17 (100)	16.83 (100)	6.59 (100)	7.06 (100)
1,2-dibromoethane	0.01 (26)			ND (0)	ND (0)	ND (0)	ND (0)	ND (0)
Tetrachloroethene	0.67 (100)			0.10 (100)	0.10 (100)	0.19 (100)	0.12 (100)	0.13 (100)
m-p-xylene	2.81 (100)	9.75 (100)		3.47 (100)	3.14 (100)	7.15 (100)	3.77 (100)	4.08 (100)
Styrene				0.33 (100)	0.38 (100)	0.79 (100)	0.36 (100)	0.70 (81)
o-xylene	1.30 (99)			1.25 (100)	1.14 (100)	2.32 (100)	1.40 (100)	1.46 (100)
m-dichlorobenzene (b)				0.00 (7)	0.00 (6)	0.01 (19)	0.00 (6)	0.00 (6)
p-dichlorobenzene (b)				0.03 (29)	0.05 (86)	0.08 (88)	0.06 (44)	0.07 (38)
o-dichlorobenzene (b)				0.00 (21)	0.02 (19)	0.01 (19)	ND (0)	ND (0)

(a) Estimates of mean concentrations from the field study are based on the lognormal model except as explained under (b).

(b) Simple averages were used to estimate the mean concentrations for these chemicals due to outliers or a large number of concentrations below the detection limit.

ND = Not Detected.

dichloromethane measured in either an automated sample or a bag or canister sample before transport was 1.27 ppb. But, the average concentration in a transported bag sample was 3.35 ppb. Also, six of the sixteen transported bag samples had concentrations exceeding 5.0 ppb. These results suggest that ARB's reported concentrations of dichloromethane may be off by a factor of 10. There may also be large errors in the reported concentrations of 1,1,1-trichloroethane, trichloroethene, toluene, m+p-xylene, and o-xylene. Smaller effects were identified for most of the other target compounds.

Another problem that can be identified in Table I-3.4 is the apparent residual contamination in canister samples. Although the transportation and storage effects for canisters are minimal (this is discussed later), the average measured concentrations of certain chemicals is significantly higher for canister samples than for AGC samples or samples collected in bags and immediately analyzed. However, for each of these chemicals the higher concentrations were observed for the same set of five canisters. Therefore, it is reasonable to conclude that the problem is caused by residual contamination from previous samples. Unfortunately, because we did not receive information about the previous use of the canisters or the procedures used in cleaning them, we cannot identify specific causes of the contamination. The canisters that are suspected of being contaminated have the following ID numbers: 9195, 9143, 9162, 9192, and 9190.

A result that is apparent in Table I-3.4 is that the effect of transportation and storage on canister samples is relatively small. We did find statistically significant effects for several chemicals, but the effect was less than ten percent for all but one of them. A 23 percent increase (1.17 to 1.44 ppb) in the concentration of dichlorodifluoromethane in canisters was apparently due to transportation and storage.

3.3.2 Graphical Analysis. A graphical analysis was used to identify obvious effects due to collection method and transportation and storage. It also helped us to develop a statistical analysis approach for identifying more subtle effects. The statistical approach and the results of the analyses are presented in Section 3.3.3.

Our preliminary analysis consisted of plotting the data as illustrated in Figures I-3.2 and I-3.3. The measured concentrations from

the AGC (denoted by the letter A) and the initial concentrations measured in the bag (B) and canister (C) samples are plotted against the time of sample collection in Figure I-3.2 for the chemical dichloromethane. Notice that there are several sample sets in which the TAC concentrations in the canisters were much higher than the concentrations measured directly or in the bag. Similar plots are provided for all of the target chemicals in Appendix I-B. These plots show the distribution of ambient concentration levels during the 7-day sample collection period. They are also useful for identifying obvious large differences between concentrations measured by AGC and measured concentrations of collocated samples collected in bags and cans.

In Figure I-3.3, and similar figures in Appendix I-C, the effects of transportation and storage on samples collected in Tedlar bags are documented. Each bag sample is identified by the numbers 1 through 9 or the letters A through G (representing samples 10 through 16). The circled numbers or letters identify the measured concentrations following transport between laboratories. Notice that the concentrations are presented on a log scale.

3.3.3 Statistical Analysis. The statistical model for analyzing the field study data is a log-linear model based on two general assumptions:

- (A) The natural logarithm of a measured sample concentration is the sum of the fixed and random effects due to measurement error, sample-to-sample variation, sample collection method, and the effects of storage and transportation;
- (B) The random effects on the log of the measured concentrations are normally distributed with means equal to zero and variances unknown.

The basic concept of the model follows:

Let AGC, B1, B2, C1, and C2 represent the measured concentration from the automated time integrated sample, the initial and final bag samples, and the initial and final canister samples, respectively. Each of these measurements is affected by different sets of factors that are of interest. For example, the automated sample is affected by changes in the ambient air concentrations and measurement error. Thus we assume

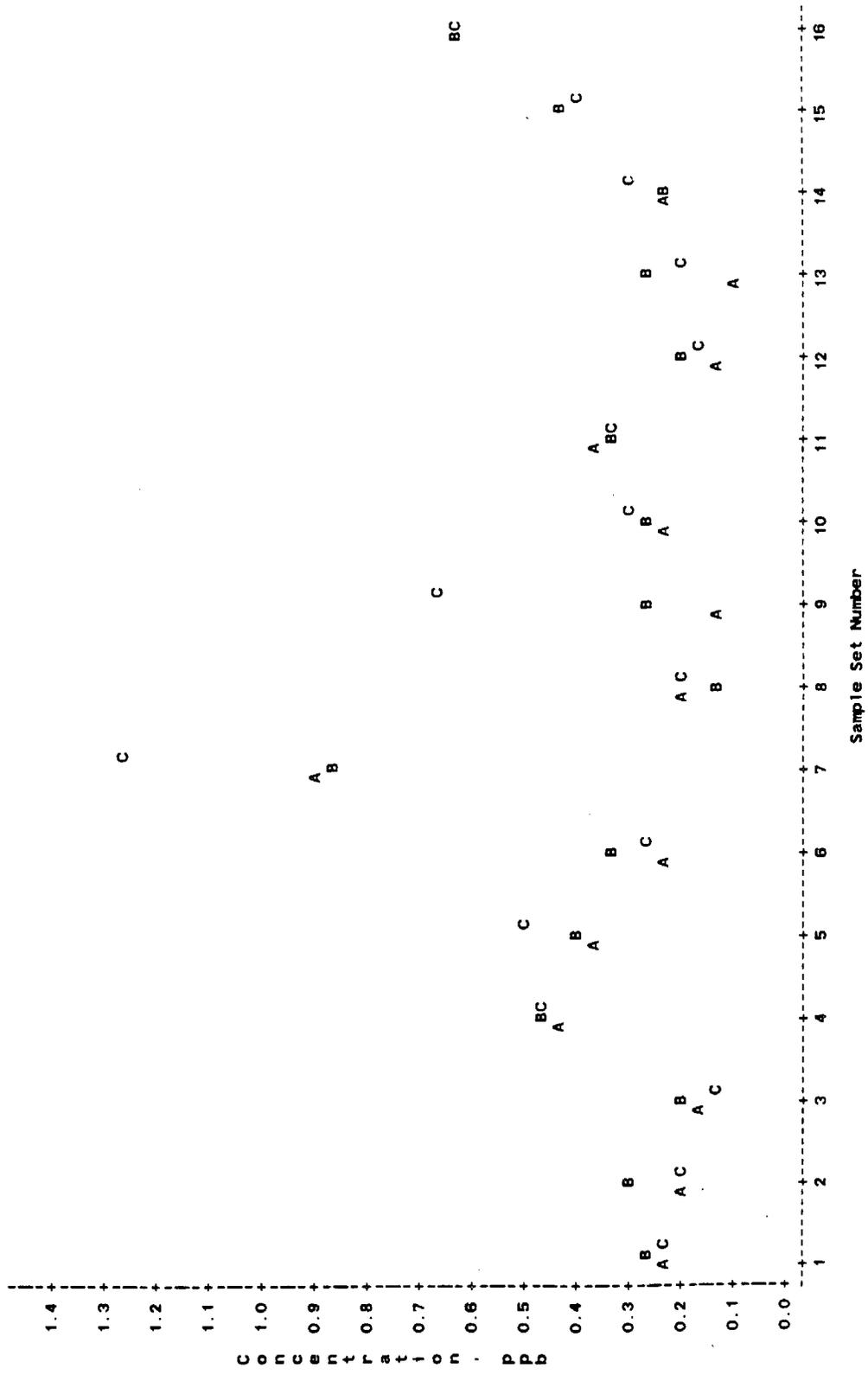


FIGURE I-3.2. PLOT OF DICHLOROMETHANE CONCENTRATIONS FOR AUTO-GC (A), INITIAL BAG (B), AND INITIAL CAN (C) SAMPLES VERSUS SAMPLE SET NUMBER

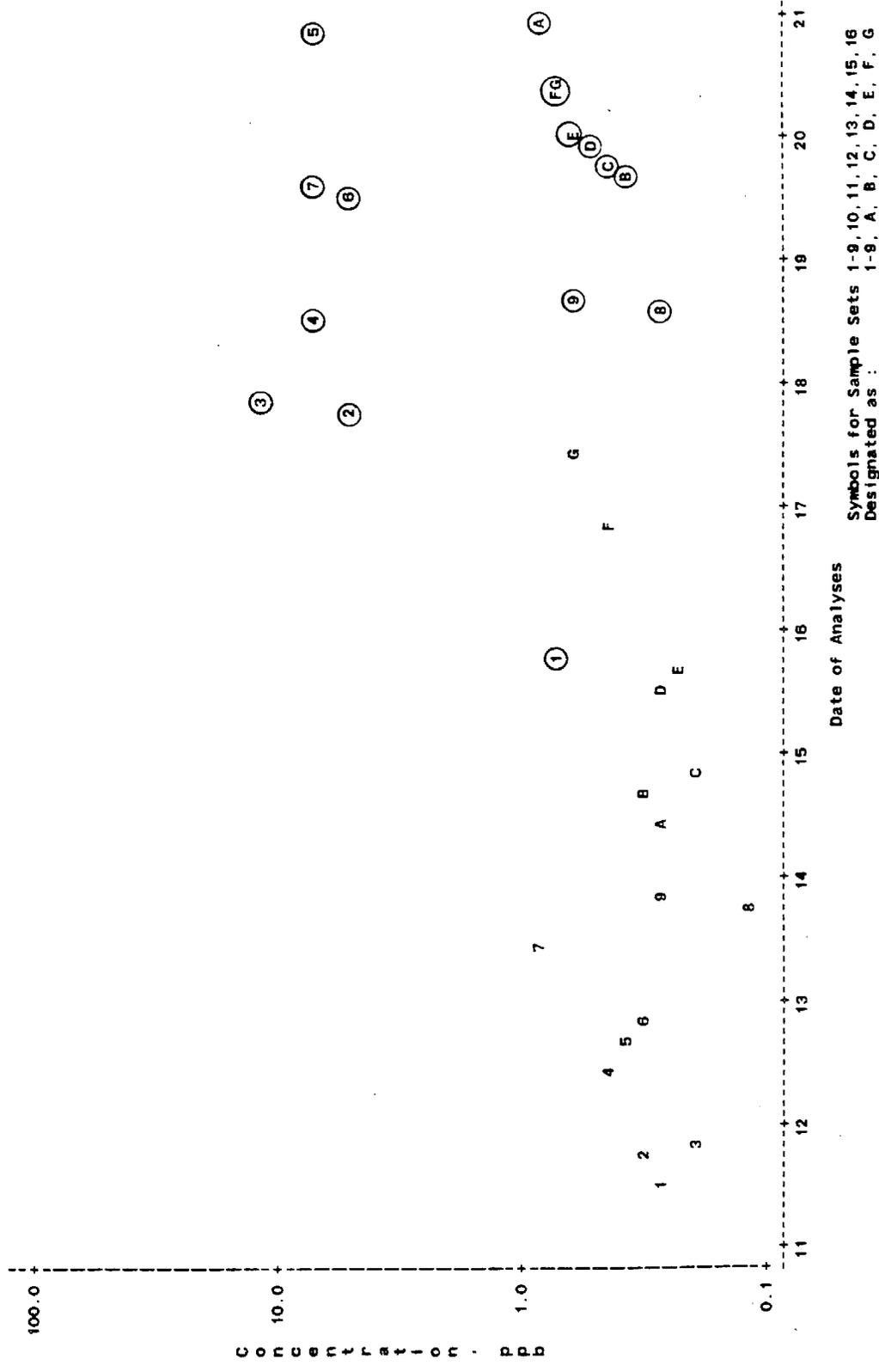


FIGURE I-3.3. PLOT OF DICHLOROMETHANE CONCENTRATIONS FOR INITIAL AND REPEAT BAG SAMPLE ANALYSES. CIRCLED SYMBOLS REPRESENT REPEAT ANALYSES.

$$\ln(\text{AGC}) = \mu + S + e,$$

where  $\mu$  is the average log-concentration in ambient air at a fixed location,  $S$  is the random effect due to sample-to-sample differences at the sampling location, and  $e$  is the random effect due to measurement error. Both random effects are assumed to have a statistical expectation of zero (ie.,  $E[S]=E[e]=0$ ). This means that the method of collecting and analyzing an automated sample does not affect the average measured log-concentration.

On the other hand, we assume that there are both fixed and random effects associated with measured concentrations in bag and canister samples. The statistical models for the measured bag concentrations are

$$\ln(\text{B1}) = \mu + S + B + e,$$

and

$$\ln(\text{B2}) = \mu + S + B + \text{BT} + e,$$

where  $B$  represents the effect of collecting a sample in a bag, and  $\text{BT}$  represents the effect of transporting and storing an air sample in a bag. We assume that each of these effects has fixed and random components. For example, we assume that expected value of  $B$  is  $B_0$  ( $E[B]=B_0$ ) and the standard deviation of  $B$  is  $\sigma_B$  ( $\text{Std}[B]=\sigma_B$ ). Also, the expected value and standard deviation of  $\text{BT}$  are  $\text{BT}_0$  and  $\sigma_{\text{BT}}$ , respectively. Similar models were used to express  $\text{C1}$  and  $\text{C2}$  in terms of the canister effect  $C$  and the transportation and storage effect  $\text{CT}$ .

The statistical analysis of collection and transportation and storage effects was performed using variance component analysis and modified t-tests to test for the statistical significance of the estimated effects. First we calculated differences

$$Z_B = \ln(\text{B1}) - \ln(\text{AGC}),$$

$$Z_{\text{BT}} = \ln(\text{B2}) - \ln(\text{B1}),$$

$$Z_C = \ln(\text{C1}) - \ln(\text{AGC}), \text{ and}$$

$$Z_{\text{CT}} = \ln(\text{C2}) - \ln(\text{C1}),$$

and computed averages over the 14 or 16 sample sets. The sample averages, denoted by  $\bar{Z}_B$ ,  $\bar{Z}_{BT}$ ,  $\bar{Z}_C$ , and  $\bar{Z}_{CT}$ , have the following statistical expectations and standard errors:

Sample Average	Expected Value	Standard Error
$\bar{Z}_B$	$B_0$	$(\sigma_B^2/N + \alpha_1\sigma_\epsilon^2)^{1/2}$
$\bar{Z}_{BT}$	$BT_0$	$(\sigma_{BT}^2/N + \alpha_2\sigma_\epsilon^2)^{1/2}$
$\bar{Z}_C$	$C_0$	$(\sigma_C^2/N + \alpha_3\sigma_\epsilon^2)^{1/2}$
$\bar{Z}_{CT}$	$CT_0$	$(\sigma_{CT}^2/N + \alpha_4\sigma_\epsilon^2)^{1/2}$

The terms  $\sigma_B^2$ ,  $\sigma_{BT}^2$ ,  $\sigma_C^2$ , and  $\sigma_{CT}^2$  are the variance components associated with the random effects of the factors being tested; and  $\sigma_\epsilon^2$  is the variance component due to measurement error. The coefficients  $\alpha_i$  are determined by the contribution of measurement error and the correlation among the data. Variance component analysis, using the Z variables and the QC data, was used to estimate the variance components in each of the standard errors.

Finally, t-statistics were computed to test the specific hypotheses about collection and transportation and storage effects. For example, to test the hypothesis that  $B_0 = 0$  we calculated

$$T_B = \bar{Z}_B / SE(\bar{Z}_B) ,$$

where  $SE(\bar{Z}_B)$  is the estimated standard error of  $\bar{Z}_B$ . According to Satterthwaite (see, for example, Johnson and Leone <sup>(5)</sup>)  $T_B$  has approximately a Student's t-distribution with  $\gamma$  degrees of freedom. He also provides a formula for estimating  $\gamma$ . The statistical significance of the bag collection effect was established by comparing the absolute value of  $T_B$  with the 97.5 percentile of the t-distribution. Similar tests were performed for the effects of BT, C, and CT. These tests are called modified t-tests because we had to use Satterthwaite's approximation and make adjustments to the estimated standard errors to account for correlation among the data. The log normal model also produces more precise estimates

of the average concentration levels and the effects of sample collection and handling conditions. The specific effects of interest in this study are described below:

1. The bag collection effect is the expected difference between the concentration measured by the automated system and the concentration measured in a bag sample immediately after the sample is collected,
2. The bag transportation and storage effect is the expected difference between the concentrations measured in a bag sample before and after the sample is transported between laboratories,
3. The canister collection effect is the expected difference between the concentration measured by the automated system and the concentration measured in a canister sample immediately after the sample is collected,
4. The canister transportation and storage effect is the expected difference between the concentrations measured in a canister sample before and after the sample is transported between laboratories.

In addition to estimating the average change in concentrations we also estimated the probability that an individual sample concentration will increase due to each of the specified effects. If there was no effect of collecting a sample in a bag, for example, then we would expect one-half (50%) of the bag samples to have higher concentrations than their collocated AGC samples. The estimated probability of increase provides an alternative test for the presence of the effect. Using a sign test (see, for example, Hollander and Wolfe <sup>(4)</sup>) we tested the hypothesis that the probability is different from 50%. The sign test does not rely on the assumption of a log normal model for the data. This is particularly important when the log normal model cannot be applied due to a large number of concentrations that are below the detection limit. In general, we used both the t-test and the sign test to determine if an estimated effect is statistically significant. However, if we encountered a large number of concentrations below the detection limit or if the log normal model was not appropriate due to the presence of outliers, we relied only on the sign test to determine if the estimated effect was significant.

The estimated effects that were found to be statistically significant (at the 0.05 level of significance) based on either the modified

t-test or the sign test are presented in Tables I-3.5 and I-3.6. Except as indicated in the tables, the estimated effects were calculated using the maximum likelihood method for a log normal model. Each table contains the estimated collection effects and transportation and storage effects for a bag or canister sample in absolute (ppb) and relative (%) units, and the estimated probabilities that sample concentrations will increase due to the effects. Also presented for each chemical are the estimated average ambient concentration determined from the automated samples, the coefficient of variation (c.v.) for the 1/2-hour time integrated sample, and the percent of the AGC samples in which the chemical was detected.

We see, for example, that dichloromethane was found in 100% of the AGC samples and the average ambient concentration was 0.28 ppb with a coefficient of variation of 60%. The average concentration in a collocated bag sample was 0.08 ppb (29%) higher than the average of the automated samples and 79% of the sample sets had bag sample concentrations that were higher than the corresponding AGC samples. The sign test determined that this percentage was significantly higher than 50% at the 0.05 level of significance. Furthermore, the average concentration of dichloromethane in the bag sample following transportation and storage was 3.00 ppb (839%) higher than the average concentration measured immediately after the sample was collected. Finally, an increase in concentration was observed in all 16 (100%) of the samples collected.

In general we see that there are significant collection and transportation and storage effects on bag samples for nearly all of the chemicals. The concentrations of dichloromethane and 1,1,1-trichloromethane were significantly higher in the bag samples immediately after sample collection, but for most of the other chemicals we found a significant decrease in sample concentrations. However, when the bag samples were reanalyzed following transport between the field site and the ARB laboratory, nearly all of the chemicals showed significant increases in concentrations.

One of the more unusual results occurred with the chemical p-dichlorobenzene. Among the fourteen sample sets for which we had data from the AGC, this chemical was not detected in ten of the automated samples. But in eight of these ten sample sets we detected it in the bag sample. On the other hand, in three of the four sample sets in which the AGC sample had

TABLE I-3.5. ESTIMATED COLLECTION AND TRANSPORTATION AND STORAGE EFFECTS ON SAMPLES COLLECTED IN TEDLAR BAGS

#	Chemical Name	Automated Sample			Bag Collection Effect			Bag Storage Effect		
		Avg Conc	C. V. (a)	Det	Avg. Increase	Pr (B1)AGC (c)	Avg. Increase	Pr (B2>B1) (e)		
		(ppb)	(%)	(%)	(ppb)	(%)	(ppb)	(%)		
1	Dichlorodifluoromethane	1.14	100.9	100	-	-	0.88	79	81*	
4	Vinyl Chloride	ND	-	0	ND	-	ND	-	-	
8	1,1-dichloroethene	ND	-	0	ND	-	ND	-	-	
9	Dichloromethane	0.28	60.0	100	0.081	29	3.00	839	100*	
11	1,1,2-trichloro-1,2,2-trifluoroethane	0.13	21.1	100	-	-	-	-	63	
14	Trichloromethane	0.01	335.7	21	-	-	0.02(g)	343(g)	88*	
15	1,2-dichloroethane	0.00	166.6	7	-	-	0.25(g)	4960(g)	100*	
16	1,1,1-trichloroethane	0.45	35.9	100	0.042	9	2.73	554	81*	
17	Benzene	2.35	114.6	100	-0.245	-10	-	-	38	
18	Carbon Tetrachloride	0.13	23.2	100	-0.005	-4	0.01	6	75*	
20	Trichloroethene	ND	-	0	ND	-	0.10(g)	-	100*	
24	Toluene	5.52	137.6	100	-0.344	-6	11.66(g)	226(g)	75*	
25	1,2-dibromoethane	ND	-	0	ND	-	ND	-	-	
26	Tetrachloroethene	0.10	54.1	100	-0.002	-2	0.09	85	81*	
29	m+p-xylene	3.47	164.6	100	-0.326	-9	4.01	127	56	
30	Styrene	0.33	190.0	100	-	-	0.41	107	63	
32	o-xylene	1.25	161.1	100	-0.116	-9	1.18	104	56	
37	m-dichlorobenzene	0.00	82.0	7	- (f)	- (f)	0.03(g)	59(g)	100	
38	p-dichlorobenzene	0.03	937.6	29	- (f)	67	-	-	86*	
39	o-dichlorobenzene	0.00	209.1	21	-	-	-	-	50	

(a) The coefficient of variation (CV) includes sampling and analysis error.  
 (b) The collection effect is represented by the average increase in concentration (ppb and percent) due to collection of the sample in a Tedlar bag. (Only effects that are statistically significant (.05 level) are presented.)  
 (c) Percent of bag samples that have higher concentrations than collocated automated samples.  
 (d) The storage effect is represented by the average increase in sample concentration (ppb and percent) due to transportation and storage in a Tedlar bag. (Only effects that are statistically significant (.05 level) are presented.)  
 (e) Percent of bag samples that have higher measured concentrations after transport than before.  
 (f) The bag effect on p-dichlorobenzene depends on the ambient concentration level.  
 (g) Estimates are based on simple averages due to outliers or a large number of not detected values.  
 \* = Means that the estimated probability is different from 50% at the .05 level of significance.  
 ND = Not detected.

TABLE I-3.6. ESTIMATED COLLECTION AND TRANSPORTATION AND STORAGE EFFECTS ON SAMPLES COLLECTED IN CANISTERS

#	Chemical Name	Automated Sample		Canister Collection Effect		Canister Storage Effect			
		Avg Conc (ppb)	C.V. (a) (%)	Det (%)	Avg. Increase (ppb)	Pr(C1>AGC) (c) (%)	Avg. Increase (ppb)	Pr(C2>C1) (e) (%)	
1	Dichlorodifluoromethane	1.14	100.9	100	-	-	0.27	23	75*
4	Vinyl Chloride	ND	-	0	ND	-	ND	-	-
8	1,1-dichloroethene	ND	-	0	ND	-	ND	-	-
9	Dichloromethane	0.28	60.0	100	0.12	42	79*	-	44
11	1,1,2-trichloro-1,2,2-trifluoroethane	0.13	21.1	100	0.43	323	64	-	56
14	Trichloromethane	0.01	335.7	21	-	-	-	-	50
15	1,2-dichloroethane	0.00	186.6	7	-	-	-	-	50
16	1,1,1-trichloroethane	0.45	35.9	100	1.27	281	50	-	31
17	Benzene	2.35	114.6	100	-0.08	-3	15*	-	56
18	Carbon Tetrachloride	0.13	23.2	100	-	-	46	-	56
20	Trichloroethene	0.00	0.0	0	-	-	-	-	100
24	Toluene	5.52	137.6	100	-	-	0.46	7	88*
25	1,2-dibromoethane	ND	-	0	ND	-	ND	-	-
26	Tetrachloroethene	0.10	54.1	100	-	-	0.01	7	69
29	m-p-xylene	3.47	164.6	100	-	-	0.30 (f)	6	88*
30	Styrene	0.33	100.0	100	-	-	-	-	31
32	o-xylene	1.25	161.1	100	0.15	12	64	4	75*
37	m-dichlorobenzene	0.00	82.0	7	-	-	-	-	100
38	p-dichlorobenzene	0.03	937.6	29	-	-	-	-	71
39	o-dichlorobenzene	0.00	209.1	21	-	-	-	-	-

(a) The coefficient of variation (CV) includes sampling and analysis error.  
 (b) The collection effect is represented by the average increase in concentration (ppb and percent) due to collection of the sample in a canister. (Only effects that are statistically significant (.05 level) are presented.)  
 (c) Percent of canister samples that have higher concentrations than collocated automated samples.  
 (d) The storage effect is represented by the average increase in sample concentration (ppb and percent) due to transportation and storage in a canister. (Only effects that are statistically significant (.05 level) are presented.)  
 (e) Percent of canister samples that have higher measured concentrations after transport than before.  
 (f) Canister storage effects for styrene were unusual because styrene was not detected in 3 canisters following transport yet others showed increases. Ambient levels were quite variable.  
 \* = Means that the estimated probability is different from 50% at the .05 level of significance.  
 ND = Not detected.

a positive concentration of p-dichlorobenzene, its concentration in the bag sample was significantly lower. Because of this unusual behavior, and because of large number of concentrations below the detection level, it is not possible to confirm these results statistically. However, because the canister sample results consistently agree with those from automated samples, we believe that the effect observed is real. Perhaps the effect is caused by the chemical adhering to the walls of the bag. This could result in low measured concentrations when the chemical is present in the air and high readings, due to contamination, when the chemical is not present. This may also explain the initial bag collection effects observed for many other chemicals.

Comparing Tables I-3.5 and I-3.6 we see a dramatic difference in the collection and transportation and storage effects between bag and canister samples. Although we found significantly higher concentrations of four chemicals (#9, 11, 16, 32) in the initial canister sample compared to the AGC sample, it appears as though the effect is due to the failure to clean five of the canisters properly. Notice that we found the average increase to be statistically significant for all four chemicals but the probability of a higher concentration in the canisters was significant only for dichloromethane.

A rather unusual collection effect was discovered for benzene. We found that the average initial canister concentration and the probability of a higher concentration in canister samples were significantly lower than expected according to our statistical tests. Because the effect is small (3.3%) it is not a major concern. However, after careful review of the data we cannot explain why this effect occurs.

We also found statistically significant effects on the concentrations of five chemicals due to transportation and storage of the canister samples. This shows that contamination can occur in canister samples; however, the largest effect was only 23.1% for dichlorodifluoromethane. The effects on the other four chemicals were less than 10%. These are relatively small effects compared to the effects found for Tedlar bag samples. Also, as mentioned earlier, the canisters made round trips between the field laboratory and the ARB laboratory, and the period between analyses was as much as 9 days. Typically, ARB will analyze field samples within 48 hours of sample collection.

### 3.4 Quality Assurance

Numerous quality assurance activities were employed during the field study to guarantee the acquisition of valid data. These activities are discussed as they relate to the sampling and analytical efforts of the study.

3.4.1 Sampling. Bag and canister sampling were tested prior to the field study and were found to be free of contamination of the 41 component mixture (i.e., below detection limit). Estimated detection limits for the target compounds are listed in Section 3.4.2. Just prior to sampling, both units along with the automated GC were connected to the sampling manifold and checks were made to assure that the entire system was leak-free.

Bags were visually inspected before use to make sure that they contained zero nitrogen. Immediately before use, the bags were "pumped down" (i.e., nitrogen was exhausted) and examined to make sure that no leaks were present and that the bag valve was sealing properly. Bags were never removed from their shipping containers. After collection, the bag valves were closed and the containers were sealed and then immediately shipped to the Sacramento office. Upon return to the field laboratory a visual inspection was made to make sure that the bag valve was closed and that the bag volume was unchanged.

Canisters were initially checked with a certified pressure-vacuum gauge to make sure that the vacuum reading was 29 in Hg. Each canister was also equipped with its own gauge for cross-reference. The canister pressure was recorded immediately after collection and after each analysis.

3.4.2 Analyses. Prior to the field sampling effort, several analyses of calibration mixtures and ultra-zero air (Linde) were carried out to ensure that the GC instrument was performing adequately.

Duplicate calibration samples were analyzed each day of the study. The first sample was analyzed before any field samples were analyzed, and the second was analyzed at approximately midway through the day. The results were used to (1) monitor the performance of the analytical system,

(2) provide estimates of the analytical precision, and (3) calculate daily response factors.

Table I-3.7 displays the challenge concentration in the calibration sample, the estimated relative standard deviation (within a day), and the estimated detection limit for each of the target chemical. With the exception of dichlorodifluoromethane, the estimated relative standard deviations are quite small, especially considering the large sample-to-sample variations and the large effects of sample collection and storage that were observed. This excellent precision allowed us to establish statistically some of the more subtle effects such as the effects of sample collection in Tedlar bags.

During the course of this project Battelle was analyzing audit samples for the Quality Assurance Division of US EPA as part of our analytical effort on the Toxic Air Monitoring System (TAMS) program. EPA reported that our measurements showed values within  $100 \pm 10$  percent of challenge concentrations ranging from 1 to 5 ppb.

3.4.3 Data Handling. All field activities were recorded in a laboratory record book. These activities include bag and canister inspection data, daily log comments and tracking information for all collected samples.

All analytical data were stored on flexible disks. However, hard copy printout was also obtained for each sample run as backup data. All raw peak areas were key-punched onto a VAX computer. The key-punched data were reviewed by the research staff prior to further use.

### 3.5 Comparison of Field and Laboratory Results

The TAC concentration changes in Tedlar bags that were observed during the Bakersfield field study were compared with the earlier laboratory studies at Battelle and with previous ARB field data. For all of these studies we show in Table I-3.8 the median TAC concentration changes in the bags that are due to storage or transportation effects. As mentioned earlier these studies were conducted under a wide variety of conditions ranging from very typical storage and transport to extreme conditions of temperature and storage time. As a result there are inconsistencies among

TABLE I-3.7. CALIBRATION SAMPLE CONCENTRATIONS, ANALYTICAL PRECISION, AND DETECTION LIMITS

Chemical	Challenge Conc. (ppb)	Relative Std. Dev. (%)	Detection Limit (ppb)
Dichlorodifluoromethane	2.60	25.2	0.01
Vinyl Chloride	4.61	6.3	0.03
1,1-Dichloroethene	3.22	4.6	0.03
Dichloromethane	4.11	3.2	0.02
1,1,2-Trichloro-1,2,2-trifluoroethene	2.72	3.6	0.02
Trichloromethane	3.45	2.0	0.01
1,2-Dichloroethane	3.34	2.9	0.02
1,1,1-Trichloroethane	2.66	5.9	0.02
Benzene	2.83	3.6	0.01
Carbon Tetrachloride	2.96	1.7	0.01
Trichloroethene	2.93	3.6	0.02
Toluene	2.45	4.4	0.01
1,2-Dibromoethane	3.06	2.8	0.01
Tetrachloroethene	2.51	3.4	0.01
m+p-Xylene	2.14	7.3	0.01
Styrene	2.25	8.8	0.02
o-Xylene	2.14	4.8	0.01
m-Dichlorobenzene	2.16	5.8	0.01
p-Dichlorobenzene	1.78	5.9	0.01
o-Dichlorobenzene	2.16	6.1	0.01

TABLE I-3.8. MEDIAN TAC CONCENTRATION CHANGES IN TEDLAR BAGS DUE TO STORAGE AND TRANSPORTATION EFFECTS

#	Compound Name	Median Concentration Increase (ppb)							
		Average Ambient Conc (ppb) (1)	ARB Bag Swap (2)	ARB Bag/Can (3)	0.5 ppb Bag/Can Storage (4)	Bag Storage Study (5)	Zero Air Bag/Can Storage (4)	Field Storage (6)	
1	Dichlorodifluoromethane		---	---	NS	ND	ND	0.88	
4	Vinyl Chloride		---	---	NS	ND	ND	ND	
8	1,1-Dichloroethene		---	---	NS	ND	ND	ND	
9	Dichloromethane	2.3	0.40	0.40	0.52	1.19	0.67	3.00	
11	1,1,2-Trichloro-1,2,2-Trifluoroethane		---	---	NS	ND	NS	NS	
14	Trichloromethane	0.08	NS	NS	NS	0.16	NS	0.02	
15	1,2-Dichloroethane		NS	NS	-0.11	INT	NS	0.25	
16	1,1,1-Trichloroethane	2.0	0.09	NS	0.10	ND	0.13	2.73	
17	Benzene	2.8	NS	-0.30	84.54	ND	13.92	NS	
18	Tetrachloromethane	0.13	NS	NS	NS	ND	ND	0.01	
20	Trichloroethene	0.36	0.03	0.08	NS	ND	0.08	0.10	
24	Toluene	7.9	---	---	1.07	7.10	0.42	11.66	
25	1,2-Dibromoethane	0.006	NS	---	-0.23	ND	ND	ND	
26	Tetrachloroethene	0.67	0.03	NS	NS	0.73	0.06	0.09	
29	m+p-Xylene	2.8	---	---	0.45	ND	0.46	4.01	
30	Styrene		---	---	0.37	---	0.85	0.41	
32	o-Xylene	1.3	---	---	0.25	ND	0.18	1.18	
37	m-Dichlorobenzene		---	---	-0.25	---	0.02	NS	
38	p-Dichlorobenzene		---	---	-0.18	---	0.09	0.03	
39	o-Dichlorobenzene		---	---	-0.26	---	0.03	NS	

NS - Indicates that the estimated change was not significantly different from zero at 0.05 level.

ND - Not detected.

INT - Interference

(1) - Based on 1985 Toxic Air Quality Data Summary.

(2) - Median increase between initial and replicate analysis at the same lab.

(3) - Median difference between analyses of bag and collocated canister samples.

(4) - Median (average) increase over the 7 day test.

(5) - Median increase among samples from several experiments in which bags were stored at 50°C.

(6) - Average increase in concentrations due to transportation and storage (Field Study).

the various experiments. For instance, benzene shows considerable concentration changes during the bag/can (0.5 ppb and zero air) laboratory storage studies at Battelle. However no significant changes were observed during the field experiments. Dichloromethane, on the other hand, shows significant concentration changes for all studies. Furthermore, the amount of change found for each study represents a significant fraction of the reported ambient concentration of dichloromethane (based on 1985 Toxic Air Quality Data Summary). As a result, the reported ambient concentration of dichloromethane is probably grossly over-estimated. Similar extrapolations can also be made for several of the other TAC compounds based upon their concentration changes and reported ambient concentrations.

#### 4.0 Conclusions and Recommendations

Our studies of storage and transportation effects on TAC concentrations in Tedlar bags and stainless steel canisters lead us to conclude the following:

- Transportation and storage of air samples in Tedlar bags significantly affects the concentrations of many TACs of interest to ARB. The effects are as large as ten times the average ambient concentrations for certain TACs.
- The effects of transportation and storage on some TAC concentrations in air samples collected in stainless steel canisters are statistically significant; however, these effects were much smaller than the effects found in Tedlar bags. Also, under a typical ARB sampling and analysis schedule, the effects may not even be detectable.
- Storage of air samples in Tedlar bags for more than 24 hours is not recommended because TAC concentrations will increase in the bags with time. The specific contaminants and level of contamination will depend upon the storage conditions. In most cases, the level of contamination found in our studies represented a significant fraction of the reported ambient air concentrations in California.
- No appreciable storage and transportation effects on TAC concentrations in stainless steel canisters were found. Sample integrity can be maintained if canisters are used as storage devices for the TAC compounds. However, caution should be used to ensure that the initially evacuated canister has been properly cleaned.

Based upon our findings we recommend that ARB replace their Tedlar bag sampling devices with stainless steel canisters as soon as possible. In the mean time ARB should minimize the storage time of air samples collected with Tedlar bags. We recommend that storage times not exceed 48 hrs. Before converting to stainless steel canisters, the procedures for cleaning the canisters should be reviewed and documented.



## CHAPTER II. EVALUATION OF SELECTED WHOLE AIR SAMPLING DEVICES

### 1.0 Introduction

The Air Resources Board is interested in finding out whether or not alternative whole air sampling approaches may offer "improved" replacements for their current Tedlar bag sampling system. ARB is particularly interested in syringe and canister based sampling systems.

In Section I of this report, stainless steel canisters treated by the Summa passivating process were shown to be excellent storage containers for ppb levels of toxic air contaminants. Whole air sampling with these canisters can be accomplished either manually or automatically. In the manual mode of operation, the evacuated canister is taken to the sampling location, and its valve is opened to obtain a grab sample. The automated mode of operation is used to collect time integrated samples. In this mode of operation, whole air is drawn into a sampling train that consists of an evacuated canister and upstream components that serve to regulate the rate and duration of air sampling. In some sampler designs, the canister is filled by action of a pump under control of an electronic or mechanical flow controller. In other designs there is no pump, and differential pressure between the atmosphere and the evacuated canister causes flow into the system. A mass flow controller or critical orifice is placed in-line to regulate the flow rate. In both systems the flow rate and sample duration must be matched in order to maintain constant flow during the sampling period.

The other whole air sampling approach that may serve as a comparable means of collecting time integrated samples involves the use of a sequential syringe sampler. The most obvious advantage of this type of sampler is that a pump/flow control valve assembly is not needed. The syringe sampler is equipped with 12 Summa polished stainless steel syringes and can be programmed to collect air samples sequentially over a period from several minutes up to 24 hours.

We evaluated the ability of commercially available syringe and canister based sampling devices to collect and deliver reliable and valid samples to the analytical system. A cleaning and certification program was established that ensures that the canister samplers are free of

contamination and that sample integrity is maintained during the use of samplers. The results of our examination and our certification program are discussed in the following sections.

## 2.0 Experimental

The apparatus and experimental procedures used to evaluate the syringe sampler and canister sampler are described below.

### 2.1 Syringe Sampler

A battery-operated sequential syringe sampler (S.I.S., Moscow, Idaho) was examined. The sampler consists of 12 syringe drives that sequentially acquire air samples at a preselected rate of one sample per hour. The syringes (150 cm<sup>3</sup>) are made of stainless steel and are internally Summa-polished to passivate the metal surface and therefore minimize VOC adsorption. Each syringe is designed to allow both closure at the end of sample collection and automatic release at the start of an analysis. Figure II-2.1 illustrates the opening/sealing mechanism.

The electronics on the syringe sampler permit either normal sequential operation or operation triggered by an external signal. The normal position is used during sample collection and is activated by the field operator. Operation automatically ceases after the 12 samples are collected. In the external mode of operation the gas chromatographic (GC) system triggers syringe injection (contact closure relay). We installed additional circuitry (RC-filter) to the GC to prevent the syringe sampler from receiving spurious "start" signals.

To ensure that the syringe contents are transferred to the GC system, a manifold assembly was connected to the syringe sampler during analysis (see Figure II-2.2). Flow to the GC system is maintained at 35 cm<sup>3</sup>/min with a mass flow controller positioned downstream of the GC's cryogenic trapping system. The syringe expels sample at a rate of 15 cm<sup>3</sup>/min. The remaining flow to the GC is obtained with excess zero air (Aadco, Inc.).

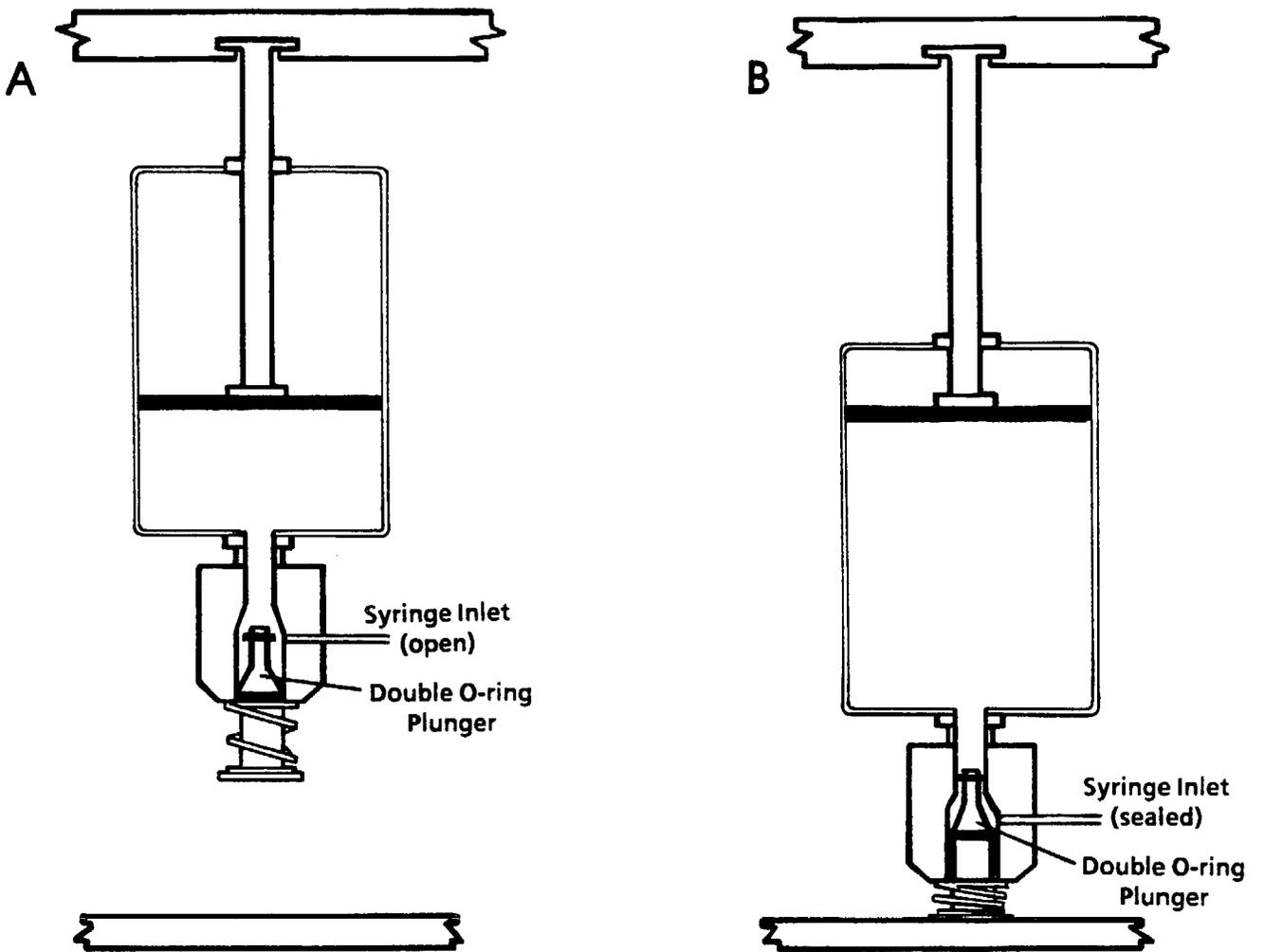


FIGURE II-2.1. ILLUSTRATION OF THE OPENING (A) AND SEALING (B) MECHANISM OF THE SYRINGE SAMPLER

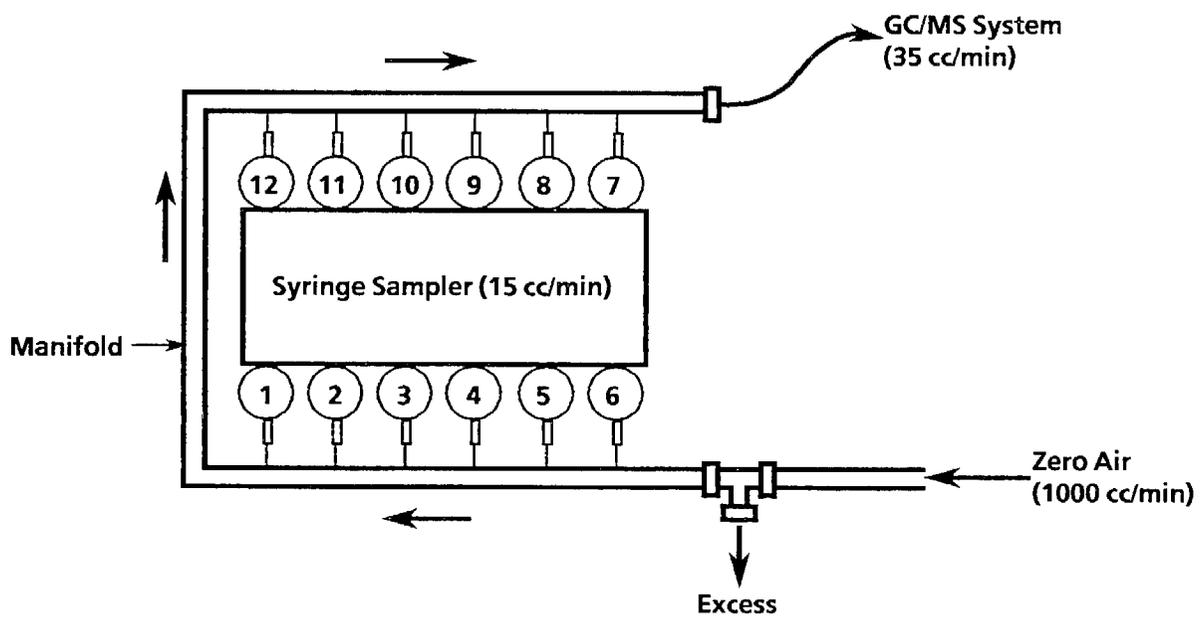


FIGURE II-2.2. FLOW PATH FROM SYRINGE SAMPLER TO GC SYSTEM. THE GC REQUIRES 35 cc/MIN, THE SYRINGE EXPELS SAMPLE AT 15 cc/MIN, AND ZERO AIR IS SUPPLIED AT ~1000 cc/MIN

## 2.2 Canister Sampler

The Model 910A canister sampler (Xontech, Inc.) draws air from a sample manifold and directs it into the sampler via an internal pump. A small portion of the air is passed through an electronic flow controller and to the evacuated canister. The remaining sampled air is vented. Figure II-2.3 shows a flow diagram of the Model 910A.

The pump's internal parts are composed of stainless steel and Teflon. The pump head is sealed with a Viton O-ring. The head pressure of the pump is adjusted with the needle valve located upstream of the exhaust port. The pump head pressure is set so that a differential pressure of at least 5 psig is maintained across the flow controller at all times. This differential pressure will allow the flow controller to deliver a constant flow to the canister during sample collection. A capillary restrictor is installed upstream of the mass flow controller to dampen pressure pulses from the pump.

## 2.3 Analytical Method

The automated GC system described in Section I of this report was used during the syringe and canister sampler tests.

## 2.4 Experimental Procedures

Initial experiments with the syringe sampler were designed to determine how well the syringes seal following the collection of an air sample. Storage periods of two hours, two days, and five days were chosen and represent typical sampling/analysis cycles. Test runs were initiated by filling a Tedlar bag with 1 ppb of the tracer gas, SF<sub>6</sub>. The bag was analyzed in triplicate each day before and after syringe analyses to assure that stable and consistent SF<sub>6</sub> levels were maintained. SF<sub>6</sub> analyses were carried out with a gas chromatograph/electron capture detector equipped with a 1 cm<sup>3</sup> loop/valve assembly. A 2 m mole sieve 5A column held isothermally at 60°C was used to elute SF<sub>6</sub>. Following these bag analyses, the syringe manifold was connected to the bag and the syringe sampler was activated. Each syringe was filled sequentially at a rate of 30 cm<sup>3</sup>/min

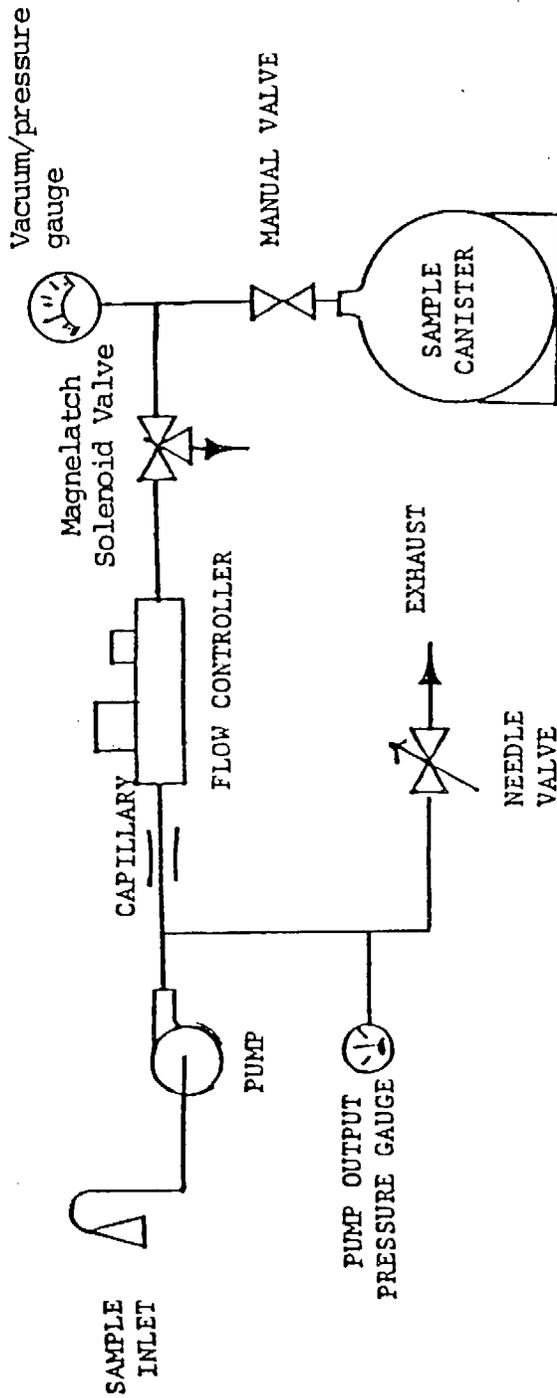


FIGURE II-2.3. FLOW DIAGRAM OF THE MODEL 910A CANISTER SAMPLER

(5 min/syringe). When the above storage time had elapsed, the 12 syringes were sequentially analyzed (5 min/syringe). The 12 syringes were refilled after each test run.

Following the storage tests, the syringe sampler was taken to a residence and placed in operation to collect twelve one-hour integrated samples sequentially. Simultaneously, a canister sampler was used to collect a sample over the same twelve hours.

Initial canister sampler tests involved challenging the commercial units with humidified zero air (Aadco, Inc.) to certify that the samplers were "clean". To accomplish this task zero air was directed through a midjet impinger containing ~15 ml of water at a rate of 1 liter/minute and then directed to the canister sampler which is operated at its normal sampling rate. The sampler exhaust (prior to entering the canister) was sampled with the GC/MS system and compared with the results obtained when sampling directly downstream of the impinger.

The canister samplers were then challenged with dilute calibration mixture in a very similar fashion. In this instance the calibration gas was first mixed with Aadco air and then passed through the impinger and into the canister sampler. In more recent studies the impinger solution was replaced with a (12" long by 1/4" O.D.) Nafion tube that was immersed in a beaker of water. Figure II-2.4 shows diagrams of both of the above humidification approaches.

### 3.0 Results and Discussion

In this section we discuss the experiments that were carried out with the syringe and canister sampling devices.

#### 3.1 Sequential Syringe Sampler

Table II-3.1 shows the results of storing 1 ppb of the tracer, SF<sub>6</sub>, in the twelve syringes. Storage periods of two hours, two days and five days were examined. Average SF<sub>6</sub> concentrations and standard deviations found for these three storage periods are 1.01 ± 0.02 ppb, 0.90 ± 0.04 ppb and 0.91 ± 0.06 ppb. Triplicate analyses of the SF<sub>6</sub> standard on each of the three test days gave values of 1.00 ± 0.02 ppb. In viewing the data, it is

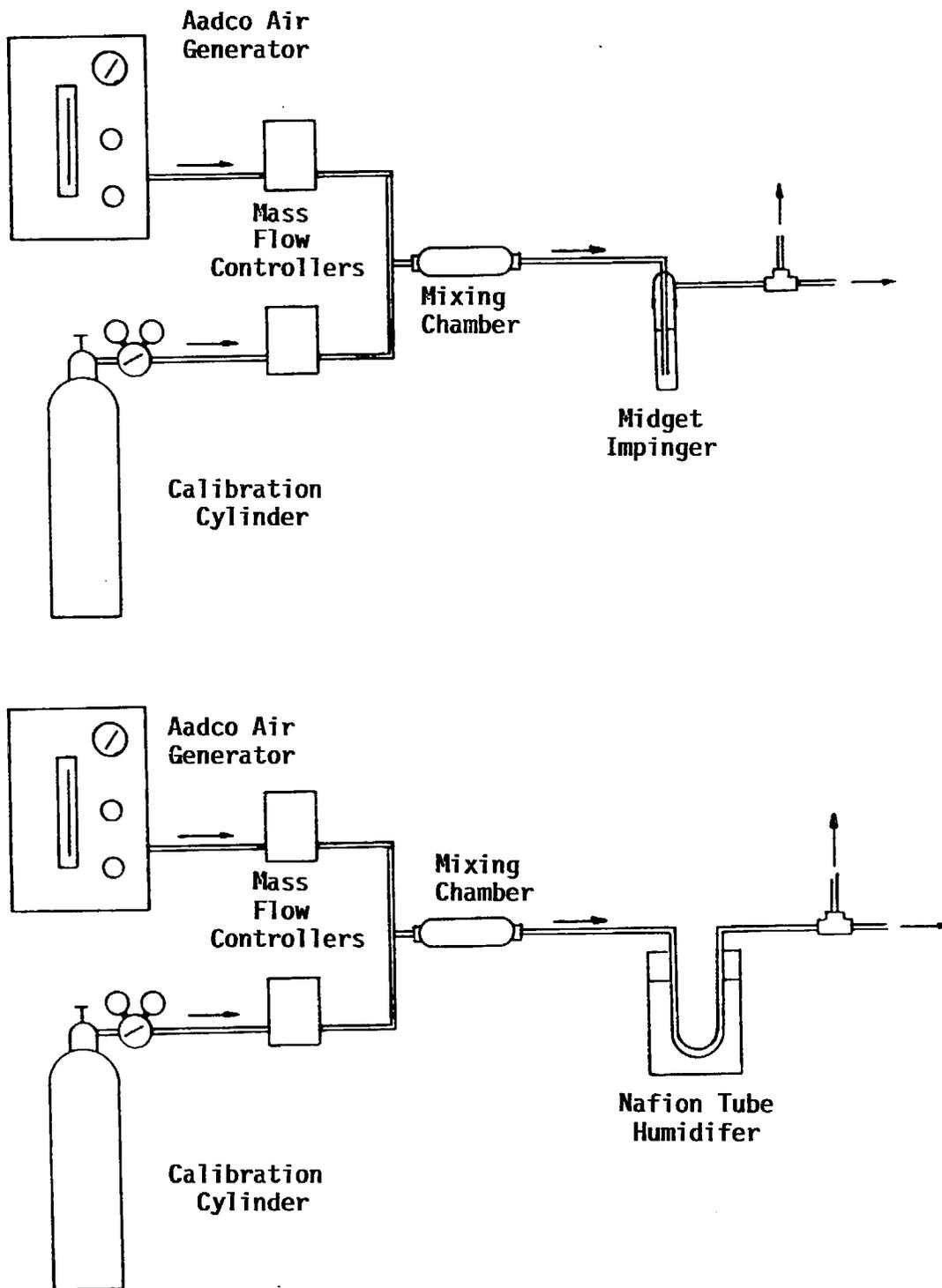


FIGURE II-2.4 DIAGRAMS OF TWO AIR HUMIDIFICATION APPROACHES

TABLE II-3-1.1. RESULTS OF STORING 1 PPB SF6 IN THE SEQUENTIAL SYRINGE SAMPLER

Test Run	Syringe #												Avg.	Std. Dev.	
	1	2	3	4	5	6	7	8	9	10	11	12			
2 Hours	1.03	1.02	0.97	1.03	1.02	1.02	1.02	1.01	1.02	0.99	0.97	1.01	1.01	1.01	0.02
2 Days	0.93	0.87	0.88	0.95	0.90	0.87	0.91	0.92	0.89	0.95	0.84	0.93	0.90	0.90	0.04
5 Days	0.94	0.83	0.88	0.97	0.90	0.96	0.97	0.89	0.96	0.81	0.94	0.87	0.91	0.91	0.06

clear that no losses of SF<sub>6</sub> occurred after several hours of storage. After storage for two or more days, however, some loss of SF<sub>6</sub> did occur. The fact that increased losses are not observed between Day 2 and Day 5 suggest that leakage may not be the cause for the SF<sub>6</sub> decrease. We suspect that the observed SF<sub>6</sub> loss of ~10 percent is probably due to compound adsorption onto the inner surfaces of the syringe itself and therefore very likely dependent upon initial SF<sub>6</sub> concentration. The ~10 percent difference at the 1 ppb level was not deemed to be of practical significance, therefore, experiments to explore the possibility of concentration dependence were not undertaken.

### 3.2 Syringe Versus Canister Sampling Devices

Results from the comparison of the syringe and canister sampling devices at two residences are shown in Table II-3.2. At these residences, sampling was carried out over 12-hour time periods (4:00 p.m. to 4:00 a.m.). During this time frame, 12 one-hour integrated samples were taken with the syringe sampler along with two canister samples. One canister was positioned indoors next to the syringe sampler, the other unit was placed outdoors. Analyses were focused on the 17 toxic air contaminants of interest to the California Air Resources Board. In viewing the data it is apparent that significant differences exist between the collocated canister and syringe samplers. In most cases the concentrations from the canister are 15 to 30 percent greater than the corresponding concentrations found from averaging the 12 syringe samples. However, for several compounds the syringe results are much higher than the canister values. There does not appear to be any consistency between compound and percent difference (e.g. canister benzene value is higher than the syringe benzene value at House B but the opposite is true at House H).

It is also interesting that at both homes, the indoor concentrations for most of the compounds are at least 10 times greater than the outdoor levels. Carbon tetrachloride and freon-113 are exceptions and show similar concentrations as evidenced by the low indoor/outdoor ratios in Table II-3.2. The hourly indoor concentrations obtained from the syringe samples also show a consistent pattern over the 12 hour sampling period. In viewing the concentrations of the more predominant target compounds, we observe a cycling pattern with the lowest concentrations occurring during

TABLE II-3.2. COMPARISON OF SYRINGE AND CANISTER SAMPLING DEVICES AT TWO RESIDENCES

Compound	House B			House H			Can Ratio			
	Can Outdoors ppb	Can Indoors ppb	Syringe Indoors ppb	% Diff	Can Outdoors ppb	Can Indoors ppb	Syringe Indoors ppb	% Diff	Indoor/Outdoor House B	Indoor/Outdoor House H
Freon-12	0.70	7.43	5.62	24.36	0.57	8.27	8.18	1.09	10.61	14.51
Vinyl chloride	*	*	*	*	*	*	*	*	*	*
Freon-11	0.25	2.02	1.78	11.88	0.25	10.53	8.81	16.33	8.08	42.12
Dichloromethane	0.20	2.05	2.65	-29.27	0.18	32.84	26.63	18.91	10.25	182.44
Freon-113	0.10	0.15	0.19	-26.67	0.09	0.19	0.34	-78.95	1.50	2.11
Trichloromethane	0.02	3.04	1.66	45.39	0.03	1.06	0.87	17.92	152.00	35.33
1,2-Dichloroethane	0.02	0.13	0.10	23.08	*	0.07	0.08	-11.43	6.50	*
1,1,1-Trichloroethane	0.35	4.18	3.08	26.32	0.33	4.89	8.15	-66.67	11.94	14.82
Benzene	0.36	17.41	13.33	23.43	0.33	1.26	1.30	-3.17	48.36	3.82
Carbon tetrachloride	0.12	0.13	0.13	0.00	0.11	0.14	0.13	7.14	1.08	1.27
Trichloroethene	*	3.25	2.33	28.31	*	0.05	0.27	-440.00	*	*
Toluene	0.67	39.95	30.26	24.26	1.03	32.05	21.05	34.32	59.63	31.12
1,2-Dibromomethane	*	*	*	*	*	*	*	*	*	*
Tetrachloroethene	0.05	0.56	0.55	1.79	0.08	2.68	1.76	34.33	11.20	33.50
Ethylbenzene	0.14	4.94	3.40	31.17	0.13	1.44	1.03	28.47	35.29	11.08
m,p-Xylene	0.35	17.14	10.29	39.96	0.32	3.59	2.57	28.41	48.97	11.22
o-Xylene	0.16	6.23	4.17	33.07	0.16	1.74	1.25	28.16	38.94	10.88

\* No data.

$$\% \text{ Diff} = 100 \left( \frac{\text{Can Indoors} - \text{Syringe Indoors}}{\text{Can Indoors}} \right)$$

the 6:00 to 8:00 p.m. dinner period (high period of ventilation) and the highest concentrations occurring during the early morning hours of 2:00 to 4:00 a.m. (period of low ventilation). Ratios of highest to lowest concentrations for these species range from 2 to 3.

As demonstrated earlier in this report, we have a good deal of experience in using canister sampling units and are confident in their ability to collect reliable samples. Although the above differences between the canister and syringe data sets are of concern, we do not believe they are of sufficient magnitude to warrant rejecting the syringe sampling approach. As pointed out in the earlier SF<sub>6</sub> experiments, the low recovery with the syringe sampler may be due to compound adsorption onto the inner syringe surfaces. Likewise, additional bias may be introduced when comparing 12 one-hour integrated syringe concentrations with the one 12-hour integrated canister concentrations. Finally, two comparisons are not of sufficient size to permit valid inferences to be made.

### 3.3 Cleaning and Testing of Canister Samplers

Initial tests with the canister samplers involved checking the units for air leaks. A calibrated flow meter (0 to 50 cm<sup>3</sup>/min) was placed at the inlet of the sampler, and the outlet was closed off. The relief valve on the unit was also capped. A reading of zero was observed on the flow meter. Next the calibrated flow meter was placed at the exit of the sampler, and the inlet was sealed. Again the flow meter read zero. These checks provided a quick method of determining if gross leaks were present.

Once the sampler passed the above leak checks, the unit then underwent a more rigorous test to establish the "cleanliness" of the sampler. This process was two-fold. The sampler was initially challenged with humidified zero air (Aadco, Inc.) containing less than 0.1 ppb of the individual organic species of interest. Air was sampled at the canister sampler exhaust port with a GC system to determine contamination. The unit was declared "clean" when the exhaust air contained less than 0.1 ppb of the targeted species. The "clean" sampler was then challenged with humidified zero air spiked with a known level of organic species. The sampler exhaust was again analyzed and compared with results from the direct GC analysis of

the spiked mixture. Recoveries greater than 90 percent were targeted in order to demonstrate sample stability of the compounds of interest.

The use of humidified air was determined early on in our studies to be crucial in certifying the canister sampling units for operation. Initial efforts of challenging the samplers with dry air containing diluted target compounds resulted in unacceptable recovery of many of the less volatile species. At challenge concentrations of 2 ppb, compounds less volatile than benzene gave recoveries ranging from 10 to 40 percent (similarly low recoveries were also obtained when the canisters themselves were directly filled with dry air spiked with low ppb levels of the target compounds). We suspect that the less volatile compounds had adsorbed onto the very dry surfaces of the sampler and/or canister. The use of humidified air likely passivates the surfaces and thereby minimizes adsorptive losses of the target compounds.

The humidification process used during the early phase of the study involved bubbling the diluted calibration mixture through a midjet impinger filled with water (as described in the experimental section). This approach gave consistent relative humidities ranging from 60 to 80 percent and excellent recovery of all the target compounds. However the system required a lengthy equilibration period (~1 to 2 hours at 1 liter/min air flow) before stable 1 to 2 ppb concentrations were obtained. Also, water droplets would often form and occasionally transfer from the impinger to the sampling unit and cause sampling and analytical problems. In one instance, the water droplets settled in the mass flow controller assembly of the canister sampler and temporarily caused erroneous flow readings. Flow rates greater than 1 liter/min were not possible with the impinger system because of the increased water droplet formation and because of the very rapid depletion of the water reservoir.

The current system for humidifying dilute calibration mixtures makes use of a Nafion tube immersed into a beaker of water and thereby circumvents the disadvantages found when using the water/impinger approach. The Nafion tube "wetter" produces very consistent relative humidities (RH) that are a function of air flow rate through the tube. At a flow rate of 1 liter/min RH values of  $75 \pm 3$  percent are obtained. A flow rate of 5 liters/min reduces the RH to  $55 \pm 3$  percent.

Results of the above canister sampler certification process are shown in Figures II-3.1 and II-3.2. In Figure II-3.1 we show two chromatographic outputs from the flame ionization detector. The lower tracing depicts the result of analyzing humidified Aadco zero air directly. No chromatographic peaks are observed. Chromatographic peak threshold is set to integrate the target compounds at concentrations  $\geq 0.1$  ppb. The upper chromatogram shows the results of analyzing the same humidified zero at the exit of the canister sampler. In viewing this chromatogram it is clear that considerable contamination results.

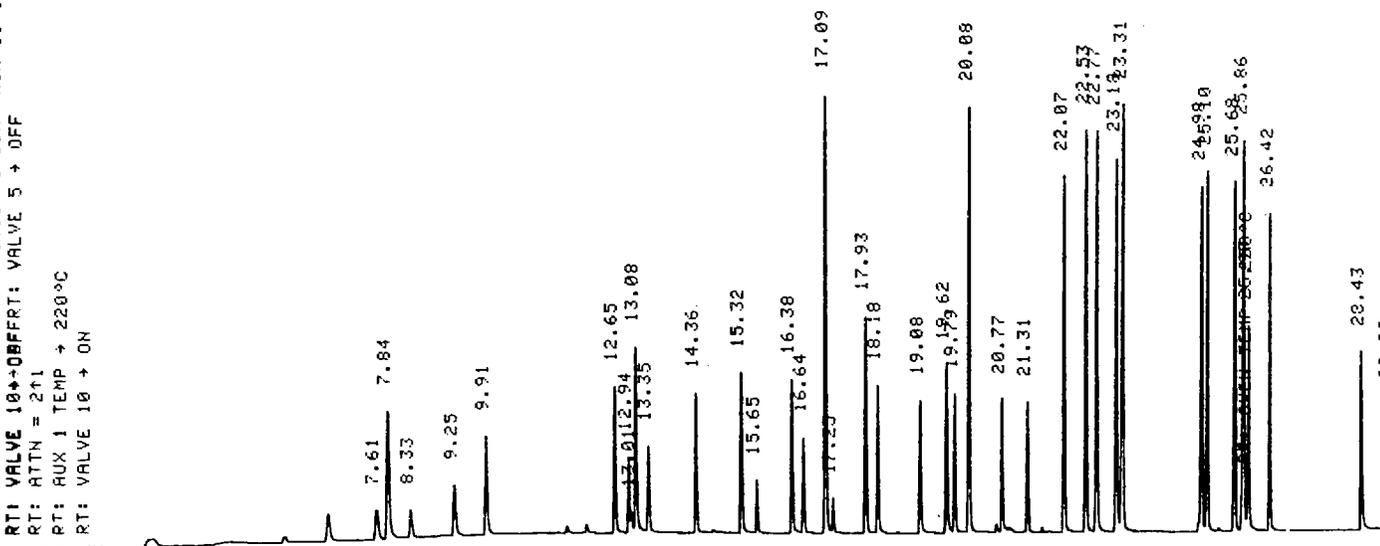
Several of the peaks are identified and quantified. Upon close inspection of the tracing, we concluded that it looked very similar to typical chromatograms of laboratory air. We examined the sampler again and found that the pump head was not sealing properly resulting in the mixing of laboratory air with the incoming humidified zero air. Recommendations were then made to the vendor to purchase and install pump heads containing Viton o-ring seals rather than the currently used Teflon seals. A challenge of the modified system with humidified zero air showed no contamination. The modified sampler was also challenged with humidified zero air spiked with the 41 component target mixture (~2 ppb nominal concentration). A comparison of those results with the direct analysis of the spiked mixture directly is shown in Figure II-3.2. The lower chromatogram depicts the analysis of the spiked mixture directly; the upper chromatogram shows the results after passing the spiked mixture through the sampler. For illustrative purposes several of the 41 peaks are labelled. It is clear that excellent recoveries are obtained for all 41 components ( $100 \pm 10$  percent). There are also a few extraneous peaks present in the analysis of the sampler's exhaust. However these compounds are not a subset of the 41 target species, and we estimate these concentrations to be less than 0.2 ppb.

#### 4.0 Conclusions and Recommendations

The commercial syringe and canister based sampling devices of interest to ARB have been examined and shown to deliver reliable and valid samples to the analytical system. A certification process has been presented that ensures that the canister samplers are free of contamination



FID SAMPLE# 1 FROM TC020401 400CC 41 COMP MIX 10/1000 DIL  
 RT1 VALVE 10 OFF RT: VALVE 5 ON  
 RT: ATTN = 211  
 RT: AUX 1 TEMP + 220°C  
 RT: VALVE 10 ON



FID SAMPLE# 1 FROM CB020402 400CC 41 COMP MIX 10/1000 THRU XONTECH  
 RT1 VALVE 10 OFF RT: VALVE 5 ON  
 RT: ATTN = 211  
 RT: AUX 1 TEMP + 220°C  
 RT: VALVE 10 ON

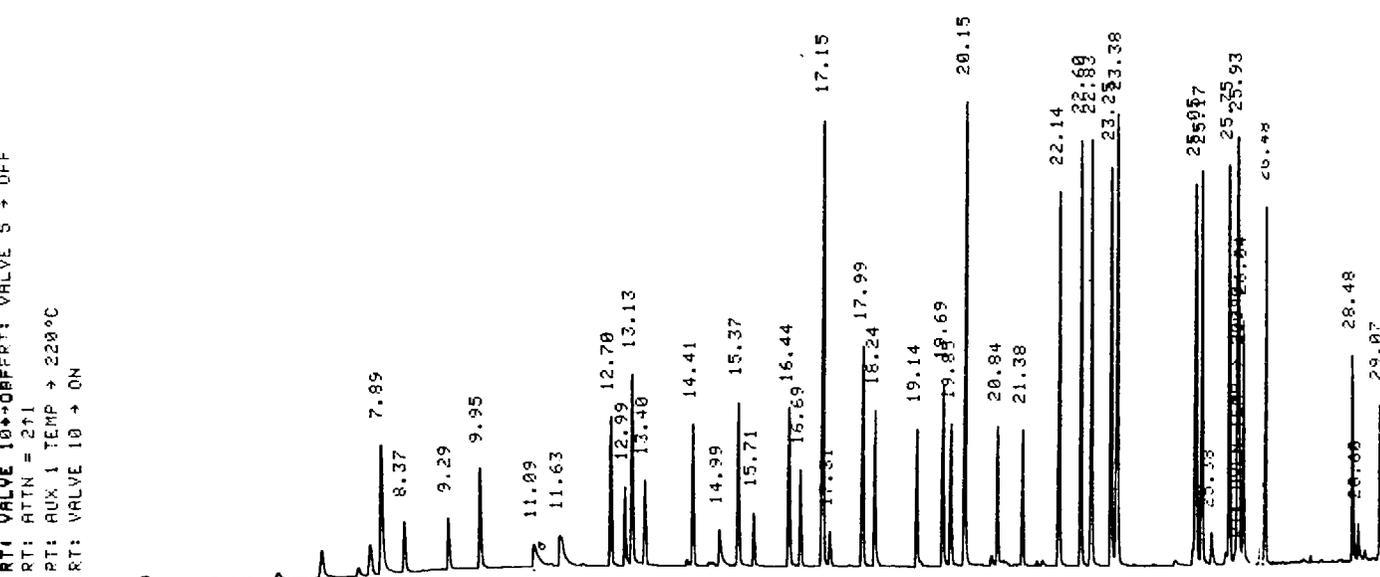


FIGURE II-3.2 TWO CHROMATOGRAMS FROM THE FLAME IONIZATION DETECTOR SHOWING THE ANALYSES OF HUMIDIFIED AADCO ZERO AIR SPIKED WITH 2 ppb LEVEL OF BATTELLE'S 41 COMPONENT CALIBRATION MIXTURE. (LOWER TRACE WAS FROM DIRECT ANALYSIS OF DILUTED MIXTURE. UPPER TRACE WAS FROM ANALYSIS AFTER PASSING THROUGH CANISTER SAMPLER)

and that sample integrity is maintained during use of the above sampling systems. We recommend that this certification process be employed as an integral part of all sampling and analysis programs involving the canister based sampling devices.



CHAPTER III. EVALUATION OF ARB'S  
ANALYTICAL METHOD

1.0 Introduction

ARB currently employs a Tenax preconcentration technique described by Method No. ADDL002 as their primary means of identifying and quantifying 17 toxic air contaminants (TACs) and freon compounds. Method No. ADDL002 utilizes a glass column (3 m long by 2 mm i.d.) packed with 1 percent SP-1000 on Carbopack B for compound separation. A tandem electron capture/photoionization detection system is used for identification and quantitation of the TACs and freon compounds.

Although ARB has utilized this method extensively to analyze for the TACs and freon compounds, they believe that a more detailed examination of the current chromatographic separation and detection system is needed. ARB has indicated three problem areas that may require modifications to the current method. ARB is not satisfied with the current column resolution of ethylene dichloride from Freon-113. Minimum detection limits for the mono- and di-chlorinated hydrocarbons are unacceptably high. Finally, measured ambient chloroform concentrations exhibit unusually large variations.

Battelle's evaluation of the current analytical method initially involved setting up a gas chromatographic (GC) system configured to match the ARBs system as described in Method No. ADDL002. Then we conducted tests to examine the following:

- Collection/recovery efficiencies vs sample volume
- "Carry over" from previous samples
- Effects of moisture removal by a Nafion dryer on the analysis.

Alterations to the current analytical method were also carried out. GC operating parameters of flow rate, temperature programming rate and detector temperature were examined to determine if improved sensitivity, peak resolution and precision could be realized. Several capillary columns were substituted for the current packed column to determine if better peak resolution could be achieved. Oxygen doping of the detector system was employed to enhance the signal-to-noise response for the mono- and di-chlorinated species.

## 2.0 Experimental

The apparatus and procedures used to evaluate ARB analytical Method No. ADDL002 and modifications of it are described below.

### 2.1 Apparatus

A Varian Model 3700 gas chromatograph equipped with tandem electron capture and photoionization (HNU Model 52-02A) detectors served as our analytical system. Hewlett Packard 3390 integrators provided peak detection and integration.

The Tekmar LSC-2 sample concentrator described in Method No. ADDL002 was replaced with a comparable 6-port Valco valve and a Supelco Tenax trap (Model No. 2-0295). The schematic of the valve-trap system is shown in Figure III-2.1 and is identical in function to the original ARB methodology.

Gas standards were supplied via a dynamic dilution system that mixed the primary cylinder gas containing the 17 target compounds (at ~50 ppb per component) with pure air (Aadco generator). Humidified air was generated by placing the Nafion tube/H<sub>2</sub>O beaker downstream of the dilution system. A diagram of this humidification system is shown in Section II-2.4.

Capillary column tests were conducted with 30 meter megabore DB-624 and OV-1 fused silica columns. Capillary column operating conditions were as follows:

start temperature	-50°C
initial hold	4 minutes
program rate	5°/minute
final temperature	150°C.

### 2.2 Procedures

During the initial phase of evaluating Method ADDL002, our chromatographic runs of standard mixtures contained a considerable number of co-eluting contaminant peaks and unacceptable "column bleed". Several modifications were made to the gas chromatographic system to eliminate these

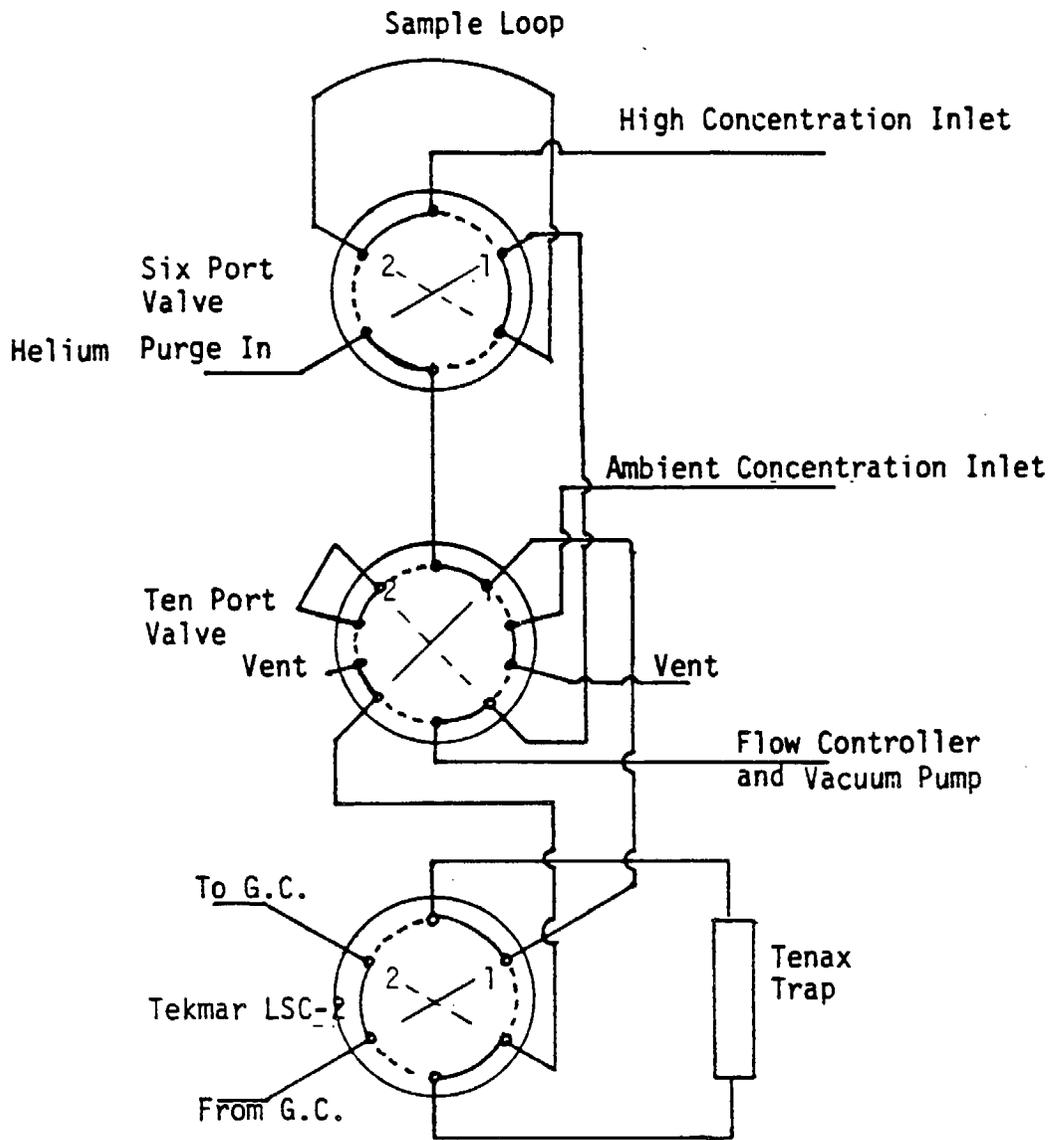


FIGURE III-2.1. DIAGRAM OF VALVE/TRAP SYSTEM FOR METHOD ADDL002

problems. First of all, a 5A molecular sieve trap (60/80 mesh packing in a stainless steel tube 30 cm long by 0.5 cm i.d.) was placed in the carrier flow line between the Tenax trap and the helium flow controller. The trap was immersed into a dewar containing liquid nitrogen during GC runs and then heated to 200°C at the end of each work day. This modification to the system removed the co-eluting contaminant peaks. The high "column bleed" was considerably reduced by replacing 10 cm of chromatographic packing with glass wool at the detector end of the column.

During subsequent experiments the tandem detector system was configured to pass the column effluent first through the photoionization detector and then into the electron capture detector (as described in Method ADDL002). However, very poor reproducibility on the ECD system was obtained following injection of standard mixtures. We found that the photoionization detector base was not properly sealed and believed that loss of sample and infiltration of oxygen was seriously affecting chromatographic results from the ECD detector. None of our attempts to re-seal the detector base was entirely successful. As a compromise, we hooked up the electron capture detector to the column exit and then connected the photoionization detector to the ECD exhaust line. In this configuration, more reproducible chromatographic results were obtained. The increased flow to the PID as a result of additional gas from the ECD make-up line did not reduce the sensitivity of the PID to the responding compounds.

To facilitate our evaluation of Method ADDL002, a calibration cylinder containing the 17 target compounds was made with nominal concentrations of 50 ppb per component. The compounds and corresponding concentrations are shown in Table III-2.1. The cylinder was prepared using a 10 to 1 dilution of one of our primary calibration cylinders. Preparation of these primary cylinders was described in Section I.

The gas chromatographic conditions for Method ADDL002 evaluation were as follows:

Column:	3 m by 2 mm i.d. glass column, packed with 1 percent SP-1000 on Carbopack B 60/80 mesh (Supelco).
Temperatures:	Injector: 200°C Detector: 350°C (ECD), 250°C (PID) Oven: 45°C, hold for four minutes, 5°C/minute ramp, to 210°C, hold for eight minutes

TABLE III-2.1. CALIBRATION CYLINDER USED DURING  
EVALUATION OF ARB'S METHOD ADDL002

Compound	Concentration ( $\pm$ 5 ppb)
Dichlorodifluoromethane	25
Vinyl chloride	45
Dichloromethane	50
1,1-Dichloroethene	40
Trichloromethane	40
1,1,2-Trichloro- 1,2,2-trifluoroethane	40
1,2-Dichloroethane	40
1,1,1-Trichloroethane	30
Carbon tetrachloride	40
Trichloroethene	40
Benzene	40
1,2-Dibromoethane	40
Tetrachloroethene	50
Toluene	30
o-Xylene	60
m+p-Xylene	60

Flow Rates: Carrier: He, 20 cm<sup>3</sup>/min  
 ECD make up: N<sub>2</sub>, 40 cm<sup>3</sup>/min

Detectors: ECD: Range X 10  
 PID: Range X 1, 10.2 eV lamp

Tenax/6-port Valve: Purge: 4 minutes  
 (substitute for Desorb: 4 minutes at 180°C  
 Tekmar LSC-2) Bake: 8 minutes at 225°C

All air samples were drawn through the 10-port sampling valve and into the Tenax trap/6-port valve via a pump/mass flow controller system at 40 cm<sup>3</sup>/min for five minutes (200 cm<sup>3</sup>). The Tenax trap was purged with 40 cm<sup>3</sup> of helium to remove any trapped moisture. Compounds in the Tenax trap were then thermally desorbed onto the head of the GC column. The column was temperature programmed, and component peaks were sequentially detected and quantified, first by the electron capture detector and then by the photoionization detector. The components were identified by retention times.

The operational steps and corresponding valve positions were as follows:

Operational Step	Valve Position			
	6-Port (Valve 1)	10-Port (Valve 2)	Tenax/6-Port (Valve 3)	Purge Gas
Loop Fill	1	1	1	Off
Loop Trap	2	1	1	On
Ambient Trap	1	2	1	Off
Trap Desorb	1	1	2	Off
Trap Bake Out	1	1	1	On

Moisture removal studies made use of a Perma Pure dryer (Model MD-125-48F). The dryer was connected to the sample inlet line during appropriate tests. The dryer was backflushed with ultra-zero air (200 cm<sup>3</sup>/min). All dilutions of the calibration cylinder were carried out with a gas phase dilutor (two mass flow controllers - Tylan, Model FC260). Aadco air served as the diluent gas.

Carry over studies made use of the gas phase dilutor with the calibration cylinder to generate spiked dilution mixtures as well as a canister sample from a highly polluted urban location. The ARB method was examined by alternatively injecting and analyzing the urban air and humidified ultra-zero air samples throughout the day. The following day the system was repeatedly challenged with spiked air (~ 2 ppb) and then humidified ultra-zero air.

2.2.1 Alterations to Method ADDL002 Procedures. Operating parameter changes with the packed column were designed to determine if improved peak resolution could be achieved and included the following:

<u>Variables</u>	<u>Variable Ranges</u>
start temperature	35 to 45°C
initial hold	0 to 8 minutes
program rate	4° to 8°/minute
final temperature	no change
carrier flow	15 to 30 cm <sup>3</sup> /min

Oxygen doping was accomplished by adding ultra-zero air (Matheson) through the H<sub>2</sub> line of the Varian 3700 GC. This line entered the base of the ECD detector. Air flow was maintained with a Tylan mass flow controller. ECD and PID temperatures were not varied (i.e. stated Method ADDL002 values). The pack column was also operated at Method ADDL002 stated conditions. The OV-1 megabore column was held at -50° for 4 minutes and then temperature programmed to 150°C at 5°/minute during oxygen doping experiments. All oxygen doping runs were made with 200 cm<sup>3</sup> samples of a 20/1 dilution of the calibration mixture identified in Table III-2.1.

2.2.2 Procedures Involving Automated GC. The Tenax, Tenax-Carbosieve S-II, and cryogenic trapping comparisons made use of the automated GC system described in Section I. The flame ionization detector output was used to obtain the experimental results. The Tenax trap was equivalent to the Method ADDL002 trap (~ 0.3 grams adsorbent). The Tenax-Carbosieve S-II contained equal amounts of each adsorbent (~ 0.13 grams).

The cryogenic trap contained 60/80 mesh silanized glass beads. All three traps were externally identical to the Method ADDL002 trap.

### 3.0 Results and Discussion

#### 3.1 Moisture Removal Studies

Moisture removal studies were carried out to determine the effect of a Nafion tube dryer on the concentrations of the target compounds in air supplied by the calibration cylinder. The Nafion dryer is used to remove water vapor selectively from a dilute mixture of the above calibration cylinder. Replicate analyses of the humidified dilution mixture with and without the Nafion dryer in-line were made at a target concentration of ~ 2 ppb. Table III-3.1 shows the actual challenge concentration of each chemical along with analytical precision values. The ratio of concentrations observed with and without the use of the dryer are also shown in the table. Further dilutions of the calibration mixture were also carried out to estimate the detection limit (ppb) for the 17 compounds. These values are also listed in the table along with detection limits specified in Method ADDL002.

At the indicated challenge concentrations acceptable precision ( $\pm 15\%$ ) was obtained for most compounds. The two compounds that showed the highest relative standard deviation (RSD) values are carbon tetrachloride and 1,2-dibromoethane (dryer out of line). We are not sure why carbon tetrachloride shows high RSD values. Samples subsequently analyzed at lower concentrations showed RSD values less than 10%. The high RSD values for 1,2-dibromoethane found in the above runs were also observed in subsequent analyses during the evaluation study. In all cases, increasing instrument response for 1,2-dibromoethane was obtained for each successive injection of the same dilution mixture. We suspected that either the Tenax trap was not efficiently releasing this compound or that column/compound interactions were occurring. Subsequent experiments with a similar Tenax trap but with a capillary column showed that dibromoethane was efficiently adsorbed and desorbed at the same operating conditions. Therefore, we believe that column/compound interactions are occurring for this compound.

TABLE III-3.1. RESULTS OF USING A NAFION DRYER TO REMOVE WATER VAPOR SELECTIVELY FROM AIR CONTAINING TARGET COMPOUNDS

	Challenge Concentration (ppb)	% RSD		Ratio Dryer/No Dryer	Detection Limit (ppb)	
		No Dryer	Dryer		Battelle	Method ADDL002
Dichlorodifluoromethane	1.0	13	8	1.06	0.8	ND
Vinyl chloride	1.8	ND*	ND	ND	1.8	0.8
Dichloromethane	1.6	13	8	0.89	1.1	0.6
1,1-Dichloroethene	2.0	7	6	0.96	0.1	0.05
Trichloromethane	1.6	14	9	1.17	0.01	0.02
1,1,2-Trichloro-1,2,2-trifluoroethane	1.6	6	7	0.92	0.05	ND
1,2-Dichloroethane	1.6	14	8	0.93	1.6	0.1
1,1,1-Trichloroethane	1.2	6	7	1.02	0.004	0.01
Carbon tetrachloride	1.6	23	3	1.26	0.002	0.01
Trichloroethene	1.6	11	9	1.00	0.004	0.02
Benzene	1.6	3	1	0.99	0.1	0.5
1,2-Dibromoethane	1.6	58	11	1.92	0.01	0.005
Tetrachloroethene	2.0	12	9	1.03	0.002	0.01
Toluene	1.2	1	16	1.08	0.2	ND
o-Xylene	2.4	17	11	1.11	0.3	ND
m+p-Xylene	2.4	10	14	0.94	0.2	ND

\*ND = no data available

The concentrations from samples processed with and without the dryer in-line compared very well for most compounds as indicated by ratio values being close to 1.00 ( $1 \pm 0.1$ ). Again the same two compounds showed higher than expected ratios ( $>1.10$ ). Although the Nafion dryer is not specified in Method ADDL002, it might be needed for moisture removal if capillary columns are employed rather than the current packed column methodology.

Detection limits were established by incrementally diluting the 2 ppb calibration mixture down to 0.06 ppb. The detection limit (DL) was the lowest generated concentration showing a measured peak area response. For those compounds giving a peak area response at the lowest generated concentration (0.06 ppb), DL values were derived by extrapolation to twice the instrument noise level. In viewing Table III-3.1, the DL values found in our evaluation generally are within a factor of 3 of the Method ADDL002 values. The one exception is 1,2-dichloroethane. For this compound the DL values differs by a factor of 16.

### 3.2 Collection/Recovery Studies

A 200 cm<sup>3</sup> sample volume is specified for Method ADDL002. During our evaluation of the method, we carried out several experiments to determine if larger volume samples could be obtained without experiencing "breakthrough" of the compounds in the Tenax trap. Sample volumes of 200 cm<sup>3</sup> of the 1 ppb dilution mixture were collected, followed by the addition of incremental amounts of Aadco zero air. The analytical results are shown in Table III-3.2. For the compounds, trichloroethene through m+p-xylene, no "breakthrough" occurred for sample volumes up to 4,200 cm<sup>3</sup>. For the compounds, 1,1-dichloroethene, trichloromethane, 1,1,2-trichloro - 1,2,2-trifluoroethane, 1,1,1-trichloroethane, and carbon tetrachloride, breakthrough did occur at sampled volumes between 200 and 4,200 cm<sup>3</sup>. No breakthrough data were obtained for dichlorodifluoromethane, vinyl chloride, dichloromethane and 1,2-dichloroethane because they were below the detection level.

In studies with the automated GC system described in Section I, we compared the relative performance of a similar Tenax trap, a Tenax-Carbosieve S-II trap and a cryogenic trap using a similar dilution mixture

TABLE III-3.2. RESULTS FROM THE ANALYSES OF THE TENAX TRAP SPIKED WITH 200 cm<sup>3</sup> OF THE DILUTED CALIBRATION MIX AND WITH INCREMENTAL AMOUNTS OF AADCO ZERO AIR

Compound	Addition of Aadco Air to 200 cm <sup>3</sup> Sample (cm <sup>3</sup> )					
	0	200	400	1,000	2,000	4,000
Dichlorodifluoromethane	←———— no GC peak found (0.5 ppb) —————→					
Vinyl chloride	←———— no GC peak found (0.9 ppb) —————→					
Dichloromethane	←———— no GC peak found (1.0 ppb) —————→					
1,1-Dichloroethene	1.0	0.8	0	0	0	0
Trichloromethane	0.8	0.8	0.8	0.7	0.5	0.2
1,1,2-Trichloro- 1,2,2-trifluoroethane	0.8	0.4	0	0	0	0
1,2-Dichloroethane	←———— no GC peak found (0.8 ppb) —————→					
1,1,1-Trichloroethane	0.6	0.5	0.3	0.3	0.3	0.2
Carbon tetrachloride	0.8	0.8	0.8	0.5	0.4	0.3
Trichloroethene	0.8	NC*	NC	NC	NC	NC
Benzene	0.8	NC	NC	NC	NC	NC
1,2-Dibromoethane	0.8	NC	NC	NC	NC	NC
Tetrachloroethene	1.0	NC	NC	NC	NC	NC
Toluene	0.6	NC	NC	NC	NC	NC
o-Xylene	1.2	NC	NC	NC	NC	NC
m+p-Xylene	1.2	NC	NC	NC	NC	NC

NC\* = No change.

of the above target compounds. In Table III-3.3 we have summarized these results. At the indicated challenge concentrations, 3 different sample volumes were collected with the Tenax and Tenax-Carbosieve S-II traps and then individually ratioed with the equivalent volume sampled with the cryogenic trapping procedure. Dichlorodifluoromethane, vinyl chloride and 1,1,2-trichloro-1,2,2-trifluoroethane were not efficiently trapped with just the Tenax adsorbent alone, and as we expected, the recovery efficiency decreased for each of the three compounds as the sampled volume increased. The Tenax-Carbosieve S-II trap, however, showed excellent recovery of all the 17 target compounds when ratioed to the cryogenic trap recovery values.

The Tenax-Carbosieve S-II trap was operated at the same desorption (180°C) and bakeout (225°C) temperatures as specified for the Method ADDL002 Tenax trap. However, the sample flow had to be directed through the Tenax adsorbent first, and during sample desorption the helium purge was backflushed through the traps (flow through the Carbosieve trap first). In this configuration the less volatile components were trapped on the Tenax adsorbent; the more volatile components were retained with the Carbosieve S-II material. If the flow direction was reversed all components would be trapped onto the Carbosieve S-II and unacceptably high desorption temperatures (400°C) would be needed to release these materials. At a 400°C desorption temperature the Carbosieve material releases numerous artifact peaks and gives low recovery for several of the target compounds. Additionally, the two adsorbents would no longer be compatible since the Tenax material would decompose at these temperatures.

### 3.3 Carry Over Effects from Previously Collected Samples

Experiments were conducted with the Tenax trap used with Method ADDL002 to determine if collected material would completely desorb and elute from the GC column during analysis. If incomplete desorption of trapped components or insufficient GC elution time occurred then we would expect "carry over" of sampled compounds to subsequent GC runs. Carry over effects were studied over a two day period. During the first day alternative runs were made with the canister sample containing urban air and with humidified Aadco air. A total of eight runs were analyzed. The target compounds were quantified and RSD values were computed. The RSD values were then compared

TABLE III-3.3. PERFORMANCE OF A TENAX TRAP AND A TENAX-CARBOSIEVE S-II TRAP COMPARED WITH CRYOGENIC TRAPPING

	Challenge Concentration (ppb)	Tenax/Cryogenic Trap			Tenax-Carbosieve/Cryogenic Trap		
		290 cm <sup>3</sup>	580 cm <sup>3</sup>	870 cm <sup>3</sup>	290 cm <sup>3</sup>	580 cm <sup>3</sup>	870 cm <sup>3</sup>
Dichlorodifluoromethane	2.6	0.00	0.00	0.00	0.98	0.98	0.90
Vinyl chloride	4.6	0.43	0.21	0.14	1.13	1.10	1.09
Dichloromethane	4.1	0.90	0.94	0.94	0.95	0.94	0.94
1,1-Dichloroethene	3.2	0.96	0.95	0.92	0.98	0.94	0.93
Trichloromethane	3.5	0.85	0.90	0.94	1.08	0.99	0.97
1,1,2-Trichloro-1,2,2-trifluoroethane	2.7	0.76	0.51	0.36	1.10	0.99	0.97
1,2-Dichloroethane	3.3	0.90	0.93	0.92	0.95	0.93	0.93
1,1,1-Trichloroethane	2.7	0.90	0.92	0.91	0.93	0.91	0.91
Carbon tetrachloride	3.0	0.86	0.93	1.01	0.93	0.99	1.01
Trichloroethene	2.9	0.83	0.86	0.85	0.90	0.86	0.86
Benzene	2.8	1.05	1.00	0.97	1.07	0.99	0.98
1,2-Dibromoethane	3.1	0.90	0.93	0.92	0.94	0.93	0.93
Tetrachloroethene	2.5	0.91	0.92	0.91	0.94	0.91	0.91
Toluene	2.5	0.96	0.95	0.93	0.97	0.93	0.93
o-Xylene	2.1	0.90	0.94	0.92	0.96	0.93	0.92
m+p-Xylene	2.1	0.93	0.95	0.93	0.98	0.94	0.93

to the earlier calculated precision values for the diluted standard mixture. No differences were observed. During the second day, the spiked Aadco air was used in place of the canister sample. The same calculation and comparison were made. Again precision values for the target compounds compared reasonably well. Examination of the chromatograms from the humidified Aadco air samples on both days did show several extraneous peaks. However, the peak area amounts were low, and no consistent pattern could be established.

The tests were designed to determine over the short term if higher molecular weight species initially captured on the Tenax trap would gradually elute with time (from trap and/or column) and cause quantification problems. Although the above results showed no significant quantification anomalies, we can not rule out the possibility that other air matrices will contain component peaks that will interfere and create quantification errors for the 17 target compounds.

#### 3.4 Alteration of GC Operating Conditions

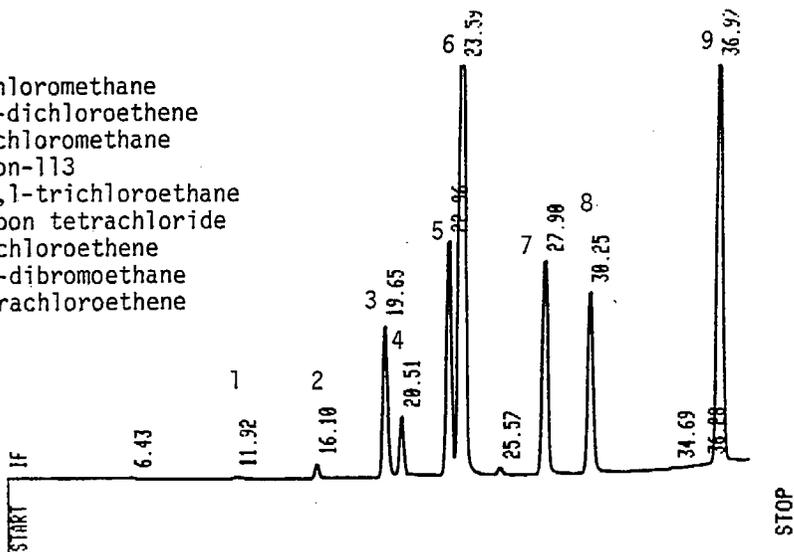
Following the above experiments, several GC operating parameters were changed to determine if improvements in peak resolution could be achieved. Operating parameters that were changed included column flow, column temperature programming conditions and carrier gas (He versus N<sub>2</sub>). Efforts were focused on improving the resolution of the three closely eluting compounds of trichloromethane, freon-113 and 1,2-dichloroethane. None of the changes (described in the experimental section) offered improved resolution of the above compounds.

#### 3.5 Use of Capillary Columns

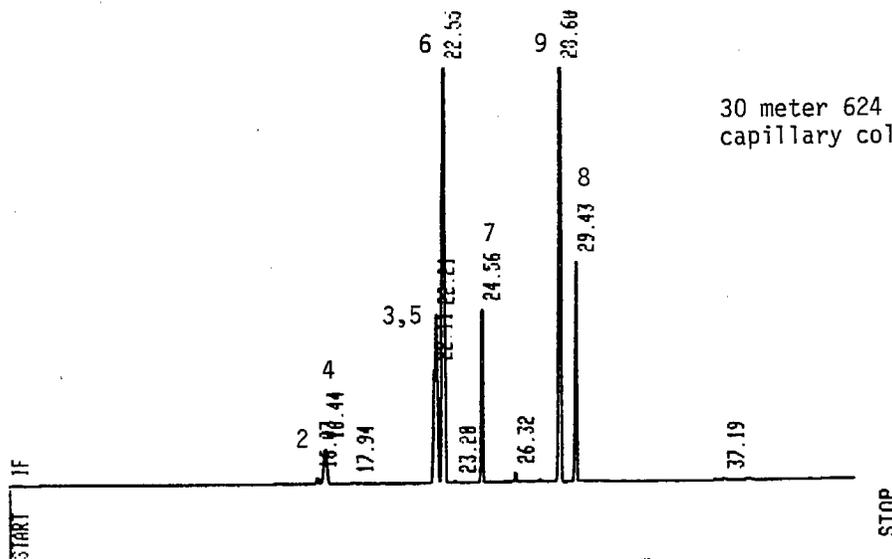
The Method ADDL002 packed column was then replaced first with a 30-meter, 624 (J&W Scientific) megabore fused silica capillary column and then with a OV-1, fused silica capillary column to determine if peak resolution could be enhanced. Representative ECD chromatograms for all three columns are shown in Figure III-3.1. For all three runs 1,2-dichloroethane was either at or below the detection limit. In viewing the chromatograms, it is clear that the 624 megabore column does not offer

1. dichloromethane
2. 1,1-dichloroethene
3. trichloromethane
4. freon-113
5. 1,1,1-trichloroethane
6. carbon tetrachloride
7. trichloroethene
8. 1,2-dibromoethane
9. tetrachloroethene

Method ADDL002  
Packed Column



30 meter 624 megabore  
capillary column



30 meter OV-1 megabore  
capillary column

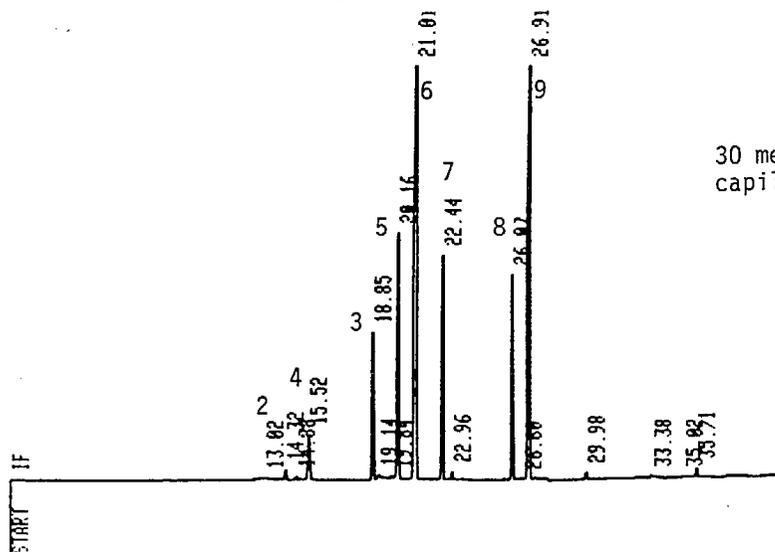


FIGURE III-3.1. THREE CHROMATOGRAMS FROM THE ELECTRON CAPTURE DETECTOR SHOWING THE ANALYSES OF A CALIBRATION MIXTURE (~1 ppb)

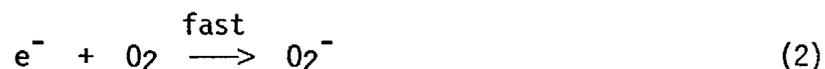
any improvement in overall resolution of the calibration mixture. Trichloromethane and 1,1,1-trichloroethane co-elute, and 1,1-dichloroethene and freon-113 are not well resolved. However the OV-1 column does offer a substantial improvement in overall resolution because all component peaks are separated at the baseline. Although 1,2-dichloroethane is not observed in this chromatogram, subsequent chromatograms show that this peak is completely resolved from the other target compounds.

### 3.6 Oxygen Doping Techniques

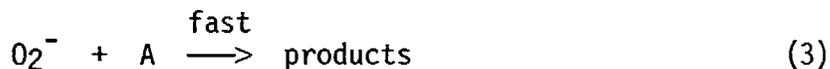
The addition of oxygen to the nitrogen carrier gas of a constant-current electron capture detector has been shown by several investigators to provide improved sensitivity to compounds having few or particularly only one chlorine atom (Grimsrud and Miller <sup>(1)</sup> and Grimsrud and Stebbins <sup>(2)</sup>). Oxygen doping has also been shown to enhance instrument response to polycyclic aromatic hydrocarbons (Grimsrud et al, <sup>(3)</sup>). These authors have discussed various aspects of the oxygen-doped ECD technique. Briefly, for molecules that exhibit weak ECD responses under normal operating conditions of the detector, a slow electron capture reaction takes place:



However the presence of oxygen in the carrier gas



produces  $O_2^{-}$  ions which in turn also react with the sample molecule A but at a much faster rate.



Thus, the normal ECD response to a compound usually reflects the rate of electron capture, while the oxygen-doped response (if significant) reflects the rate of  $O_2^{-}$  attack on the sample molecule.

It was our intent to utilize the oxygen doping technique to demonstrate the peak enhancements that could be achieved for the target compounds currently analyzed by Method ADDL002 (a packed column is specified). However, because the OV-1 megabore column was in the GC system at the initiation of these experiments, preliminary runs were completed with this capillary column in place. In Figure III-3.2 we show two ECD chromatograms. The top chromatogram was obtained with no O<sub>2</sub>-doping. Dichloromethane and 1,2-dichloroethane peaks are just above baseline noise; the bottom chromatogram shows that with minimal O<sub>2</sub>-doping (~ 0.06% of carrier flow), better than 10-fold increases in peak area responses were obtained for the two compounds. No increase in baseline noise was observed with the added oxygen.

In subsequent experiments, the capillary column was replaced with the packed column, and a series of runs was made at various oxygen doping levels. These results are summarized in Table III-3.4. Peak area responses for each target compound at the various oxygen doping levels are ratioed to the corresponding peak area obtained with no oxygen doping. Oxygen doping levels ranged from 0 to 2.0 percent (total flow). All data were obtained with the GC operating according to column and detector conditions specified in Method ADDL002. At the challenge concentration of ~ 2 ppb, substantial peak area enhancements are observed for two of the compounds. Dichloromethane shows a relative response increase of ~ 130 at an oxygen doping level of 2.0 percent while 1,2-dichloroethane gives a relative response increase of ~ 200 at this same doping level. The remaining compounds show no appreciable changes in peak area response. In fact for the more strongly electrophilic species (e.g., carbon tetrachloride and tetrachloroethene) slightly lower peak area response are observed at the higher oxygen doping levels.

Oxygen doping did not appear to affect peak areas for compound detected by the PID. The addition of oxygen actually decreased the "column bleed" observed with the PID detector during typical temperature programming but gave a corresponding higher "column bleed" on the ECD system. The column bleed level is shown in Figures III-3.3 and III-3.4. Figure III-3.3 shows the ECD chromatograms; Figure III-3.4 shows the PID chromatograms.

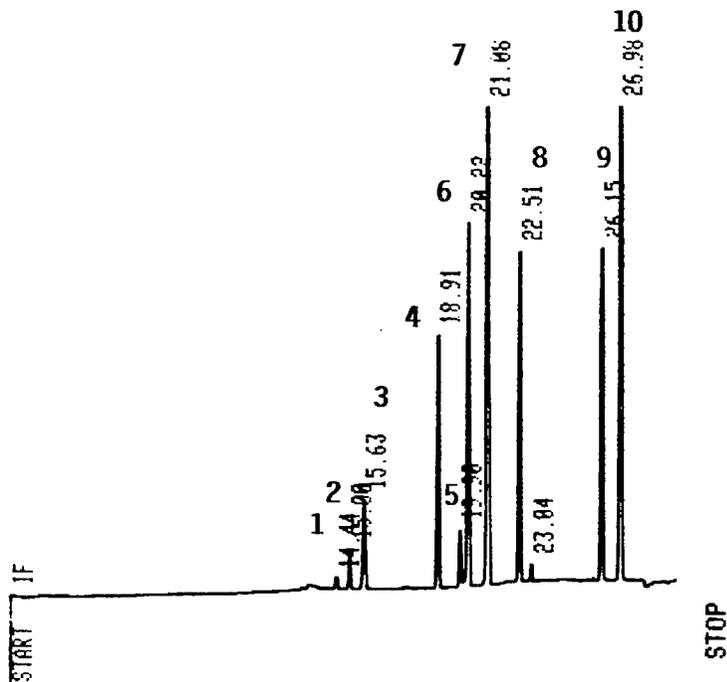
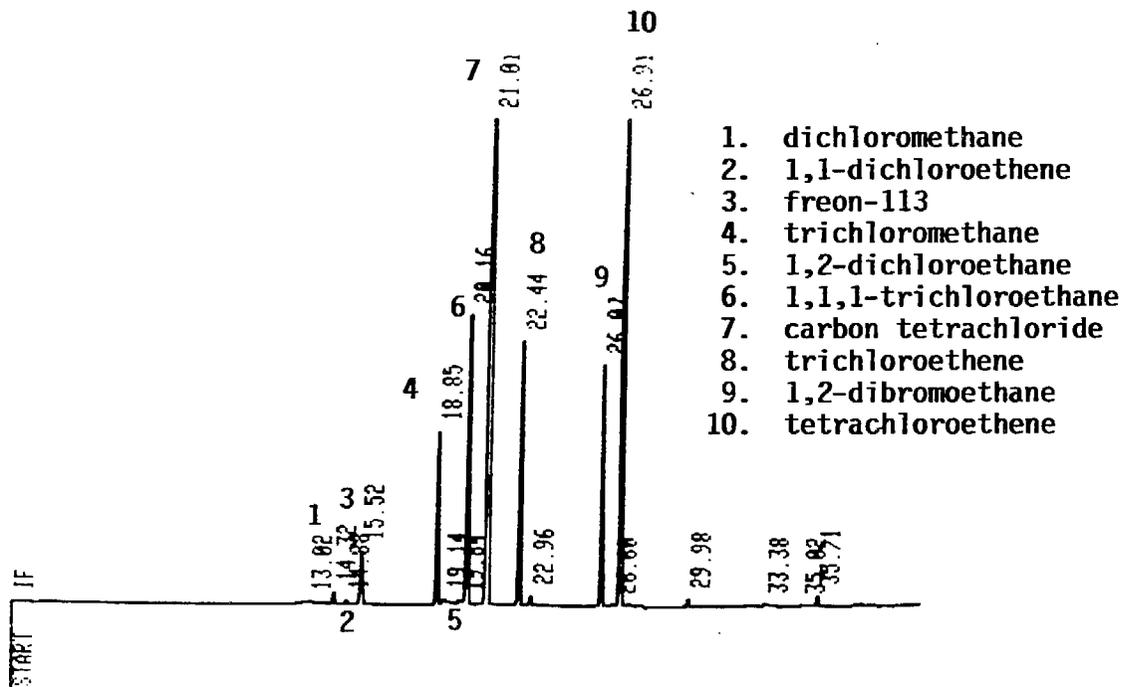


FIGURE III-3.2. TWO CHROMATOGRAMS (30 Meter Megabore OV-1 Column) WITH AN ELECTRON CAPTURE DETECTOR SHOWING THE ANALYSIS OF A CALIBRATION MIXTURE (~2 ppb) with (Lower Trace) AND WITHOUT (Upper Trace) OXYGEN OF THE CARRIER GAS

TABLE III-3.4. RELATIVE RESPONSE OF ELECTRON CAPTURE DETECTOR TO TARGET COMPOUNDS  
(NOMINALLY ~ 2 PPB) AS A FUNCTION OF OXYGEN DOPING LEVEL

Compound	Percent O <sub>2</sub> in Carrier Gas									
	0	0.06	0.12	0.2	0.4	0.8	1.2	2.0		
Dichlorodifluoromethane	NP	NP	NP	NP	NP	NP	NP	NP	NP	NP
Vinyl chloride	1.0	1.07	1.53	0.78	2.09	0.63	1.33	1.37		
Dichloromethane	1.0	10	26	56	90	102	135	131		
1,1-Dichloroethene	1.0	1.11	1.13	1.23	1.44	1.37	1.29	1.31		
Trichloromethane	1.0	1.28	1.35	1.44	1.51	1.28	1.46	1.29		
1,1,2-Trichloro- 1,2,2-trifluoroethane	1.0	1.38	1.81	0.99	1.20	1.08	2.08	1.67		
1,2-Dichloroethane	1.0	17	51	112	168	164	209	196		
1,1,1-Trichloroethane	1.0	1.02	1.05	0.92	0.95	0.69	0.61	0.52		
Carbon tetrachloride	1.0	1.14	1.14	1.05	1.00	0.76	0.71	0.57		
Trichloroethene	1.0	1.15	1.18	1.17	1.15	0.92	0.94	0.81		
1,2-Dibromoethane	1.0	1.23	1.30	1.38	1.48	1.25	1.32	1.22		
Tetrachloroethene	1.0	1.00	1.08	0.77	0.70	0.74	0.78	0.61		

NP = no peak

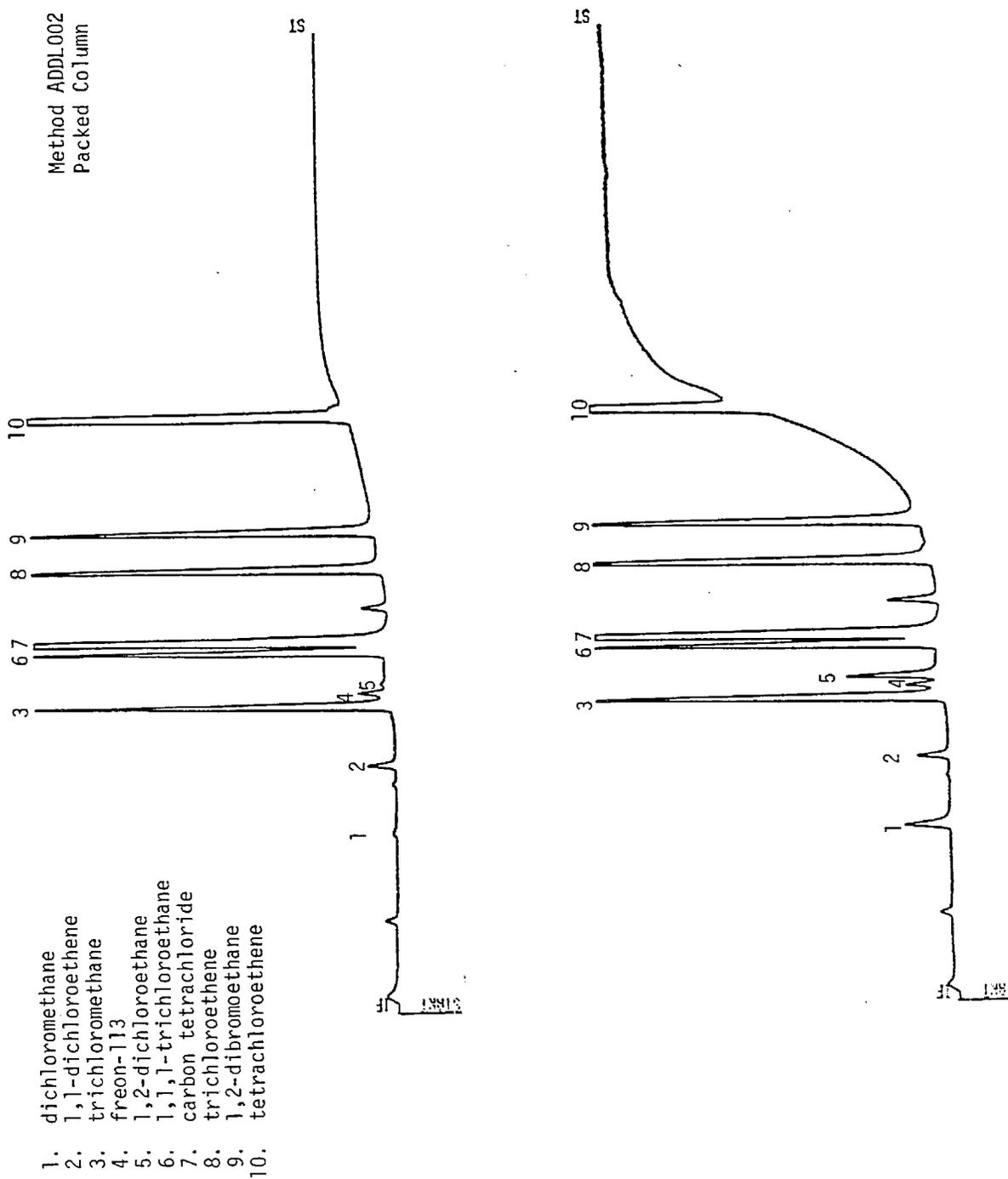


FIGURE III-3.3. TWO CHROMATOGRAMS FROM THE ELECTRON CAPTURE DETECTOR SHOWING THE ANALYSES OF A CALIBRATION MIXTURE (~2 ppb) WITH (Lower Trace) AND WITHOUT (Upper Trace) OXYGEN DOPING OF THE CARRIER GAS

1. 1,3-butadiene
2. 1,1-dichloroethene
3. trichloroethene
4. benzene
5. tetrachloroethene
6. toluene
7. o-xylene
8. m,p-xylene

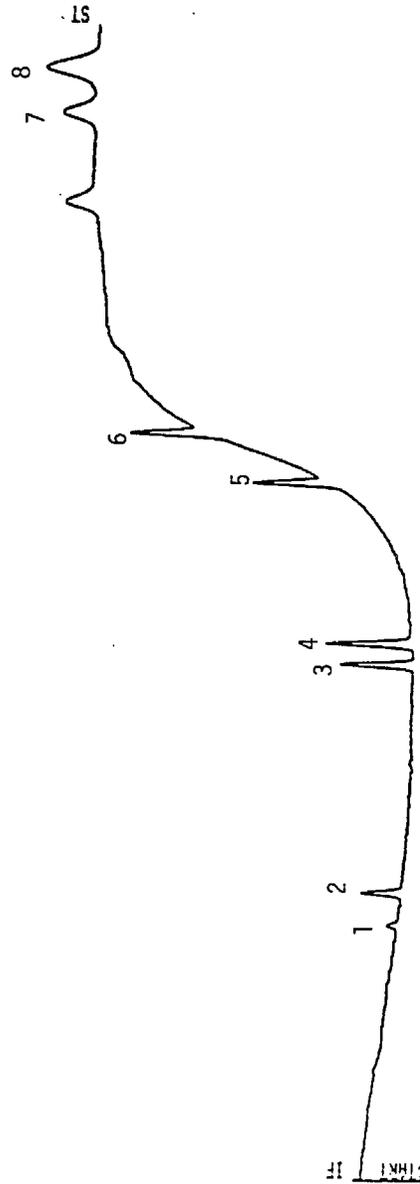
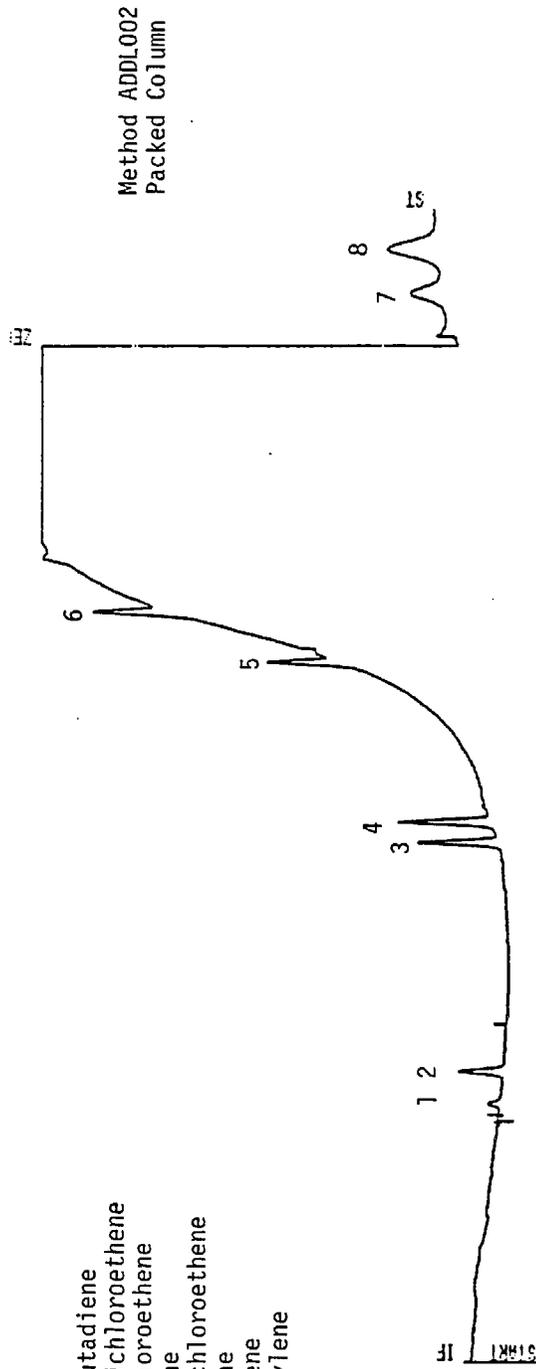


FIGURE III-3.4. TWO CHROMATOGRAMS FROM THE PHOTOIONIZATION DETECTOR SHOWING THE ANALYSES OF A CALIBRATION MIXTURE (~2 ppb) WITH (Lower Trace) AND WITHOUT (Upper Trace) OXYGEN DOPING OF THE CARRIER GAS

#### 4.0 Conclusions and Recommendations

Method ADDL002 has been examined, and we conclude the following:

- Method ADDL002 provides a very suitable technique for determining ambient concentrations of most of the 17 target compounds. Dichlorodifluoromethane, vinyl chloride and 1,1,2-trichloro-1,2,2-trifluoroethane are not determined adequately by Method ADDL002. GC operating parameters of flow rate, temperature programming rate and detector temperatures appear to be optimally set for peak resolution. Precision and detection levels stated in the Method were reproduced. Current trap desorption/bakeout temperatures, column temperature and run times are adequate. No "carry over" effects from previous samples or standards were observed.
- Collection and recovery studies showed that dichlorodifluoromethane, vinyl chloride, and 1,1,2-trichloro-1,2,2-trifluoroethane are not adequately retained with the existing Method ADDL002 Tenax trap. A Tenax/Carbosieve S-II trap gave much improved collection/recovery efficiencies. Values of  $100 \pm 10\%$  were obtained when comparing the Tenax/Carbosieve S-II to a cryogenic trap.
- A Nafion tube dryer was shown to remove water vapor selectively from the target mixtures. This dryer did not offer improvements with the current method but could be advantageously used if capillary columns were to be used for separation purposes.
- A 30-meter megabore, OV-1, capillary column offered much improved resolution of the 17 target compounds when compared to the packed column specified in Method ADDL002. However, cryogenic cooling of the column is necessary for optimal resolution. We recommend that ARB switch to the megabore OV-1 capillary column.
- Oxygen doping of the carrier gas to the ECD detector demonstrated that significantly enhanced peak area responses (100 to 200 fold) for the compounds, dichloromethane and 1,2-dichloroethane could be easily achieved. Because these two species are of particular interest to ARB, we recommend that Method ADDL002 be modified to include oxygen doping procedures.

## CHAPTER IV. ALTERNATIVE ANALYTICAL APPROACHES

### 1.0 Introduction

Method ADDL002 currently serves as ARB's primary means for analyzing for the 17 toxic air contaminants and freon compounds mentioned earlier. In Chapter 3 we evaluated this method and, for the most part, found it to be a very good method for analyzing the current target compounds.

During our evaluation of Method ADDL002 we also modified the existing procedures to determine if alternative approaches might provide an "improved" method. We examined the use of capillary columns, multi-adsorbent traps and oxygen doping techniques. As experimental data indicated, all three modifications provided improvement to the existing method. In this chapter we have prioritized these "improved" approaches along with two other proposed items that were discussed in Chapter 1-- automated GC system and automated sampler/analyzer.

### 2.0 Prioritization of Modifications to Current Analytical Method

#### 2.1 Minimal Modifications

Two alternative approaches to Method ADDL002 that will provide significant improvement yet will involve very minimal changes to the method are oxygen doping techniques and the use of a multi-adsorbent trap. Oxygen doping can be easily activated by connection of an oxygen line to the existing nitrogen line (make-up gas) of the electron capture detector. As discussed earlier, significant signal-to-noise enhancement of the mono and di-chlorinated hydrocarbons can be achieved without detrimental effects occurring to the analytical column or to measurements of other compounds. The insertion of a multi-adsorbent trap can also be made without major modification to the current analytical system. During our experimental work, the Tenax/Carbosieve S-II showed better recoveries of the more volatile organic compounds when compared to the Method ADDL002 Tenax trap. This multi-adsorbent trap also compared very well with the cryogenic trapping procedure currently in use with Battelle's automated GC system.

Our third recommendation calls for automating the sample introduction and processing procedures. Currently, Method ADDL002 requires a good deal of operator action during initial sample flushing, loading and injection operations. We have recently developed a sequential canister sampler (Figure IV-2.1) that can not only be used in the field to collect samples sequentially, but as shown in Figure IV-2.2, also be interfaced to the GC system for sequential analysis of samples. In the figure, the GC system is programmed to analyze four canister samples sequentially without requiring operator action. Another unit permits the unattended sampling and analysis of eight canister samples. This alteration to our system has significantly reduced operator/interface time and has doubled sample throughput to the GC system. This "auto-sampler" approach was used during the Bakersfield field site and proved to be very advantageous. An operator's manual is available which provides more detail concerning the use of the auto-sampler and the automated gas chromatographic system (contact Battelle staff).

## 2.2 Major Modification

A major modification to the existing Method involves the use of a megabore capillary column in place of the packed column. However incorporation of a capillary column will require the use of liquid nitrogen to cryo-focus the desorbed target compounds onto the head of the capillary column. Optimal operating conditions will need to be reestablished, along with documentation of component retention times and interfering species.

## 2.3 Automated GC/MSD-FID System

Although Method ADDL002 serves very adequately for analyzing the current target compounds of interest to ARB, this list of species is continually expanding. We believe that a gas chromatographic/mass spectrometric system will be better able to meet future analytical needs. Battelle currently employs an automated GC system which is equipped with parallel flame ionization and mass spectrometric detectors. The unit is equipped with cryogenic trapping capabilities and uses capillary columns for compound separation. The mass spectrometer is normally operated in the

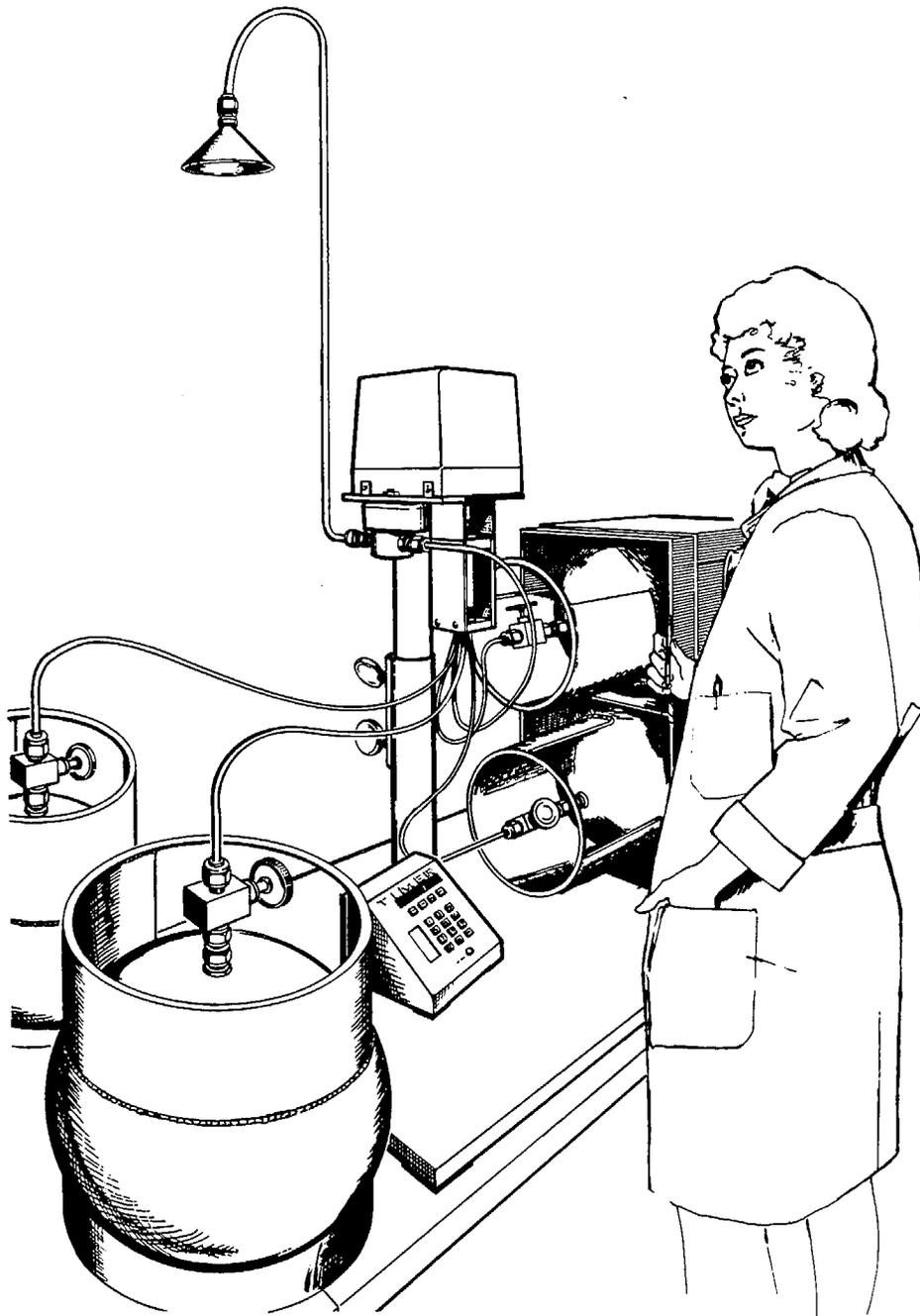


FIGURE IV-2.1. SEQUENTIAL CANISTER SAMPLER

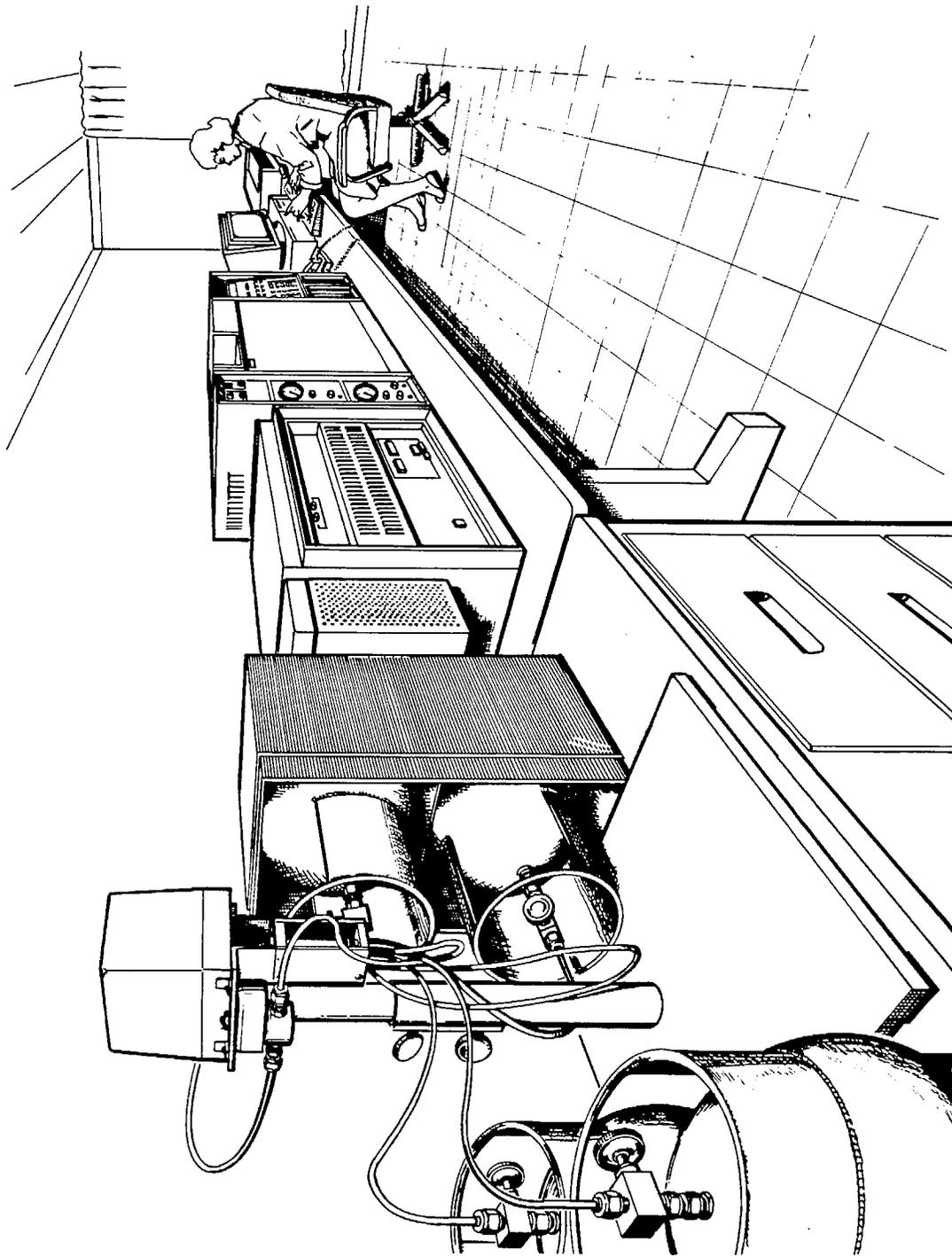


FIGURE IV-2.2. AUTOMATED GAS CHROMATOGRAPHIC SYSTEM SEQUENTIALLY ANALYZING FOUR CANISTER SAMPLES

selective ion monitoring mode (SIM) and provides a detection limit of ~0.01 ppb for most of the seventeen compounds of interest to ARB. Operational details of the system have already been provided in Chapter 1.

### 3.0 Recommendations

We recommend that oxygen doping and multi-adsorbent trapping be incorporated into ARB's current methodology in the near future in order to improve present deficiencies of the method (i.e. low sensitivity and recovery of some species). The automation of the analytical system for sample introduction and processing should also be actively pursued in the near term.

If ARB anticipates that their list of target compounds will expand, we recommend that they seriously consider using capillary columns for better peak resolving capability and eventually employing gas chromatography with a mass spectrometric detector as their primary detection system.



## CHAPTER V. EVALUATION OF ARB QUALITY CONTROL PROCEDURES

### 1.0 Introduction

One of the objectives of this program was to evaluate ARB's quality control methods and quantitative techniques and to estimate the precision, accuracy, and sensitivity of ARB's analytical and sampling procedures for monitoring TACs. In this part of the report we concentrate mainly on the quality control and quantitative procedures associated with the analytical portion of the ARB procedures. The sampling methodologies were discussed in great detail in Chapters I and II.

Section 2.0 contains a discussion of performance evaluation methods and quantitative techniques that we recommend for ARB. These methods are illustrated in Section 3.0 with statistical analyses of ARB's multipoint calibration and daily calibration and control sample data. Some additional quality control methods are discussed in Section 4.0. Finally, in Section 5.0 we summarize our recommendations.

### 2.0 Performance Evaluation Methods

To evaluate the characteristics of ARB's sampling and analytical techniques it is important to have a clear understanding of various statistical terms and concepts used in the method performance evaluation. Therefore, in Section 2.1 we describe some of the performance measures and objectives used by ARB and present our interpretation of them. In Section 2.2 we present some quantitative techniques for characterizing the accuracy, precision, and sensitivity of ARB's analytical procedures using the multipoint calibration data and data from the daily calibration and control sample analyses.

#### 2.1 Performance Measures and Objectives

The performance of sampling and analytical methods can be characterized in many ways. The most common approaches involve the concepts of accuracy, precision, sensitivity, and statistical control. These

concepts, as applied to ARB sampling and analytical methods, are defined and discussed below.

Accuracy. In the general sense accuracy is the degree of agreement of a measurement with an accepted reference or true value. Accuracy is often described by error limits such as  $\pm 10\%$ . This usually means that a specified percentage of the measurements (e.g. 95%) will lie within 10% of the accepted reference value. Accuracy limits should include all sources of random and systematic errors. It is not always the case that accuracy will be constant for all reference values. Whether accuracy is calculated in absolute or relative units it is important to state the range of values for which the accuracy limits apply and to describe the procedures for calculating the limits.

The term accuracy is also used to describe the lack of systematic bias in the measurement process. In this context an accurate measurement is one whose average value is close to the accepted reference value. Measurement bias is estimated by the difference  $X - X_0$ , where  $X$  is the average of replicate measurements of a sample having a known reference value  $X_0$ . With this definition of accuracy we can have a measurement process that is accurate but not precise. See the definition of precision below.

The primary source of bias in the analytical method is nonlinearity of the instrument response relative to sample concentrations. This can occur even when linearity is demonstrated in a multipoint calibration study if the measured concentration is outside of the linear range of the instrument. This is discussed further in Section 2.2.

Precision. Precision is a measure of mutual agreement among individual measurements or estimates of the same quantity, usually made under similar conditions. Precision is concerned with the closeness of results to each other and is not affected by bias.

The standard deviation of replicate measurements is the most common estimate of measurement precision. However, it is often the case that the standard deviation is a function of the concentration being measured. When this occurs it is recommended that a precision function be established. The statistical procedure for estimating a precision function is discussed in Section 2.2.

When measurements are subject to many sources of error, such as day-to-day variations and within-day variations, variance component analysis should be used to estimate the total random error of the measurement process. In such cases, the standard deviation of consecutive measurements will often underestimate the total variation in the measurement process. However, this may not be a concern if separate calibrations are performed each day.

Sensitivity. Sensitivity of an analytical method refers to the ability to detect the presence of small quantities of a target analyte. The chemistry literature contains many conflicting and ill-defined terms used to characterize analytical sensitivity. The terms most often used are limit of detection (LOD), minimum detectable limit (MDL) instrument detection limit (IDL), and method detection limit, also called the MDL. Unfortunately, there is little agreement on either the definition of these terms or on the statistical procedures for estimating the associated quantities. ARB quality control documents and standard operating procedures describe different methods for calculating the LOD and MDL. Furthermore, the documents do not clearly distinguish the meanings of these terms.

Throughout this report we will refer to the minimum detectable limit (MDL) as smallest "true" concentration that can be consistently detected by the instrument. This means that if we challenge the instrument with a sample containing a target analyte at a concentration equal to the MDL (the true concentration) we will detect the presence of the analyte with probability greater than 99% (i.e., consistently). Further discussion of this topic, along with a recommended procedure for calculating the MDL, is presented in Section 2.2.

Statistical Control. A measurement process is in a state of statistical control if the measurement errors exhibit only random or chance variations. These random variations are due to many sources, each contributing a relatively small and indistinguishable random error to every measurement. When a measurement process is in a state of statistical control there are no systematic or assignable causes of variability. Such causes result in identifiable trends or sudden large changes in the measurement errors.

Control charts are the best methods for determining if a process is in a state of statistical control. A control chart is a graphical plot of test results (such as periodic measurements of standards) with respect to time or sequence of measurement. Control limits, which define the boundaries of normal variability under steady state operation, are calculated so that as long as the plotted measurements remain between the control limits, there is some assurance that the process is in a state of statistical control. In addition to using control limits, runs tests and warning limits can be used to detect trends in the data.

Control charts can be used to monitor many characteristics of the measurement process. Some examples include the mean and standard deviation (or range) of replicate measurements of standards, daily response factors, and results from collocated or parallel sampling analyses.

## 2.2 Quantitative Techniques

The procedures used to calibrate analytical instruments and calculate measured (found) concentrations can have a significant effect on the accuracy and precision of reported values. These procedures, and some of the quantitative techniques used by ARB to characterize method performance are discussed below. Section 2.2.1 contains a discussion of statistical techniques for analyzing multipoint calibration data. The procedures for analyzing daily calibration and control sample data are discussed in Section 2.2.2. Finally, in Section 2.2.3 we discuss the relationship between ambient concentration levels and these used in the calibration and control sample analyses.

2.2.1 Multipoint Calibration Procedures. ARB performs multipoint calibrations of their analytical methods between four and six times each year. These calibrations are not used to quantify sample concentrations. Instead they are used primarily to characterize analytical precision, accuracy, linearity, and sensitivity. In general, estimates of precision and accuracy obtained from a multipoint calibration can be misleading. The data are obtained over a relatively short period of time and they do not take into account the variability and bias introduced by daily calibration activities. However, the multipoint calibrations do provide the means of

assessing instrument linearity, characterizing the relationship between precision and concentration level, and estimating method detection limits (minimum detectable levels).

ARB's multipoint calibration consists of two or three replicate analyses of four concentrations for each of the target chemicals. The four concentrations are achieved by challenging the instrument with different volumes of a standard calibration gas.

ARB uses descriptive statistics and simple linear regression to obtain estimates of the method precision and minimum detectable levels (MDLs). Precision is characterized by the relative standard deviation (RSD) determined from two or three replicate analyses at a specified concentration level. MDLs are calculated by the formula

$$MDL = x + 3 \cdot RSD \cdot x,$$

where  $x$  is the absolute value of the x-intercept from the simple linear regression of peak area on concentration and RSD is the relative standard deviation of the peak areas at the specified concentration level. There does not appear to be a procedure for testing the linearity of the responses.

ARB's procedures for estimating precision and sensitivity are reasonable. However, the methods are based on restrictive assumptions and they do not make the best use of the available data. Furthermore, under certain conditions the results can be misleading. The procedures we recommend for characterizing precision, estimating MDLs, and demonstrating linearity are outlined below.

The approach is based on the more general assumption that precision is a function of concentration level. The basic difference from the method used by ARB is that we use weighted least squares statistical procedure instead of simple linear (unweighted) regression.

The first step is to establish a model for precision as a function of concentration. Most measurement processes have standard deviations that increase with the concentration level. That is

$$S_j = g(c_j) + \text{error},$$

where  $S_i$  is the sample standard deviation of the instrument responses at the challenge concentration  $c_i$ , and  $g(c)$  is an increasing function. Usually we assume that

$$g(c) = a_0 + b_0 \cdot c,$$

where  $a_0$  and  $b_0$  are unknown constants.

The precision model is established by first calculating the sample standard deviation ( $S_i$ ) of responses (peak areas) at each concentration level  $c_i$ . Then use simple linear regression to estimate the coefficients  $a_0$  and  $b_0$ . The estimates of  $a_0$  and  $b_0$  under this model are

$$\hat{b}_0 = \frac{\sum_i (c_i - \bar{c}) S_i}{\sum_i (c_i - \bar{c})^2},$$

and

$$\hat{a}_0 = \bar{S} - \hat{b}_0 \bar{c},$$

where  $\bar{S}$  and  $\bar{c}$  are the average values of  $S_i$  and  $c_i$ , respectively. To test the hypothesis that  $a_0 = 0$  compute

$$t = \hat{a}_0 / \left( \frac{\sum_i c_i^2}{k \sum_i (c_i - \bar{c})^2} \right)^{1/2},$$

where  $k$  is the number of challenge concentrations. Compare this value to the 95th percentile of the  $t$ -distribution with  $k-1$  degrees of freedom, and reject the hypothesis of a proportional precision model if the absolute value of  $t$  exceeds the 95th percentile. If the intercept is not significantly different from zero, as determined by a  $t$ -test, then the proportional precision model can be adopted. That is,

$$g(c) = b_0 \cdot c.$$

Under this model the least squares estimate of  $b_0$  is

$$\hat{b}_0 = \frac{\sum_i c_i S_i}{\sum_i c_i^2} .$$

In our analysis of the ARB data (Section 3.0), we found that we can ignore the intercept term. The estimated coefficient  $\hat{b}_0$  will be used later to characterize precision.

The next step in our analysis is to establish a calibration model using weighted least squares regression. Weighted least squares produces more precise estimates of the calibration parameters than simple (unweighted) least squares. Furthermore, if the standard deviation of responses increases with concentration, unweighted least squares cannot make use of all of the data to estimate the method precision. Instead we could only rely on estimated standard deviations (determined from two or three analyses) at each concentration level. The weighted least squares procedure uses weights that are inversely proportional to the square of the standard deviations of the responses.

The data obtained from the multipoint calibration can be represented by  $R_{ij}$ , the  $j$ -th ( $j=1, \dots, n_j$ ) response (peak area) obtained at the  $i$ -th ( $i=1, \dots, k$ ) concentration level  $c_i$ . The calibration model is

$$R_{ij} = a_1 + b_1 * c_i + \text{error},$$

where  $a_1$  and  $b_1$  are unknown constants and the error is assumed to be approximately normally distributed with a standard deviation  $g(c) = b_0 * c$ . We now apply the weighted least squares algorithm using weights

$$w_i = (1/g(c_i))^2$$

to estimate the calibration coefficients  $a_1$  and  $b_1$ . The weighted least squares formulas are presented at the end of this section.

One of the statistics calculated in the weighted least squares algorithm is the mean squared error (MSE). In unweighted regression the square root of the MSE is an estimate of the measurement standard deviation. In weighted regression the expected value of the MSE is the average value of

$w_i * g^2(c_i)$ , where  $g(c_i)$  is the standard deviation of the response  $R_{ij}$ . Thus if we had properly chosen our weights to be the inverse of the square of the standard deviation, the MSE from the regression analysis should be equal to 1. The reason that this does not always occur is due to lack of fit. The MSE measures the average squared deviation from the regression line, but the previously estimated standard deviations only account for the variation about the average responses. If the average responses at the challenge concentrations do not form a straight line we recommend accounting for this lack of fit by adjusting the estimated standard deviations. The adjusted standard deviations are

$$g'(c) = g(c) * (MSE)^{1/2} .$$

To determine if there is lack of fit we first calculate the sum of squares for pure error (SSPE) by the formula

$$SSPE = \sum_i \sum_j w_i (R_{ij} - \bar{R}_i)^2$$

where  $\bar{R}_i$  is the average response at the  $i$ -th challenge concentration. Next, the sum of squares for lack of fit is calculated by

$$SSLF = SSE - SSPE$$

where  $SSE = MSE * (N-2)$  is the sum of squares for error and

$$N = \sum_i n_i$$

is the total number of measurements at the  $k$  unique concentration levels.

Finally we calculate the F-statistic

$$F = \frac{SSLF (N-k)}{SSPE (k-2)}$$

and compare this value with the 0.05 percentile of the F distribution with

k-2 and N-k degrees of freedom. If the value of F exceeds the critical value then we have demonstrated at the 0.05 level of significance that there is a lack of fit due to nonlinearity of the instrument response.

When we find a statistically significant lack of fit there may not be a practical solution to the problem. Lack of fit often occurs because there are errors in determining the "true" challenge concentrations. Figure V-2.1 shows that the relationship between the found and true concentration for dichloromethane is not exactly linear. Unless the instrument response can be corrected by changes in the analytical method the only solution is to adjust the instrument precision using the MSE as described earlier.

The final steps in our analysis of the multipoint calibration data are performed using the found concentrations calculated by

$$\hat{C}_{ij} = (R_{ij} - \hat{a}_1) / \hat{b}_1 ,$$

where  $\hat{a}_1$ , and  $\hat{b}_1$  are the weighted least squares estimates of the calibration coefficients. Using the model for the standard deviation of  $R_{ij}$ , defined earlier, we can now establish a model for standard deviation of the found concentration,  $\hat{C}$ . Because we estimated the standard deviation of  $R_{ij}$  by the function  $g'(c)$ , the estimated standard deviation of the found concentration is approximately

$$G(c) = g'(c) / \hat{b}_1 .$$

If the proportional precision model holds, this reduces to

$$G(c) = \hat{b}_0 * c * (MSE)^{1/2} / \hat{b}_1 .$$

Also the relative standard deviation of the found concentration is simply  $\hat{b}_0 * (MSE)^{1/2} / \hat{b}_1$ .

Finally, to estimate the MDL, we calculate prediction bounds  $\hat{C} = c \pm 3 * G(c)$ . If the errors are normally distributed we would expect at least 99% of the found concentrations to fall within these bounds. Next we solve the equation

$$DL = MDL - 3 * G(MDL) ,$$

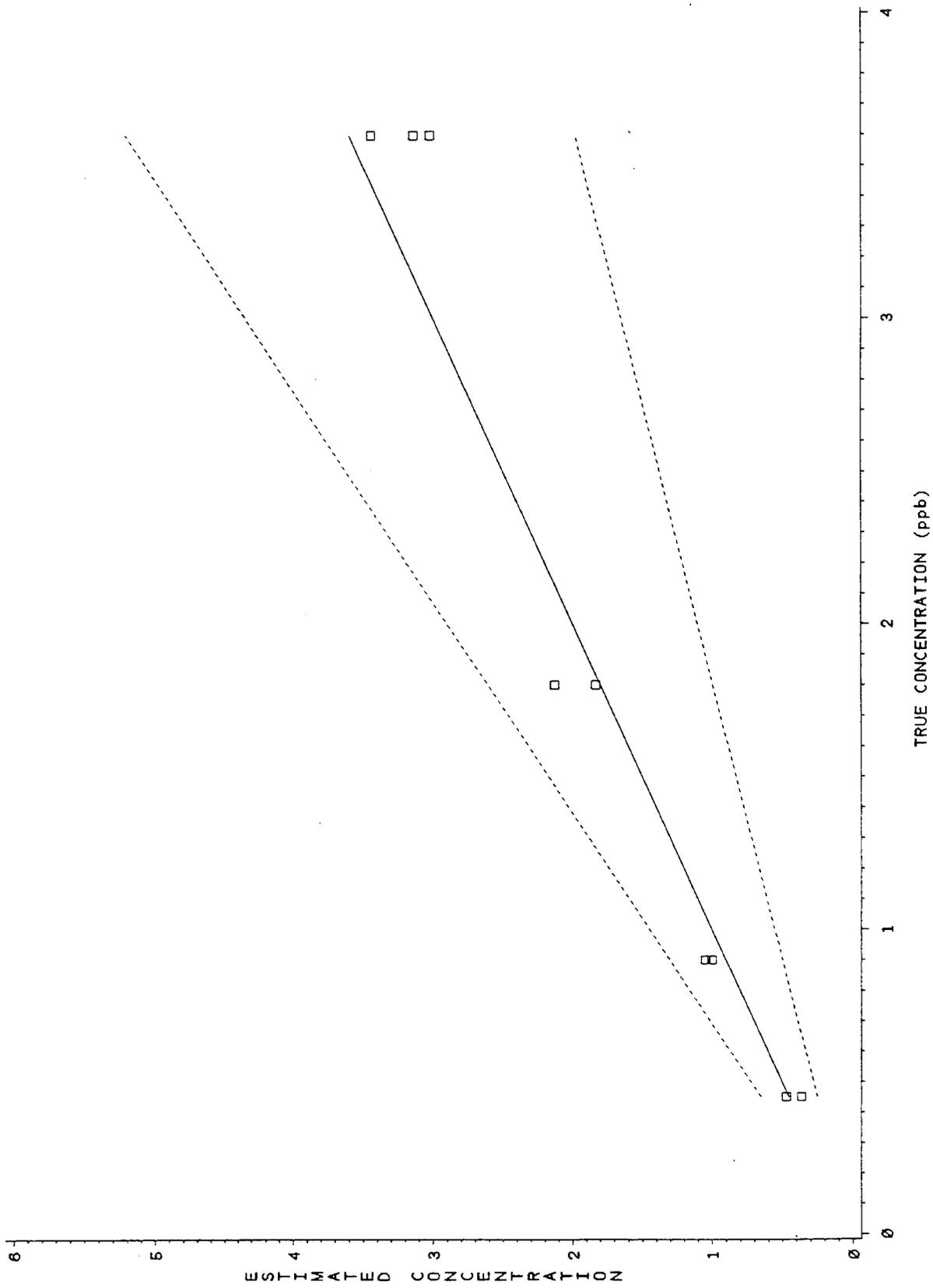


FIGURE V-2.1. THE RELATIONSHIP BETWEEN ESTIMATED (FOUND) CONCENTRATION AND TRUE CONCENTRATION IS NOT PERFECTLY LINEAR FOR DICHLOROMETHANE

where  $DL = 3 \cdot G(0)$  is the method decision limit. The DL is the smallest found concentration for which we can say with 99% confidence that the chemical is present. The solution (MDL) to this equation is the true concentration level that we can say with at least 99% confidence will produce a found concentration that is greater than the method decision limit (DL).

Because the estimation of the MDL involves extrapolation of the calibration curve we recommend a simple modification to the above procedure. The precision function is estimated from calibration data obtained over a limited range of challenge concentrations. We have no assurances that it can be extrapolated to a zero concentration. Often there are fixed sources of variation that affect instrument responses at very small concentrations. Therefore, we recommend that the precision function  $G(c)$  be replaced by the value  $G(c_1)$  for concentrations below the smallest challenge concentration  $c_1$ . Thus the estimated MDL is the solution to the equation

$$3 \cdot G(c_1) = MDL - 3 \cdot G(MDL).$$

This approach is illustrated in Figure V-2.2.

In Section 3.0, we summarize this approach and apply the methods to a set of multipoint calibration data provided by ARB. Below we provide the formulas for calculating weighted least squares estimates.

Weighted Least Squares Estimates Applied to Calibration of Instruments with Replicate Calibration Sample. Let  $R_{ij}$  be the response obtained from the  $j$ th replicate sample at the  $i$ -th challenge concentration level  $c_i$ . The number of unique challenge concentrations is  $k$  and the number of replicates at the  $i$ -th concentration is  $n_i$ . We assume that

$$R_{ij} = a_1 + b_1 c_i + \text{error} ,$$

where  $a_1$  and  $b_1$  are unknown constants and the standard deviation of the error is proportional to a function  $g(c)$ . Then the weighted least squares estimates of  $a_1$  and  $b_1$  are

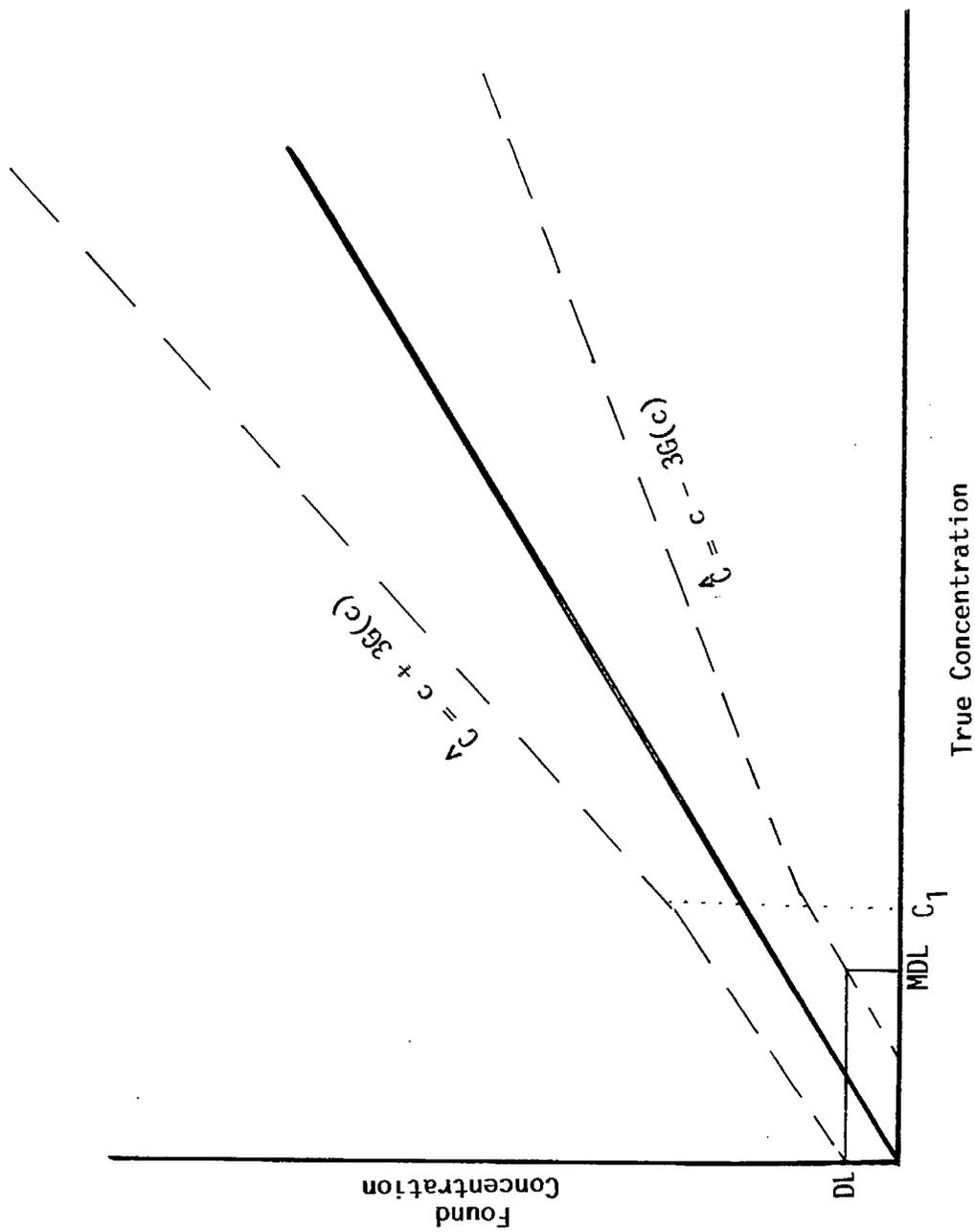


FIGURE V-2.2. ESTIMATING THE MDL USING 99% PREDICTION BOUNDS ON THE FOUND CONCENTRATION. C1 IS THE SMALLEST CHALLENGE CONCENTRATION.

$$\hat{b}_1 = \frac{(\sum_i n_i w_i) (\sum_{i,j} \sum w_i R_{ij} c_i) - (\sum_{i,j} \sum w_i R_{ij}) (\sum_i n_i w_i c_i)}{(\sum_i n_i w_i) (\sum_i n_i w_i c_i^2) - (\sum_i n_i w_i c_i)^2}$$

and

$$\hat{a}_1 = \frac{\sum_{i,j} \sum w_i R_{ij} - \hat{b}_1 \sum_i n_i w_i c_i}{\sum_i n_i w_i},$$

where  $w_i$  is proportional to  $(1/g(c_i))^2$ . The mean squared error is

$$MSE = \sum_i \sum_j w_i (R_{ij} - \hat{a}_1 + \hat{b}_1 c_i)^2.$$

The estimated standard deviation of the response  $R_{ij}$  is

$$\hat{\sigma}_R(c_i) = (MSE/w_i)^{1/2},$$

or if

$$w_i = (1/g(c_i))^2,$$

then

$$\hat{\sigma}_R(c_i) = g(c_i) (MSE)^{1/2}.$$

2.2.2 Daily Calibration Procedures. The daily calibration procedure for the primary GC/ECD method ADDL002 is described in the standard operating procedure (SOP). The SOP specifies that response factors (RF = concentration/peak area) are to be calculated daily for each target compound. If the daily RFs agree to within  $\pm 15\%$  of historical values, the historical RFs are updated (ie., replaced) for subsequent analyses. Otherwise the historical value is used. Next a control sample is run immediately following the calibration sample and a found concentration is calculated using the equation

$$\hat{C} = RF * Area.$$

If the found concentration is not within  $\pm 15\%$  of the known concentration the problem must be resolved before field samples can be run.

We reviewed some of ARB's daily calibration and control sample data obtained during a fifteen day period in 1987 and found the application of this procedure difficult to follow. Without more detailed descriptions of this procedure by ARB personnel it is difficult for us to recommend specific procedures to be followed. However, as presented in Section 3.2, we analyzed the daily calibration and control data for this fifteen day period and found that by simply updating the daily RF regardless of its value, we obtained better precision for the control sample analyses than would have been obtained by following the procedure outlined in ARB's SOP. Some general recommendations are provided in Section 3.2.

2.2.3 Selection of Calibration Standards. The multipoint calibrations and the daily analyses of calibration and control samples serve two separate purposes: (1) Evaluation of method performance, and (2) Quantification of sample analyses. The multipoint calibration is used only for evaluating method performance, while the daily analyses are performed with both purposes in mind.

An important consideration in designing a multipoint calibration study or in selecting standard samples for the daily calibration and control analyses, is the relationship between the ambient concentrations of the target chemicals and the concentrations used in these activities. Ideally, the concentrations used in the multipoint calibration span the range of concentrations that are typically found in the environment. This ensures that the instrument's performance is evaluated over the entire range of interest.

The concentration of the daily calibration sample should be close to the average ambient concentration. This will help reduce the bias in the reported average ambient concentration if the instrument response is not exactly proportional to the challenge concentration. This can occur if the response is nonlinear or if the intercept of the calibration curve is significantly different from zero. However, if the instrument response is proportional to the concentration level, then we can improve the precision

of the measured concentrations by selecting a calibration standard with a concentration that is above the ambient concentration levels. Taking both accuracy and precision into account it is generally acceptable to choose a calibration standard that is in the upper half of the ambient concentration range.

Since the purpose of the control sample is to monitor the performance of the instrument on a daily basis, it best to choose a control standard with a concentration near the center (mean, median, or midrange) of the ambient range of concentrations. If the control sample concentration is too large or too small than the estimated precision from the control sample data may not properly characterize the precision for ambient samples.

Table V-2.1 contains a summary of the TAC ambient levels and the concentrations used by ARB in calibration and control sample analyses for the primary analytical method. We used the results from the automated GC analyses in the Bakersfield field study to estimate the range of ambient concentrations. Although these data are not representative of ambient levels throughout California, they are the only ambient data we had available that do not include the contamination effects of Tedlar bags. The extreme concentration listed in the table is the largest concentration that was observed in any sample (including bags and cans) during the field study.

In most cases the calibration range covers the ambient range. The only notable exceptions are dichloromethane, 1,2-dichloroethane, and toluene. For other chemicals it might also be helpful to include smaller concentrations in the multipoint calibration. However, this depends on the sensitivity of the instrument.

Of greater concern are the large control sample concentrations for 1,1,1-trichloroethane, trichloroethene, 1,2-dibromoethane, and tetrachloroethene. The large values for 1,1,1-trichloroethane and 1,2-dibromoethane may explain the poor precision that was demonstrated for these chemicals using the ARB procedure for updating response factors in Section 3.2.

Dispite these goals, we recognize that it is not always possible to have the ideal relationship between the standard samples and ambient levels. The problem is particularly difficult because it is necessary to use a single sample that contains all chemicals at precise levels. Also, reliable reference standards are hard to find.

TABLE V-2.1. SUMMARY OF TAC AMBIENT LEVELS AND ARB'S CALIBRATION AND CONTROL SAMPLE CONCENTRATIONS

Chemical	Ambient Range(a)	Extreme(b)	Calibration Range(c)	Control Sample(d)
Vinyl chloride	ND	--	1.25-10.0	NA
Dichloromethane	0.1-1.0	10.0	0.45-3.6	3.10
Trichloromethane	ND-0.1	0.1	0.02-0.16	0.12
1,2-Dichloroethane	ND-0.1	1.5	0.14-1.10	0.12
1,1,1-Trichloroethane	0.2-1.0	18.3	0.24-1.9	2.80
Benzene	0.5-9.5	29.3	0.61-4.9	4.70
Tetrachloromethane	0.1-0.2	0.2	0.02-0.17	0.23
Trichloroethene	ND	0.5	0.11-0.90	2.40
Toluene	1.0-25.3	84.7	1.25-10.0	NA
1,2-Dibromoethane	ND	--	0.04-0.32	1.10
Tetrachloroethene	0.1-0.3	0.5	0.02-0.19	1.00

NA Not available.

(a) Range of concentrations measured by Battelle's automated GC during the Bakersfield study.

(b) Largest concentration measured in all samples from the Bakersfield field study.

(c) Concentrations used in multipoint calibration. The largest concentration is used to calculate response factors.

(d) Control sample concentration.

### 3.0 Performance Evaluation - Analytical Systems

To characterize the accuracy, precision, and sensitivity of ARB's analytical systems ARB provided Battelle with two sets of data. The first set was obtained from a 1988 multipoint calibration of ARB's primary method ADDL002. The second set consisted of daily calibration and control sample data (peak areas) from the primary analytical method during a fifteen day period in 1987. Section 3.1 contains a statistical analysis of the multipoint calibration data to assess the precision and sensitivity of the method under controlled conditions. An analysis of the daily calibration and control data is presented in Section 3.2.

#### 3.1 Analysis of Multipoint Calibration Data

ARB periodically performs multipoint calibrations of their primary GC/ECD analytical system. Data from one of these calibrations, November 1988, were provided to Battelle for statistical analysis. The data consist of two or three peak area measurements of eleven compounds, each at four concentration levels. The four concentrations were achieved by challenging the instrument with the standard calibration mixture using injection volumes of 25, 50, 100 and 200  $\text{cm}^3$ . Table V-3.1 shows the challenge concentrations and number of measurements taken at each of the different levels for the 11 compounds. The actual peak areas are listed in Appendix V-A.

Along with the data, ARB also supplied the results of their analysis of the data. ARB analyzed the multipoint calibration data by performing simple linear regression on the mean peak areas at each concentration level. The estimated regression parameters were used to compute MDLs according to the method described in their SOP. (Also described in Section 2.2 of this report.) To characterize the method precision, ARB reported the sample relative standard deviations of the peak areas at the concentrations corresponding to an injection volume of 100  $\text{cm}^3$ . In most cases we were able to reproduce ARB's results. The only exceptions were in the results for tetrachloroethene, apparently due to an error in reading one of the peak areas, and 1,1,1-trichloroethane, for which no explanation has been found for the discrepancy.

TABLE V-3.1. CHALLENGE CONCENTRATIONS AND NUMBER OF MEASUREMENTS  
TAKEN DURING AN ARB MULTIPOINT CALIBRATION

Chemical	ppb at 200 cm <sup>3</sup>	Injection Volume (cm <sup>3</sup> )			
		25	50	100	200
Vinyl chloride	10.0	2	2	2	-*
Dichloromethane	3.6	2	2	2	3
Trichloromethane	0.16	2	2	2	3
1,2-Dichloroethane	1.1	2	2	2	3
1,1,1-Trichloroethane	1.9	2	2	2	3
Benzene	4.9	2	2	2	3
Carbon tetrachloride	0.17	2	2	2	3
Trichloroethene	0.9	2	2	2	3
Toluene	10.0	2	2	2	3
1,2-Dibromoethane	0.32	2	2	2	3
Tetrachloroethene	0.19	2	2	2	2

\* The peak areas for vinyl chloride at this level exhibited such a deviation from a line that they were excluded from analysis by both ARB and Battelle.

We reanalyzed the multipoint calibration using the weighted linear regression. The weighting was done to take into account the nonhomogenous variance in peak areas at different concentration levels. As described in Section 2.2, the analysis was carried out in following steps:

1. Calculate the sample standard deviation at each concentration level,
2. Use simple linear regression to fit the linear model of standard deviation versus concentration level,
3. Fit a line to the peak areas versus concentration level using weighted least squares regression with weights equal to the reciprocal of the square of the predicted standard deviations from step 2,
4. Test for lack of fit,
5. Convert the peak areas into found concentrations using the estimated intercepts and slopes from the weighted regression analysis,
6. Calculate the estimated standard deviations ( $G(c)$ ) of the found concentrations by dividing the predicted peak area standard deviations (step 2) by the estimated peak area slope (step 3) and multiplying by the root mean squared error from the weighted regression analysis (step 3),
7. Calculate prediction bounds on the found concentrations using the equations

$$C = c \pm 3 * G(c)$$

then extend these bounds to the origin by replacing  $G(c)$  with its value at the smallest challenge concentration  $G(c_1)$ ,

8. Plot the found concentrations and prediction bounds and calculate the MDL by solving the equation

$$3 * G(c_1) = MDL - 3 * G(MDL),$$

9. Report the MDLs and estimated standard deviations.

The standard deviations can be reported in absolute ( $G(c)$ ) or relative ( $100 * G(c) / c$ ) terms. They should be reported as a function of concentration. However, if the proportional precision model holds (as we demonstrated in step 2), the relative standard deviations will be independent of the concentration level.

The results of this analysis are presented in Appendix V-B and Tables V-3.2 and V-3.3. Appendix V-B contains plots of the found concentrations with prediction bounds of  $\pm 3$  standard deviation limits overlaid. Table V-3.2 contains the calibration parameters (intercept and slope) obtained from the weighted regression analysis, and Table V-3.3 contains the estimated MDLs and relative standard deviations (RSD) from the above analysis along with the corresponding values reported by ARB. Also reported in Table V-3.3 are the lowest concentration levels used in the multipoint calibration.

In general there is good agreement between ARB's results and the Battelle results determined by weighted least squares analysis. The only significant differences are in the MDLs and RSDs reported for 1,1,1-trichloroethane and in the RSDs reported for 1,2-bromoethane. With both chemicals the weighted least squares analysis is more conservative.

Several of the chemicals have estimated MDLs that are much smaller than the lowest concentration used in the multipoint calibration. This means that the estimation of the MDL involves significant extrapolation; therefore, the estimates may not be reliable. To avoid this problem, smaller challenge concentrations (perhaps corresponding to a 12.5 cm<sup>3</sup> injection volume) should be included in the multipoint calibration procedure. Even if this results in concentrations below the detection limits for other chemicals, the results will help to verify the estimated MDLs.

For three of the chemicals (dichloromethane, 1,2-dichloroethane, and toluene) the estimated RSDs are quite large. This is mainly due to the nonlinearity of the instrument response confirmed by lack of fit tests. Examination of the plots in Appendix V-B reveals that there is substantial nonlinearity displayed by most of the chemicals. However, except for these three chemicals the effect may not be of practical importance.

### 3.2 Analysis of Daily Calibration and Control Data

ARB also supplied daily calibration and control sample data for nine compounds over a fifteen day period from 12/16/87 through 12/31/87. Analyses were performed on twelve of these days and control samples were run on ten days. ARB reported control sample concentrations on each day using

TABLE V-3.2. CALIBRATION PARAMETERS ESTIMATED WITH WEIGHTED  
LEAST SQUARES ANALYSIS

Chemical	Intercept	Slope
Vinyl chloride	2,312.7	3,620
Dichloromethane	328.3	4,955
Trichloromethane	394.8	208,290
1,2-Dichloroethane	-53.8	7,483
1,1,1-Trichloroethane	33,228.5	422,745
Benzene	6,642.0	32,048
Carbon tetrachloride	6,893.5	1,744,732
Trichloroethene	3,803.4	228,220
Toluene	25,055.7	30,116
1,2-Dibromoethane	2,246.9	249,242
Tetrachloroethene	12,759.9	1,303,443

TABLE V-3.3. MINIMUM DETECTABLE LEVELS (MDL) AND  
RELATIVE STANDARD DEVIATIONS (RSD)  
DETERMINED FROM MULTIPOINT CALIBRATION DATA(a)

Chemical	Lowest Conc.	MDL		RSD	
		ARB	Battelle	ARB	Battelle
Vinyl chloride	1.25	0.56	0.28	2.1	3.8
Dichloromethane	0.45	0.4	0.40	10.2	14.9
Trichloromethane	0.02	0.004	0.007	7.5	5.6
1,2-Dichloroethane	0.138	0.11	0.19	10.3	19.4
1,1,1-Trichloroethane	0.238	0.09	0.10	2.2	6.8
Benzene	0.61	0.28	0.13	5.2	3.6
Carbon tetrachloride	0.021	0.008	0.005	3.4	4.2
Trichloroethene	0.1125	0.042	0.036	5.7	5.3
Toluene	1.25	0.76	0.92	12.8	12.2
1,2-Dibromoethane	0.04	0.012	0.008	0.5	3.3
Tetrachloroethene	0.0238	0.014	0.007	5.0	4.8

(a) ARB results are those reported with the data. Battelle results were determined from weighted least squares analysis.

a procedure for computing and updating daily response factors (RFs). This procedure is described in their SOP. The objective of our analysis of the daily calibration and control data was two-fold:

1. To estimate the relative standard deviation (RSD) of the reported control sample concentrations, and
2. To evaluate two alternatives to the ARB procedure for updating daily response factors: a) automatically updating the RF every day, and b) using a constant RF over a given period of time.

The data received from ARB are listed in Appendix V-C. Table V-3.4 is the data listing for 1,2-dibromoethane. Included in the tables are the peak areas and reported concentrations for the daily calibration and control samples. We also computed the response factors used in the reported concentrations and estimated a second concentration for the control sample based on a daily response factor calculated from the reported peak area for the calibration sample and its known concentration. These estimates simulate the control sample concentrations that would be reported if the response factor was automatically updated each day.

A third estimated control sample concentration was calculated using a single response factor determined by averaging the daily response factors. We did not include daily response factors from days on which the control samples were not analyzed.

Table V-3.5 shows the estimated relative standard deviations determined from each of the three sets of calculated control sample concentrations. It is clear that the use of an average response factor is not practical due to daily changes in the analytical instrument. There is clearly a significant day-to-day source of error in the measurement process. The results also show that the RSDs calculated from the estimated control sample concentrations are generally smaller than the RSDs calculated from ARB's reported values. This is particularly true for the chemicals 1,2-dibromoethane and 1,1,1-trichloroethane. In both cases we found that there were between two and four days on which the response factor used by ARB to calculate the control sample concentration was significantly different from the factor calculated from the daily calibration sample analysis. The reason for these differences is likely due to the fact that estimated calibration sample concentrations on those days were not within 15% of the

TABLE V-3.4. LISTING OF DAILY CALIBRATION & CONTROL DATA FOR 1,2-DIBROMOETHANE

Date (YYMMDD)	Calibration Samples										Control Samples			
	RUN NUMBER	VOLUME	PEAK AREA	DAILY RFx10K	REPORTED CONC	%DIFF FROM TRUE	IMPUTED RFx10K	RUN NUMBER	VOLUME	PEAK AREA	CALC CONC	REPORTED CONC	IMPUTED RFx10K	
871216	710	200	89801	0.036	0.2284	29.2	0.025	711	200	487186	1.7361	1.2284	0.025	
871217	716	200	93771	0.034	0.2360	26.3	0.025	717	200	469232	1.6613	1.2000	0.026	
871218	727	200	97757	0.033	0.2465	23.0	0.025	728	200	475840	1.5570	1.1993	0.025	
871219	738	200	96732	0.033	0.2439	23.8	0.025	.	.	.	.	.	.	
871219	739	100	40866	0.046	0.2020	36.9	0.025	.	.	.	.	.	.	
871219	746	50	17112	0.047	0.1720	46.3	0.025	.	.	.	.	.	.	
871221	704	200	19927	0.101	0.0502	84.3	0.025	.	.	.	.	.	.	
871221	705	200	121467	0.026	0.3063	4.3	0.025	.	.	.	.	.	.	
871222	709	200	87221	0.037	0.2199	31.3	0.025	710	200	444258	1.6299	1.1202	0.025	
871223	721	200	86834	0.037	.	.	.	722	200	445060	1.6401	1.6000	0.038	
871224	732	200	84233	0.038	0.3100	3.1	0.037	733	200	434720	1.6515	1.6515	0.038	
871228	739	200	75183	0.043	0.3200	0.0	0.043	740	200	361949	1.5408	1.5406	0.043	
871229	746	200	74910	0.043	0.3200	0.0	0.043	747	200	367172	1.6539	1.6200	0.042	
871230	753	200	78170	0.041	0.3200	0.0	0.041	755	200	390064	1.5968	1.5968	0.041	
871231	760	200	79884	0.040	.	.	.	761	200	395391	1.5678	1.5878	0.040	

TABLE V-3.5. COMPARISON OF ESTIMATED CONTROL SAMPLE RSDs USING THREE METHODS FOR CALCULATING RESPONSE FACTORS

Compound	Relative Standard Deviation		
	ARB Method <sup>(a)</sup>	Daily Calibration <sup>(b)</sup>	Average RF <sup>(c)</sup>
Dichloromethane	2.2	2.2	19.8
Trichloromethane	2.1	1.7	6.0
1,2-Dichloroethane	5.7	5.7	22.7
1,1,1-Trichloroethane	19.0	6.4	27.3
Carbon tetrachloride	2.1	2.0	12.7
Trichloroethene	2.4	2.3	6.9
1,2-Dibromoethane	15.8	3.4	10.2
Tetrachloroethene	3.3	3.4	5.0
Benzene	2.3	3.2	3.5

- (a) RF calculated according to ARB method.  
 (b) RF updated each day.  
 (c) Daily RFs were averaged.

known concentrations. However, this favors the idea that a procedure of strictly updating the response factor should be used.

The procedure for updating response factors described in the SOP is difficult to follow. There appear to be situations that can occur in practice that are not specified in the SOP. For example, what happens if the calculated calibration sample concentration is outside the 15% bounds but the calculated control sample concentrations are within the bounds using both the previous or new response factor? Also, how many times should the calibration or control sample analyses be performed if the reported concentrations are not within the bounds?

This analysis is not sufficient to make concrete recommendations on how to establish daily response factors. It only demonstrates that the current procedure should be reevaluated. We also recommend the current or any revised procedure be written to include all possible outcomes of the daily calibration and control samples analyses. Furthermore, by recording the peak areas for both the calibration and control sample analyses in a log or computerized database, the method's performance could be more closely monitored and it would be easier to perform more frequent analyses of this type. The database could also be used to construct the control charts that are currently done by hand. Finally, we also recommend that control charts be established for the daily response factors or calibration sample peak areas to more closely monitor the changes in instrument performance.

#### 4.0 ARB Quality Control Program

The monitoring program for TACs is managed by ARB's Monitoring and Laboratory Division. Historically, the analytical and sampling methods for the program were developed in two separate laboratories. The two laboratories were also jointly running the TAC program by dividing up both the sampling and analysis responsibilities. The Northern Laboratory in Sacramento was responsible for sampling sites in northern California and the Southern Laboratory in El Monte was responsible for sites in the south. During these early years of the program the laboratories cooperated on many method development and evaluation programs. However, in 1988 (in the middle of this contract with Battelle) the TAC program was consolidated and is now

managed solely by the Northern Laboratory. Their responsibilities include sampling, analysis, method development, and quality control.

The original intent of this task (Task 5 in the request for proposals) was to review a wide range of quality control activities conducted at the two laboratories. Our first quarterly report contained a general discussion of these activities. However, it was decided to devote more of the project effort to documenting the results of the laboratory and field studies and to evaluating the accuracy and precision for ARB's analytical methods. The accuracy and precision analysis was discussed in Sections 2.0 and 3.0. The following sections contain some recommendations regarding the use of data quality objectives and ARB's procedures for documenting procedures and reporting laboratory data.

#### 4.1 Quality Objectives

The Environmental Protection Agency's Quality Assurance Management Staff (EPA/QAMS) requires that Data Quality Objectives (DQOs) be prepared in advance of all large surveys or monitoring activities. DQOs are statements of the quality of data needed to support a specific decision or action. Data quality requirements are determined by study objectives, rather than equipment or analysis method characteristics. By stating the DQOs it is much easier to focus on method performance characteristics that need to be improved in order to meet the objectives. For example, the analytical methods may surpass the DQOs for analytical accuracy and precision but the sampling techniques may need significant improvement before the sampling DQOs can be achieved.

Although ARB's TAC program is not bound by the requirements of EPA/QAMS, we recommend that DQOs be established to help define the minimum requirements for monitoring TACs. The DQOs should clearly state the types of decisions made with monitoring data and the risks associated with inaccurate measurements. These objectives will be used to establish minimum requirements for method accuracy, precision, sensitivity, selectivity, and other measurement characteristics. Ultimately this will lead to QC activities that are aimed at ensuring these performance characteristics.

## 4.2 Documentation and Reporting

The documentation for ARB's sampling and analytical methods consists of a QC manual and individual SOPs for each of the sampling and analytical methods. The performance of these methods is reported in monthly QC reports that regularly contain results from control sample analyses and duplicate analyses of field samples. Periodically, the QC reports also contain results from special studies such as confirmation analyses, performance audits, collocated sample studies.

ARB's QC manual is well written and provides sufficient detail on the sampling and analytical methods. However, the latest revision of this document is dated May, 1986; and there have been numerous changes to the sampling and analytical methods that have not been included. The individual SOPs are also well written, but they contain different levels of detail depending on when they were written. Not all of the SOPs contain method performance data. Also, the SOP for the primary method has not been updated since 1986.

There is one area in which it would be helpful if the QC manual and SOPs were more specific. This is in the area of data reporting. Currently there are procedures for reporting results of daily control sample analyses and duplicate analyses. This could be expanded to include daily and multipoint calibration data and various types of performance data such as confirmation analyses and performance audits. Data from the QC activities and studies are now presented in a variety of forms and with different levels of detail. For example, the data from duplicate analyses are provided in tabular form in the monthly QC reports. On the other hand, the control sample analysis results are presented in hand written control charts.

The control sample data, as well as the daily and multipoint calibration data, are valuable for performing periodic statistical analyses of the method's accuracy, precision, and sensitivity. However, with the current system for reporting and handling data, this can be very difficult. In order to evaluate the daily calibration data it is necessary to compile data from daily logs. Also, the daily control sample data are not sufficient to perform a meaningful analysis. The monthly QC reports present the data in graphical form; but, even if available in tabular form they only

represent the measured concentrations of the control sample analyses. Without going back to the daily logs it is not possible determine the response factor used in the calculation, or whether the response factor was determined from the current or previous analysis. In our analysis of control sample data in Section 3.2, we had to impute the response factor from the peak area to determine which calibration run produced the response factor.

Our primary recommendation is for ARB to review all of the data management needs in the laboratory and to pay particular attention to how specific types of data will be used in evaluating the performance of the sampling and analytical methods. Also, if an automated data system can be developed, we recommend that the use of control charts be expanded. At a minimum control charts should be used to track daily calibration analyses and possibly instrument performance measures. Finally, before making any decisions about which type of data to include in a laboratory data management system, we recommend that ARB take a close look at how these data will be statistically analyzed and how the analyses will be used to evaluate method performance.

## 5.0 Conclusions and Recommendations

The broad range of QC activities documented in ARB's QA manual, SOPs, and monthly QC reports demonstrate ARB's strong commitment to ensuring quality in the TAC sampling and measurement processes. In addition to the routine activities (such as duplicate analyses, daily control samples, multipoint calibrations, performance audits) ARB has conducted numerous special studies such as the "bag swap" and "bag/canister" studies to address additional quality issues.

Our investigation of ARB's Quality Control program focussed primarily on the daily calibration activities and the quantitative techniques used to characterize the performance of the analytical methods. We also performed statistical analyses of selected ARB QC data to evaluate the accuracy, precision, and sensitivity of ARB's primary analytical method. These activities resulted in recommendations to apply new statistical procedures to the multipoint calibration data and to revise or clarify the protocol for updating daily response factors. Finally, we made some general

recommendations regarding the documentation of QC procedures, data reporting, and data management. Our conclusions and recommendations are summarized below:

1. ARB currently uses simple linear regression and descriptive statistics on the multipoint calibration data to characterize the accuracy, precision, and sensitivity of their analytical method. In most cases these procedures produce acceptable results. However, the method characterization could be improved by applying the more general statistical procedures described in Sections 2.0 and 3.0. These procedures are used to establish a precision function, estimate calibration parameters and the MDL, and test the linearity of the calibration function.
2. ARB's protocol for updating daily response factors is difficult to follow and may not cover all possible outcomes of the daily calibration and control sample analyses. Our statistical analysis of ARB supplied data demonstrated that precision may be improved by simply updating the daily response factor each day. Without more detailed information and access to additional data it is not practical for us to make specific recommendations for calculating response factors. Instead, we recommend that ARB closely monitor the daily calibration and control sample data and reevaluate their current protocol. This can be facilitated by recording peak areas for the daily calibration and control sample analyses in a log or computerized database. More frequent statistical analyses should be performed and control charts should be maintained for the daily response factors or calibration sample peak areas.
3. ARB's selection of calibration and control sample concentrations is appropriate for most of the TACs being monitored. It may be helpful to include smaller concentrations in the multipoint calibration for some chemicals. However, the concentrations in the daily calibration sample appear to be appropriate for all of the TACs. On the other hand, there are several chemicals for which the control sample concentrations are significantly higher than the ambient concentrations. This could affect the validity of the instrument's performance assessment.
4. The documentation of ARB's laboratory and field procedures contained in the QA manual, SOPs, and monthly QC reports is quite detailed. However, the QA manual and the SOPs need to be updated to reflect changes that have been implemented in practice.
5. ARB reports the results of routine and special QC activities in a monthly QC reports. However, the procedures for reporting and managing the great volume of data could be

improved by developing a comprehensive laboratory data management system. Also, the value of some of the data that are routinely reported could be enhanced by further and more frequent statistical analysis. This is especially true for data obtained in the daily calibration and control sample analyses, and the data obtained from duplicate analyses of field samples. A computerized data management system would greatly facilitate these activities. It would also make it feasible to increase the use of control charts to monitor instrument parameters, daily response factors, or other routinely collected data.

6. ARB should consider developing a set of data quality objectives (DQOs) as recommended by EPA's Quality Assurance Management Staff. DQOs are statements of the quality of data that must be achieved in various segments of a monitoring program. Only after the objectives are defined can the required amount and type of QC data be decided, and also what type of statistical procedures will be used to demonstrate that the objectives are being met.



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APPENDIX I-A

DATA FROM BAKERSFIELD FIELD STUDY



## APPENDIX I-A

### DATA FROM BAKERSFIELD FIELD STUDY

The data consists of five measured concentration (ppb) of 20 target chemicals for each of 16 sample sets. The five measurements are:

- A = Air sample analyzed directly by automated GC,
- B1 = Initial analysis of the bag sample,
- B2 = Repeat analysis of the bag sample following transport,
- C1 = Initial analysis of the canister sample, and
- C2 = Repeat analysis of the canister sample following transport.

CONCENTRATIONS OF SELECTED COMPOUNDS (PPB) BY SAMPLE SET

Chemical Number=1 Chemical Name=Dichlorodifluoromethane

Sample Set	Auto GC (A)	Initial Bag (B1)	Repeat Bag (B2)	B1 -A % Chg	B2 -B1 % Chg	Initial Can (C1)	Repeat Can (C2)	C1 -A % Chg	C2 -C1 % Chg
1	0.78	0.72	0.68	-0.06	-0.05	0.70	0.69	-0.09	-0.00
2	0.99	0.97	1.02	-0.02	0.05	0.92	0.99	-0.07	0.08
3	0.68	0.67	4.30	-0.01	3.63	0.84	0.67	-0.04	0.03
4	0.41	0.58	2.06	0.17	1.48	0.40	1.38	-0.01	0.98
5	0.49	0.34	1.21	-0.15	0.87	0.36	0.89	-0.13	0.53
6	0.30	0.22	1.32	-0.08	1.10	0.25	0.83	-0.05	0.38
7	11.22	14.81	17.64	3.60	2.83	14.70	17.05	3.48	2.36
8	0.62	0.90	1.24	0.29	0.34	0.88	1.04	0.26	0.16
9	0.48	0.68	1.09	0.20	0.41	0.99	1.06	0.51	0.06
10	2.24	0.99	1.52	-1.25	0.53	2.29	2.28	0.05	0.05
11	0.62	0.59	0.63	-0.02	0.04	0.58	0.60	-0.05	0.04
12	0.52	0.56	0.57	0.03	0.02	0.55	0.55	0.02	0.01
13	0.65	0.65	0.64	-0.01	-0.01	0.63	0.69	-0.03	0.06
14	0.64	0.54	0.54	-0.10	-0.00	0.54	0.51	-0.10	-0.03
15		1.61	2.05		0.44	1.83	1.88		0.15
16		2.30	2.30		0.00	2.25	2.23		-0.03

Chemical Number=4 Chemical Name=Vinyl Chloride

Sample Set	Auto GC (A)	Initial Bag (B1)	Repeat Bag (B2)	B1 -A % Chg	B2 -B1 % Chg	Initial Can (C1)	Repeat Can (C2)	C1 -A % Chg	C2 -C1 % Chg
1	ND	ND	ND	ND	ND	ND	ND	ND	ND
2	ND	ND	ND	ND	ND	ND	ND	ND	ND
3	ND	ND	ND	ND	ND	ND	ND	ND	ND
4	ND	ND	ND	ND	ND	ND	ND	ND	ND
5	ND	ND	ND	ND	ND	ND	ND	ND	ND
6	ND	ND	ND	ND	ND	ND	ND	ND	ND
7	ND	ND	ND	ND	ND	ND	ND	ND	ND
8	ND	ND	ND	ND	ND	ND	ND	ND	ND
9	ND	ND	ND	ND	ND	ND	ND	ND	ND
10	ND	ND	ND	ND	ND	ND	ND	ND	ND
11	ND	ND	ND	ND	ND	ND	ND	ND	ND
12	ND	ND	ND	ND	ND	ND	ND	ND	ND
13	ND	ND	ND	ND	ND	ND	ND	ND	ND
14	ND	ND	ND	ND	ND	ND	ND	ND	ND
15	ND	ND	ND	ND	ND	ND	ND	ND	ND
16	ND	ND	ND	ND	ND	ND	ND	ND	ND

CONCENTRATIONS OF SELECTED COMPOUNDS (PPB) BY SAMPLE SET

----- Chemical Number=8 Chemical Name=1,1-dichloroethane -----

Sample Set	Auto GC (A)	Initial Bag (B1)	Repeat Bag (B2)	B1 -A % Chg	B2 -B1 % Chg	Initial Can (C1)	Repeat Can (C2)	C1 -A % Chg	C2 -C1 % Chg
1	ND	ND	ND	ND	ND	ND	ND	ND	ND
2	ND	ND	ND	ND	ND	ND	ND	ND	ND
3	ND	ND	ND	ND	ND	ND	ND	ND	ND
4	ND	ND	ND	ND	ND	ND	ND	ND	ND
5	ND	ND	ND	ND	ND	ND	ND	ND	ND
6	ND	ND	ND	ND	ND	ND	ND	ND	ND
7	ND	ND	ND	ND	ND	ND	ND	ND	ND
8	ND	ND	ND	ND	ND	ND	ND	ND	ND
9	ND	ND	ND	ND	ND	ND	ND	ND	ND
10	ND	ND	ND	ND	ND	ND	ND	ND	ND
11	ND	ND	ND	ND	ND	ND	ND	ND	ND
12	ND	ND	ND	ND	ND	ND	ND	ND	ND
13	ND	ND	ND	ND	ND	ND	ND	ND	ND
14	ND	ND	ND	ND	ND	ND	ND	ND	ND
15	ND	ND	ND	ND	ND	ND	ND	ND	ND
16	ND	ND	ND	ND	ND	ND	ND	ND	ND

----- Chemical Number=9 Chemical Name=Dichloromethane -----

Sample Set	Auto GC (A)	Initial Bag (B1)	Repeat Bag (B2)	B1 -A % Chg	B2 -B1 % Chg	Initial Can (C1)	Repeat Can (C2)	C1 -A % Chg	C2 -C1 % Chg
1	0.25	0.27	0.70	0.02	0.43	0.24	0.20	-0.00	-0.04
2	0.19	0.30	5.47	55.4	5.17	0.19	0.21	0.00	0.02
3	0.17	0.20	10.95	23.2	10.74	0.14	0.15	-0.02	0.00
4	0.43	0.47	7.36	9.9	6.89	0.47	0.42	0.05	-0.05
5	0.36	0.39	7.52	8.6	7.13	0.50	0.54	0.14	0.05
6	0.23	0.33	5.00	42.2	4.67	0.27	0.23	0.04	-0.04
7	0.92	0.87	7.79	-5.5	6.93	1.27	1.30	0.35	0.03
8	0.19	0.12	0.29	-34.9	0.17	0.19	0.19	3.8	-0.00
9	0.15	0.26	0.59	80.1	0.32	0.68	0.65	351.2	-0.01
10	0.24	0.28	0.81	18.3	0.53	0.30	0.23	27.2	-0.07
11	0.36	0.33	0.38	-8.9	0.05	0.33	0.33	-10.4	0.00
12	0.12	0.20	0.48	60.1	0.28	0.17	0.16	0.05	-0.01
13	0.11	0.26	0.53	134.9	0.27	0.21	0.24	91.1	0.03
14	0.22	0.25	0.64	12.4	0.40	0.31	0.27	41.3	-0.04
15		0.42	0.73		0.31	0.41	0.53		0.12
16		0.62	0.73		0.11	0.63	0.60		-0.02

CONCENTRATIONS OF SELECTED COMPOUNDS (PPB) BY SAMPLE SET

Chemical Number=11 Chemical Name=1,1,2-trichloro-1,2,2-trifluoroethane

Sample Set	Auto GC (A)	Initial Bag (B1)	Repeat Bag (B2)	B1 -A % Chg	B2 -B1 % Chg	Initial Can (C1)	Repeat Can (C2)	C1 -A	C1 -A % Chg	C2 -C1	C2 -C1 % Chg
1	0.20	0.15	0.15	-0.05	-0.00	0.17	0.12	-0.03	-14.6	-0.05	-31.3
2	0.15	0.15	0.14	-0.01	-0.00	0.14	0.14	-0.01	-6.5	-0.00	-1.0
3	0.13	0.12	0.09	-0.01	-0.02	0.05	0.11	-0.08	-62.6	0.06	119.4
4	0.18	0.14	0.15	-0.04	0.00	0.19	0.14	0.01	6.4	-0.05	-24.1
5	0.11	0.09	0.16	-0.02	0.06	1.44	1.48	1.32	1155	0.04	2.6
6	0.11	0.14	0.19	0.03	0.05	0.12	0.12	0.01	8.0	0.00	4.1
7	0.15	0.18	0.16	0.03	-0.01	1.51	1.53	1.37	929.9	0.01	0.8
8	0.14	0.11	0.11	-0.03	0.00	0.38	0.37	0.24	175.5	-0.00	-0.9
9	0.15	0.07	0.15	-0.08	0.09	3.67	3.82	3.52	2391	0.16	4.3
10	0.10	0.16	0.53	0.06	0.37	0.16	0.14	0.06	54.3	-0.02	-14.2
11	0.12	0.12	0.12	-0.00	0.00	2.0	0.14	-0.03	-23.6	0.04	44.9
12	0.12	0.12	0.09	-0.00	-0.03	0.12	0.11	-0.00	-1.3	-0.01	-6.7
13	0.11	0.14	0.13	0.03	-0.02	0.12	0.13	0.01	8.9	0.01	9.2
14	0.09	0.11	0.13	0.02	0.02	15.9	0.34	0.26	283.5	-0.01	-2.1
15		0.11	0.16		0.04	35.5	0.22			0.03	15.4
16		0.11	0.12		0.01	5.2	0.13			0.01	5.8

Chemical Number=14 Chemical Name=Trichloromethane

Sample Set	Auto GC (A)	Initial Bag (B1)	Repeat Bag (B2)	B1 -A % Chg	B2 -B1 % Chg	Initial Can (C1)	Repeat Can (C2)	C1 -A	C1 -A % Chg	C2 -C1	C2 -C1 % Chg
1	0.03	0.01	0.02	-0.02	0.02	0.03	0.03	0.00	11.2	-0.00	-5.3
2	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
3	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
4	0.03	0.02	0.02	-0.02	0.00	0.03	ND	-0.00	-5.7	-0.03	-100
5	ND	ND	0.11	ND	0.11	ND	ND	ND	ND	ND	ND
6	ND	ND	0.11	ND	0.11	ND	ND	ND	ND	ND	ND
7	0.07	0.03	0.07	-0.03	0.03	0.08	0.09	0.01	14.3	0.02	23.4
8	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
9	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
10	ND	ND	0.05	ND	0.05	ND	ND	ND	ND	ND	ND
11	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
12	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
13	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
14	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
15		ND	0.05		0.05	ND	ND	ND	ND	ND	ND
16		0.05	0.05		-0.00	0.02	0.05			0.02	92.0

CONCENTRATIONS OF SELECTED COMPOUNDS (PPB) BY SAMPLE SET

Chemical Number=15 Chemical Name=1,2-dichloroethane

Sample Set	Auto GC (A)	Initial Bag (B1)	Repeat Bag (B2)	B1 - A % Chg	B2 - B1	B2 - B1 % Chg	Initial Can (C1)	Repeat Can (C2)	C1 - A % Chg	C2 - C1	C2 - C1 % Chg
1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2	ND	ND	1.23	ND	1.23	ND	ND	ND	ND	ND	ND
3	ND	ND	1.42	ND	1.42	ND	ND	ND	ND	ND	ND
4	ND	ND	1.17	ND	1.17	ND	ND	ND	ND	ND	ND
5	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
6	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
7	0.07	0.06	0.07	-0.02	0.02	28.2	0.08	0.09	0.9	0.01	16.4
8	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
9	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
10	ND	ND	0.09	ND	0.09	ND	ND	ND	ND	ND	ND
11	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
12	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
13	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
14	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
15	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
16	ND	0.02	0.07	ND	0.05	286.8	0.09	0.01	ND	-0.08	-92.4

Chemical Number=16 Chemical Name=1,1,1-trichloroethane

Sample Set	Auto GC (A)	Initial Bag (B1)	Repeat Bag (B2)	B1 - A % Chg	B2 - B1	B2 - B1 % Chg	Initial Can (C1)	Repeat Can (C2)	C1 - A % Chg	C2 - C1	C2 - C1 % Chg
1	0.34	0.34	0.58	-0.01	0.25	73.0	0.32	0.37	-0.03	0.06	17.5
2	0.33	0.41	8.46	26.3	8.04	1958	0.32	0.36	-0.01	0.04	13.0
3	0.24	0.33	18.31	38.2	17.98	5447	0.25	0.28	0.01	0.03	13.2
4	0.66	0.68	10.13	0.02	9.45	1394	0.60	0.55	-0.07	-0.05	-7.8
5	0.48	0.51	4.76	2.6	4.25	834.0	3.57	3.31	3.09	644.1	-7.2
6	0.39	0.59	4.34	0.21	3.74	629.0	0.45	0.44	0.06	-0.01	-2.9
7	1.09	1.05	0.97	-0.04	-0.08	-7.9	11.12	9.86	10.03	920.7	-11.4
8	0.41	0.43	0.41	0.02	-0.01	-2.8	1.22	1.07	0.81	199.2	-12.2
9	0.41	0.48	0.57	0.08	0.08	16.7	11.01	8.48	10.61	2608	-13.9
10	0.48	0.47	0.88	-0.02	0.41	87.8	0.47	0.38	-0.01	-2.8	-18.2
11	0.42	0.39	0.35	-0.03	-0.04	-10.3	0.42	0.37	0.01	-1.6	-11.8
12	0.40	0.40	0.42	0.00	0.03	6.4	0.20	0.33	-0.20	0.14	70.8
13	0.37	0.34	0.41	-0.03	0.07	20.0	0.36	0.29	-0.01	-3.1	-18.3
14	0.34	0.37	0.44	0.03	0.07	18.0	1.28	1.09	0.94	274.2	-14.8
15	ND	0.43	0.54	ND	0.11	26.3	0.69	0.76	ND	0.07	10.6
16	ND	0.42	0.48	ND	0.06	15.3	0.45	0.44	ND	-0.01	-2.7

CONCENTRATIONS OF SELECTED COMPOUNDS (PPB) BY SAMPLE SET

Sample Set	Auto GC (A)	Initial Bag (B1)	Repeat Bag (B2)	B1 -A		B2 -B1		Initial Can (C1)	Repeat Can (C2)	C1 -A		C2 -C1	
				B1 -A	% Chg	B2 -B1	% Chg			C1 -A	% Chg	C2 -C1	% Chg
1	3.67	3.27	2.85	-0.40	-10.9	-0.42	-12.7	3.41	3.32	-0.25	-6.9	-0.10	-2.8
2	0.89	0.71	0.68	-0.17	-19.6	-0.04	-5.0	0.88	0.81	-0.02	-2.8	-0.05	-5.6
3	0.61	0.54	0.58	-0.07	-11.4	0.04	7.1	0.55	0.51	-0.06	-9.5	-0.04	-7.2
4	4.89	4.35	3.85	-0.54	-11.0	-0.50	-11.5	4.68	4.63	-0.21	-4.2	-0.05	-1.0
5	0.78	0.71	0.81	-0.05	-6.4	0.10	14.0	0.73	0.80	-0.03	-3.9	0.07	9.7
6	0.58	0.50	0.64	-0.08	-13.8	0.14	28.1	0.57	0.58	-0.01	-2.1	0.01	1.7
7	9.48	8.84	7.91	-0.65	-6.8	-0.92	-10.5	9.11	9.38	-0.38	-4.0	0.27	3.0
8		0.56	2.55			1.99	352.0	0.61	0.63			0.02	3.6
9	0.61	0.53	3.08	-0.08	-13.2	2.54	478.0	0.69	0.72	0.08	12.3	0.03	4.0
10	3.50	3.33	28.34	-0.17	-4.9	26.00	779.8	3.56	3.51	0.05	1.4	-0.05	-1.4
11	0.99	0.85	0.83	-0.14	-13.8	-0.02	-2.0	0.92	0.97	-0.07	-7.3	0.06	6.5
12	1.02	0.91	0.88	-0.11	-10.8	-0.04	-3.9	0.96	0.99	-0.06	-5.8	0.03	2.8
13	2.34	2.33	1.98	-0.01	-0.5	-0.35	-15.0	2.28	2.33	-0.08	-2.4	0.05	2.1
14	1.35	1.19	1.17	-0.15	-11.4	-0.03	-2.2	1.28	1.26	-0.09	-6.5	-0.00	-0.1
15		4.23	4.11			-0.12	-2.7	4.42	4.95			0.53	11.9
16		12.44	10.60			-1.84	-14.8	12.65	12.49			-0.16	-1.3

Chemical Number=17 Chemical Name=Benzene

Sample Set	Auto GC (A)	Initial Bag (B1)	Repeat Bag (B2)	B1 -A		B2 -B1		Initial Can (C1)	Repeat Can (C2)	C1 -A		C2 -C1	
				B1 -A	% Chg	B2 -B1	% Chg			C1 -A	% Chg	C2 -C1	% Chg
1	0.14	0.11	0.12	-0.02	-18.0	0.01	6.4	0.14	0.12	0.00	0.4	-0.02	-11.2
2	0.15	0.11	0.10	-0.04	-23.5	-0.01	-9.2	0.13	0.12	-0.02	-15.9	-0.00	-1.2
3	0.13	0.13	0.12	0.00	3.1	-0.01	-8.1	0.13	0.14	-0.00	-2.4	0.01	8.2
4	0.12	0.12	0.12	-0.01	-5.1	0.00	0.2	0.13	0.13	0.00	3.8	-0.00	-0.9
5	0.16	0.12	0.15	-0.03	-20.6	0.03	20.2	0.15	0.14	-0.00	-2.2	-0.01	-7.1
6	0.13	0.10	0.13	-0.03	-24.6	0.03	28.0	0.14	0.13	0.01	7.3	-0.01	-7.8
7	0.14	0.12	0.15	-0.02	-11.1	0.03	23.3	0.14	0.13	0.01	7.0	-0.01	-7.8
8		0.10	0.11			0.01	13.1	0.12	0.12			-0.00	-3.0
9	0.06	0.11	0.11	0.05	83.5	0.00	1.6	0.11	0.12	0.04	72.6	0.01	10.6
10	0.12	0.11	0.12	-0.01	-11.2	0.01	6.3	0.11	0.12	-0.01	-7.8	0.01	8.5
11	0.12	0.11	0.11	-0.00	-1.4	-0.00	-3.7	0.11	0.13	-0.01	-5.9	0.02	17.4
12	0.11	0.11	0.12	-0.00	-1.3	0.00	3.6	0.10	0.14	-0.01	-9.9	0.03	32.7
13	0.12	0.11	0.11	-0.01	-6.8	0.01	5.2	0.12	0.12	0.00	0.3	0.01	4.9
14	0.13	0.12	0.11	-0.01	-7.5	-0.01	-4.6	0.12	0.13	-0.01	-3.9	0.01	5.4
15		0.11	0.11			0.00	4.3	0.12	0.13			0.01	7.7
16		0.12	0.13			0.01	5.4	0.12	0.13			0.01	9.7

Chemical Number=18 Chemical Name=Carbon Tetrachloride

CONCENTRATIONS OF SELECTED COMPOUNDS (PPB) BY SAMPLE SET

Sample Set	Auto GC (A)	Initial Bag (B1)	Repeat Bag (B2)	Chemical Number=20		Chemical Name=Trichloroethene		Initial Can (C1)	Repeat Can (C2)	C1 -A		C2 -C1	
				B1 -A % Chg	B2 -B1 % Chg	B1 -A % Chg	B2 -B1 % Chg			C1 -A % Chg	C2 -C1 % Chg	C1 -A % Chg	C2 -C1 % Chg
1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2	ND	0.37	0.37	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
3	ND	0.51	0.51	ND	0.37	0.51	ND	ND	ND	ND	ND	ND	ND
4	ND	0.39	0.39	ND	0.51	0.39	ND	ND	ND	ND	ND	ND	ND
5	ND	0.10	0.10	ND	0.39	0.10	ND	ND	ND	ND	ND	ND	ND
6	ND	0.12	0.12	ND	0.10	0.12	ND	ND	ND	ND	ND	ND	ND
7	ND	0.08	0.08	ND	0.12	0.08	0.07	0.08	0.07	0.07	0.01	9.4	9.4
8	ND	ND	ND	ND	0.08	ND	ND	ND	ND	ND	ND	ND	ND
9	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
10	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
11	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
12	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
13	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
14	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
15	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
16	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

Sample Set	Auto GC (A)	Initial Bag (B1)	Repeat Bag (B2)	Chemical Number=24		Chemical Name=Toluene		Initial Can (C1)	Repeat Can (C2)	C1 -A		C2 -C1	
				B1 -A % Chg	B2 -B1 % Chg	B1 -A % Chg	B2 -B1 % Chg			C1 -A % Chg	C2 -C1 % Chg	C1 -A % Chg	C2 -C1 % Chg
1	8.70	7.63	7.69	-1.06	0.06	-12.2	0.8	8.33	9.23	-0.36	0.89	-4.2	10.7
2	1.96	1.86	12.49	-0.10	10.63	-5.0	572.3	1.91	1.86	-0.04	-0.05	-2.2	-2.5
3	1.31	1.34	9.92	0.03	8.58	1.9	640.6	1.31	1.11	-0.01	-0.20	-0.6	-15.3
4	13.49	11.95	21.24	-1.54	9.28	-11.4	77.8	13.06	14.40	-0.43	1.34	-3.2	10.2
5	2.04	1.81	44.81	-0.23	43.00	-11.2	2375	2.73	3.23	0.69	0.50	34.0	18.4
6	1.21	1.18	37.71	-0.03	36.54	-2.5	3108	1.13	1.22	-0.07	0.08	-6.1	7.2
7	25.30	23.00	21.75	-2.30	-1.26	-9.1	-5.5	28.10	32.80	2.80	4.70	11.1	16.7
8	1.08	1.07	6.30	-0.01	5.24	-1.2	491.4	1.25	1.51	0.17	0.26	15.7	20.8
9	1.13	1.22	7.01	0.09	5.79	7.7	473.8	4.08	4.79	2.95	0.71	260.0	17.3
10	9.66	8.81	84.66	-0.85	75.84	-8.8	860.5	9.71	9.80	0.05	0.08	0.5	0.9
11	2.08	1.78	1.81	-0.29	0.03	-14.2	1.8	2.02	2.15	-0.05	0.12	-2.5	6.2
12	1.99	1.85	2.37	-0.14	0.52	-7.1	28.2	1.92	2.07	-0.07	0.15	-3.5	7.6
13	5.91	5.34	4.92	-0.58	-0.42	-9.8	-7.8	5.65	5.86	-0.27	0.21	-4.5	3.7
14	2.81	2.55	3.09	-0.06	0.54	-2.2	21.3	2.92	2.98	0.32	0.04	12.1	1.4
15	11.61	10.80	10.80	-0.80	-8.9	-7.00	-8.9	13.01	14.80	1.79	1.79	13.7	13.7
16	33.50	26.50	26.50	-7.00	-20.9	-20.9	-20.9	35.42	35.70	0.27	0.27	0.8	0.8

CONCENTRATIONS OF SELECTED COMPOUNDS (PPB) BY SAMPLE SET

Chemical Number=25 Chemical Name=1,2-dibromoethane

Sample Set	Auto GC (A)	Initial Bag (B1)	Repeat Bag (B2)	B1 -A % Chg	B2 -B1 % Chg	Initial Can (C1)	Repeat Can (C2)	C1 -A % Chg	C2 -C1 % Chg
1	ND	ND	ND	ND	ND	ND	ND	ND	ND
2	ND	ND	ND	ND	ND	ND	ND	ND	ND
3	ND	ND	ND	ND	ND	ND	ND	ND	ND
4	ND	ND	ND	ND	ND	ND	ND	ND	ND
5	ND	ND	ND	ND	ND	ND	ND	ND	ND
6	ND	ND	ND	ND	ND	ND	ND	ND	ND
7	ND	ND	ND	ND	ND	ND	ND	ND	ND
8	ND	ND	ND	ND	ND	ND	ND	ND	ND
9	ND	ND	ND	ND	ND	ND	ND	ND	ND
10	ND	ND	ND	ND	ND	ND	ND	ND	ND
11	ND	ND	ND	ND	ND	ND	ND	ND	ND
12	ND	ND	ND	ND	ND	ND	ND	ND	ND
13	ND	ND	ND	ND	ND	ND	ND	ND	ND
14	ND	ND	ND	ND	ND	ND	ND	ND	ND
15	ND	ND	ND	ND	ND	ND	ND	ND	ND
16	ND	ND	ND	ND	ND	ND	ND	ND	ND

Chemical Number=26 Chemical Name=Tetrachloroethene

Sample Set	Auto GC (A)	Initial Bag (B1)	Repeat Bag (B2)	B1 -A % Chg	B2 -B1 % Chg	Initial Can (C1)	Repeat Can (C2)	C1 -A % Chg	C2 -C1 % Chg
1	0.08	0.06	0.08	-23.4	0.02	0.07	0.07	-0.01	-6.1
2	0.09	0.08	0.24	-10.1	0.16	0.09	0.10	0.00	10.3
3	0.05	0.05	0.16	-12.6	0.12	0.05	0.08	-0.01	27.7
4	0.13	0.11	0.27	-14.0	0.16	0.13	0.12	0.00	-4.6
5	0.19	0.17	0.50	-10.3	0.33	0.21	0.22	0.03	3.4
6	0.12	0.09	0.35	-22.5	0.26	0.11	0.13	-0.01	20.4
7	0.25	0.21	0.23	-16.1	0.02	0.28	0.27	0.03	-4.8
8	0.06	0.05	0.08	-11.8	0.01	0.07	0.08	0.01	16.5
9	0.08	0.07	0.19	-5.0	0.02	0.12	0.11	0.06	-6.3
10	0.08	0.11	0.11	77.8	-0.00	0.08	0.08	0.00	2.5
11	0.13	0.11	0.11	-12.7	-0.01	0.12	0.13	0.05	23.0
12	0.05	0.07	0.07	10.7	0.02	0.07	0.07	-0.01	5.9
13	0.05	0.07	0.06	24.4	-0.01	0.07	0.07	0.01	11.4
14	0.05	0.15	0.15	0.01	0.00	0.17	0.19	0.01	13.8
15	0.05	0.09	0.09	0.00	0.00	0.10	0.10	0.02	11.1
16	0.09	0.09	0.10	2.1	0.00	0.10	0.10	-0.00	-2.5

CONCENTRATIONS OF SELECTED COMPOUNDS (PPB) BY SAMPLE SET

----- Chemical Number=29 Chemical Name=m+p-xylylene -----

Sample Set	Auto GC (A)	Initial Bag (B1)	Repeat Bag (B2)	B1 -A % Chg	B2 -B1	B1 -A % Chg	B2 -B1 % Chg	Initial Can (C1)	Repeat Can (C2)	C1 -A % Chg	C2 -C1	C1 -A % Chg	C2 -C1 % Chg
1	5.94	4.92	3.69	-1.02	-1.23	-17.1	-24.9	5.84	5.68	-0.10	-0.16	-1.7	-2.8
2	0.88	0.90	2.17	0.02	1.27	2.4	140.9	0.86	0.87	-0.02	0.02	-2.6	1.8
3	0.67	0.66	1.35	-0.01	0.69	-1.8	105.0	0.70	0.83	0.03	-0.07	4.1	-9.3
4	8.36	6.90	6.68	-1.46	-0.22	-17.5	-3.2	8.09	8.82	-0.27	0.73	-3.2	9.1
5	0.89	0.87	2.40	-0.02	1.53	-2.3	175.2	1.11	1.24	0.21	0.14	23.9	12.6
6	0.58	0.61	1.83	0.04	1.22	6.2	198.2	0.56	0.58	-0.02	0.03	-4.1	4.6
7	16.37	14.04	10.49	-2.32	-3.55	-14.2	-25.3	16.15	19.35	-0.22	3.20	-1.3	19.8
8	0.61	0.53	2.68	-0.07	2.15	-12.0	402.3	0.77	0.96	0.17	0.19	27.5	24.3
9	0.62	0.61	3.08	-0.00	2.46	-0.4	400.9	1.18	1.42	0.56	0.24	91.3	20.0
10	6.71	5.68	50.76	-1.03	45.08	-15.4	794.1	6.74	7.04	0.03	0.31	0.4	4.6
11	1.06	0.85	0.72	-0.21	-0.13	-19.8	-15.5	1.06	1.26	0.00	0.20	0.0	18.7
12	0.98	0.85	1.08	-0.13	0.23	-13.6	27.3	0.96	1.03	-0.03	0.08	-2.6	8.3
13	3.62	3.13	2.68	-0.50	-0.44	-13.8	-14.1	3.56	3.72	-0.07	0.16	-1.9	4.5
14	1.58	1.46	1.65	-0.12	0.19	-7.6	-13.1	1.61	1.73	0.03	0.12	2.2	7.6
15		7.46	6.12		-1.34	-18.0	-32.3	8.70	9.61		0.91		10.5
16		22.37	15.14		-7.23			24.09	24.94		0.85		3.5

----- Chemical Number=30 Chemical Name=Styrene -----

Sample Set	Auto GC (A)	Initial Bag (B1)	Repeat Bag (B2)	B1 -A % Chg	B2 -B1	B1 -A % Chg	B2 -B1 % Chg	Initial Can (C1)	Repeat Can (C2)	C1 -A % Chg	C2 -C1	C1 -A % Chg	C2 -C1 % Chg
1	0.27	0.20	0.16	-0.08	-0.03	-28.1	-17.7	0.24	0.17	-0.04	-0.07	-13.0	-27.9
2	0.11	0.16	0.66	0.04	0.50	38.2	318.8	0.12	ND	0.00	-0.12	2.1	-100
3	0.10	0.11	0.48	0.02	0.36	19.0	318.5	0.09	ND	-0.01	-0.09	-7.0	-100
4	0.39	0.33	0.80	-0.07	0.48	-17.4	147.0	0.38	0.33	-0.01	-0.05	-3.4	-12.1
5	0.07	0.10	0.53	0.03	0.43	50.2	432.8	0.08	0.04	0.01	-0.04	15.6	-47.4
6	0.05	0.10	0.55	0.04	0.45	80.1	460.3	0.06	ND	0.01	-0.06	18.7	-100
7	4.06	2.93	1.16	-1.13	-1.77	-27.8	-60.3	3.67	3.93	-0.38	0.26	-9.4	7.0
8	0.08	0.10	0.13	0.01	0.04	16.6	40.4	0.08	0.07	-0.00	-0.01	-1.1	-18.2
9	0.10	0.12	0.15	0.01	0.03	12.2	27.5	0.13	0.13	0.03	-0.00	26.9	-2.5
10	0.73	0.51	0.33	-0.22	-0.19	-30.0	-36.3	0.65	0.66	-0.08	0.01	-10.6	1.7
11	0.04	0.07	0.09	0.03	0.01	91.4	17.1	0.09	0.10	0.05	0.02	125.1	22.0
12	0.07	0.09	0.12	0.02	0.03	23.6	34.4	0.08	0.06	0.00	-0.01	6.1	-18.9
13	0.17	0.15	0.15	-0.02	-0.00	-12.4	-0.1	0.13	0.13	-0.03	-0.00	-19.7	-1.2
14	0.08	0.09	0.15	0.01	0.06	16.6	68.8	0.10	0.09	0.02	-0.01	28.9	-7.3
15		0.23	0.20		-0.03		-13.5	0.24	0.26		0.01		5.4
16		0.61	0.35		-0.26		-42.8	0.67	0.77		0.10		14.7

CONCENTRATIONS OF SELECTED COMPOUNDS (PPB) BY SAMPLE SET

Sample Set	Auto GC (A)	Initial Bag (B1)	Repeat Bag (B2)	Chemical Number=32			Chemical Name=o-xylene					
				B1 -A % Chg	B2 -B1 % Chg	B2 -B1 % Chg	Initial Can (C1)	Repeat Can (C2)	C1 -A % Chg			
1	2.15	1.79	1.18	-0.36	-0.61	-33.9	2.15	1.92	-0.01	-0.3	-0.23	-10.7
2	0.33	0.33	0.68	-0.00	0.33	99.1	0.35	0.34	0.02	4.5	-0.01	-2.0
3	0.22	0.23	0.43	0.00	0.21	91.2	0.25	0.24	0.03	12.6	-0.02	-5.8
4	3.02	2.47	2.15	-0.55	-0.32	-12.8	2.91	2.99	-0.11	-3.5	0.07	2.5
5	0.34	0.33	0.82	-0.01	0.48	147.1	0.45	0.47	0.11	32.2	0.02	4.8
6	0.23	0.24	0.85	0.01	0.41	172.8	0.22	0.21	-0.01	-6.0	-0.00	-0.8
7	6.25	5.35	3.34	-0.89	-2.01	-37.5	6.12	6.56	-0.12	-2.0	0.44	7.2
8	0.23	0.21	0.85	-0.01	0.64	299.5	0.32	0.36	0.10	42.0	0.04	12.1
9	0.23	0.24	1.00	0.00	0.76	312.5	0.43	0.48	0.19	77.9	0.06	13.0
10	2.31	1.94	17.42	-0.37	15.48	798.1	2.34	2.42	0.03	1.4	0.07	3.0
11	0.40	0.32	0.28	-0.08	-0.07	-20.7	0.42	0.47	0.02	3.9	0.06	13.3
12	0.38	0.31	0.33	-0.06	0.03	8.3	0.37	0.41	0.01	2.3	0.04	9.4
13	1.23	1.07	0.86	-0.17	-0.21	-19.6	1.20	1.25	-0.03	-2.5	0.05	3.9
14	0.55	0.51	0.56	-0.04	0.05	9.9	0.57	0.63	0.03	5.2	0.05	9.1
15		2.53	1.90		-0.63	-24.9	2.99	3.22			0.23	7.5
16		7.37	4.96		-2.41	-32.7	8.04	8.45			0.41	5.1

Chemical Number=37 Chemical Name=m-dichlorobenzene

Sample Set	Auto GC (A)	Initial Bag (B1)	Repeat Bag (B2)	Chemical Number=37			Chemical Name=m-dichlorobenzene					
				B1 -A % Chg	B2 -B1 % Chg	B2 -B1 % Chg	Initial Can (C1)	Repeat Can (C2)	C1 -A % Chg			
1	ND	0.03	0.06	0.03	0.03	92.0	0.03	0.04	0.03	-100	0.00	14.5
2	0.01	ND	ND	-0.01	ND	ND	ND	ND	-0.01	ND	ND	ND
3	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
4	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
5	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
6	ND	ND	0.04	ND	0.04		ND	ND	ND	ND	ND	ND
7	ND	ND	0.04	ND	0.04		ND	ND	ND	ND	ND	ND
8	ND	ND	ND	ND	ND		ND	ND	ND	ND	ND	ND
9	ND	ND	ND	ND	ND		ND	ND	ND	ND	ND	ND
10	ND	ND	ND	ND	ND		ND	ND	ND	ND	ND	ND
11	ND	ND	ND	ND	ND		ND	ND	ND	ND	ND	ND
12	ND	ND	ND	ND	ND		ND	ND	ND	ND	ND	ND
13	ND	ND	ND	ND	ND		ND	ND	ND	ND	ND	ND
14	ND	ND	ND	ND	ND		ND	ND	ND	ND	ND	ND
15		ND	ND		ND		ND	ND			ND	ND
16		ND	ND		ND		ND	ND			ND	ND

CONCENTRATIONS OF SELECTED COMPOUNDS (PPB) BY SAMPLE SET

Sample Set	Auto GC (A)	Initial Bag (B1)	Repeat Bag (B2)	Chemical Number=38			Chemical Name=p-dichlorobenzene				
				B1 - A % Chg	B2 - B1 % Chg	Initial Can (C1)	Repeat Can (C2)	C1 - A % Chg	C2 - C1 % Chg		
1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2	ND	0.05	0.09	0.05	0.04	84.9	0.02	ND	ND	ND	ND
3	ND	0.02	0.07	0.02	0.04	210.2	ND	ND	ND	ND	-100
4	0.11	0.07	0.12	-0.03	0.05	68.6	0.10	0.08	ND	ND	-15.1
5	ND	0.05	0.09	0.05	0.05	98.7	ND	ND	ND	ND	ND
6	ND	0.03	0.13	0.03	0.09	283.9	ND	ND	ND	ND	ND
7	0.19	0.12	0.12	-0.06	-0.01	-4.2	0.19	0.21	0.00	0.3	12.6
8	ND	0.04	0.07	0.04	0.03	67.3	ND	ND	ND	ND	ND
9	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
10	0.06	0.05	0.12	-0.00	0.07	128.2	0.05	0.07	-0.00	-4.0	28.4
11	ND	0.04	0.04	0.04	0.00	13.4	ND	ND	ND	ND	ND
12	ND	0.03	0.07	0.03	0.03	106.2	ND	ND	ND	ND	ND
13	0.05	0.05	0.06	-0.00	0.00	5.0	0.05	0.07	-0.00	-1.0	30.1
14	ND	0.04	0.07	0.04	0.03	76.3	ND	ND	ND	ND	ND
15	.	0.02	0.12	.	0.10	522.0	0.27	0.29	.	.	4.2
16	.	0.20	0.09	.	-0.11	-53.5	0.23	0.26	.	.	9.8

CONCENTRATIONS OF SELECTED COMPOUNDS (PPB) BY SAMPLE SET

Sample Set	Auto GC (A)	Initial Bag (B1)	Repeat Bag (B2)	Chemical Number=39			Chemical Name=o-dichlorobenzene				
				B1 - A % Chg	B2 - B1 % Chg	Initial Can (C1)	Repeat Can (C2)	C1 - A % Chg	C2 - C1 % Chg		
1	0.02	ND	ND	-0.02	ND	ND	ND	ND	-0.02	-100	ND
2	ND	0.01	ND	0.01	-0.01	-100	ND	ND	ND	ND	ND
3	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
4	0.02	ND	0.04	-0.02	0.04	ND	ND	ND	-0.02	-100	ND
5	ND	0.03	ND	0.03	-0.03	-100	ND	ND	ND	ND	ND
6	ND	ND	0.05	ND	0.05	.	ND	ND	ND	ND	ND
7	0.02	ND	0.05	-0.02	0.05	.	ND	ND	-0.02	-100	ND
8	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
9	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
10	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
11	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
12	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
13	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
14	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
15	.	0.03	ND	.	-0.03	-100	ND	ND	.	.	ND
16	.	ND	ND	.	ND	ND	ND	ND	.	.	ND



APPENDIX I-B

PLOTS OF INITIAL CONCENTRATIONS VERSUS  
COLLECTION DATE BY COLLECTION METHOD



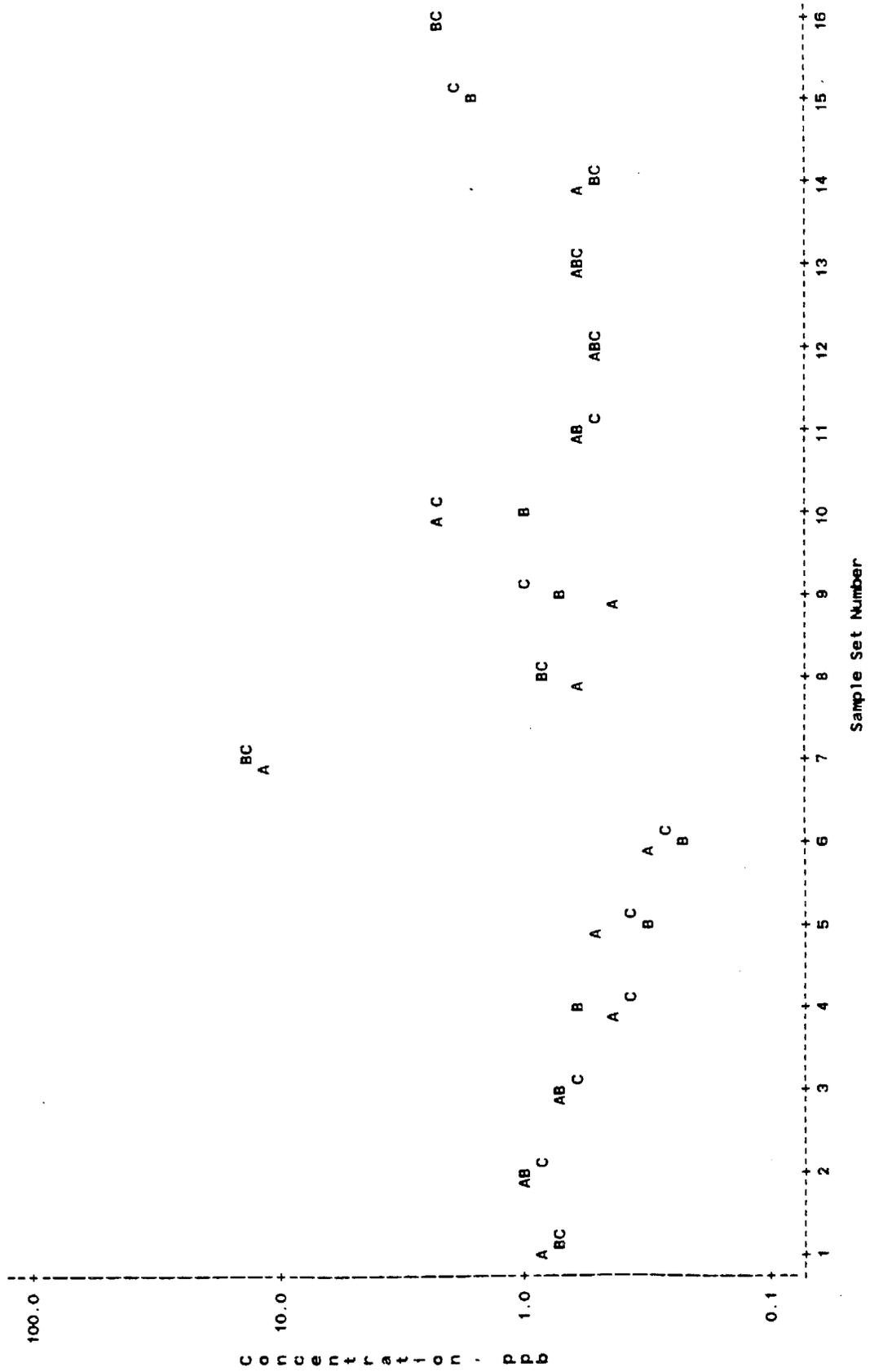
APPENDIX I-B

PLOTS OF INITIAL CONCENTRATIONS VERSUS  
COLLECTION DATE BY COLLECTION METHOD

- A = Air sample analyzed directly by automated GC
- B = Initial analysis of the bag sample
- C = Initial analysis of the canister sample

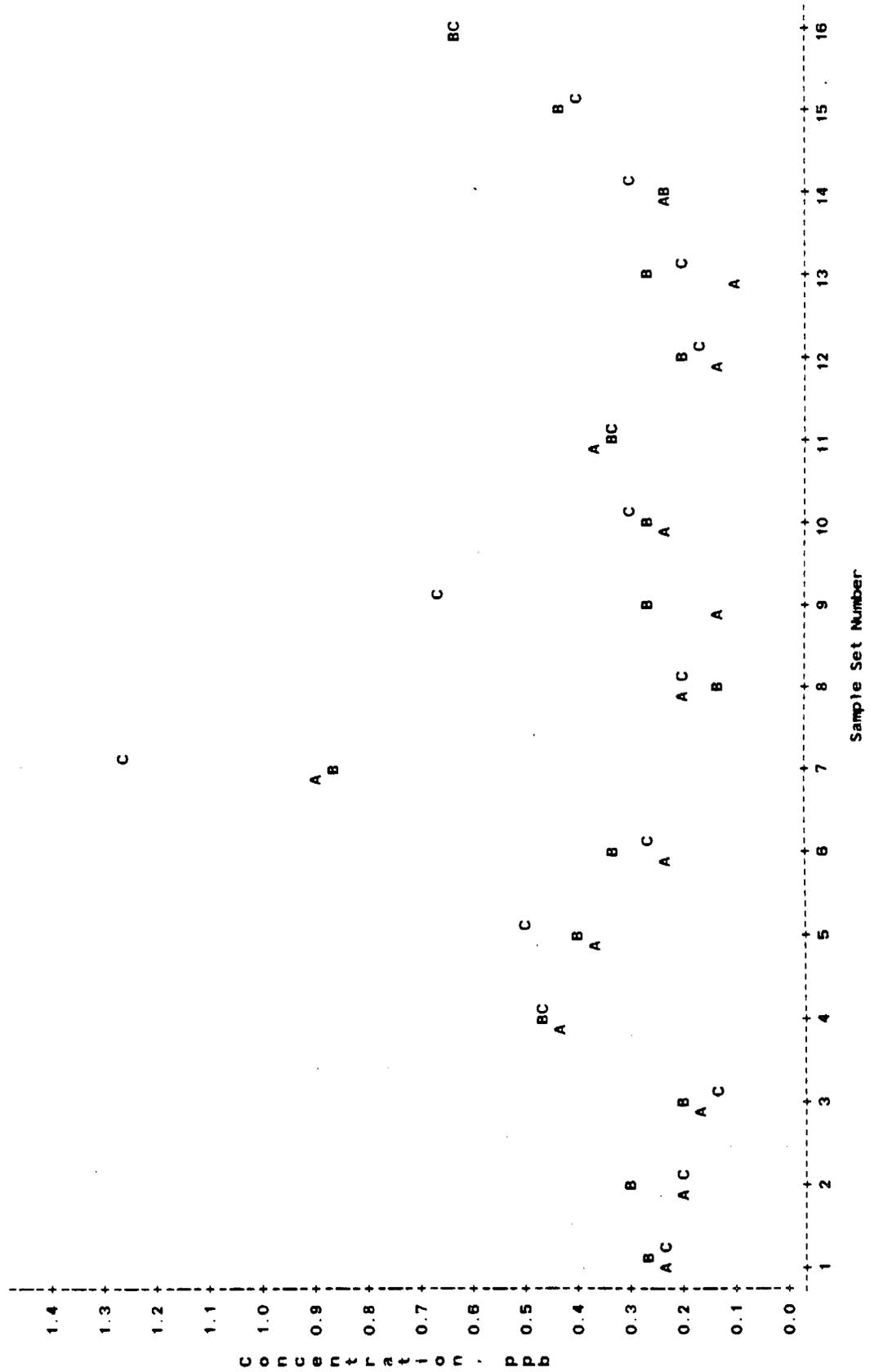
PLOTS OF CONCENTRATIONS FOR AUTO-GC (A), INITIAL BAG (B),  
AND INITIAL CAN (C) SAMPLES VERSUS SAMPLE SET NUMBER

Chemical Name = Dichlorodifluoromethane



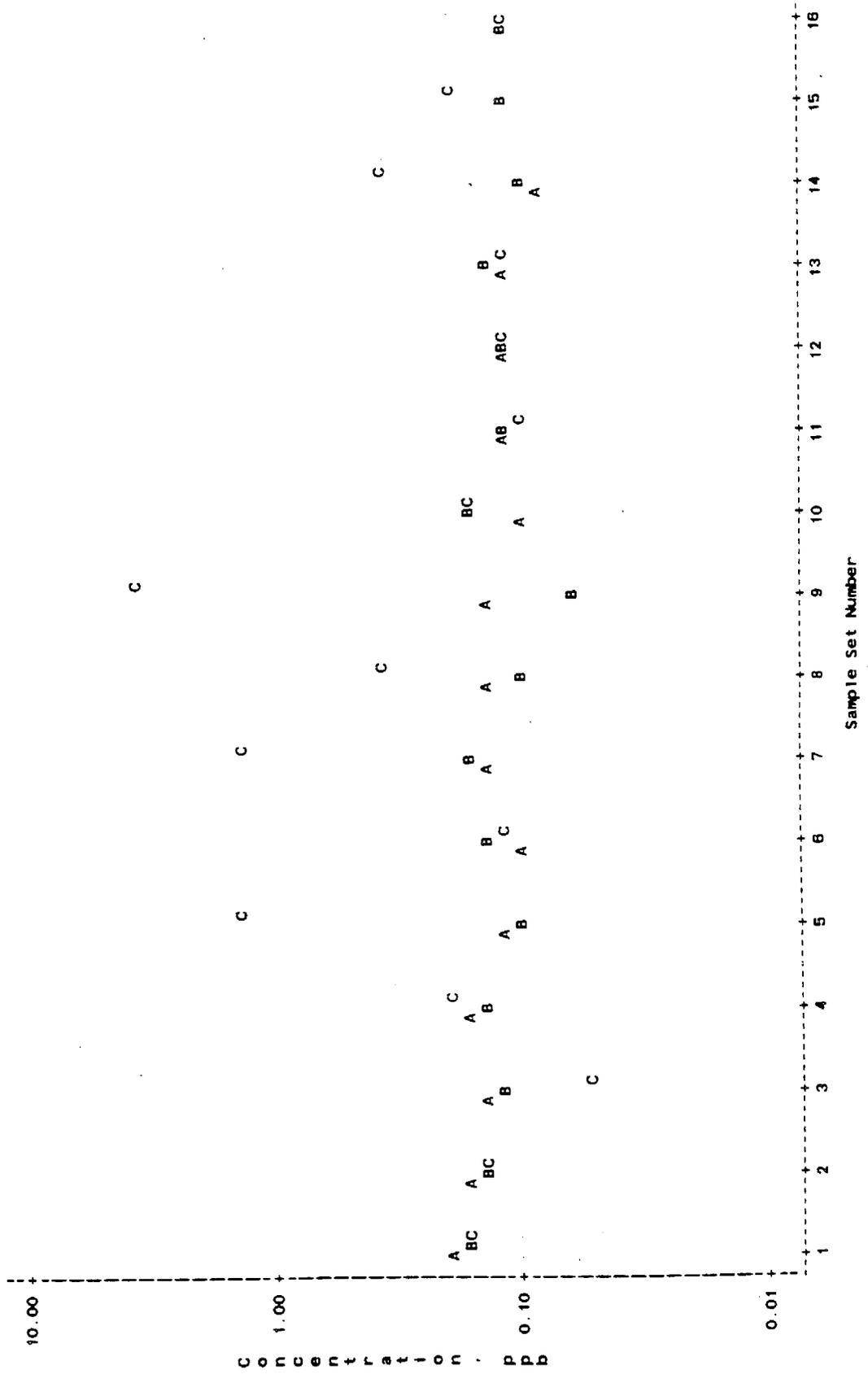
PLOTS OF CONCENTRATIONS FOR AUTO-GC (A), INITIAL BAG (B),  
AND INITIAL CAN (C) SAMPLES VERSUS SAMPLE SET NUMBER

Chemical Name = Dichloromethane



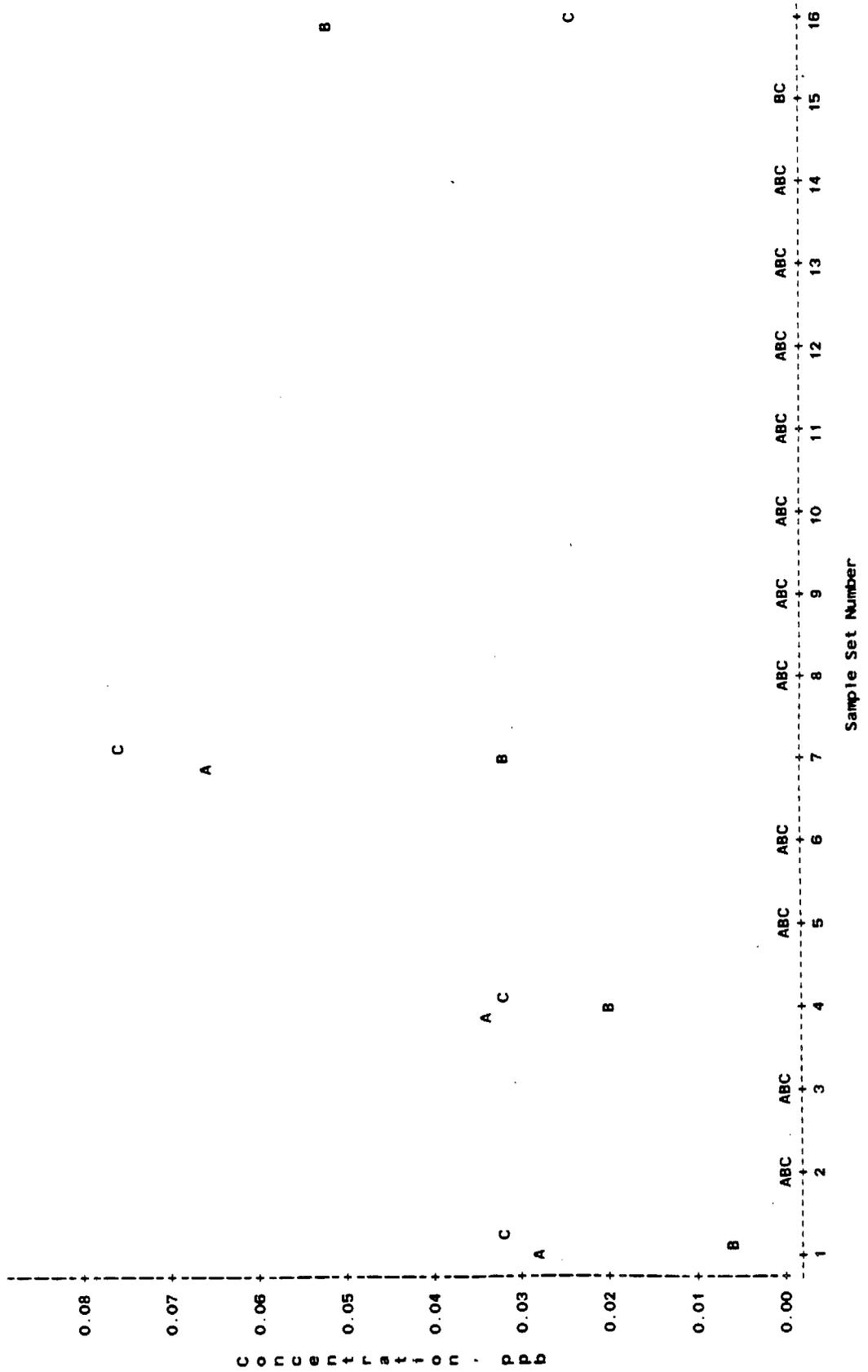
PLOTS OF CONCENTRATIONS FOR AUTO-GC (A), INITIAL BAG (B),  
AND INITIAL CAN (C) SAMPLES VERSUS SAMPLE SET NUMBER

Chemical Name = 1,1,2-trichloro-1,2,2-trifluoroethane



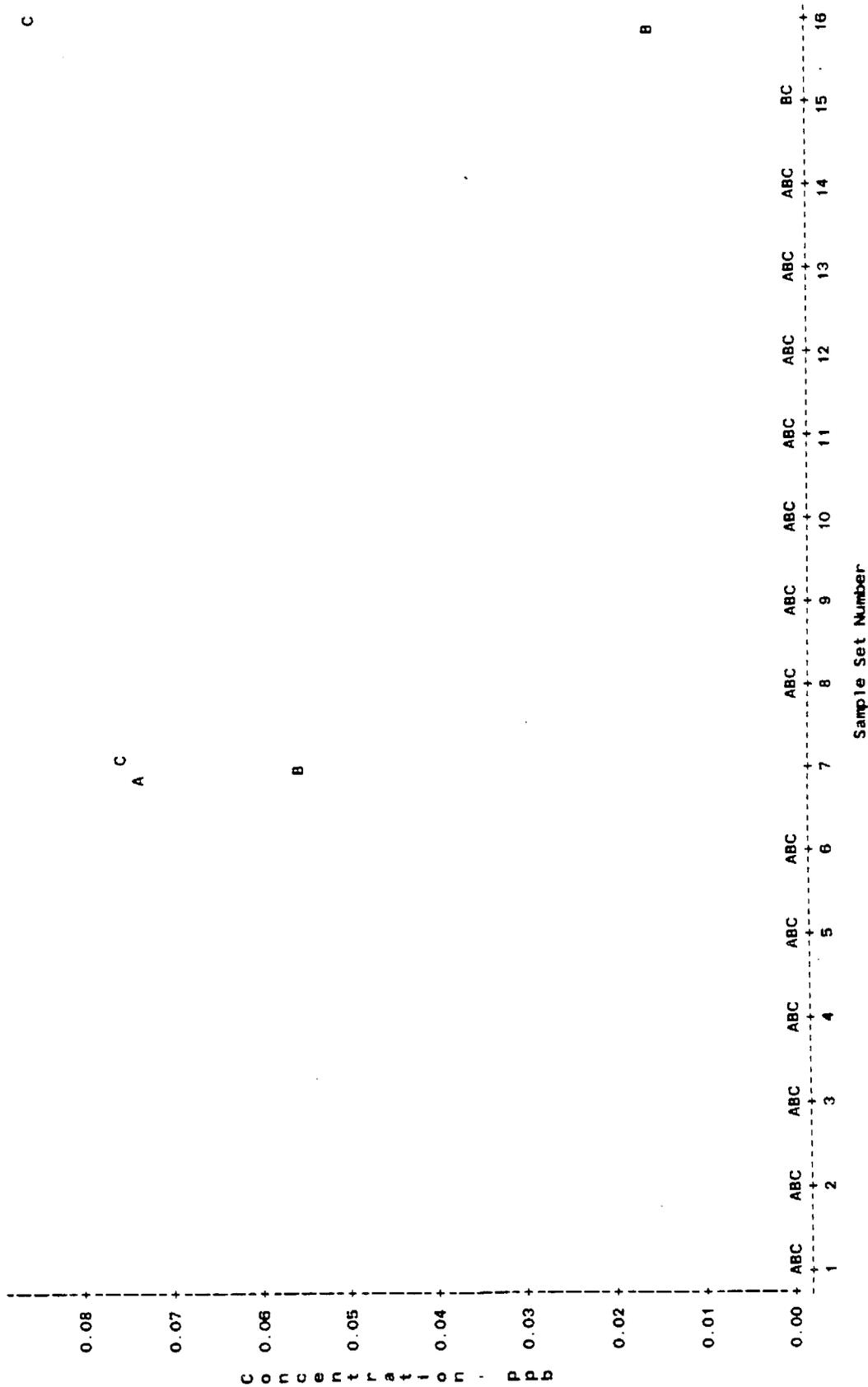
PLOTS OF CONCENTRATIONS FOR AUTO-GC (A), INITIAL BAG (B),  
AND INITIAL CAN (C) SAMPLES VERSUS SAMPLE SET NUMBER

Chemical Name = Trichloromethane



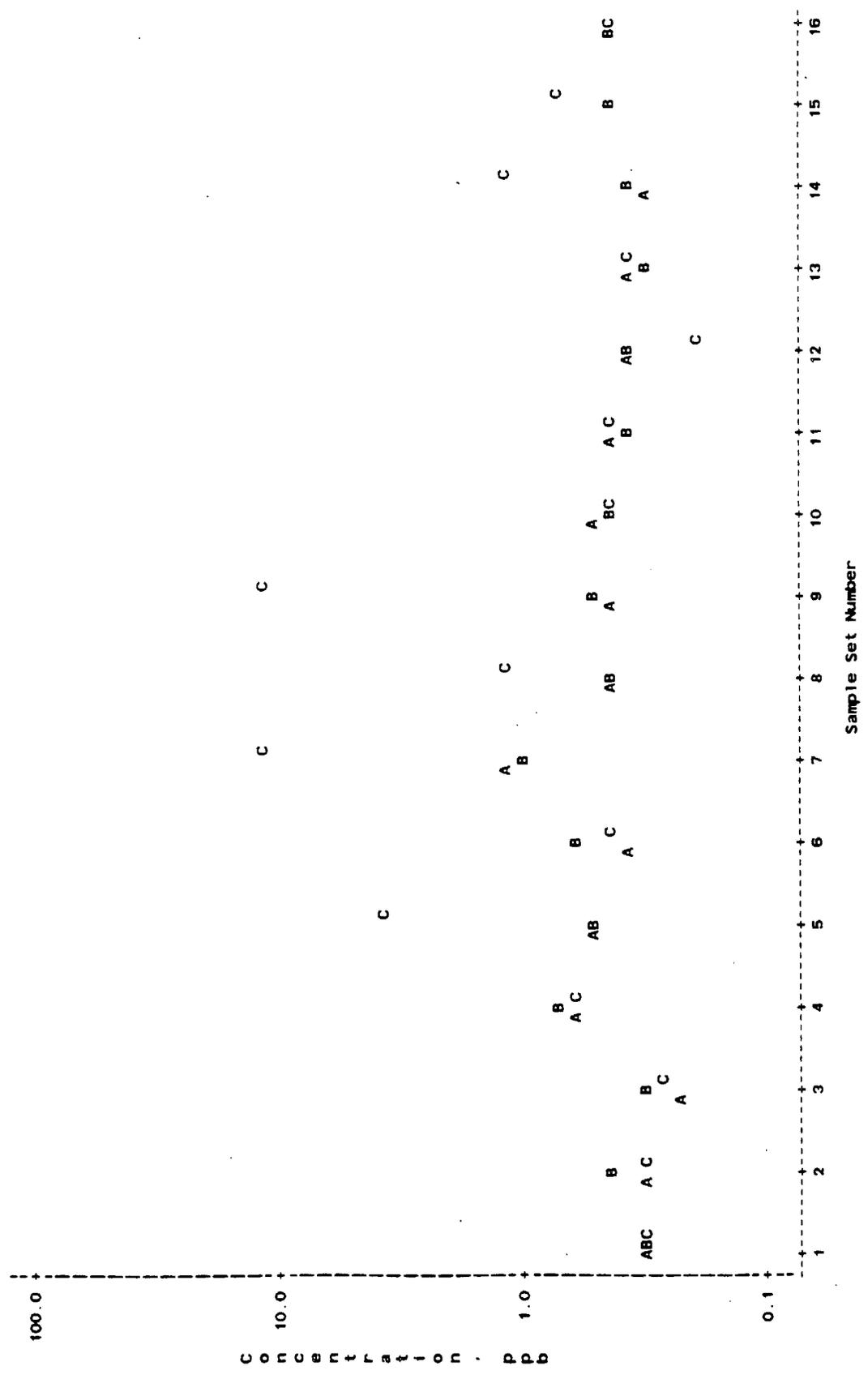
PLOTS OF CONCENTRATIONS FOR AUTO-GC (A), INITIAL BAG (B),  
AND INITIAL CAN (C) SAMPLES VERSUS SAMPLE SET NUMBER

Chemical Name = 1,2-dichloroethane



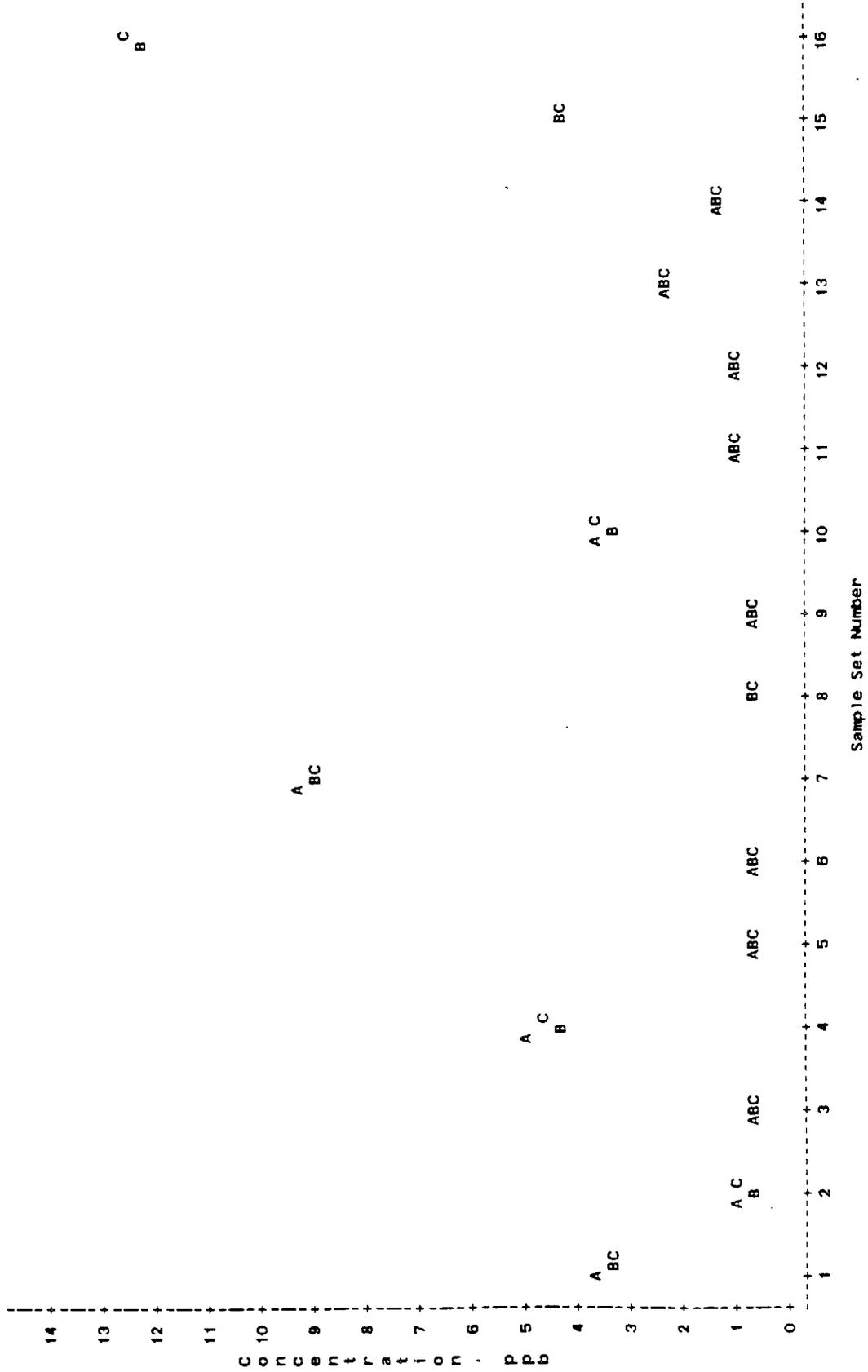
PLOTS OF CONCENTRATIONS FOR AUTO-GC (A), INITIAL BAG (B),  
AND INITIAL CAN (C) SAMPLES VERSUS SAMPLE SET NUMBER

Chemical Name = 1,1,1-trichloroethane



PLOTS OF CONCENTRATIONS FOR AUTO-GC (A), INITIAL BAG (B),  
AND INITIAL CAN (C) SAMPLES VERSUS SAMPLE SET NUMBER

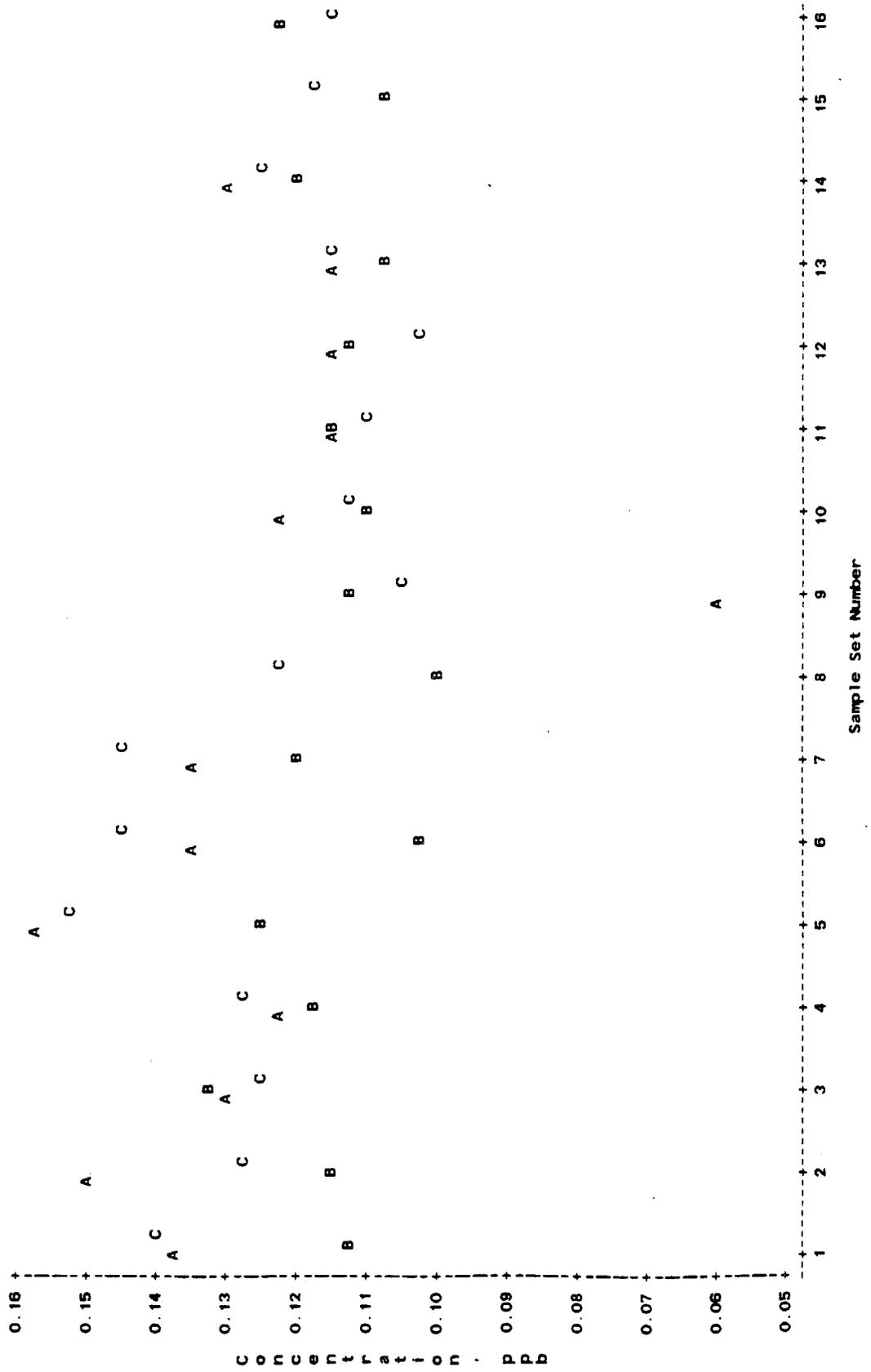
Chemical Name = Benzene



NOTE: 1 OBS HAD MISSING VALUES OR WERE OUT OF RANGE

PLOTS OF CONCENTRATIONS FOR AUTO-GC (A), INITIAL BAG (B),  
AND INITIAL CAN (C) SAMPLES VERSUS SAMPLE SET NUMBER

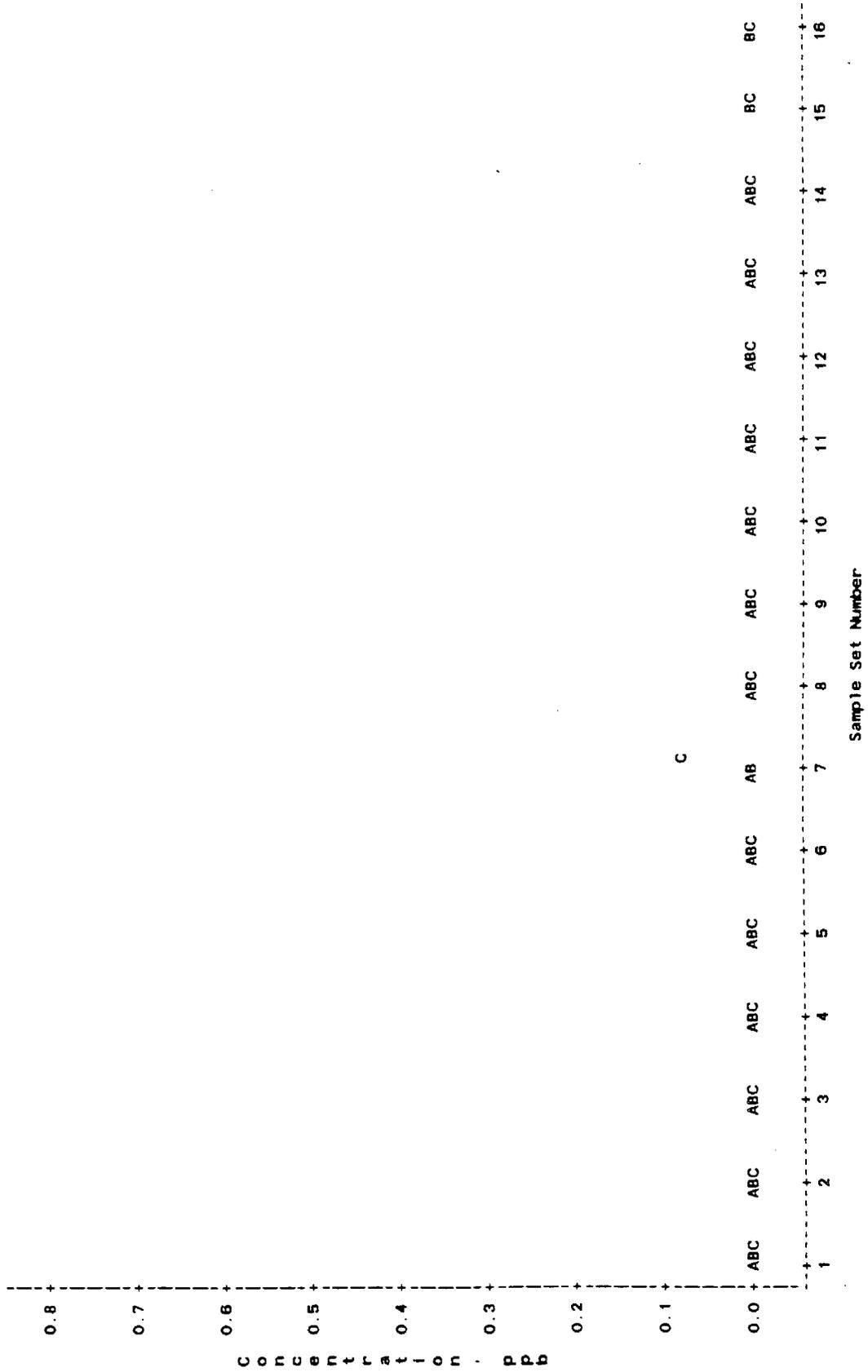
Chemical Name = Carbon Tetrachloride



NOTE: 1 OBS HAD MISSING VALUES OR WERE OUT OF RANGE

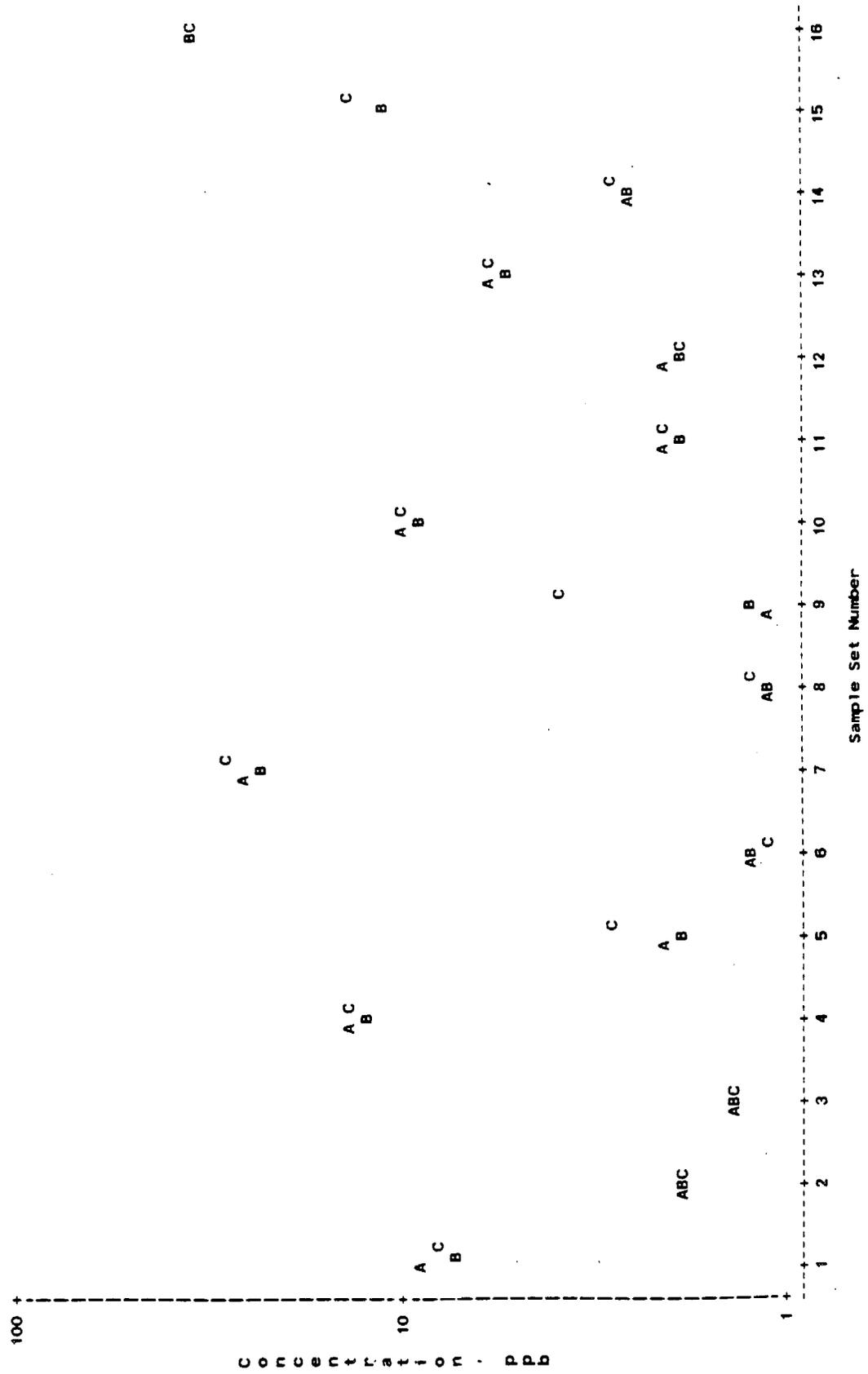
PLOTS OF CONCENTRATIONS FOR AUTO-GC (A), INITIAL BAG (B),  
AND INITIAL CAN (C) SAMPLES VERSUS SAMPLE SET NUMBER

Chemical Name = Trichloroethene



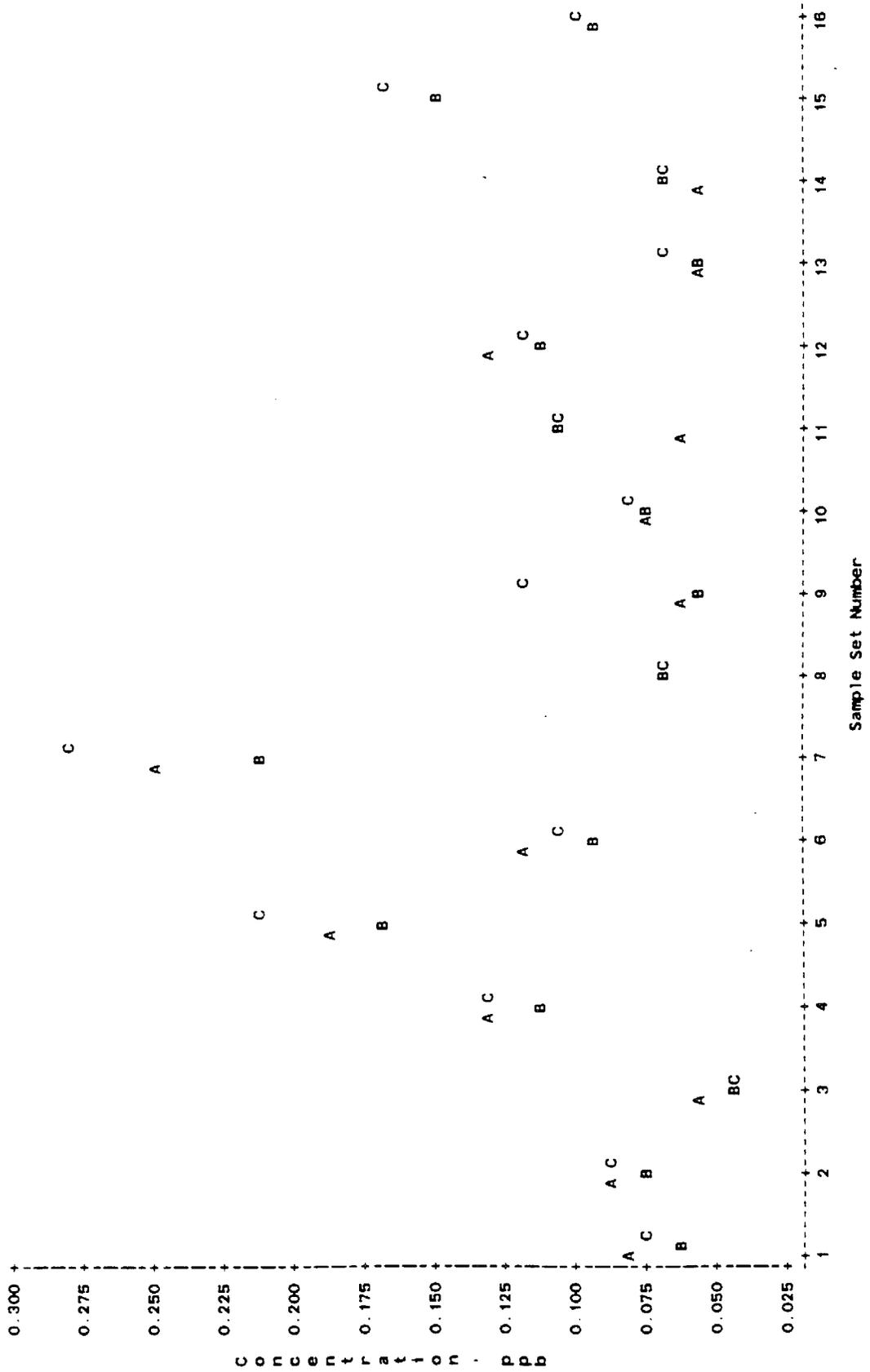
PLOTS OF CONCENTRATIONS FOR AUTO-GC (A), INITIAL BAG (B),  
AND INITIAL CAN (C) SAMPLES VERSUS SAMPLE SET NUMBER

Chemical Name = Toluene



PLOTS OF CONCENTRATIONS FOR AUTO-GC (A), INITIAL BAG (B),  
AND INITIAL CAN (C) SAMPLES VERSUS SAMPLE SET NUMBER

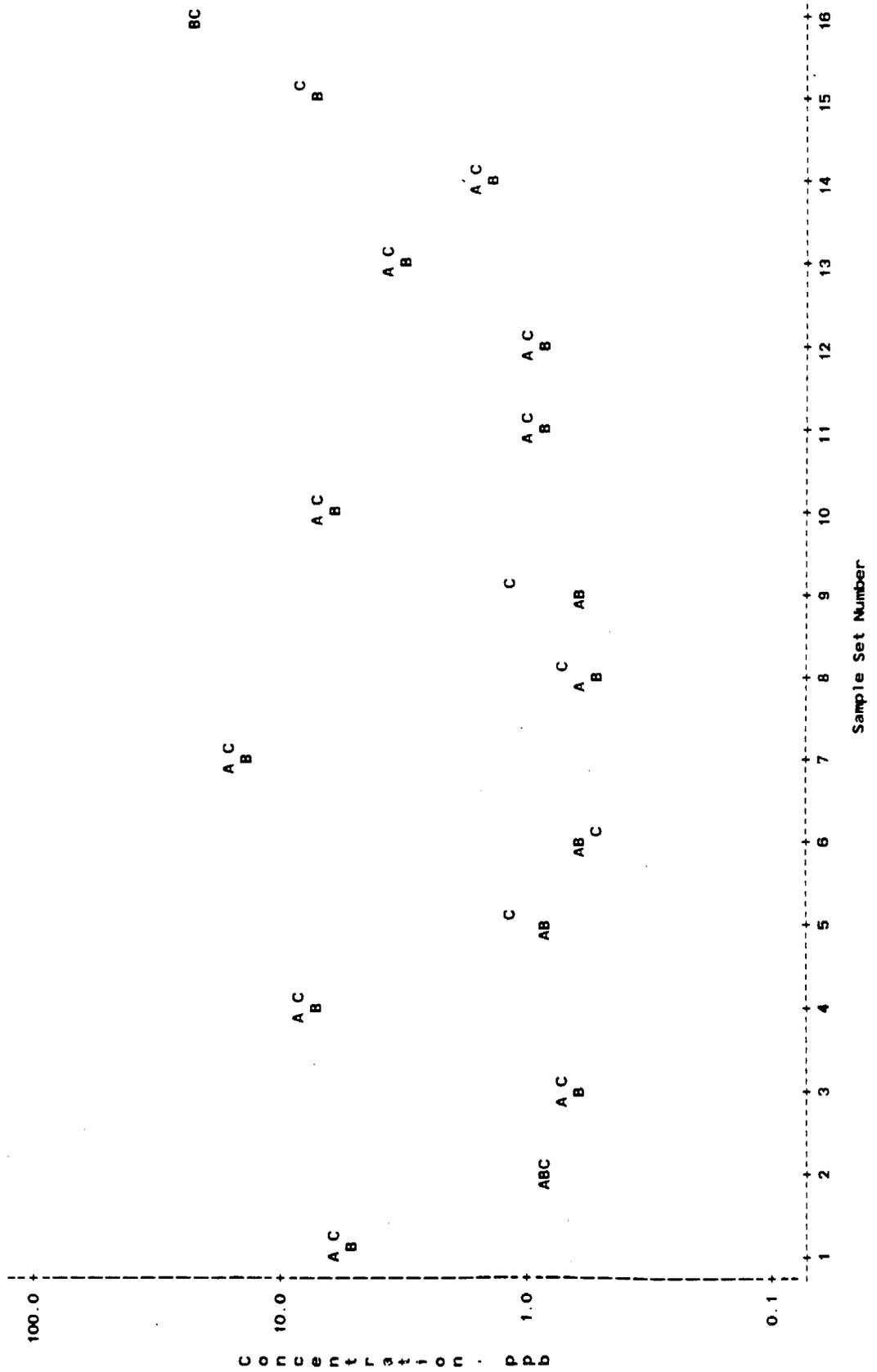
Chemical Name = Tetrachloroethene



NOTE: 1 OBS HAD MISSING VALUES OR WERE OUT OF RANGE

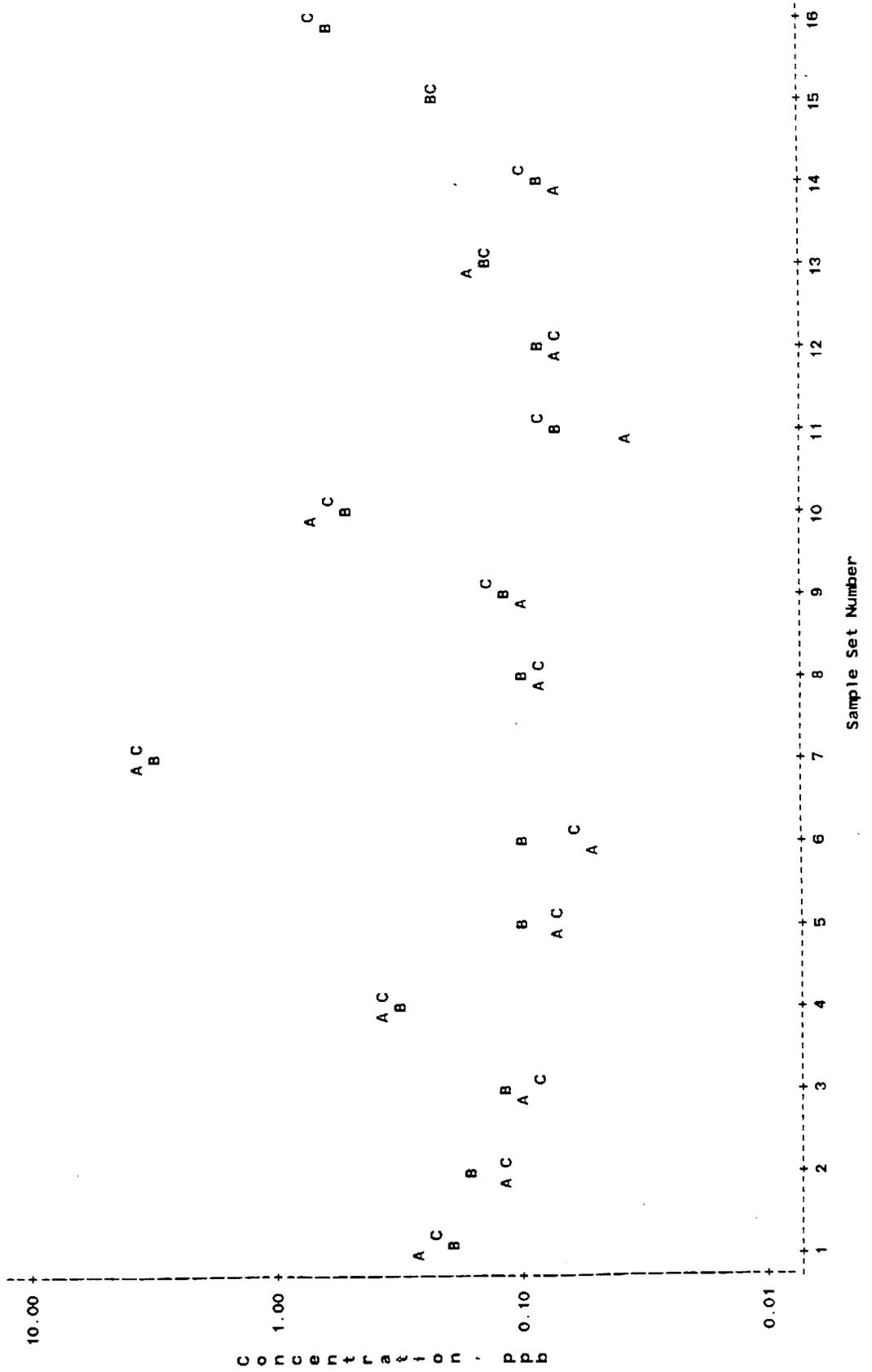
PLOTS OF CONCENTRATIONS FOR AUTO-GC (A), INITIAL BAG (B),  
AND INITIAL CAN (C) SAMPLES VERSUS SAMPLE SET NUMBER

Chemical Name = m:p-xylene



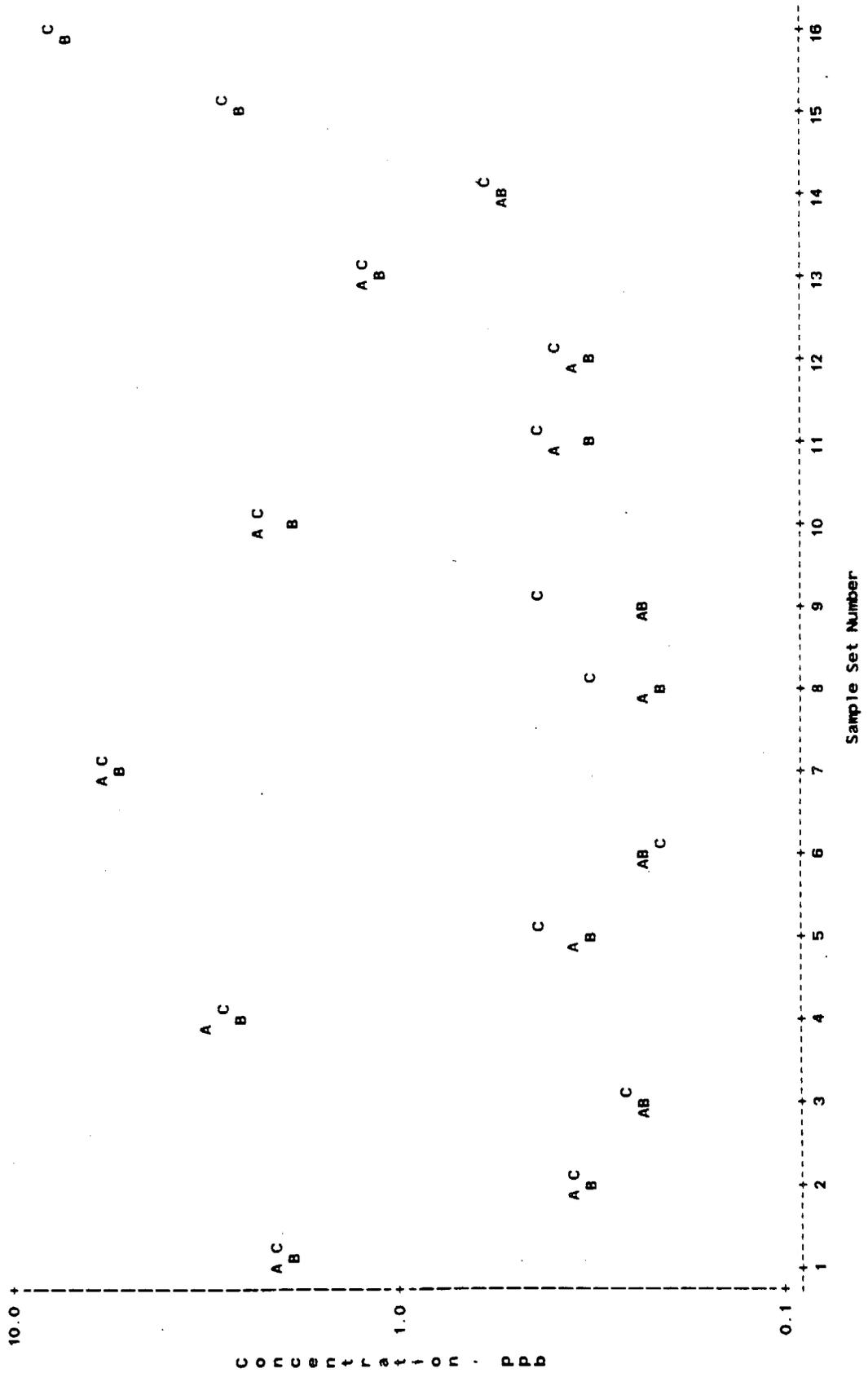
PLOTS OF CONCENTRATIONS FOR AUTO-GC (A), INITIAL BAG (B),  
AND INITIAL CAN (C) SAMPLES VERSUS SAMPLE SET NUMBER

Chemical Name = Styrene



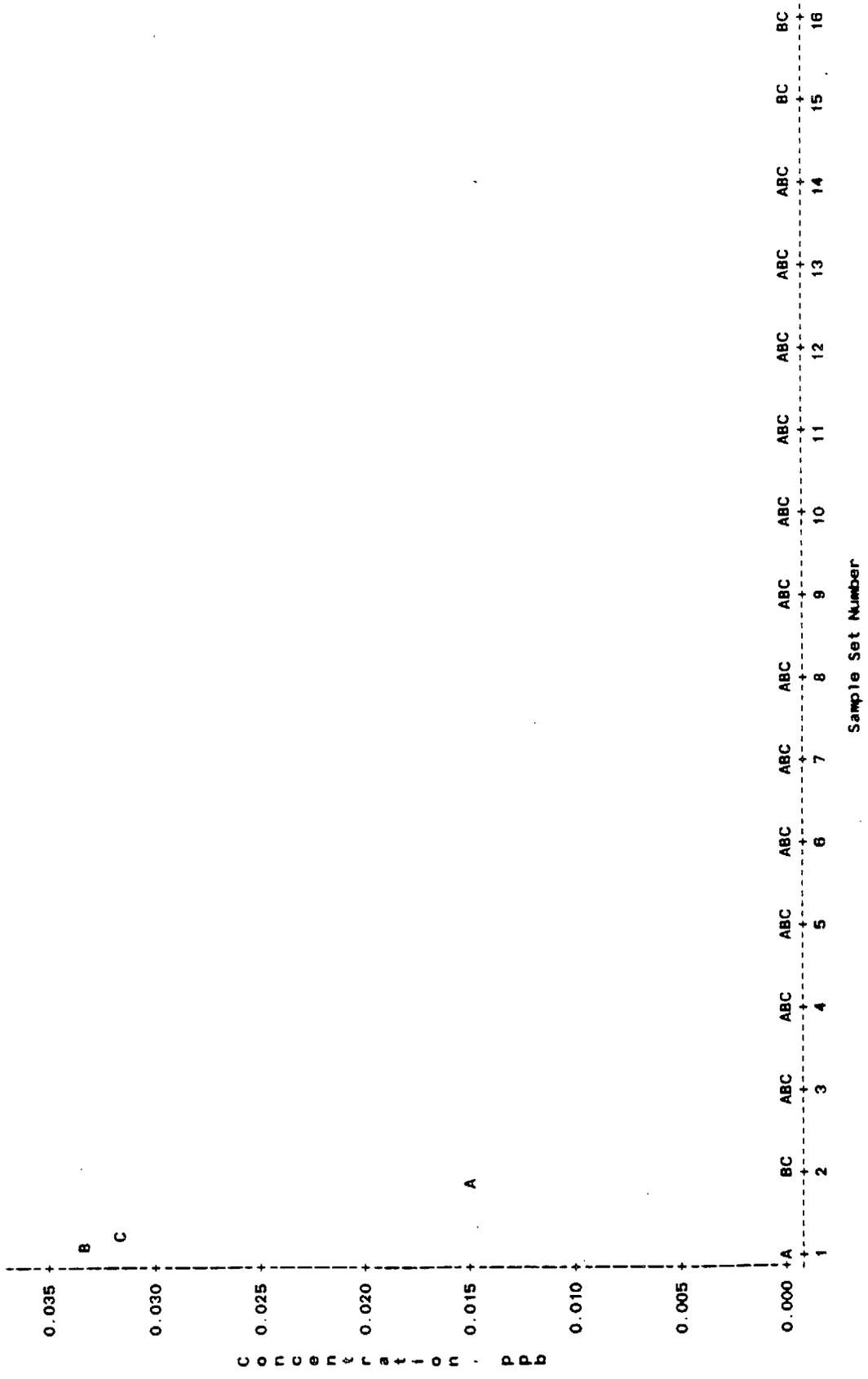
PLOTS OF CONCENTRATIONS FOR AUTO-GC (A), INITIAL BAG (B),  
AND INITIAL CAN (C) SAMPLES VERSUS SAMPLE SET NUMBER

Chemical Name = o-xylene



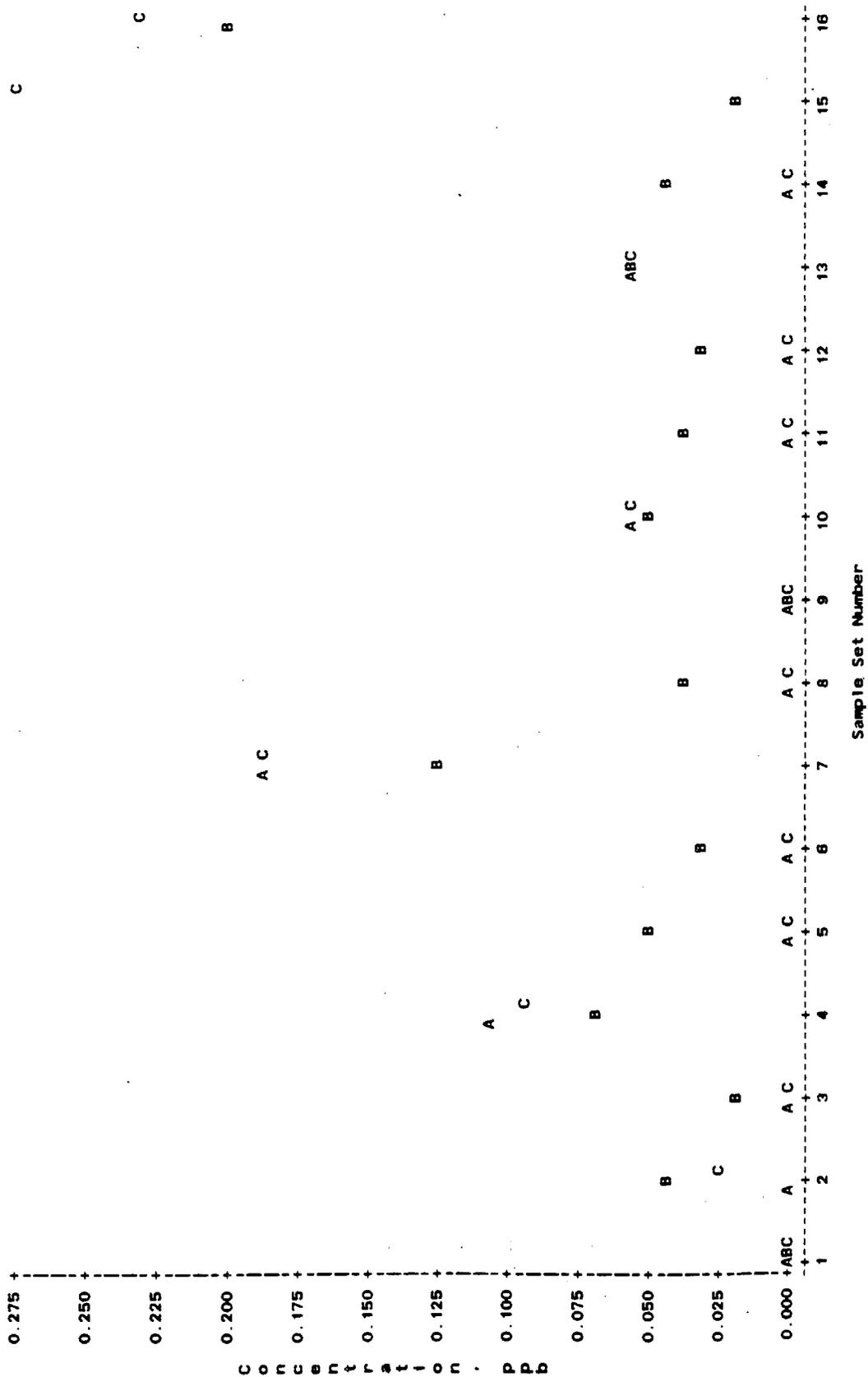
PLOTS OF CONCENTRATIONS FOR AUTO-GC (A), INITIAL BAG (B),  
AND INITIAL CAN (C) SAMPLES VERSUS SAMPLE SET NUMBER

Chemical Name = m-dichlorobenzene



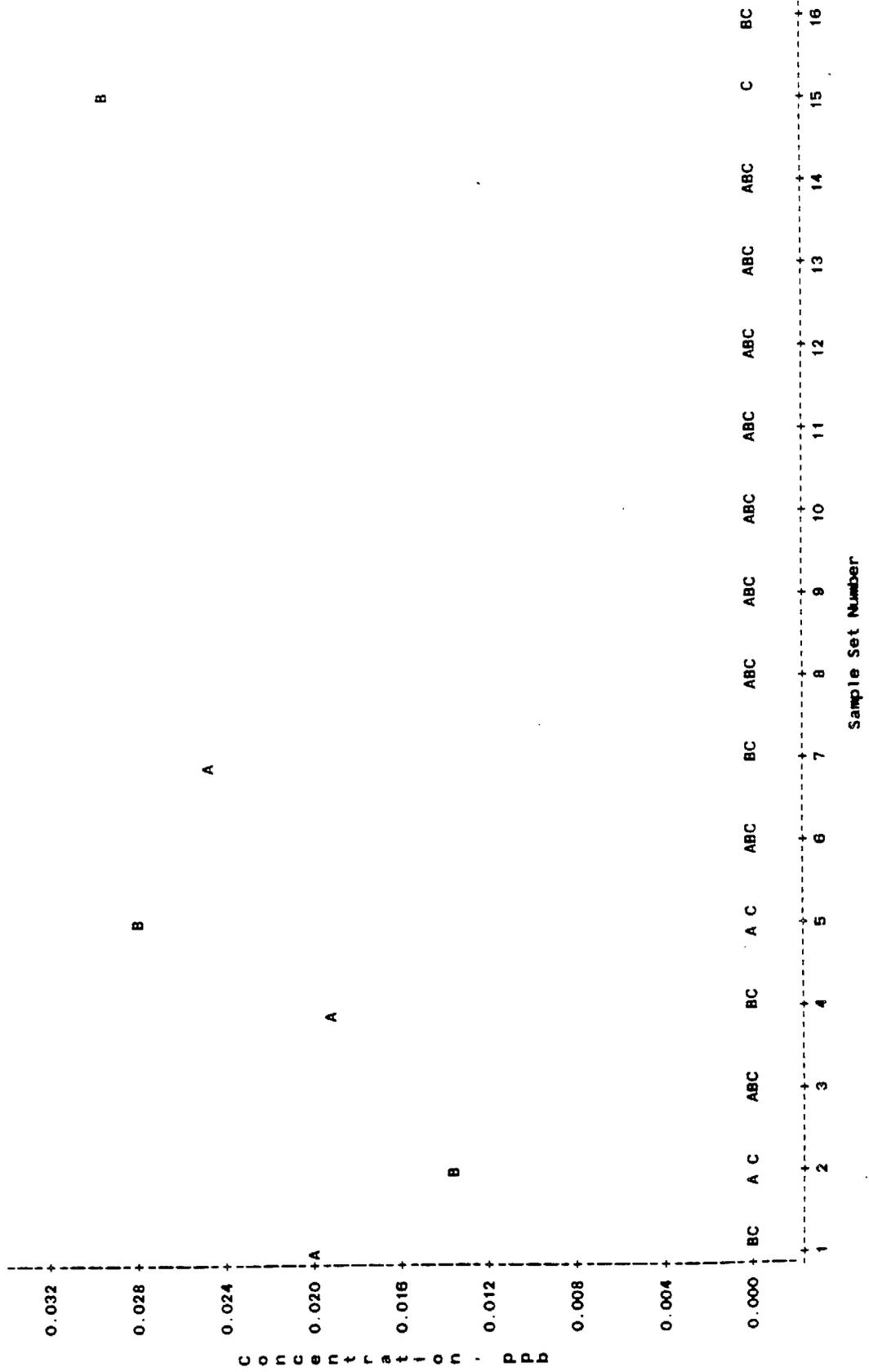
PLOTS OF CONCENTRATIONS FOR AUTO-GC (A), INITIAL BAG (B),  
AND INITIAL CAN (C) SAMPLES VERSUS SAMPLE SET NUMBER

Chemical Name = p-dichlorobenzene



PLOTS OF CONCENTRATIONS FOR AUTO-GC (A), INITIAL BAG (B),  
AND INITIAL CAN (C) SAMPLES VERSUS SAMPLE SET NUMBER

Chemical Name = o-dichlorobenzene



APPENDIX I-C

PLOTS OF INITIAL AND REPEAT ANALYSES OF BAG SAMPLES



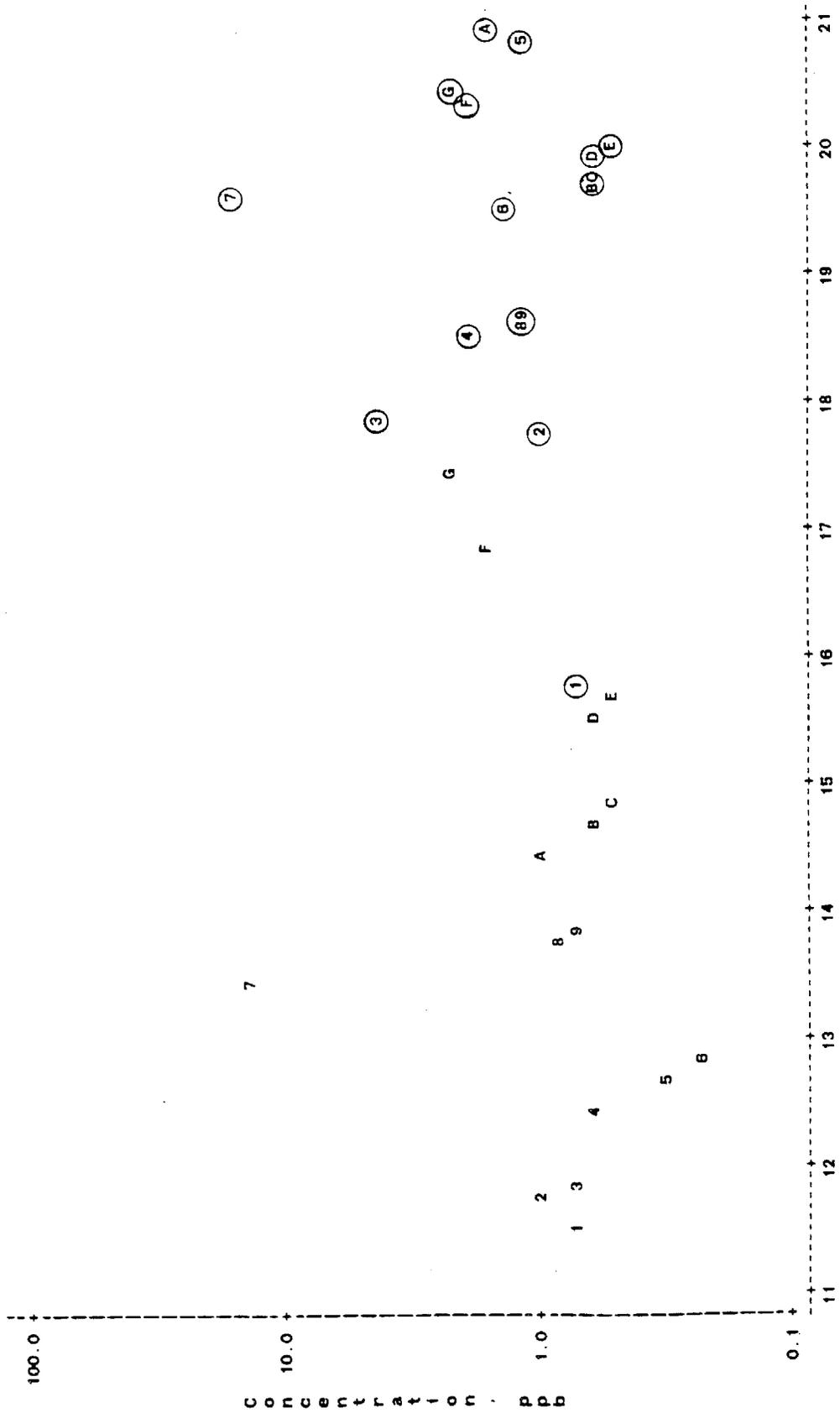
## APPENDIX I-C

### PLOTS OF INITIAL AND REPEAT ANALYSES OF BAG SAMPLES

The bag samples are identified by the numbers 1 through 9 and the letters A through G representing sample sets 1 through 9 and 10 through 16, respectively.

PLOTS OF CONCENTRATIONS FOR INITIAL AND REPEAT BAG SAMPLES

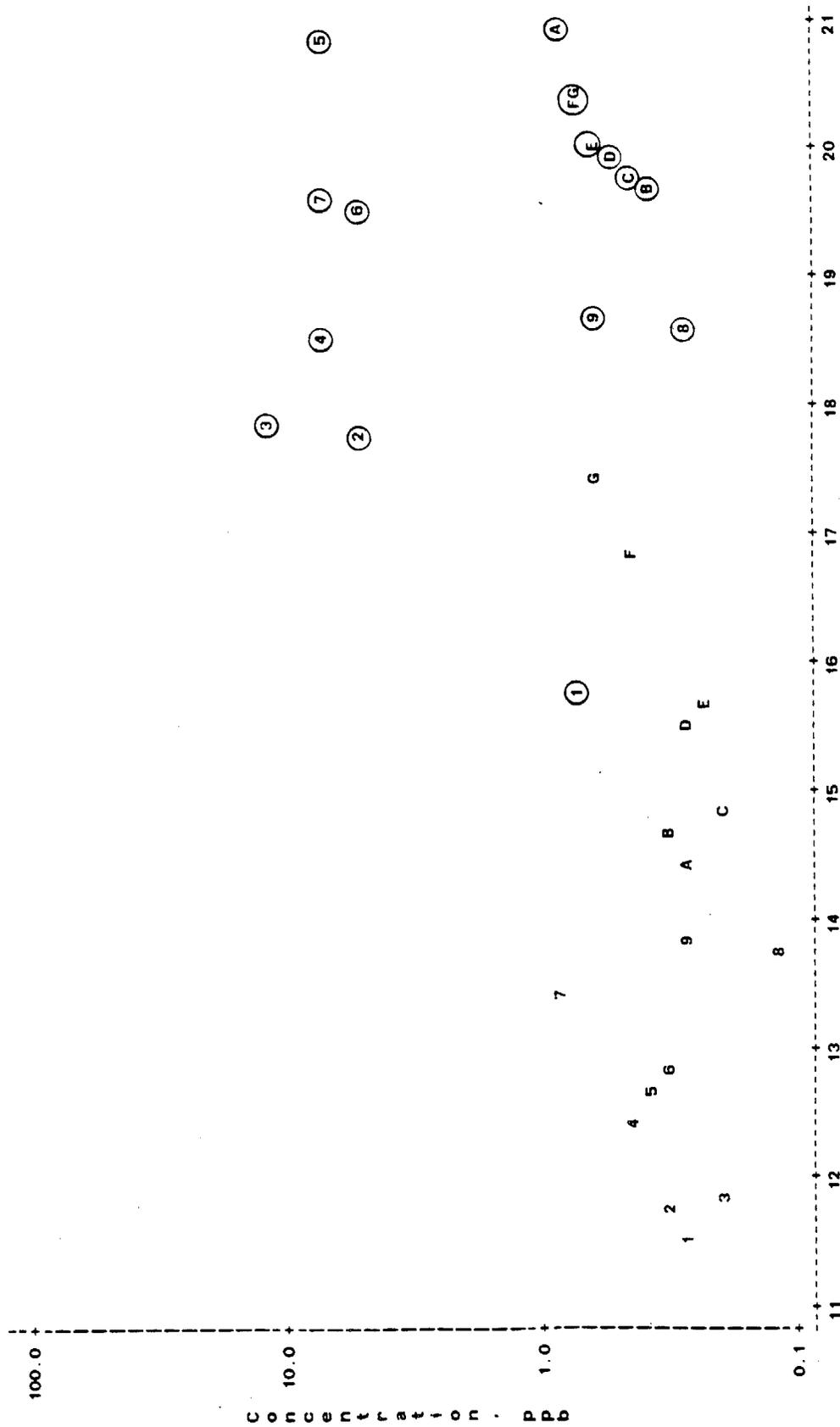
Chemical Name = Dichlorodifluoromethane



Date of Analyses  
 Symbols for Sample Sets 1-9, 10, 11, 12, 13, 14, 15, 16  
 Designated as: 1-9, A, B, C, D, E, F, G

PLOTS OF CONCENTRATIONS FOR INITIAL AND REPEAT BAG SAMPLES

Chemical Name = Dichloromethane

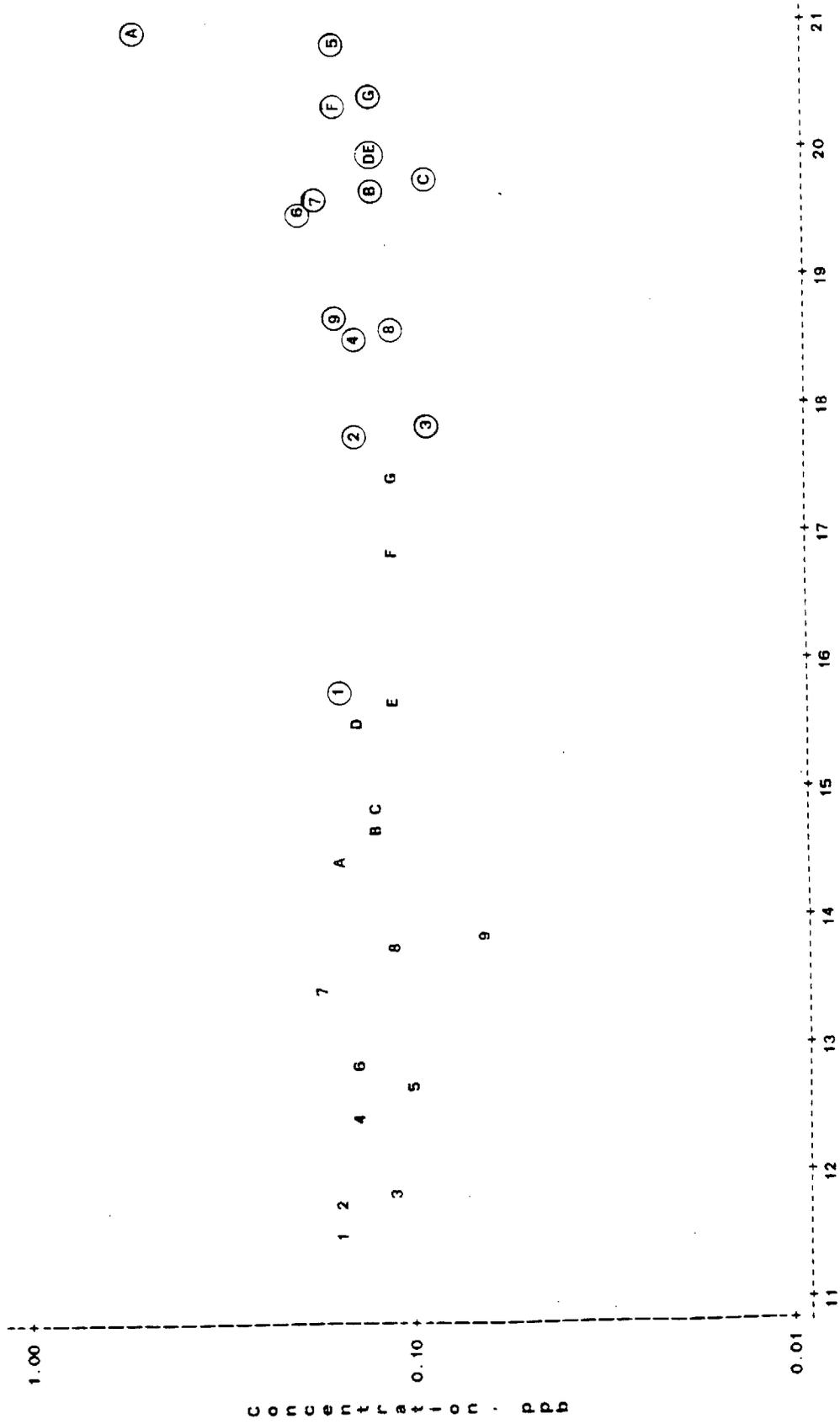


Date of Analyses

Symbols for Sample Sets 1-9, 10, 11, 12, 13, 14, 15, 16 Designated as: 1-9, A, B, C, D, E, F, G

PLOTS OF CONCENTRATIONS FOR INITIAL AND REPEAT BAG SAMPLES

Chemical Name = 1,1,2-trichloro-1,2,2-trifluoroethane

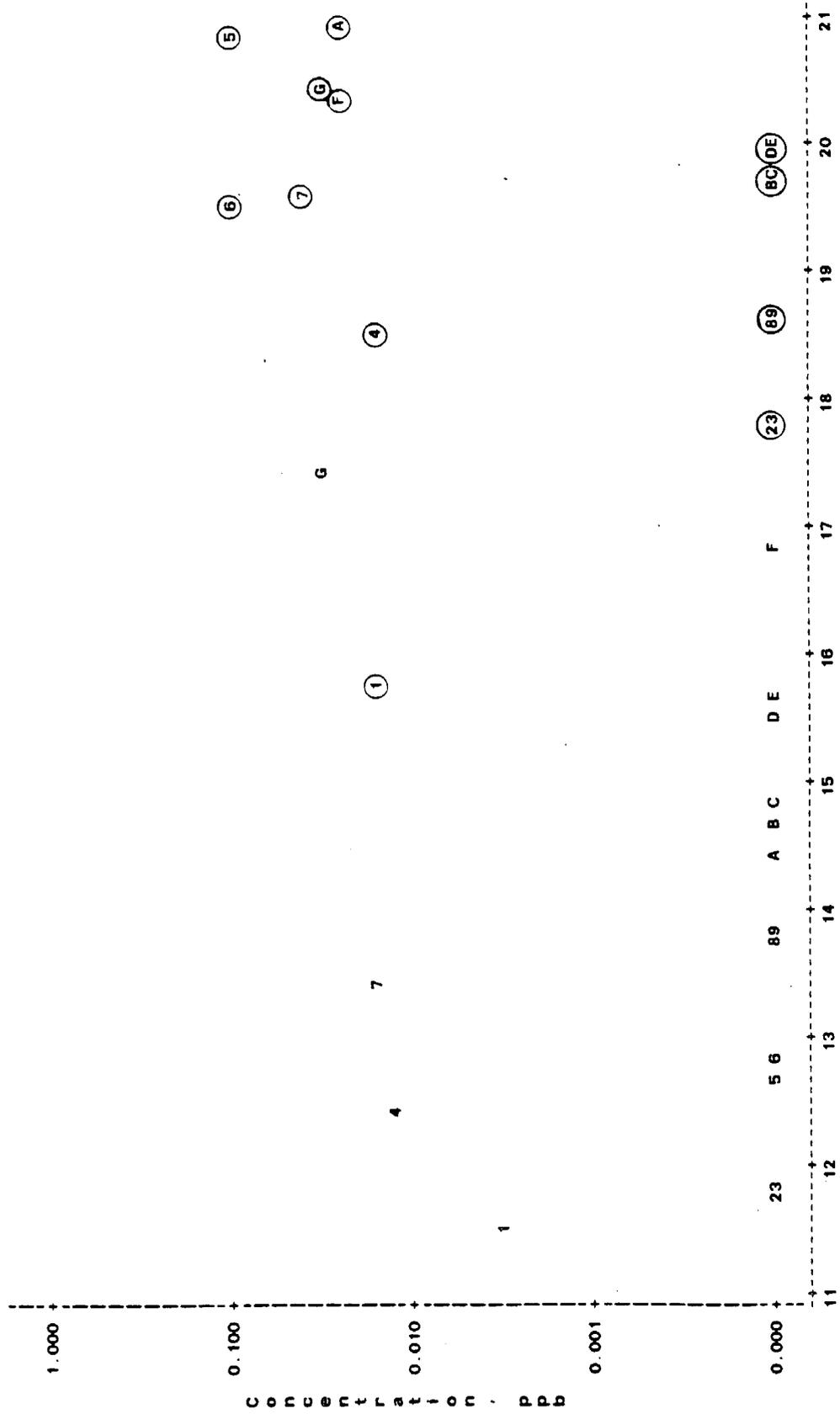


Date of Analyses

Symbols for Sample Sets 1-9, 10, 11, 12, 13, 14, 15, 16 Designated as : 1-9, A, B, C, D, E, F, G

PLOTS OF CONCENTRATIONS FOR INITIAL AND REPEAT BAG SAMPLES

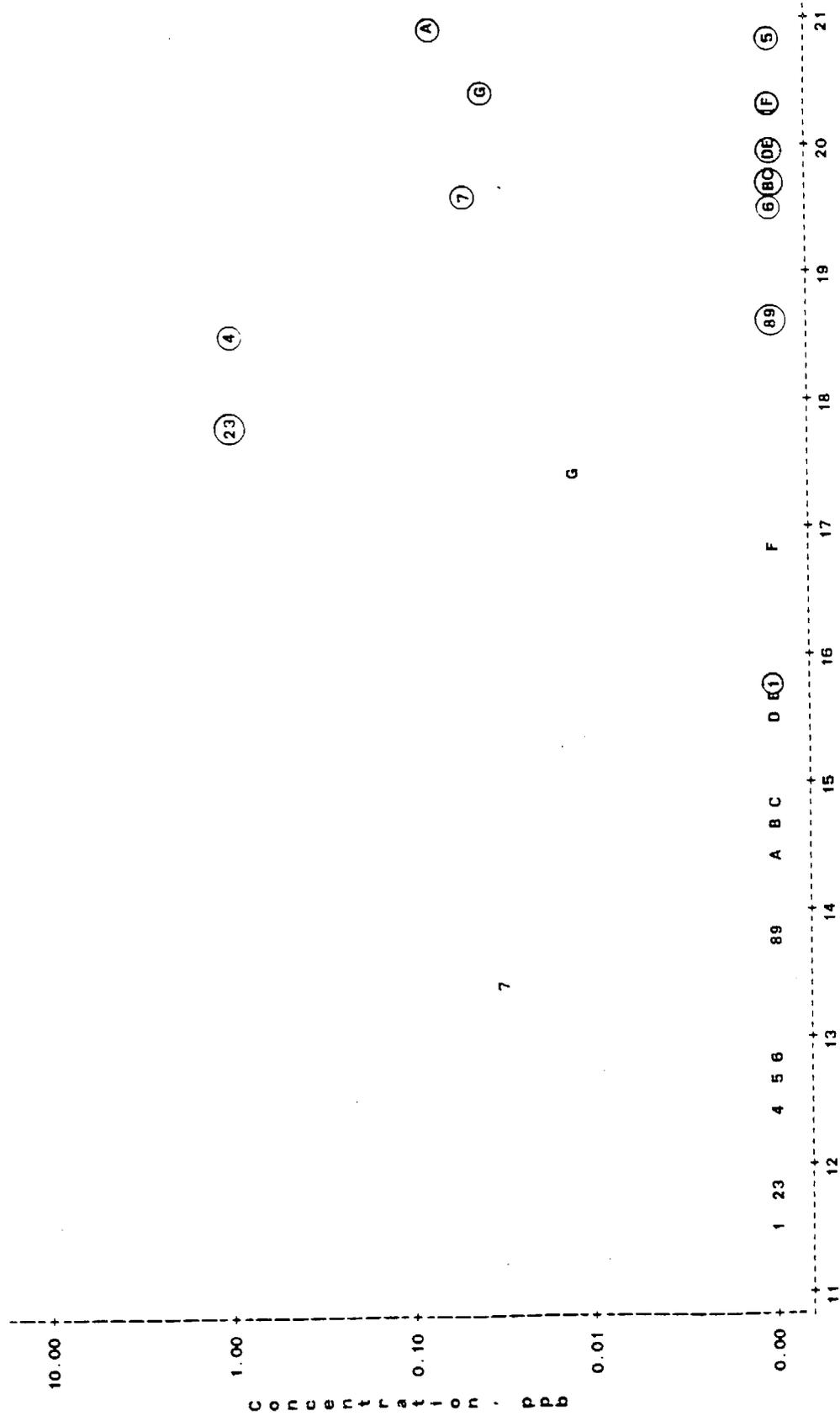
Chemical Name = Trichloromethane



Date of Analyses  
 Symbols for Sample Sets 1-9, 10, 11, 12, 13, 14, 15, 16  
 Designated as: 1-9, A, B, C, D, E, F, G

PLOTS OF CONCENTRATIONS FOR INITIAL AND REPEAT BAG SAMPLES

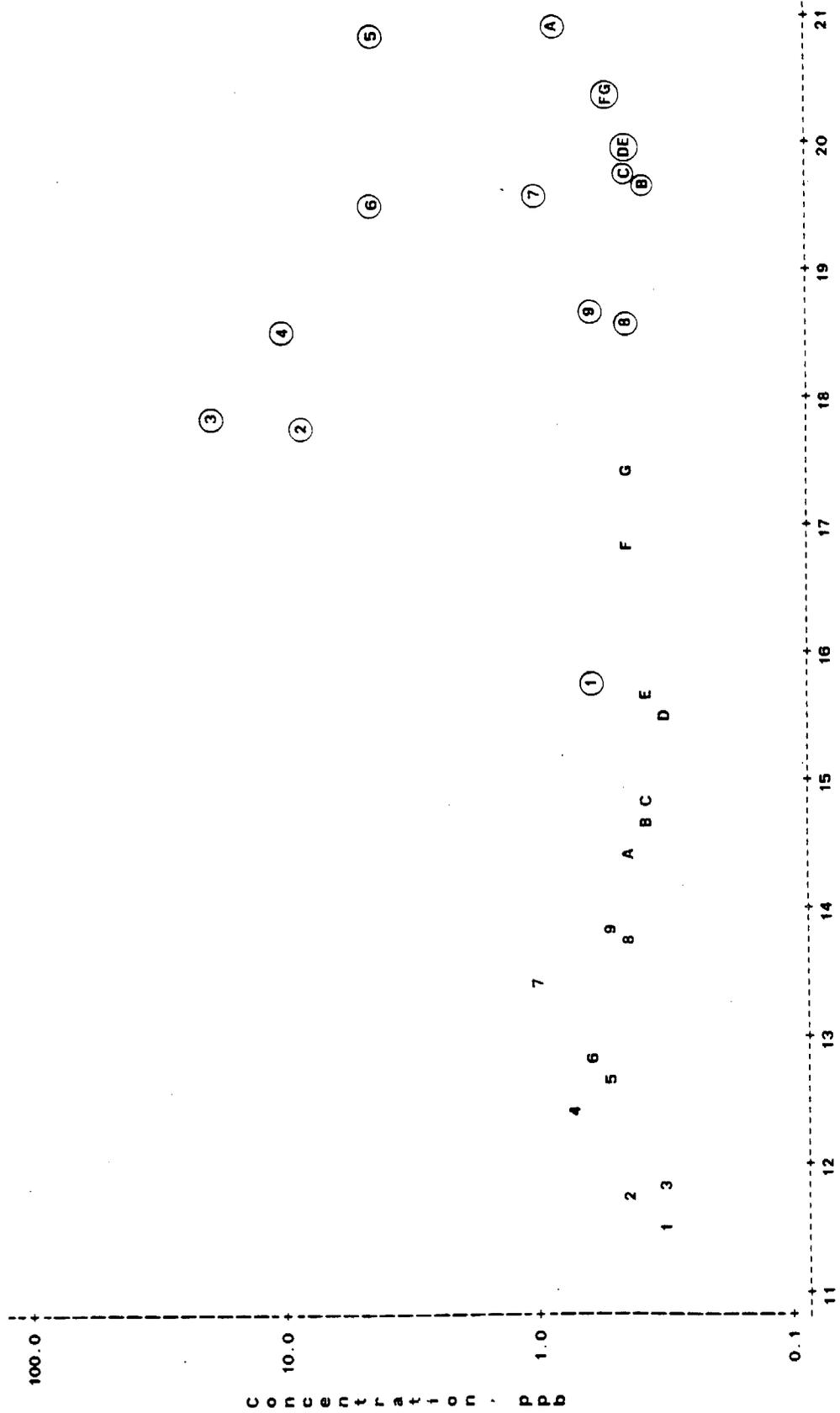
Chemical Name = 1,2-dichloroethane



Date of Analyses  
 Symbols for Sample Sets 1-9, 10, 11, 12, 13, 14, 15, 18  
 Designated as: 1-9, A, B, C, D, E, F, G

PLOTS OF CONCENTRATIONS FOR INITIAL AND REPEAT BAG SAMPLES

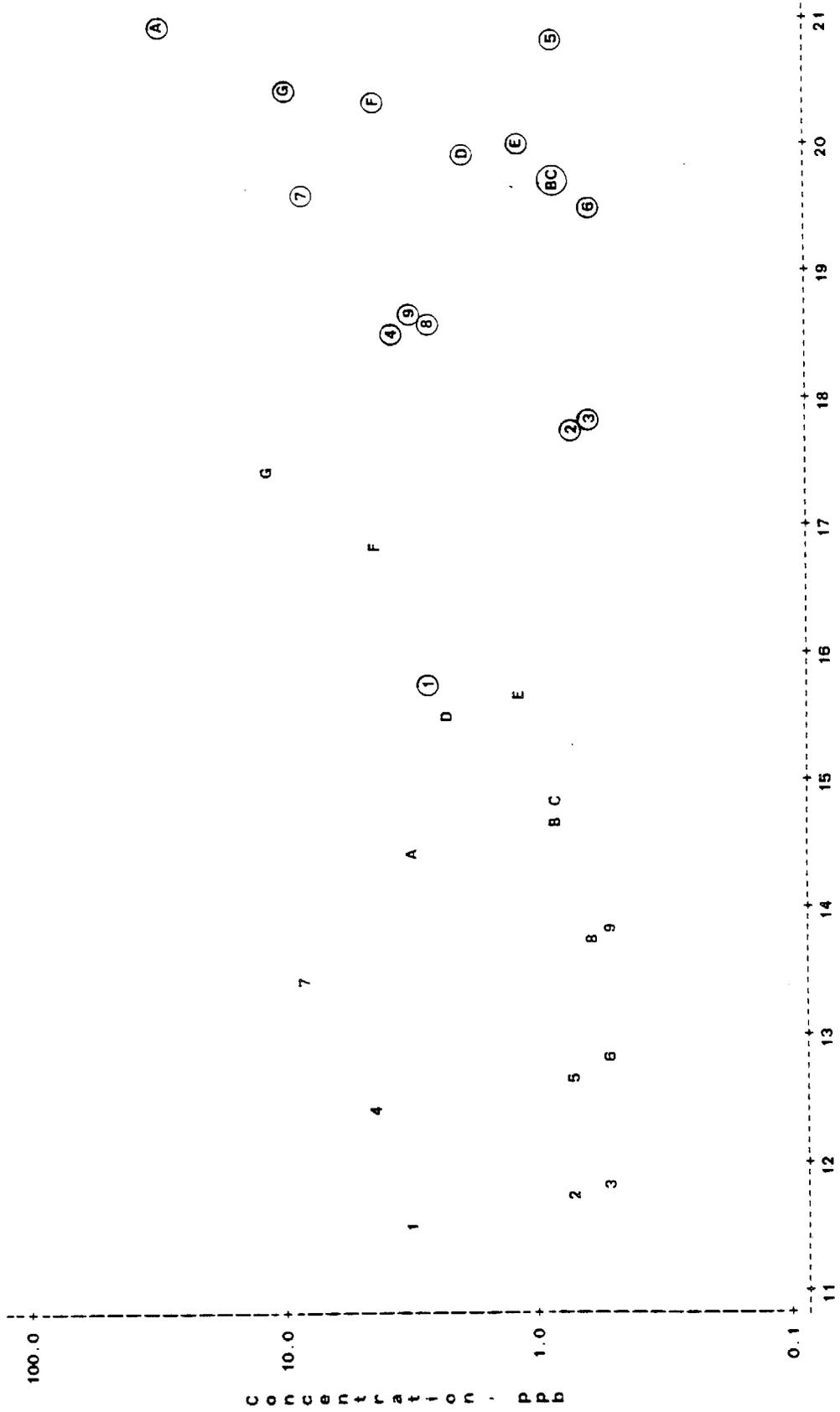
Chemical Name = 1,1,1-trichloroethane



Date of Analyses  
 Symbols for Sample Sets 1-9, 10, 11, 12, 13, 14, 15, 16  
 Designated as: 1-9, A, B, C, D, E, F, G

PLOTS OF CONCENTRATIONS FOR INITIAL AND REPEAT BAG SAMPLES

Chemical Name = Benzene



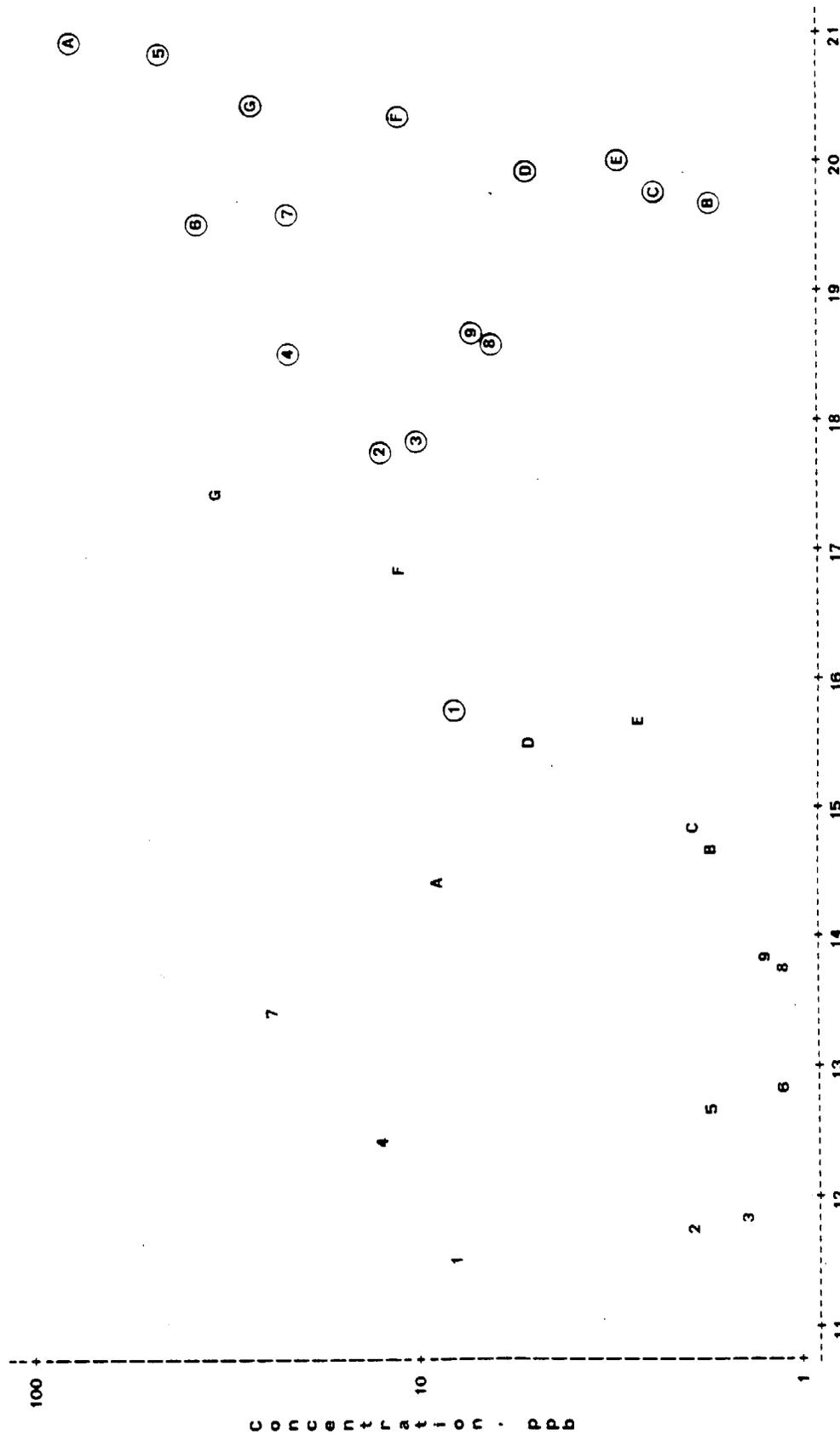
Date of Analyses  
 Symbols for Sample Sets 1-9, 10, 11, 12, 13, 14, 15, 16  
 Designated as : 1-9, A, B, C, D, E, F, G





PLOTS OF CONCENTRATIONS FOR INITIAL AND REPEAT BAG SAMPLES

Chemical Name = Toluene

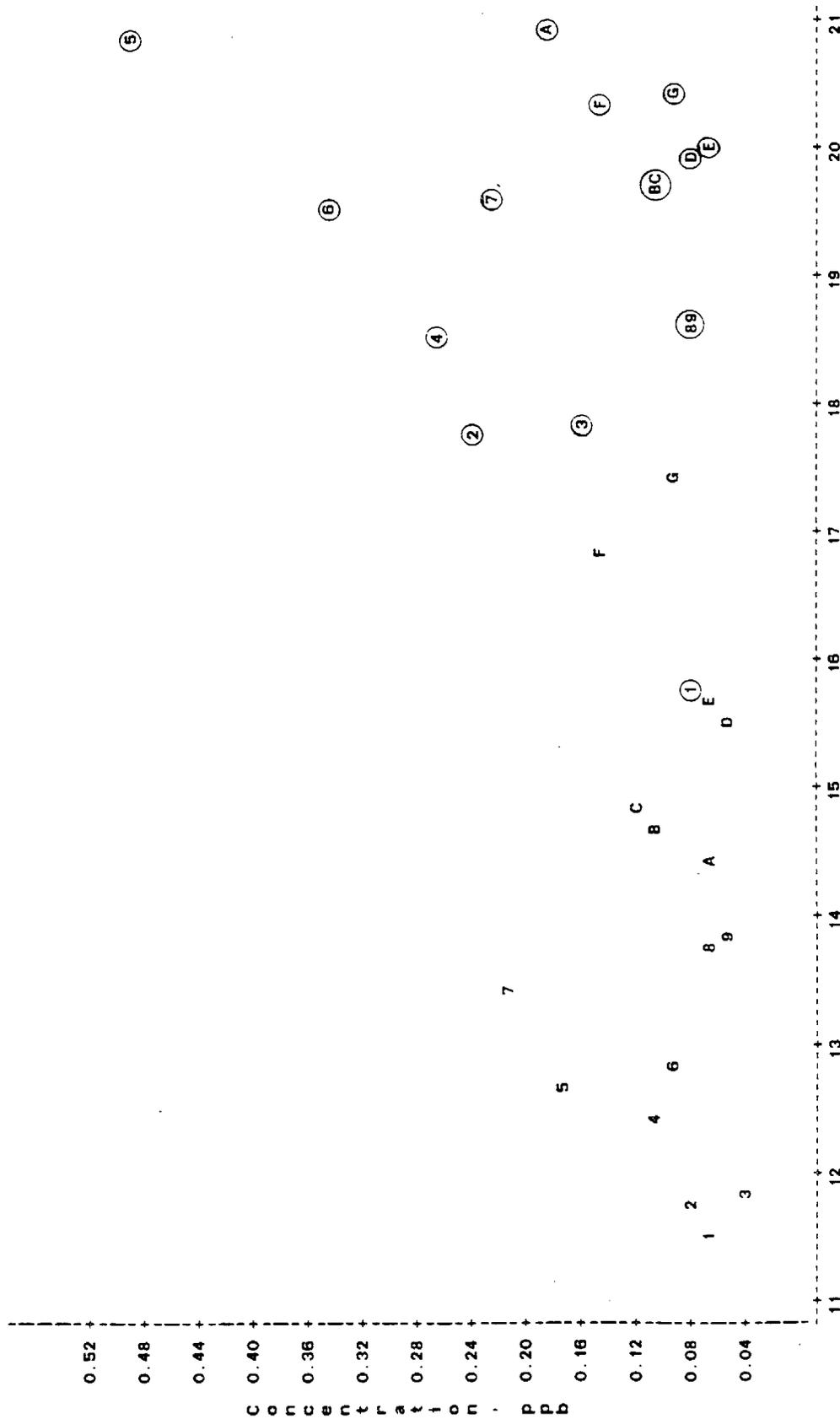


Date of Analyses

Symbols for Sample Sets 1-9, 10, 11, 12, 13, 14, 15, 16 Designated as: 1-9, A, B, C, D, E, F, G

PLOTS OF CONCENTRATIONS FOR INITIAL AND REPEAT BAG SAMPLES

Chemical Name = Tetrachloroethene

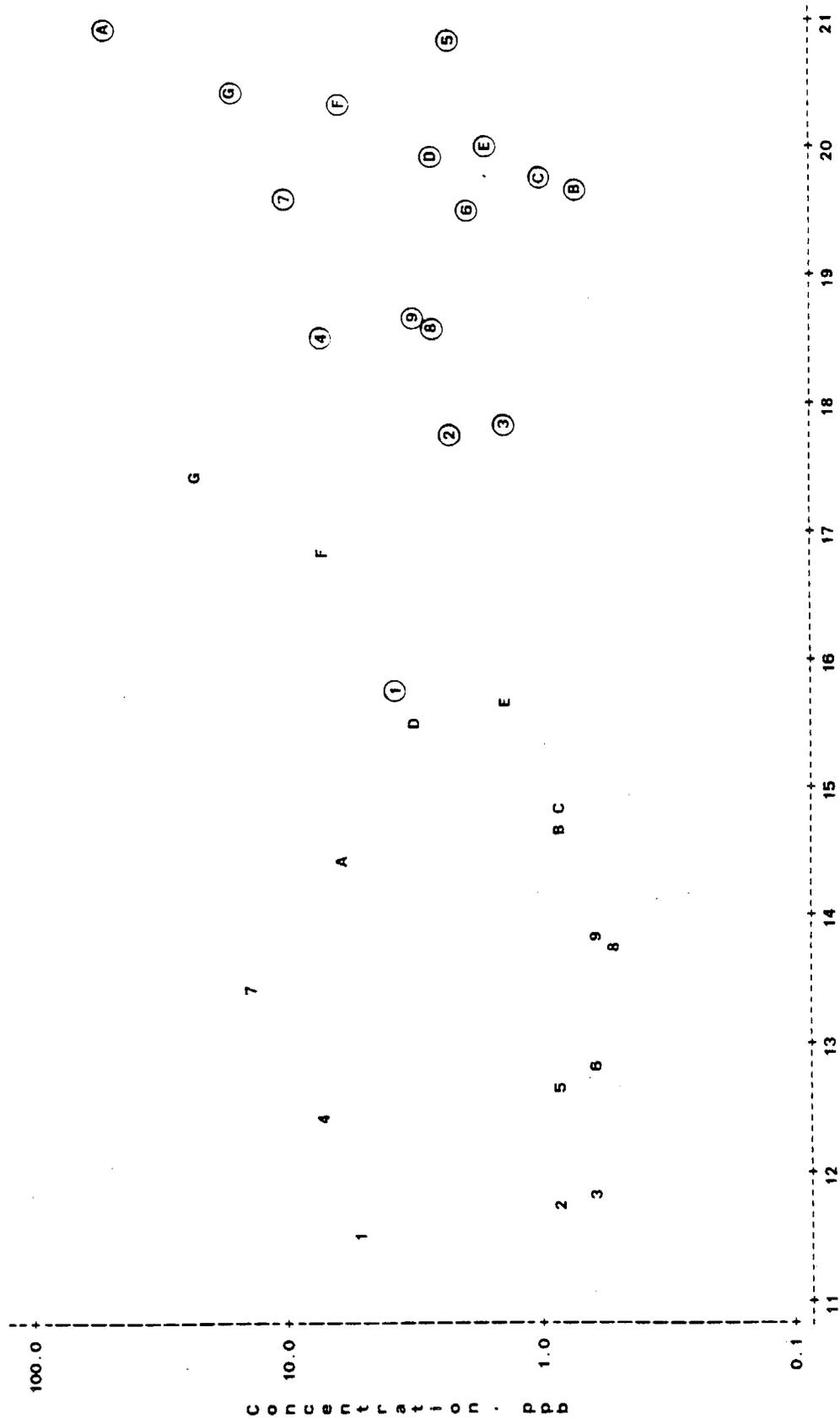


Date of Analyses

Symbols for Sample Sets 1-9, 10, 11, 12, 13, 14, 15, 16 Designated as : 1-9, A, B, C, D, E, F, G

PLOTS OF CONCENTRATIONS FOR INITIAL AND REPEAT BAG SAMPLES

Chemical Name = m+p-xylene

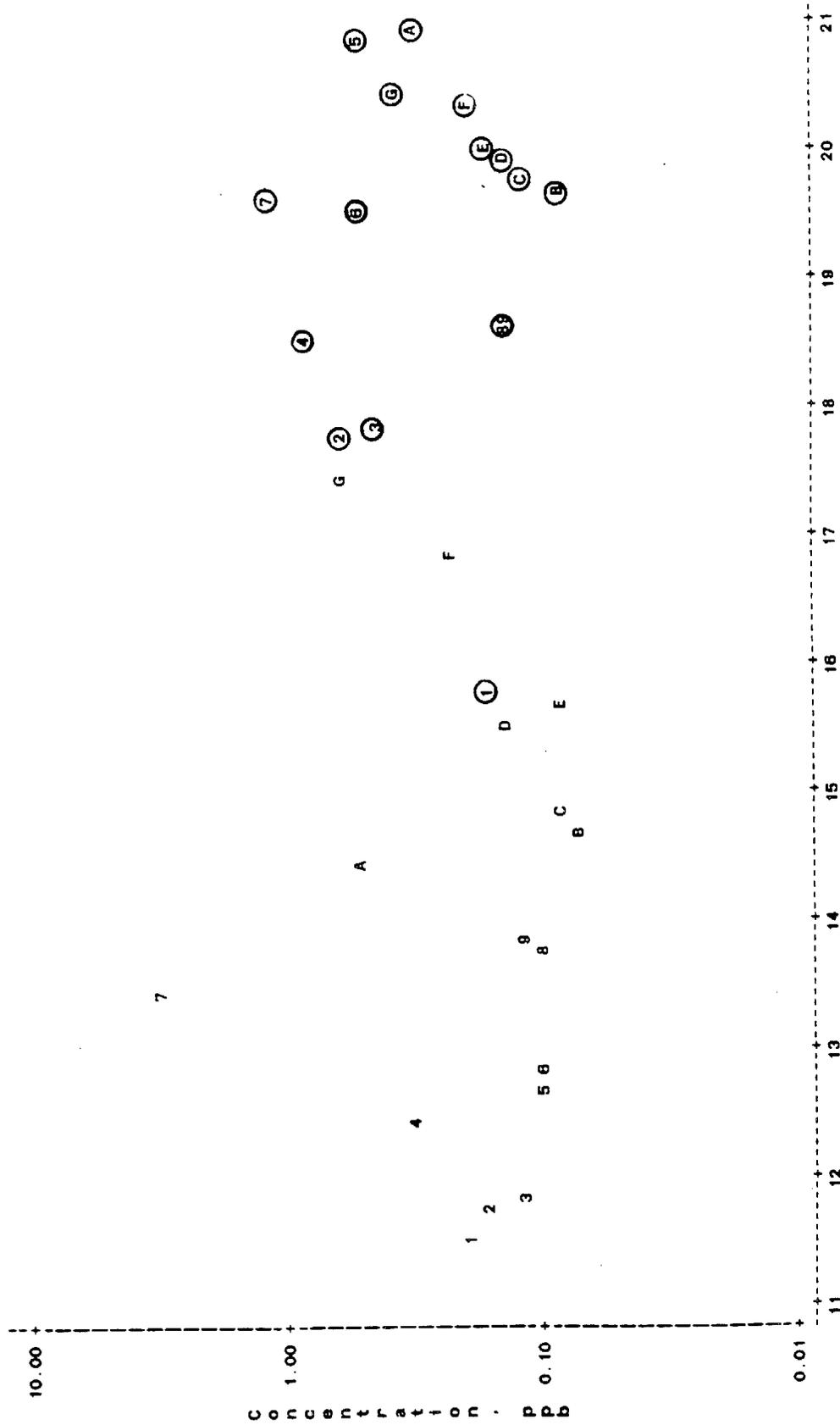


Date of Analyses

Symbols for Sample Sets 1-9, 10, 11, 12, 13, 14, 15, 16 Designated as: 1-9, A, B, C, D, E, F, G

PLOTS OF CONCENTRATIONS FOR INITIAL AND REPEAT BAG SAMPLES

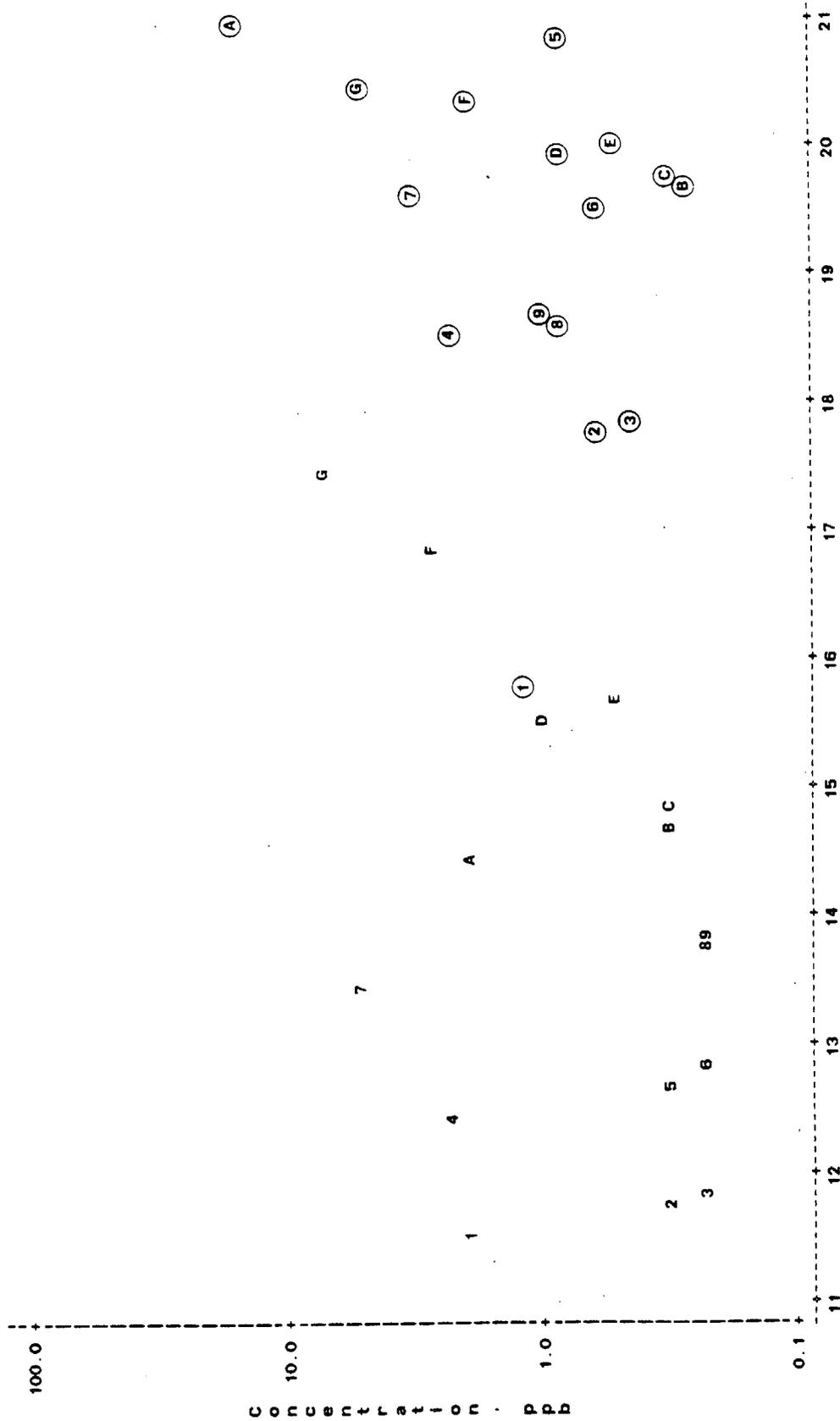
Chemical Name = Styrene



Date of Analyses  
 Symbols for Sample Sets 1-9, 10, 11, 12, 13, 14, 15, 16  
 Designated as : 1-9, A, B, C, D, E, F, G

PLOTS OF CONCENTRATIONS FOR INITIAL AND REPEAT BAG SAMPLES

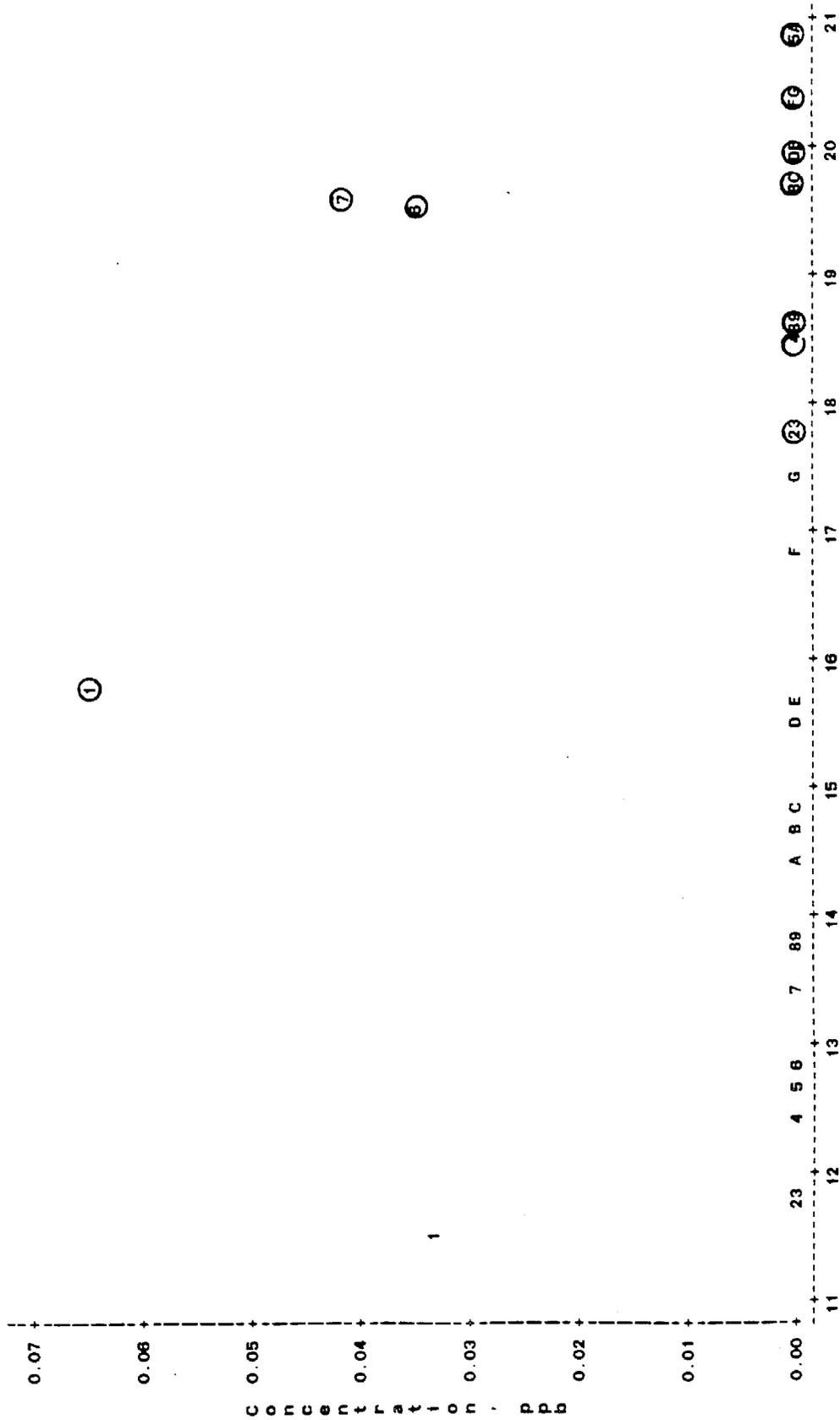
Chemical Name = o-xylene



Date of Analyses  
 Symbols for Sample Sets 1-9, 10, 11, 12, 13, 14, 15, 16  
 Designated as: 1-9, A, B, C, D, E, F, G

PLOTS OF CONCENTRATIONS FOR INITIAL AND REPEAT BAG SAMPLES

Chemical Name = m-dichlorobenzene

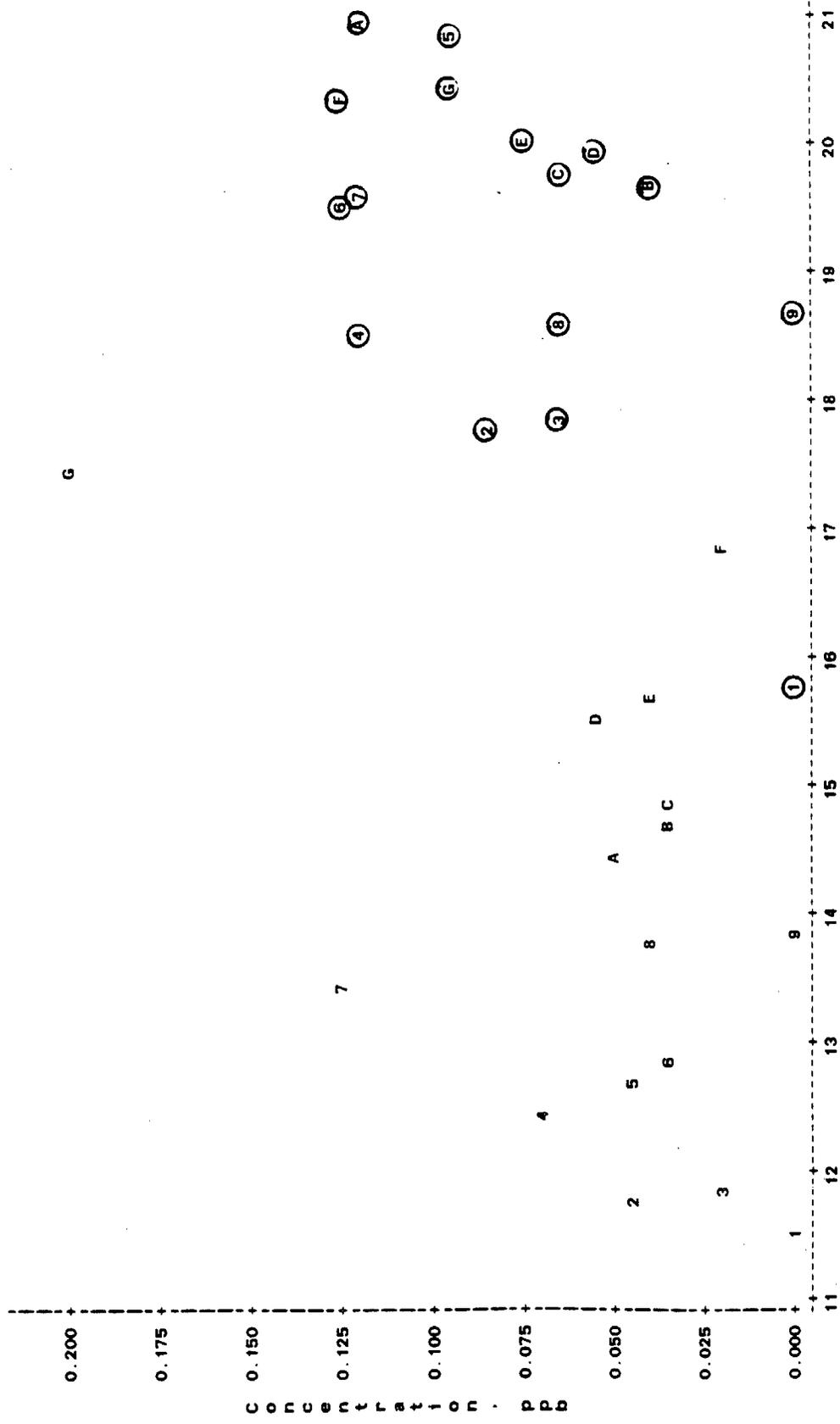


Date of Analyses

Symbols for Sample Sets 1-9, 10, 11, 12, 13, 14, 15, 16 Designated as : 1-9, A, B, C, D, E, F, G

PLOTS OF CONCENTRATIONS FOR INITIAL AND REPEAT BAG SAMPLES

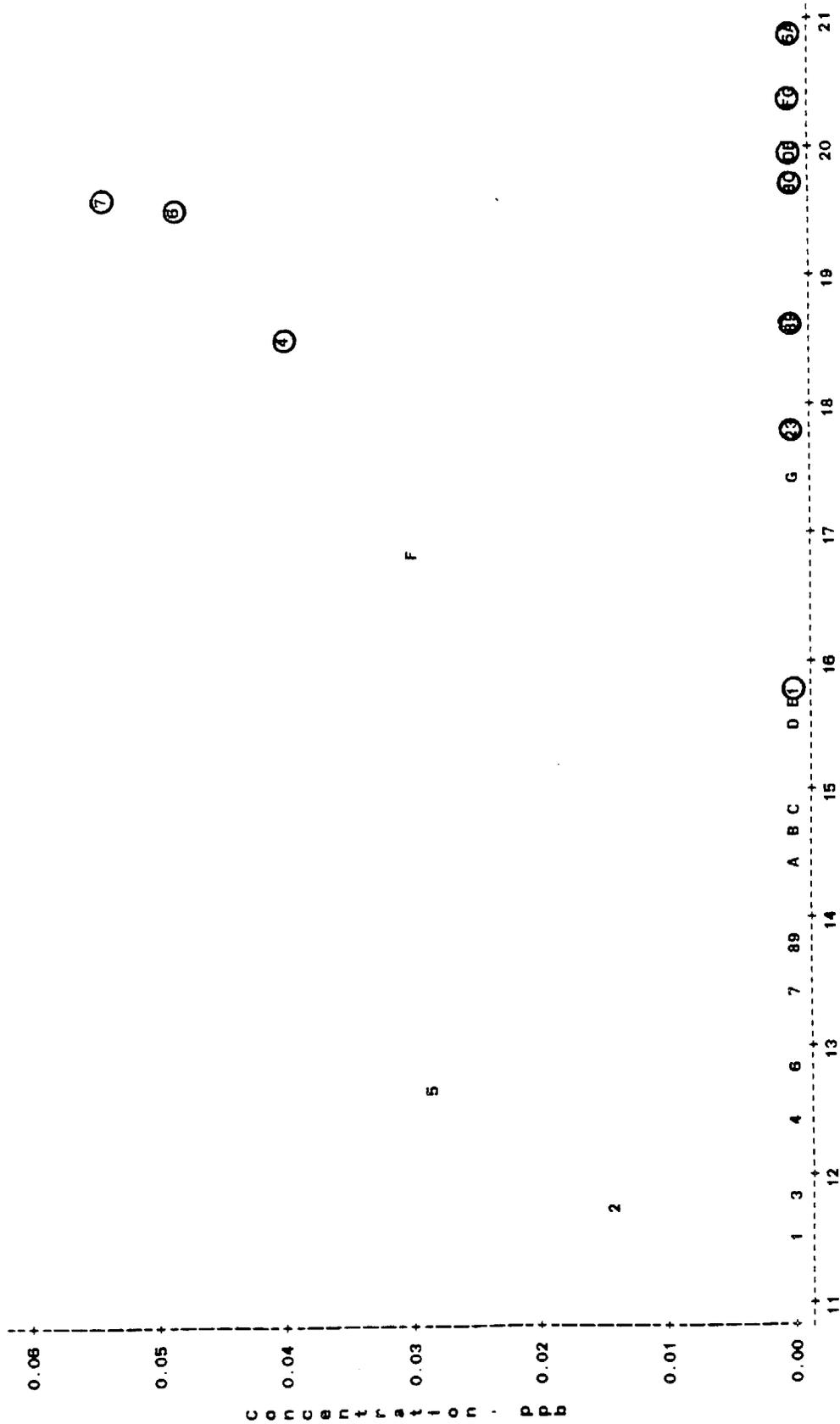
Chemical Name = p-dichlorobenzene



Date of Analyses  
 Symbols for Sample Sets 1-9, 10, 11, 12, 13, 14, 15, 16  
 Designated as : 1-9, A, B, C, D, E, F, G

PLOTS OF CONCENTRATIONS FOR INITIAL AND REPEAT BAG SAMPLES

Chemical Name = o-dichlorobenzene



Date of Analyses

Symbols for Sample Sets 1-9, 10, 11, 12, 13, 14, 15, 16  
Designated as: 1-9, A, B, C, D, E, F, G

APPENDIX V-A

LISTING OF ARB MULTIPOINT CALIBRATION DATA



APPENDIX V-A

LISTING OF MULTIPOINT CALIBRATION DATA

OBS	COMPOUND	TRUE CONCENTRATION (ppb)	AREA COUNT 1	AREA COUNT 2	AREA COUNT 3
1	dichloromethane	0.4500	2126	2664	.
2	dichloromethane	0.9000	5282	5513	.
3	dichloromethane	1.8000	9422	10883	.
4	dichloromethane	3.6000	15895	15309	17401
5	trichloromethane	0.0200	4501	4537	.
6	trichloromethane	0.0400	8737	8992	.
7	trichloromethane	0.0800	16469	18319	.
8	trichloromethane	0.1600	30997	36148	32235
9	1,1,1-trichloroethane	0.2380	129160	132701	.
10	1,1,1-trichloroethane	0.4750	240087	243985	.
11	1,1,1-trichloroethane	0.9500	460825	475096	.
12	1,1,1-trichloroethane	1.9000	777115	783730	798437
13	carbon tetrachloride	0.0210	42663	43470	.
14	carbon tetrachloride	0.0425	81158	82701	.
15	carbon tetrachloride	0.0850	159384	167175	.
16	carbon tetrachloride	0.1700	291354	292397	294879
17	trichloroethene	0.1125	28394	29767	.
18	trichloroethene	0.2250	55456	56464	.
19	trichloroethene	0.4500	108261	117325	.
20	trichloroethene	0.9000	196326	202457	203563

APPENDIX V-A (continued)

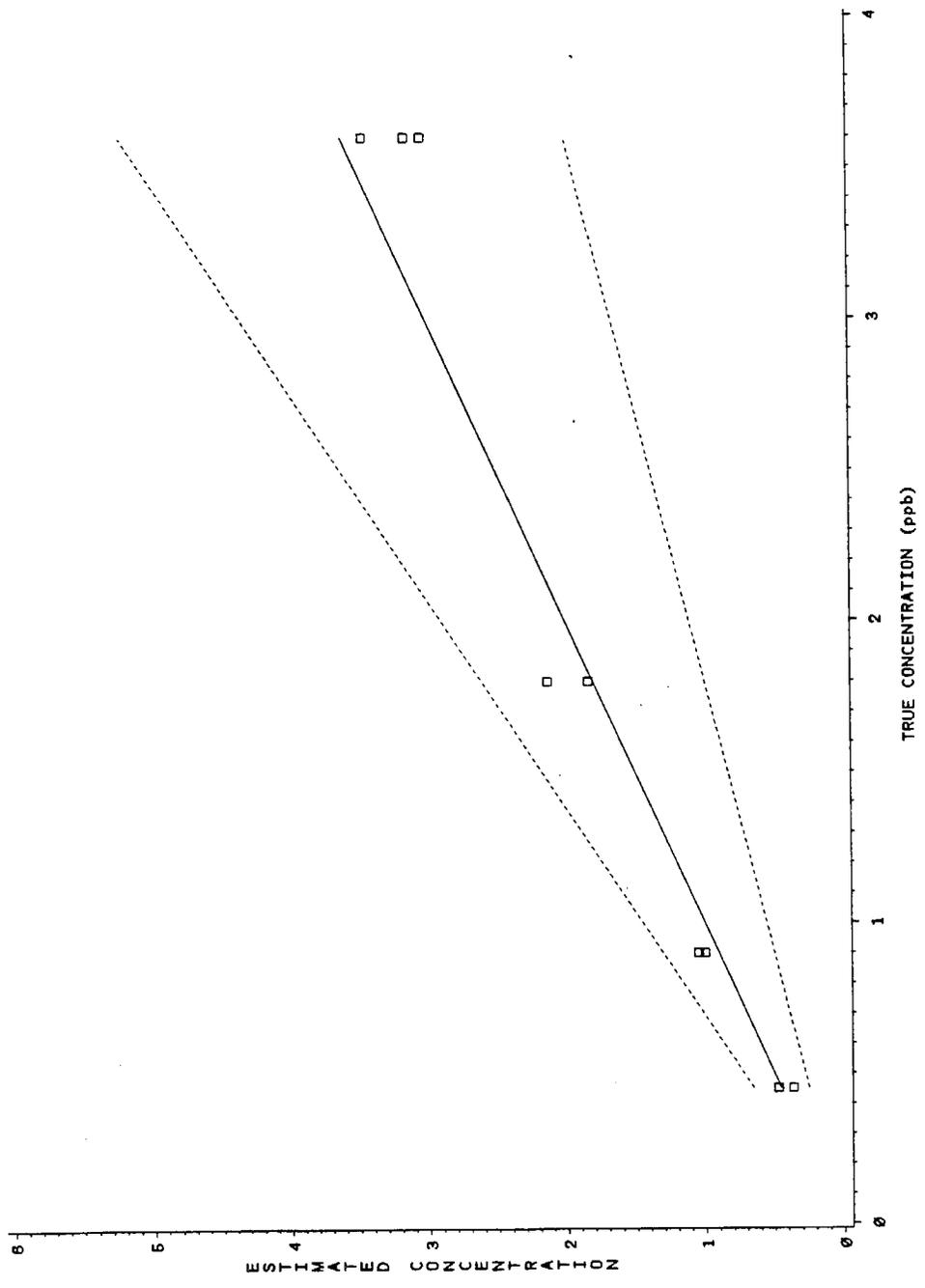
OBS	COMPOUND	TRUE CONCENTRATION (ppb)	AREA COUNT 1	AREA COUNT 2	AREA COUNT 3
21	tetrachloroethene	0.0238	45386	42023	.
22	tetrachloroethene	0.0475	75068	73465	.
23	tetrachloroethene	0.0950	136188	146184	.
24	tetrachloroethene	0.1900	251155	255769	.
25	benzene	0.6100	25566	26559	.
26	benzene	1.2250	47448	45244	.
27	benzene	2.4500	82976	89272	.
28	benzene	4.9000	166736	161674	157269
29	1,2-dichloroethane	0.1380	683	1113	.
30	1,2-dichloroethane	0.2750	2342	2204	.
31	1,2-dichloroethane	0.5500	4347	5033	.
32	1,2-dichloroethane	1.1000	6733	6682	7736
33	1,2-dibromoethane	0.0400	12381	11699	.
34	1,2-dibromoethane	0.0800	23242	22888	.
35	1,2-dibromoethane	0.1600	41931	41664	.
36	1,2-dibromoethane	0.3200	81418	80183	81520
37	vinyl chloride	1.2500	6904	6886	.
38	vinyl chloride	2.5000	11063	10977	.
39	vinyl chloride	5.0000	21321	20420	.
40	toluene	1.2500	59891	68148	.
41	toluene	2.5000	96655	93721	.
42	toluene	5.0000	154356	184990	.
43	toluene	10.0000	388214	320144	314329

APPENDIX V-B

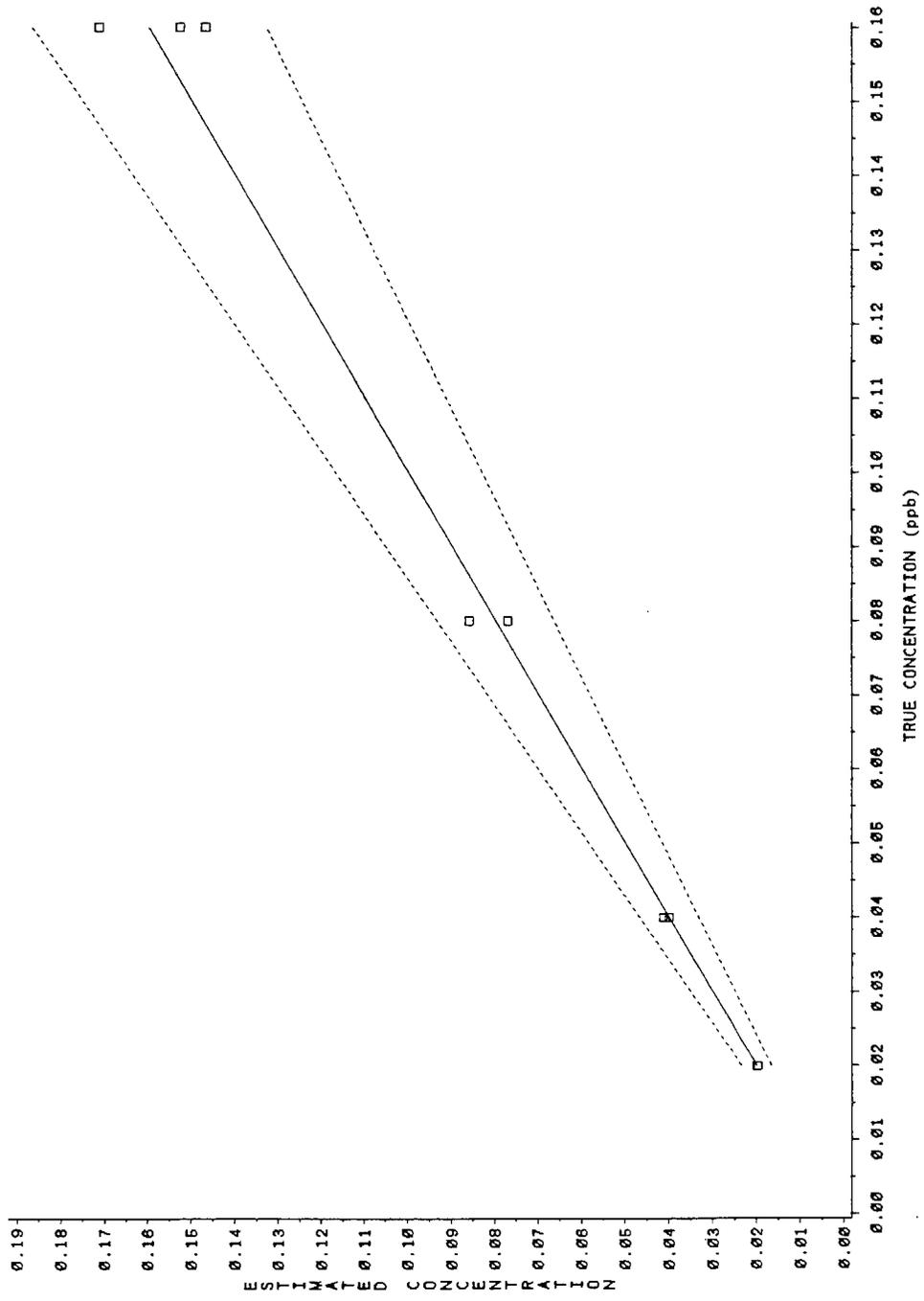
PLOTS OF ARB'S MULTIPOINT CALIBRATION DATA  
WITH 99% PREDICTION LIMITS



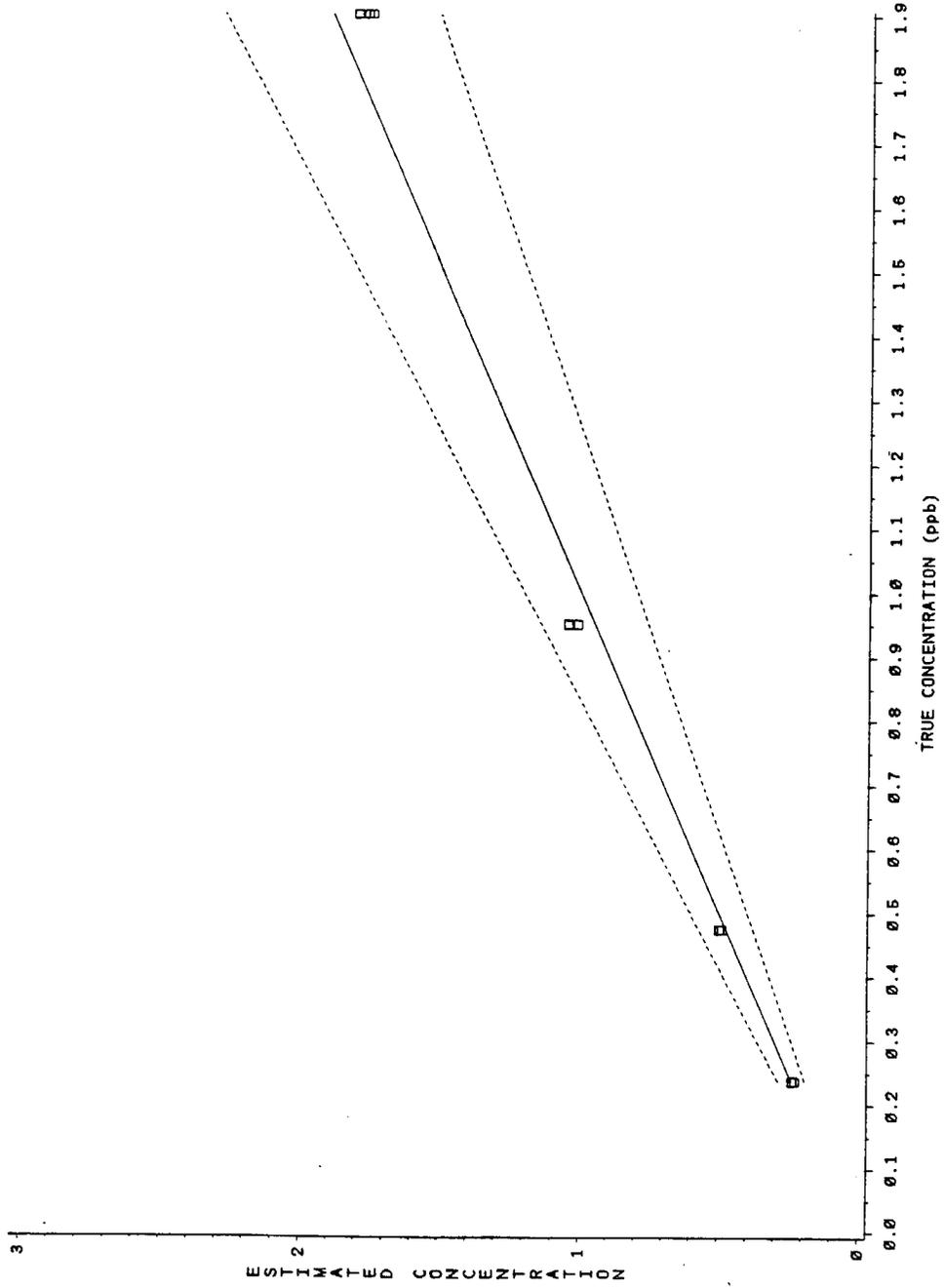
CALIBRATED DATA WITH WEIGHTED REGRESSION LINE  $\pm$  3 STDV  
COMPOUND=dichloromethane



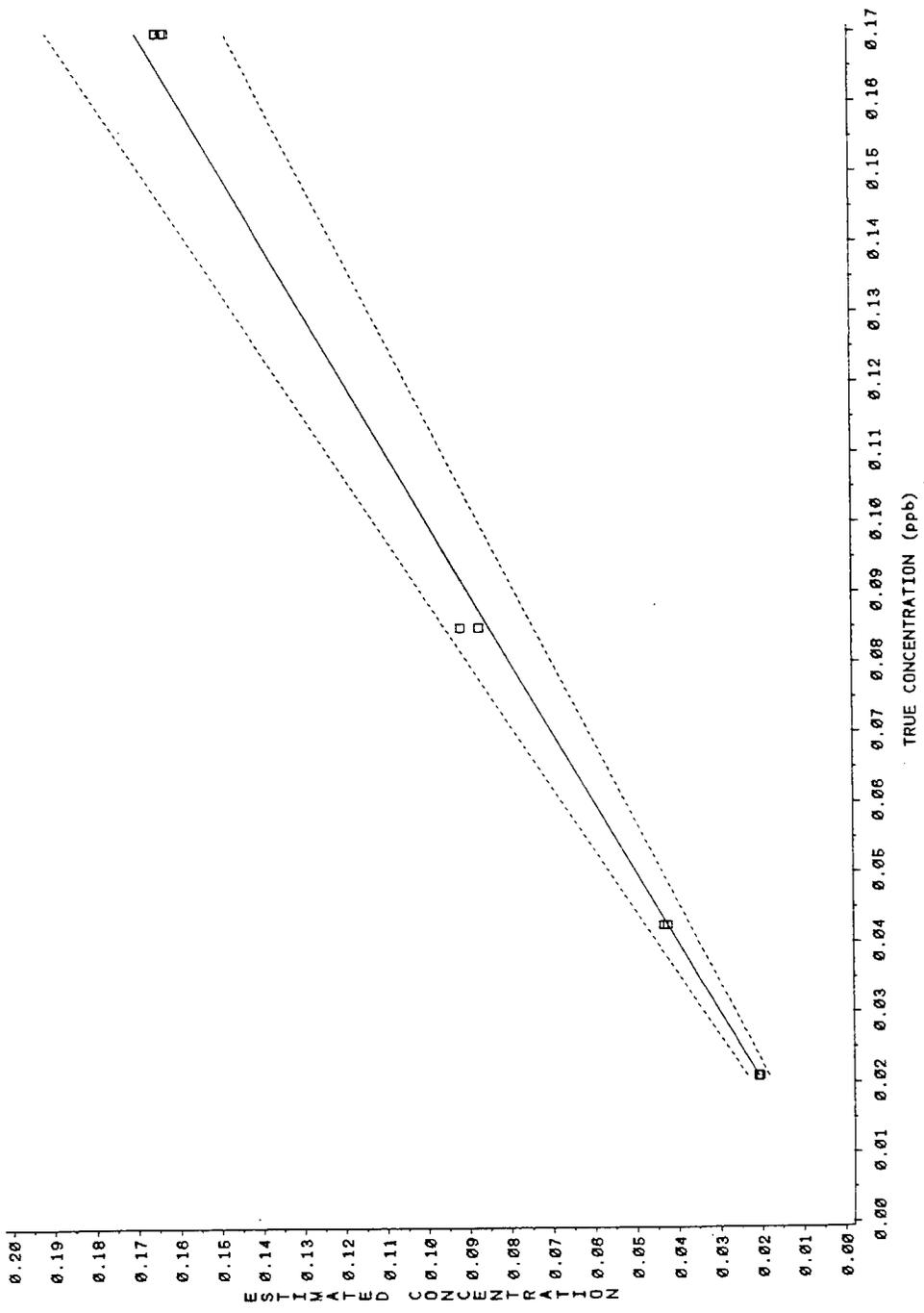
CALIBRATED DATA WITH WEIGHTED REGRESSION LINE  $\pm$  3 STDV  
 COMPOUND=trichloromethane



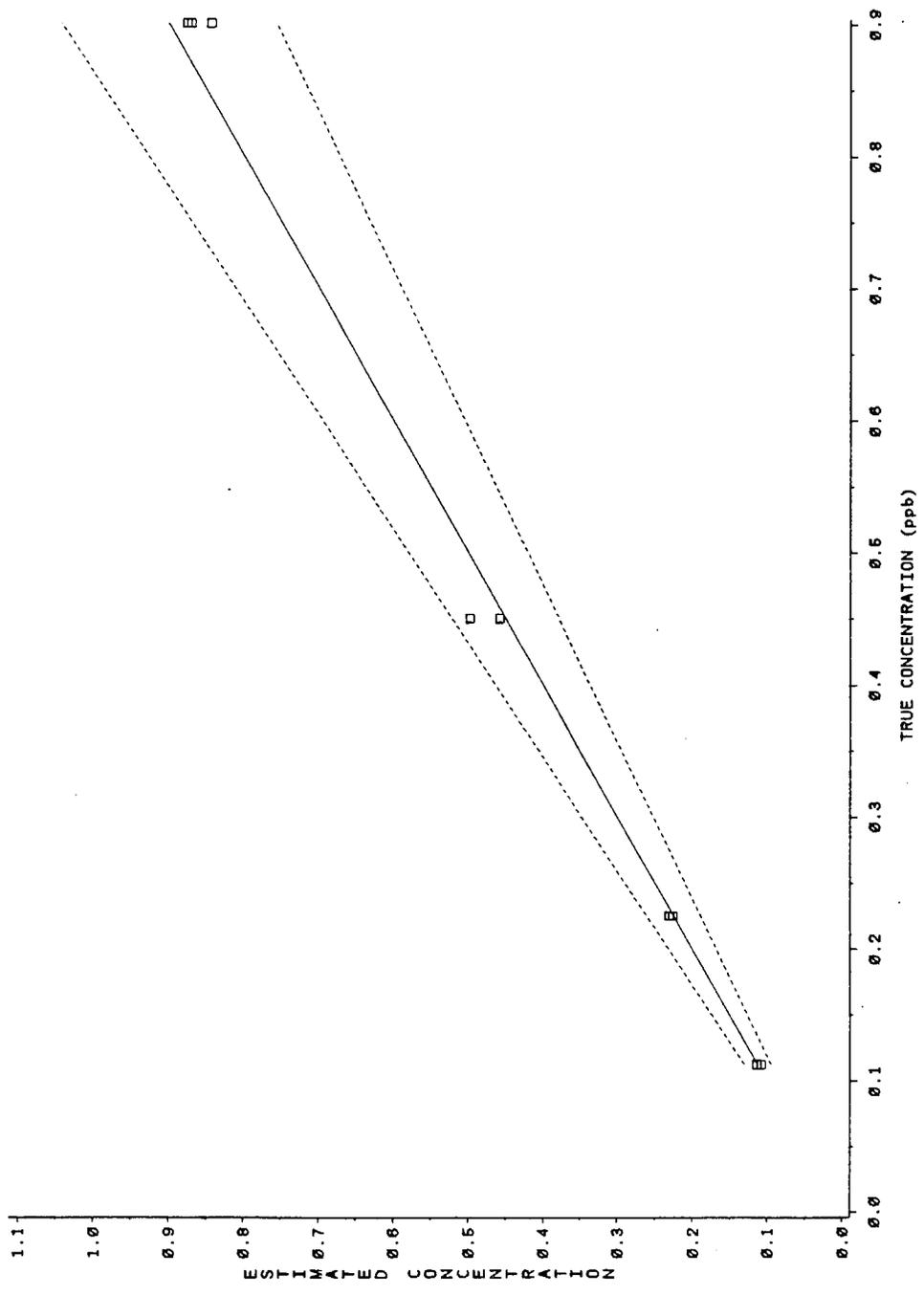
CALIBRATED DATA WITH WEIGHTED REGRESSION LINE  $\pm$  3 STDV  
COMPOUND=1,1,1-trichloroethane



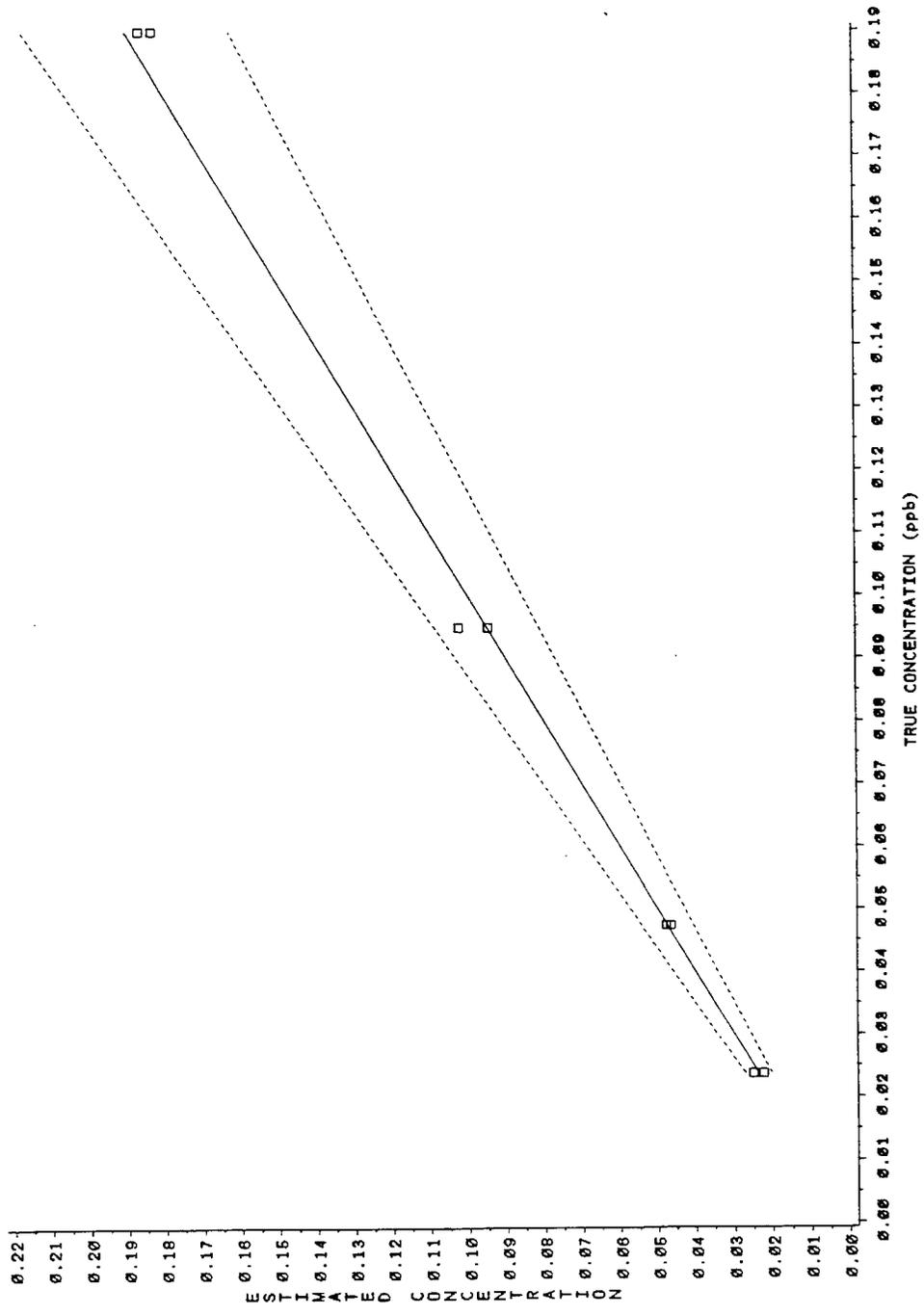
CALIBRATED DATA WITH WEIGHTED REGRESSION LINE  $\pm$  3 STDV  
 COMPOUND=carbon tetrachloride



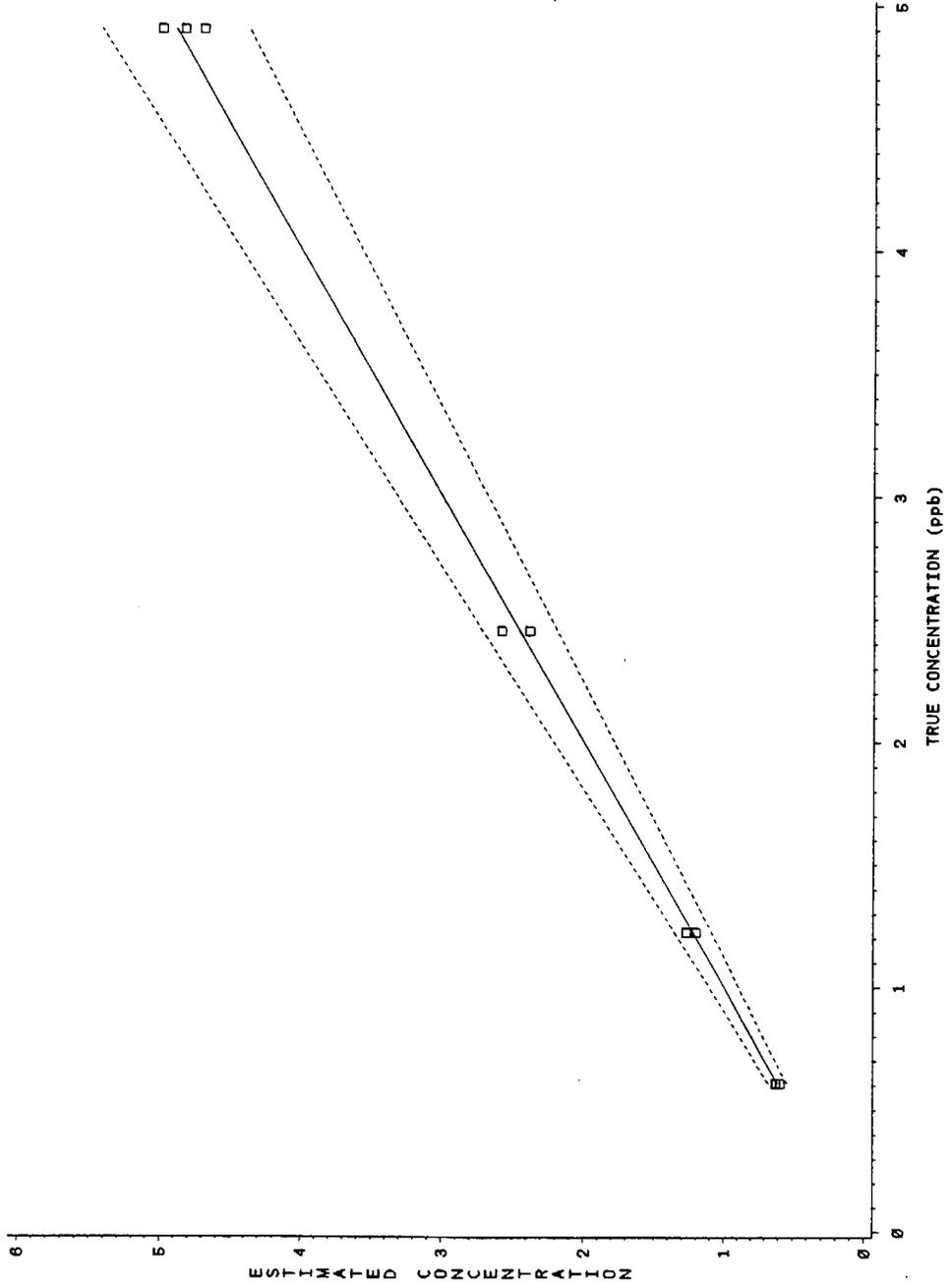
CALIBRATED DATA WITH WEIGHTED REGRESSION LINE  $\pm 3$  STDV  
COMPOUND=trichloroethene



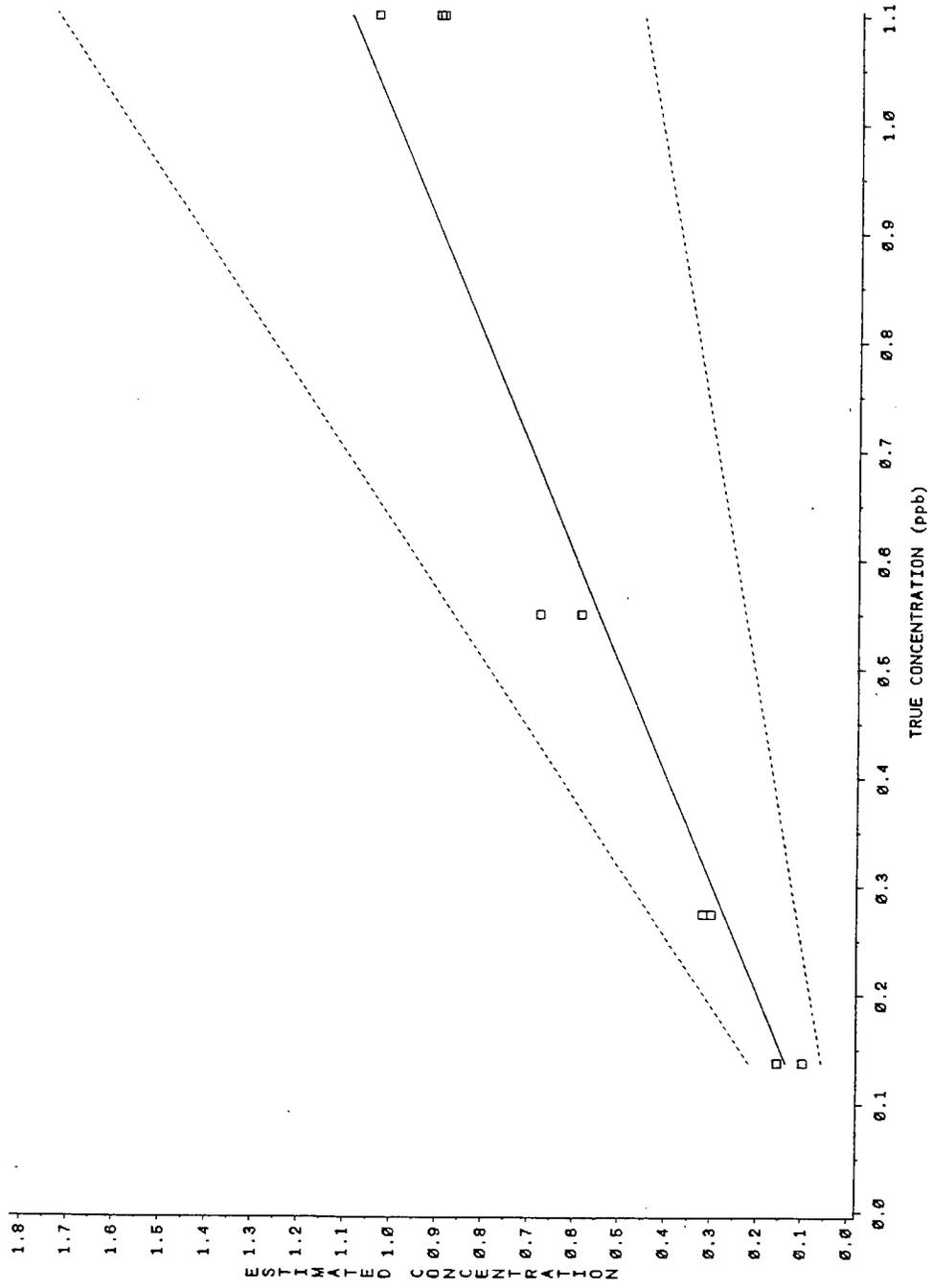
CALIBRATED DATA WITH WEIGHTED REGRESSION LINE  $\pm$  3 STDV  
 COMPOUND=tetrachloroethene



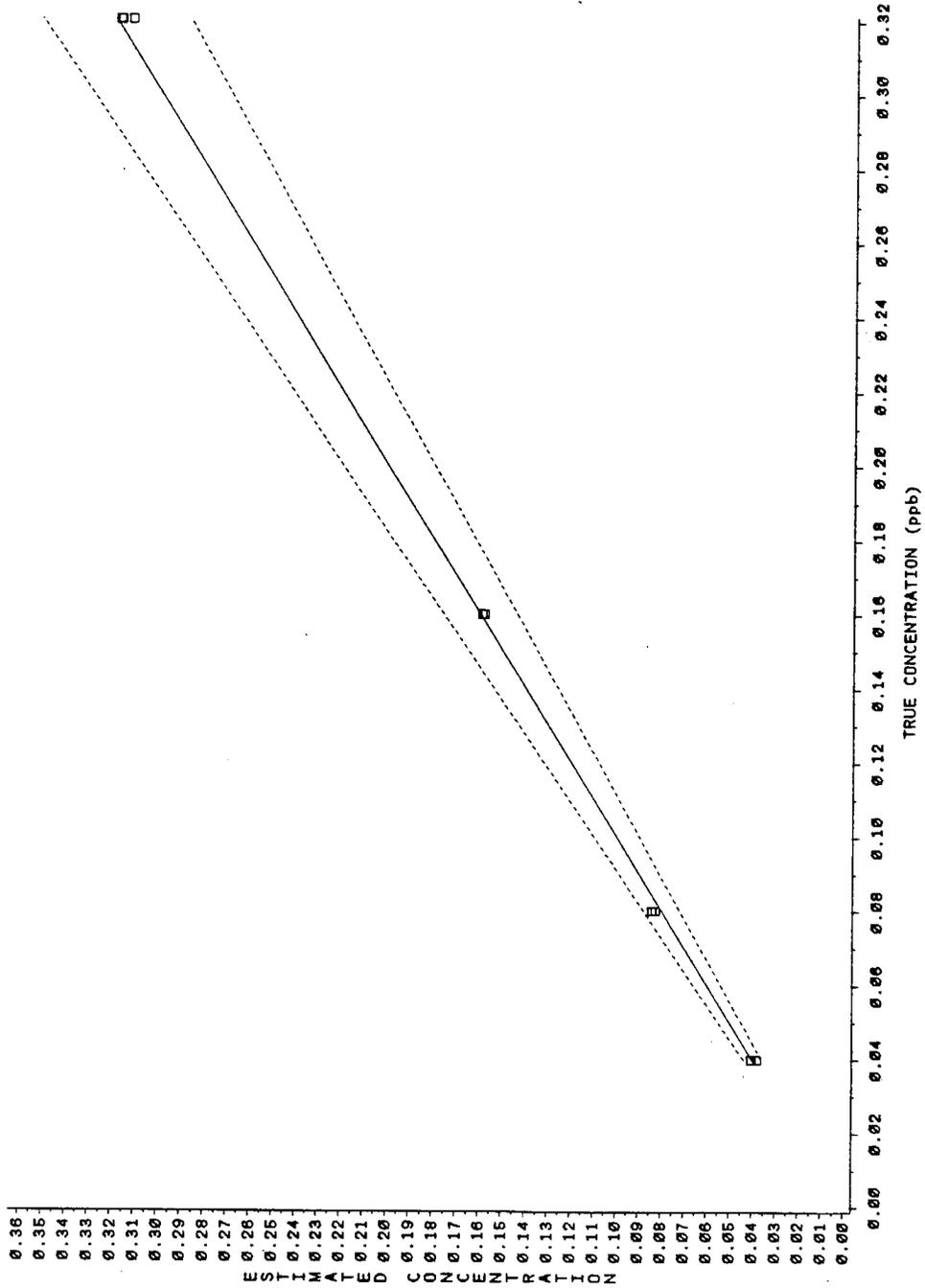
CALIBRATED DATA WITH WEIGHTED REGRESSION LINE  $\pm$  3 STDV  
COMPOUND=benzene



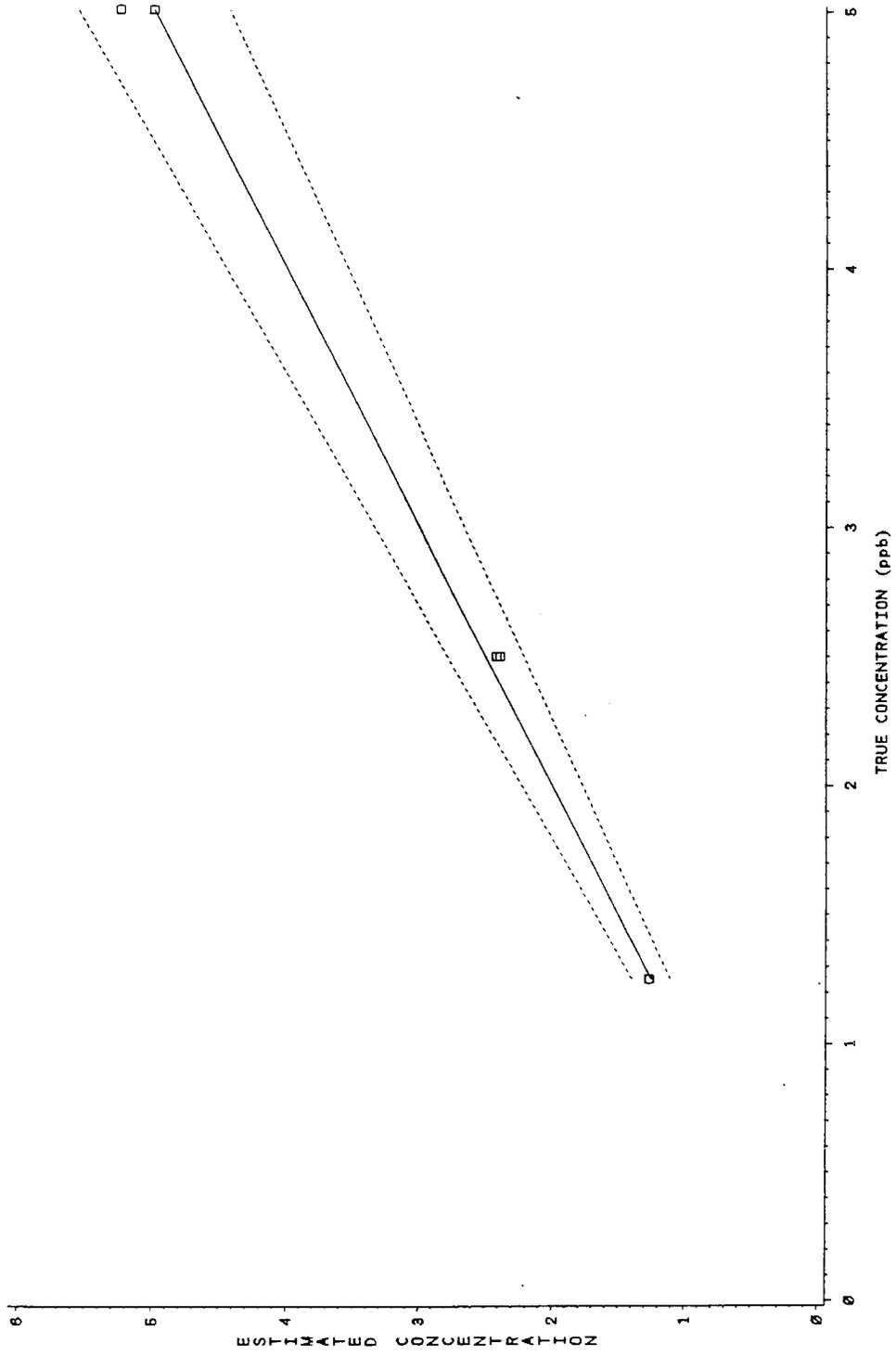
CALIBRATED DATA WITH WEIGHTED REGRESSION LINE  $\pm$  3 STDV  
COMPOUND=1,2-dichloroethane



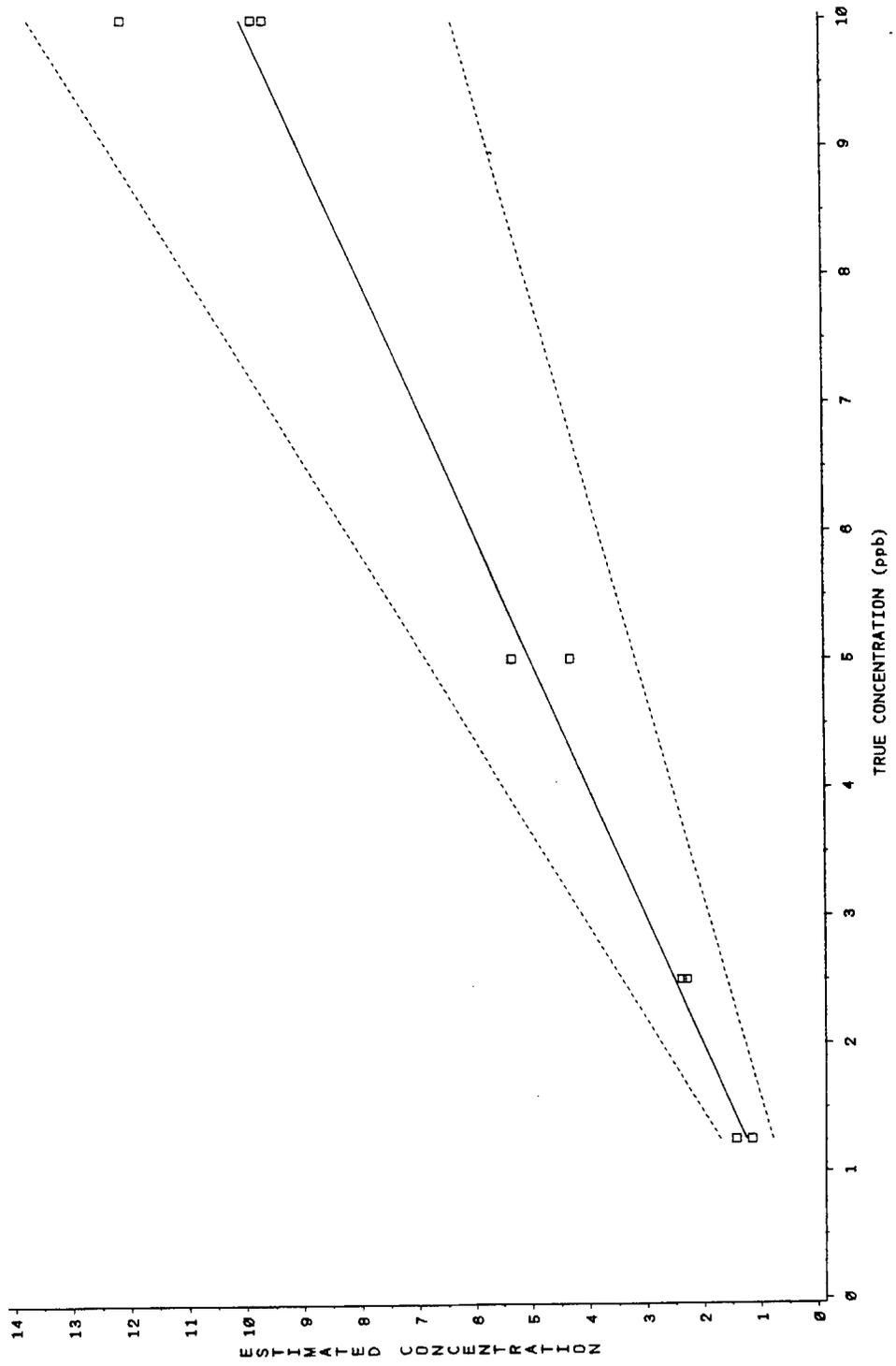
CALIBRATED DATA WITH WEIGHTED REGRESSION LINE  $+/- 3$  STDV  
 COMPOUND=1,2-dibromoethane



CALIBRATED DATA WITH WEIGHTED REGRESSION LINE  $\pm$  3 STDV  
COMPOUND=vinyl chloride



CALBRATED DATA WITH WEIGHTED REGRESSION LINE  $\pm$  3 STDV  
COMPOUND=toluene





APPENDIX V-C

CALIBRATION AND CONTROL SAMPLE DATA USED IN THE  
PRECISION ANALYSIS OF ARB'S ANALYTICAL METHOD



LISTING OF DAILY CALIBRATION & CONTROL DATA

CHEMICAL = dichloromethane

Date (YYMMDD)	Calibration Samples										Control Samples				
	RUN NUMBER	VOLUME	PEAK AREA	DAILY RFx10K	REPORTED CONC	%DIFF FROM TRUE	IMPUTED RFx10K	RUN NUMBER	VOLUME	PEAK AREA	CALC CONC	REPORTED CONC	IMPUTED RFx10K		
871216	710	200	84660	0.425	3.7000	- 2.8	0.437	711	200	68019	2.8924	2.8924	0.425		
871217	716	200	82465	0.437	3.5000	2.8	0.424	717	200	68777	3.0025	3.0000	0.438		
871218	727	200	81564	0.441	3.5607	1.1	0.437	728	200	68121	3.0067	3.0067	0.441		
871219	738	200	85157	0.423	3.7590	- 4.4	0.441	.	.	.	.	.	.		
871219	739	100	45356	0.397	4.0038	-11.2	0.441	.	.	.	.	.	.		
871219	740	50	25644	0.359	4.4216	-22.8	0.441	.	.	.	.	.	.		
871221	704	200	38623	0.932	1.6065	55.4	0.416	.	.	.	.	.	.		
871221	705	200	148594	0.242	6.1808	-71.7	0.416	.	.	.	.	.	.		
871222	709	200	57311	0.628	2.3800	33.9	0.415	710	200	47690	2.9957	3.0000	0.629		
871223	721	200	57881	0.622	.	.	.	722	200	47479	2.9530	2.9500	0.621		
871224	732	200	59058	0.610	3.7000	- 2.8	0.627	733	200	47154	2.8744	2.8744	0.610		
871228	739	200	52721	0.683	3.6000	0.0	0.683	740	200	42985	2.9352	2.9352	0.683		
871229	746	200	55402	0.650	3.5990	0.0	0.650	747	200	44407	2.8655	2.8655	0.650		
871230	753	200	56485	0.637	3.5990	0.0	0.637	755	200	44490	2.8355	2.8355	0.637		
871231	760	200	55093	0.653	.	.	.	761	200	46250	3.0222	3.0220	0.653		

LISTING OF DAILY CALIBRATION & CONTROL DATA

CHEMICAL = trichloromethane

Date (YYMMDD)	Calibration Samples										Control Samples			
	RUN NUMBER	VOLUME	PEAK AREA	DAILY RFx10K	REPORTED CONC	%DIFF FROM TRUE	IMPUTED RFx10K	RUN NUMBER	VOLUME	PEAK AREA	CALC CONC	REPORTED CONC	IMPUTED RFx10K	
871216	710	200	42834	0.037	0.1611	-0.7	0.038	711	200	31456	0.1175	0.1175	0.037	
871217	716	200	42957	0.037	.	.	.	717	200	31524	0.1174	0.1200	0.038	
871218	727	200	41955	0.036	0.1563	2.3	0.037	728	200	31194	0.1190	0.1190	0.038	
871219	738	200	43179	0.037	0.1647	-2.9	0.038	.	.	.	.	.	.	
871219	739	100	22173	0.036	0.1692	-5.7	0.038	.	.	.	.	.	.	
871219	740	50	11800	0.034	0.1800	-12.5	0.038	.	.	.	.	.	.	
871221	704	200	8352	0.192	0.0318	80.1	0.038	.	.	.	.	.	.	
871221	705	200	37484	0.043	0.1425	10.9	0.038	.	.	.	.	.	.	
871222	709	200	42030	0.036	0.1598	0.1	0.038	710	200	30772	0.1171	0.1171	0.038	
871223	721	200	42814	0.037	.	.	.	722	200	31031	0.1160	0.1200	0.039	
871224	732	200	42590	0.030	0.1600	0.0	0.038	733	200	30680	0.1153	0.1153	0.038	
871228	739	200	37556	0.043	0.1590	0.6	0.042	740	200	27078	0.1154	0.1154	0.043	
871229	746	200	38515	0.042	0.1549	3.2	0.040	747	200	27556	0.1145	0.1145	0.042	
871230	753	200	39333	0.041	0.1600	0.0	0.041	755	200	27913	0.1135	0.1135	0.041	
871231	760	200	38123	0.042	.	.	.	761	200	28513	0.1197	0.1197	0.042	

LISTING OF DAILY CALIBRATION & CONTROL DATA

CHEMICAL = 1,1,1-trichloroethane

Date (YYMMDD)	Calibration Samples										Control Samples			
	RUN NUMBER	VOLUME	PEAK AREA	DAILY RFx10K	REPORTED CONC	%DIFF FROM TRUE	IMPUTED RFx10K	RUN NUMBER	VOLUME	PEAK AREA	CALC CONC	REPORTED CONC	IMPUTED RFx10K	
871216	710	200	171473	0.111	1.1325	40.4	0.066	711	200	274555	3.0422	3.0000	0.109	
871217	716	200	234155	0.081				717	200	348181	2.8252	2.8000	0.080	
871218	727	200	246376	0.077	2.2174	-16.7	0.090	728	200	371846	2.8676	2.8676	0.077	
871219	738	200	258063	0.074	1.9901	-4.7	0.077							
871219	739	100	82703	0.115	1.2756	32.9	0.077							
871219	740	50	36617	0.132	1.1112	41.5	0.077							
871221	704	200	112805	0.168	0.7450	60.8	0.066							
871221	705	200	656151	0.029	4.3336	-128	0.066							
871222	709	200	158392	0.120	1.0460	44.9	0.066	710	200	284616	3.4141	1.8800	0.066	
871223	721	200	133782	0.142				722	200	229837	3.2842	2.3000	0.100	
871224	732	200	119710	0.159	1.2000	36.8	0.100	733	200	204959	3.2530	3.2793	0.100	
871228	739	200	117385	0.162	1.9000	0.0	0.162	740	200	201088	3.2548	3.2548	0.162	
871229	746	200	105570	0.180	1.8990	0.1	0.180	747	200	185252	3.3341	3.3341	0.180	
871230	753	200	109580	0.173	1.9000	0.0	0.173	755	200	186096	3.2267	3.2267	0.173	
871231	760	200	103599	0.183				761	200	180234	3.3055	3.3055	0.183	

LISTING OF DAILY CALIBRATION & CONTROL DATA

CHEMICAL = carbon tetrachloride

Date (YYMMDD)	Calibration Samples										Control Samples			
	RUN NUMBER	VOLUME	PEAK AREA	DAILY RFx10K	REPORTED CONC	DIFF FROM TRUE	IMPUTED RFx10K	RUN NUMBER	VOLUME	PEAK AREA	CALC CONC	REPORTED CONC	IMPUTED RFx10K	
871218	710	200	176128	0.009	0.1476	1.6	0.008	711	200	308008	0.2606	0.2606	0.009	
871217	716	200	182383	0.008	.	.	.	717	200	314482	0.2686	0.2686	0.008	
871218	727	200	187539	0.008	0.1542	- 2.6	0.008	728	200	308993	0.2471	0.2471	0.008	
871219	738	200	187365	0.008	0.1499	0.1	0.008	.	.	.	.	.	.	
871219	739	100	81309	0.009	0.1300	13.3	0.008	.	.	.	.	.	.	
871219	746	50	38416	0.010	0.1164	22.4	0.008	.	.	.	.	.	.	
871221	704	200	45787	0.033	0.0417	72.2	0.009	.	.	.	.	.	.	
871221	705	200	274547	0.005	0.2500	-66.7	0.009	.	.	.	.	.	.	
871222	709	200	162050	0.009	0.1480	1.3	0.009	710	200	270710	0.2506	0.2506	0.009	
871223	721	200	162475	0.009	.	.	.	722	200	275129	0.2540	0.2500	0.009	
871224	732	200	161281	0.009	0.1500	0.0	0.009	733	200	270811	0.2519	0.2519	0.009	
871228	739	200	135191	0.011	0.1490	0.7	0.011	740	200	223364	0.2478	0.2479	0.011	
871229	746	200	138326	0.011	0.1500	0.0	0.011	747	200	232432	0.2520	0.2522	0.011	
871230	753	200	143073	0.010	0.1500	0.0	0.010	755	200	233808	0.2451	0.2451	0.010	
871231	760	200	149187	0.010	.	.	.	761	200	246095	0.2474	0.2474	0.010	

LISTING OF DAILY CALIBRATION & CONTROL DATA

CHEMICAL = trichloroethene

Date (YYMMDD)	Calibration Samples										Control Samples				
	RUN NUMBER	VOLUME	PEAK AREA	DAILY RFx10K	REPORTED CONC	%DIFF FROM TRUE	IMPUTED RFx10K	RUN NUMBER	VOLUME	PEAK AREA	CALC CONC	REPORTED CONC	IMPUTED RFx10K		
871216	710	200	341345	0.028	0.9263	- 2.9	0.027	711	200	929905	2.4518	2.4518	0.026		
871217	716	200	336505	0.027	.	.	.	717	200	920443	2.4618	2.4600	0.027		
871218	727	200	331883	0.027	0.8876	1.4	0.027	728	200	904125	2.4518	2.4518	0.027		
871219	738	200	340616	0.026	0.9237	- 2.6	0.027	.	.	.	.	.	.		
871219	739	100	166836	0.027	0.9048	- 0.5	0.027	.	.	.	.	.	.		
871219	740	50	87228	0.026	1.0540	-17.1	0.030	.	.	.	.	.	.		
871221	704	200	53237	0.169	0.1413	84.3	0.027	.	.	.	.	.	.		
871221	705	200	266450	0.034	0.2020	77.6	0.008	.	.	.	.	.	.		
871222	709	200	373011	0.024	0.9899	-10.0	0.027	710	200	1070E3	2.5989	2.5969	0.024		
871223	721	200	371661	0.024	.	.	.	722	200	1071E3	2.5930	2.6000	0.024		
871224	732	200	367197	0.025	0.8900	1.1	0.024	733	200	1053E3	2.5820	2.5820	0.025		
871228	739	200	321066	0.028	0.9000	0.0	0.028	740	200	901530	2.5271	2.5271	0.028		
871229	746	200	346090	0.026	0.9000	0.0	0.026	747	200	957359	2.4896	2.4896	0.026		
871230	753	200	349029	0.026	0.9000	0.0	0.026	755	200	901670	2.4798	2.4798	0.026		
871231	760	200	339204	0.027	.	.	.	761	200	959584	2.5460	2.5460	0.027		

LISTING OF DAILY CALIBRATION & CONTROL DATA

CHEMICAL = tetrachloroethene

Date (YYMMDD)	Calibration Samples										Control Samples			
	RUN NUMBER	VOLUME	PEAK AREA	DAILY RFx10K	REPORTED CONC	%DIFF FROM TRUE	IMPUTED RFx10K	RUN NUMBER	VOLUME	PEAK AREA	CALC CONC	REPORTED CONC	IMPUTED RFx10K	
871216	710	200	385109	0.005	0.1905	- 0.3	0.005	711	200	2107E3	1.0391	1.0391	0.005	
871217	716	200	380052	0.005	0.1900	0.0	0.005	717	200	2084E3	1.0318	1.0300	0.005	
871218	727	200	373116	0.005	0.1865	1.0	0.005	728	200	2017E3	1.0273	1.0273	0.005	
871219	738	200	379874	0.005	0.1933	- 1.7	0.005	.	.	.	.	.	.	
871219	739	100	191271	0.005	0.1948	- 2.5	0.005	.	.	.	.	.	.	
871219	740	50	102577	0.005	0.2000	- 9.5	0.005	.	.	.	.	.	.	
871221	704	200	70622	0.027	0.0373	80.4	0.005	.	.	.	.	.	.	
871221	705	200	348797	0.005	0.1895	0.3	0.005	.	.	.	.	.	.	
871222	709	200	388107	0.005	0.2053	- 8.1	0.005	710	200	2261E3	1.1068	1.1065	0.005	
871223	721	200	387804	0.005	.	.	.	722	200	2291E3	1.1223	1.1200	0.005	
871224	732	200	382297	0.005	0.1900	0.0	0.005	733	200	2261E3	1.1236	1.1236	0.005	
871228	739	200	346016	0.005	0.1900	0.0	0.005	740	200	2003E3	1.0997	1.0997	0.005	
871229	746	200	366899	0.005	0.1900	0.0	0.005	747	200	2080E3	1.0804	1.0804	0.005	
871230	753	200	367087	0.005	0.1900	0.0	0.005	755	200	2084E3	1.0683	1.0683	0.005	
871231	760	200	367065	0.005	.	.	.	761	200	2074E3	1.0736	1.0736	0.005	

LISTING OF DAILY CALIBRATION & CONTROL DATA

CHEMICAL = benzene

Date (YYMMDD)	Calibration Samples										Control Samples			
	RUN NUMBER	VOLUME	PEAK AREA	DAILY RFx10K	REPORTED CONC	%DIFF FROM TRUE	IMPUTED RFx10K	RUN NUMBER	VOLUME	PEAK AREA	CALC CONC	REPORTED CONC	IMPUTED RFx10K	
871216	710	200	36037	1.360	4.8879	0.2	1.356	711	200	35384	4.8112	4.8112	1.360	
871217	716	200	35425	1.383	.	.	.	717	200	33763	4.6701	4.6700	1.383	
871218	727	200	34465	1.422	4.7672	2.7	1.383	728	200	35766	5.0850	4.9472	1.383	
871219	738	200	34339	1.427	4.8621	0.4	1.422	.	.	.	.	.	.	
871219	739	100	16410	1.493	4.6662	4.8	1.422	.	.	.	.	.	.	
871219	740	50	8291	1.478	4.7136	3.8	1.421	.	.	.	.	.	.	
871221	704	200	7170	6.834	0.9953	79.7	1.388	.	.	.	.	.	.	
871221	705	200	35100	1.396	4.8720	0.6	1.388	.	.	.	.	.	.	
871222	709	200	33592	1.459	4.6630	4.8	1.388	710	200	33265	4.8523	4.8523	1.459	
871223	721	200	34198	1.433	.	.	.	722	200	35100	5.0295	5.0000	1.425	
871224	732	200	33425	1.466	4.8000	2.0	1.436	733	200	32824	4.8119	4.8119	1.466	
871226	739	200	35868	1.368	4.8990	0.0	1.366	740	200	36590	4.9986	4.9986	1.366	
871229	746	200	34674	1.405	4.9000	0.0	1.405	747	200	34568	4.8570	4.8570	1.405	
871230	753	200	36363	1.347	4.9000	0.0	1.347	755	200	34080	4.5898	4.7196	1.385	
871231	760	200	34261	1.430	.	.	.	761	200	33586	4.8037	4.8037	1.430	

LISTING OF DAILY CALIBRATION & CONTROL DATA

CHEMICAL = 1,2-dichloroethane

Date (YYMMDD)	Calibration Samples										Control Samples			
	RUN NUMBER	VOLUME	PEAK AREA	DAILY RFx10K	REPORTED CONC	%DIFF FROM TRUE	IMPUTED RFx10K	RUN NUMBER	VOLUME	PEAK AREA	CALC CONC	REPORTED CONC	IMPUTED RFx10K	
871216	710	200	31074	0.354	1.1116	- 1.1	0.358	711	200	2309	0.0817	0.0817	0.354	
871217	716	200	30771	0.357	.	.	.	717	200	2444	0.0874	0.0870	0.368	
871218	727	200	30287	0.363	1.0827	1.6	0.367	728	200	2351	0.0854	0.0854	0.363	
871219	738	200	31595	0.348	1.1475	- 4.3	0.383	.	.	.	.	.	.	
871219	739	100	15879	0.348	1.1534	- 4.9	0.383	.	.	.	.	.	.	
871219	740	50	8259	0.333	1.2000	- 9.1	0.363	.	.	.	.	.	.	
871221	704	200	12287	0.895	0.4106	62.7	0.334	.	.	.	.	.	.	
871221	705	200	57591	0.191	1.9250	-75.0	0.334	.	.	.	.	.	.	
871222	709	200	17651	0.623	0.5900	46.4	0.334	710	200	.	.	.	.	
871223	721	200	22201	0.495	.	.	.	722	200	1677	0.0831	0.0830	0.495	
871224	732	200	20799	0.529	1.0300	6.4	0.495	733	200	.	.	.	.	
871228	739	200	17547	0.827	1.1000	0.0	0.627	740	200	.	.	.	.	
871229	746	200	19249	0.571	1.0990	0.1	0.571	747	200	.	.	.	.	
871230	753	200	19405	0.567	1.1000	0.0	0.567	755	200	1443	0.0818	0.0818	0.567	
871231	760	200	19326	0.569	.	.	.	761	200	1609	0.0950	0.0950	0.569	

LISTING OF DAILY CALIBRATION & CONTROL DATA

CHEMICAL = 1,2-dibromoethane

Date (YYMMDD)	Calibration Samples										Control Samples				
	RUN NUMBER	VOLUME	PEAK AREA	DAILY RFx10K	REPORTED CONC	%DIFF TRUE	FROM TRUE	IMPUTED RFx10K	RUN NUMBER	VOLUME	PEAK AREA	CALC CONC	REPORTED CONC	IMPUTED RFx10K	
871216	710	200	89801	0.036	0.2284	29.2	0.025	0.025	711	200	487186	1.7361	1.2284	0.025	
871217	716	200	93771	0.034	0.2380	26.3	0.025	0.025	717	200	469232	1.6013	1.2000	0.028	
871218	727	200	97757	0.033	0.2465	23.0	0.025	0.025	728	200	475840	1.5570	1.1993	0.025	
871219	738	200	96732	0.033	0.2439	23.8	0.025	0.025	.	.	.	.	.	.	
871219	739	100	40866	0.040	0.2020	36.9	0.025	0.025	.	.	.	.	.	.	
871219	740	50	17112	0.047	0.1720	46.3	0.025	0.025	.	.	.	.	.	.	
871221	704	200	19927	0.161	0.0582	84.3	0.025	0.025	.	.	.	.	.	.	
871221	705	200	121467	0.028	0.3063	4.3	0.025	0.025	.	.	.	.	.	.	
871222	709	200	87221	0.037	0.2199	31.3	0.025	0.025	710	200	444258	1.6299	1.1202	0.025	
871223	721	200	86834	0.037	.	.	.	.	722	200	445060	1.6401	1.6000	0.036	
871224	732	200	84233	0.038	0.3100	3.1	0.037	0.037	733	200	434720	1.6515	1.6515	0.038	
871228	739	200	75183	0.043	0.3200	0.0	0.043	0.043	740	200	361949	1.5406	1.5406	0.043	
871229	746	200	74910	0.043	0.3200	0.0	0.043	0.043	747	200	387172	1.6539	1.6200	0.042	
871230	753	200	76170	0.041	0.3200	0.0	0.041	0.041	755	200	390064	1.5988	1.5988	0.041	
871231	760	200	79684	0.040	.	.	.	.	761	200	395391	1.5878	1.5878	0.040	

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