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Abstract

Title of thesis : Organics in Ambient Air By Collection On Tenax, Thermal Desorption, and Capillary Chromatography with Parallel FID/ECD Analyses

Name of Candidate : Chih-Hsiang Liao Master of Science in Environmental Engineering, 1989.

Thesis directed by:

Dr. Barbara B. Kebbekus Date Associate Chair Department of Chemical Engineering, Chemistry & Environmental Science

Volatile organics in ambient air were regularly collected on Tenax cartridges at high (10 ml/min) and low (5 ml/min) intake flows. These Tenax samples were analyzed by using a Tekmar Automatic Thermal Desorber and capillary GC system with parallel flame ionization (FID) and electron capture detectors (ECD). A series of quality assurance procedures has been established to improve and assure the accuracy and precision of sample collecton and analysis. These procedures relate to performance of the Tekmar thermal desorber, recovery efficiency from the Tenax, and include studies on breakthrough and co-elution. The results demonstrate (1) that from ambient air data in East Central

New Jersey, chlorocarbons, including chloroform, 1,1,1trichloroethane, carbon tetrachloride, trichloroethylene and perchloroethylene, are present at lower levels than the hydrocarbons: hexane, benzene, toluene and p,m-xylene. Among the chlorocarbons, chloroform and trichloroethylene are present at very low trace levels (within 0.5 ppb) at sampling sites if compared to the other compounds; (2) the ECD is a preferred detector to accurately quantitate the chloro compounds, while hydrocarbons are bset quantitated by FID; (3) The accuracy and precision of Tenax sampling for most of the target compounds warrants its use as judged from studies of breakthrough as well as agreement between high and low flow samples; and (4) Tenax adsorbent is unable to efficiently trap light chlorocarbons such as methylchloride and dichloromethane. A statistical analysis of air data is presented based upon the above studies.

ORGANICS IN AMBIENT AIR BY COLLECTION ON TENAX, THERMAL DESORPTION, AND CAPILLARY CHROMATOGRAPHY WITH PARALLEL FID/ECD ANALYSES

ΕY

CHIH-HSIANG LIAO

Thesis submitted to the faculty of the Graduate School of the New Jersey Institute of Technology in partial fulfillment of the requirements for the degree of Master of Science in Environmental Science 1989

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APPROVAL SHEET

Title of Thesis : Organics in Ambient Air By Collection on Tenax, Thermal Desorption, and Capillary Chromatography with Parallel FID/ECD Analyses

Name of Candidate : Chih-Hsiang Liao Master of Science in Environmental Science, 1989

Thesis and Abstract Approved :

5/11/89

9 19 89

Dr. Barbara B. Kebbekus Associate Chair Department of Chemical Engineering, Chemistry & Environmental Science

MAg Dr. Joseph W. Bozzelli Date Professor Department of Chemical Engineering, Chemistry & Environmental Science

Date

Dr. Arthur Greenberg Professor Department of Chemical Engineering, Chemistry & Environmental Science

Date

Name : Chih-Hsiang Liao

;*

Permanent address :

Drgree and date to be conferred : M.S. Ev. Sc., 1989

Date of birth :

Place of birth :

Secondary education : Chien-Kuo High School, Sep. 1975

| Collegiate institutions | Attended | Date | Degree | Date |
|-----------------------------|----------|------|--------|------|
| National Cheng Kung Univers | ity | 9/78 | B.Sc | 6/82 |
| New Jersey Institute of Tec | hnology | 9/87 | M.S | 5/89 |

Major : Environmental Science

Minor : Air Pollution Analysis and Method Development Position held :

| 9/87 - present | Research Assistant Air Pollution Research Laboratory Department of Chemical Engineering Chemistry & Environmental Science New Jersey Institute of Technology Newark, New Jersey 07102 |
|----------------|--|
| 6/84 - 6/87 | Engineer Taiwan Water Supply Corporation Kaohsiung, Taiwan, R.O.C |
| 5/82 - 5/84 | Second Lieutenant military service in the Army |

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My wife, Michelle, and my son, Steven, have cheerfully waited for this "homework" to be finished. I am deeply gratefully to them for their patience.

Finally, I am indebted to my parents in Taiwan, and I would like to present this paper to them.

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I. Introduction

A. Staten Island/New Jersey Urban Air Toxics Assessment Project (SI/NJ UATAP)

The Urban Air Toxics Assessment Project for Northeastern New Jersey and Staten Island is a three year project encompassing indoor as well as outdoor air sampling and analysis. The overall objective is to characterize the air quality in the target region for selected toxic air contaminants. Ultimately, data collected during the study period will be used to develop human exposure assessments. The groups involved represent both academic communities and governmental agencies: University of Medicine and Dentistry of NJ (UMDNJ) - Robert Wood Johnson Medical School; New Jersey Institute of Technology (NJIT); College of Staten Island (CSI); NY Department of Environmental Conservation (NYDEC); NJ Department of Environmental Protection (NJDEP); NY Department of Health (NYDOH); and US Environmental Protection Agency (EPA). Four ambient pollutant monitoring sites were selected in Northeastern New Jesey, two sites in Union County and two in Middlesex County. NJIT has serviced the two sites at Elizabeth and Carteret for two years with sampling once every 6 days. Selected ambient volatile organic compounds (VOCs) include:

MeCl --- methylchloride; DCM --- dichloromethane; C6 --- hexane; CFor --- Chloroform; 1,1,1--- 1,1,1-trichloroethane;

Bz --- benzene; CC14 ---carbon tetrachloride; Tric --- trichloroethylene; Tol---toluene; Perc --- perchloroethylene; pmX--- p,m-Xylene; and oX --- o-xylene.

They are on the EPA list of priority pollutants. Seven of the above target compounds are chloro compounds (C_{1-2}) . Quarterly and annual reports of experiments data are submitted to both NJDEP and EPA for comparison with the other analytical laboratories involved in this project. To assure data quality produced by individual laboratory or agent, an intensive sampling campaign called a "shootout"- a project for interlaboratory comparison study-was held once a year with sample collection in Staten Island, New York. Before the "shoot-out", separate media for sample collection were sent to EPA for spiking with standards. Subsequent analytical results were reported to EPA with separate quality assurance analyses on Tenax samples also.

B. Tenax Sampling of Ambient Air

Volatile organic compounds in ambient air or water are present in low concentrations (ppm-ppb range). Thus preconcentration of VOCs is necessary for quantitative or qualitative gas chromatographic analysis. This preconcentration can be achieved by either loading a largevolume air sample collected in a canister into a cryogenic trap or drawing a required air volume through a cartridge

containing a sorbent medium, which retains the organic compounds while allowing the bulk constituent (air, H_2O , $CO_2...$) to pass through, then desorbing the sample for analysis.

In selecting a solid sorbent for sampling, we have considered the influence of temperature and humidity on the collection efficiency. The sorbent's affinity for water vapor in ambient air can be a limiting factor especially when a sample is to be analyzed by capillary gas chromatography. One liter of air at 50% relative humidity and 25° C will contain approximately 10 mg of water that appears as ice in the cryogenic focus area of the capillary trap. This ice can present a large problem because of the possibility of altering or plugging the carrier flow. Carrier flow variation or temporary stoppage will cause variability in retention times and may cause incomplete cryotrap desorption [1].

The ability of Tenax to collect and retain hazardous vapors from ambient air is nearly unaffected by humidity conditions commonly encountered in field sampling [2,3]. In addition to the sorption power of Tenax, (adsorbing compounds up to C_{16} (B.P 290^O C) [4]), it can easily be regenerated for repeated re-use [3]. A disadvantage, however, is the relatively small breakthrough volumes for light hydrocarbons and low molecular weight polar compounds that limit sample volumes for these species [5].

In the SI/NJ UATA project, we have used Tenax for sampling. The parameters for Tenax cartridge and sampling conditions are listed below :

| stainless steel tube | 0.64 cm (o.d) x 18 cm |
|--------------------------|---------------------------|
| weight of adsorbent | 350 mg |
| adsorbent particle size | 60/80 mesh |
| adsorbent bed | 0.60 cm (i.d) x 7 cm |
| bulk density in tube | 0.18 g/cm ³ |
| sampling flow rate | |
| low flow tube | 5 ml/min or 7 liter/day |
| high flow tube | 10 ml/min or 14 liter/day |
| sampling flow rate/cross | area |

| low flow tube | 17.7 | cm/min |
|----------------|------|--------|
| high flow tube | 35.4 | cm/min |

C. Analytical Method

After sampling, the concentrated compounds are released by thermal desorption and introduced via a carrier gas system into a cryofocusing capillary trap at the head of the GC capillary column, followed by rapidly heating this trap and injection onto the capillary GC column. The effluent of the column is split into two GC detectors- a flame ionization detector (FID) and an electron capture detector (ECD).

To quantitate the sample, a standard gas mixture containing target compounds was prepared and analyzed in

the same manner as the samples. The concentrations of unknown sample are then calculated according to the formula :

 $C_{1}/C_{2} = A_{1}/A_{2}$

where C₁ is standard concentration;

C₂ is sample concentration;

- A1 is peak area of detector response of standard;
- A₂ is peak area of detector response of sample.
- D. Evaluation and Statistical Analysis of Ambient Air Data

A careful evaluation of ambient air data obtained from Tenax sampling is a difficult and lengthy process containing much uncertainty. This paper will describe several criteria for interpretation of the precision of the entire sampling and analytical system.

In addition to the basic requirement of correct identification of target compounds, specific criteria are necessary for judging data quality statistically. These include both laboratory and field studies such as :

- performance of desorber/analytical system;
- (2) recovery efficiency and reproducibility of spikedTenax;
- (3) bias of entire system;
- (4) duplicate sampling; and
- (5) agreement between high and low flow tubes.

II. Instrumentation

A. Description of the Analytical System

shown in Figure 1, the analytical system As incorporates a Tekmar Model 5000 Automatic Desorber and a Varian Model 3700 gas chromatography equipped with an IBM PC based data acquisition system (Interactive Microware, Inc.). The Tekmar 5000 automatic on-line desorber is a microprocessor- based instrument designed for the thermal desorption and gas chromatographic injection of volatile orgranic compounds from adsorbent traps for use with capillary G.C. The interface provides direct on-column injection, by cryogenically trapping the desorbed sample into a narrow band on an uncoated inert fused silica precolumn (0.32 mm i.d). This then flash-heated for injection into the G.C. Both desorber and GC were interfaced so that the entire analysis was automated. All transfer components (tubing, valves) were heated to minimize sample loss by physical adsorption.

A 50 m x 0.21 mm i.d. cross-linked methyl fused silica column (Hewlett Packard) with 0.5 micron film thickness of OV 101 was used to resolve the target compounds. The column flow was maintained at a volume flow of 1 ml/min by using a flow controller. Zero-grade helium served as the carrier gas, and zero-grade nitrogen (28

ml/min)was used as the make-up gas to provide electron capture operation. Optimum analytical results were achieved by temperature programming the GC oven from 35 to 195° C at 6° C/min. At the end of the column, the carrier gas flow is split to the FID and ECD, with 90% of the effluent going to the FID.

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Besides, two six-port valves (shown in Figure 1) with 2 ml sampling loops were also used in order to have the flexibility to :

(1) run standard gas either by the flow routing of sample analysis or by direct injection onto the GC column; and
(2) spike the standard gas mixture onto Tenax for diverse experiments.

B. Performance of Tekmar Automatic Desorber

The Tekmar Model 5000 Automatic Desorber [6] provides both fully automatic desorption of the Tenax cartridge and fully automated interface to the G.C. Once a Tenax trap has been inserted into the furnace, it is first swept with helium before it is heated. This prepurge mode serves dual functions. It allows any water present to be purged out of the tube before the internal trap is cooled; this is particularly helpful for taking samples under high humidity or rainy conditions. The second advantage of this mode is that it removes oxygen from the tube before heating, thus increasing the life time of the reuseable

Tenax material and reducing the formation of artifacts. After prepurge the trap is heated and swept with helium into a cryogenic trap cooled by liquid nitrogen. After the desorption step is complete, an eight-port switching valve is rotated to cause the carrier gas to backflush the cold trap, which is heated rapidly to a preset temperature, and the sample is then transferred to the second cryogenic trap before the sample is injected into the G.C. After sample injection, the Tenax trap can be baked to regenerate it. All the sampling traps were analyzed under the following desorption conditions :

Prepurge 1 : 3 min at 10 ml/min; Desorb : 12 min at 210° C into a cold trap (Cryo-1) at -150° C; Transfer: 12 min at 1 ml/min and 210° C of transfer line into a second cryofocus (Cryo-2) at -150° C; Inject : 2 min at 210° C; and Bake: 15 min at 225° C.

To ensure the reliability of the Tekmar desorber, an experiment was made to compare a standard gas mixture run through the desorber and GC (Cryo-1 and 2) versus the same standard directly injected into the GC (Cryo-2 only), which are termed Method 1 and Method 3, respectively, and were automatically controlled by desorber, upon their selection.

'Table 1 presents results for a standard gas mixture analyzed on different dates using Method 1. For any given compound, the reproducibility is acceptable, since the coefficient of variation (CV) ranges from 2.4 to 10.38 %.

Similarly, Table 2 shows CV ranging from 1.37 to 6.96 % by Method 3. Comparing the CV value of a given compound, as one might expect due to the comparative simplicities, the dispersion is lower by Method 3 than by Method 1 with the exception of C6 and CFor, which are eluted at nearly the same retention time.

A criterion for judging Tekmar desorber performance under the mentioned desorption conditions is to investigate the difference between both methods(1 and 3 only). The difference was computed and shown in Table 3, which indicates that the percent difference between Method 1 and 3 ranges from -6.44 to 1.71. It thus implies that complete recovery can be obtained under the preset conditions of desorber; for any of the target compounds, the -150° C temperature of Cryo-1 and 2 is low enough to trap all target compounds at a desorption flow rate of 10 ml/min in Cryo-1 or transfer flow rate of 1 ml/min in Cryo-2. Another point is that the temperature of the transfer line and the transfer time, which are 210° C and 12 min, can be also accepted. However, we have investigated various transfer line temperatures to check the recovery efficiencies of target compounds. Table 4 presents the result of the transfer line temperature versus weight detected, and Figure 2 and 3 show the graphs plotted from Table 4 for comparison of low and high boiling points. As we can see, the quantities of pmX and oX decrease a little at 90° C but

significantly decrease at 60° C, while all the other compounds are not affected by temperatures as low as 60° C. This shows us a very important concept that the waterplugging problem in the capillary column could be solved by controlling the transfer line temperature at an optimum value, so as to retain the water vapor and water- soluble polar compounds while allowing the target compounds to be transferred to Cryo-2. Using modification on the Tekmar desorber, we can also analyze the VOCs collected by the canister method or by other solid sorbents which tend to adsorb water vapor under such analytical system.

Another experiment to test the performance of the entire analytical system including the desorber and capillary GC was made by spiking standards into 8 clean Tenax traps and then desorbing the traps. The recovery values of 8 replicates were computed in Table 5. It shows that complete recovery of target compounds can be obtained with only one exception MeCl, which will be explained later on.

Before high performance was achieved in the analytical system, we had found that a hot spot (around 80 $^{\circ}$ C) at the far end of desorber furnace existed with temperature high enough to liberate the sample adsorbed on the most concentrated end of the Tenax tube. Thus we would lose the sample during three-minute prepurge mode, even though the displayed furnace temperature was 40° C. Due to

this, we decrease the quantity of Tenax adsorbent, 500 mg to 350 mg, allowing a shorter Tenax bed (7 cm long) in the sampling tube with the bottom region (10 cm long) of the furnace empty to avoid effects of the hot spot.

C. Comparison of FID and ECD GC Detector

The FID [7] is highly sensitive to most organic compounds with the exception of certain functional groups such as carbonyl, hydroxyl, halogen, and amino. These can sometimes yield fewer ions or none at all. On the other hand, the ECD [7] is selective in its response, being highly sensitive toward molecules containing electronnegative functional groups such as halogens, peroxides, quinones, and nitro groups. ECD is insensitive toward molecular classes including amines, alcohols, and hydrocarbons. It will be shown in this work that knowing the response intensity relationships for chloro compounds between FID and ECD is of significant benefit since 7 of 12 target compounds are chloro compounds. We will show that these chloro compounds can be easily interfered with (coelution) by other hydrocarbons. This co-elution or interference is amplified further because the FID response to some of the chlorinated compounds is very small. Inaccurate quantitation may result if these are determined only by FID response. Due to this potential problem we show

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that one should consider the quantitation of chlorocarbons by ECD, instead of by FID, if good reproducibility and linear response can be achieved.

Different amounts of standard were injected into the desorber and GC using six-port valve with 2 ml sampling loop, by changing the pressure in the sampling loop (eg 1 atm, 28", 20", 10", 5", 2"). The sampling loop was set at temperature of 165 ° C. Table 6 shows the reproducibility comparison of the two GC detectors. The coefficients of variation (CV) of FID and ECD response indicate the dispersion of a group of replicate data. As for FID, all the CV values are within 10%, while they show larger variations with ECD (within 17%). However, the precision of quantitation can be better by ECD than by FID when one considers the described co-elution problem of chloro compounds with atmospheric HC's. From this experiment, sets of data on FID and ECD responses with several different amounts of standard gas were obtained. These data are shown shows that P is in Table 7. The gas law (PV=nRT) proportional to (n/V)=C (concentration) when T is constant. If linear response of both detectors is assumed, then the following expression is obtained:

 $P_1 C_1 A_1$ __ _ _ _ _ _ $P_2 C_2 A_2$

where P; is pressure

i i i i

C_i is concentration of compound

A; is peak area of compound.

Using the experimental data in Table 7, a number of regression lines of response area vs pressure are shown in Figure 4-1 through 4-12. It is apparent that high linear correlation is achieved for each of target compounds. Table 8 shows the correlation coefficients of R squared between FID/ECD and pressure for each of the twelve compounds and also the weight range being detected. In general, a high linear response exists for all target compounds with both FID and ECD. The correlation coefficients of chloro compounds from FID and ECD indicate that higher correlation is obtained for the ECD. Hence, to eliminate the interference from co-eluting peaks, we recommend quantitation of chlorinated compounds directly by ECD since this method has the higher linear correlation.

III. Characteristics of Tenax Adsorbent and Adsorbate

A. Basic Parameters

Tenax is a relatively polar porous ploymer based on 2,6-diphenyl-p-phenylene oxides. It was developed by AKZO Research laboratories and introduced as a GC column material by Van Wijk in 1969-70 [8]. Typical characteristics of Tenax TA are :

| specific surface area | 35 m ² /g; |
|-----------------------|--------------------------|
| pore volume | 2.4 cm ³ /g; |
| average pore radius | 200 nm; and |
| density | 0.16 g/cm ³ . |

With a prepared standard gas mixture containing about 5 ppm of each of the target compounds, the following series of experiments can be performed:

(1) calibrating the concentration of air sample;

(2) spiking Tenax trap for adsorption/desorption study; and

(3) spiking Tenax trap for recovery study.

Table 9 shows relevent information for the standard gas mixture and the properties of the target compounds, which are listed in the order of elution in chromatogram.

B. Adsorption/Desorption of Adsorbate

This experiment was mainly designed to understand the adsorption/desorption efficiency for all adsorbates prior to field sampling. Using the analytical system shown in Figure 1, we can connect the blank Tenax trap between the six-port valve and Tekmar furnace. The breakthrough compounds in the effluent were directed to the Tekmar desorber and detected by GC when loading 2 ml standard gas mixture into trap under the conditions of 10 ml/min carrier flow, temperature 170° C and 1 atm. After these breakthrough compounds are measured, the spiked Tenax trap is desorbed into the GC. By noting the results presented in Table 10, it is clear that most of the MeCl breaks through the Tenax trap under the above loading conditions with a total volume of carrier gas of 120 ml. Relating the conditions to field sampling, it seems that the Tenax trap is unable to retain MeCl efficiently. As for the other compounds, the average adsorption/desorption efficiencies ranged between 95 and 124.5 %.

C. Retention Tendency of Adsorbate

The real mechanism of the adsorption process on a solid sorbent is very complicated in field air sampling. It is generally determined by such synergistic parameters as the concentration of the investigated compounds, temperature, co-adsorption, sorbent particle size, gas flow-rate, gas humidity, properties of the adsorbent and adsorbate, and the number of adsorption-desorption processes[9]. To grasp some idea about retention tendency

of adsorbate under the current sampling conditions, we designed an experiment by first spiking a known amount of standard Tenax trap blank at a carrier flow 10 ml/min for time periods of 12 minutes. We then purged the traps with zero grade nitrogen (same flow direction as air sample collection) at approximate purge flow rates of 5 and 10 ml/min, respectively, for 24 hours. This is similar to routine sampling conditions.

The results are shown in Table 11. As we can expect, MeCl instead of being purged out will break through immediately at the very beginning when spiking the blank traps. We also see that DCM can be completely purged out at either low or high flow rate. CFor is purged only at high purge flow rates. With a high purge flow rate of 9.8 ml/min, approximately 60 % of C6, 1,1,1, and CCl4 were purged out. However, by purging at low flow rate of 4.8 ml/min, only 54 % of CFor was purged out.

Although this experiment does not reflect the real state of routine field sampling, which actually varies the inlet concentration with time, it demonstrates that Tenax seems unable to effectively adsorb light chloro compounds, especially MeCl and DCM. If necessary, another active sorbent can be used in series with Tenax for collection of low molecular weight compounds which break through on Tenax.

IV. Two Studies of Ambient Air Analysis

A. Co-elution Study of Chloro Compounds

There is а problem of co-elution in the chromatographic separation of several chloro compounds when analyzing routine Tenax air samples collected from both Elizabeth and Carteret, New Jersey. First, the peaks of interest in the chromatogram of a spiked air sample are identified and then chromatograms of the air sample are compared with the spiked air sample. Then the ratio of FID vs ECD response of spiked sample is compared to that of a Standard Gas Mixture to demonstrate that the use of ECD response solves the problem of co-elution in quantitating these chlorocarbons. The experimental procedures are described as follows:

 Prepare two air samples collected in Tenax traps from a field site.

(2) Spike one of the above samples with 2 ml Standard Gas Mixture under the conditions of 1 atm and temperature 165^o C. Figure 1 shows the apparatus used to spike Standard gas into Tenax trap by using a six-port valve and a 2 ml sampling loop.

(3) Analyze each of samples listed below in Tekmar Desorber/GC :

a. 2 ml Standard gas at 1 atm and 165^o C;
b. spiked air sample; and

c. plain air sample.

The results are discussed in the four points below : Figure 5 plots the relationship between temperature program and retention time for each standard in the gas mixture. The temperature program sets initial temperature at 35° C for 12 min, then, increases temperature to a final temperature of 195° C at the rate of 6° C/min. The final temperature is maintained for 5 min. The last target compound, o-Xylene, is eluted at 126° C and retention time 27.1 min.

Paired chromatograms of FID and ECD response on the standard gas, spiked air sample and air sample are shown in Figure 6-1 through 6-4, 7-1 through 7-4 and 8-1 through 8-4, respectively.

(1) Analyzing the chromatogram of spiked air sample: first, chloroform elutes on the shoulder of a hydrocarbon peak next to it. Quantitation is difficult unless high concentration is present. No separation could be expected, therefore, if its concentration is much lower than spike, is ambient as usually found in air. Secondly, trichloroethylene comes out between two hydrocarbon peaks which are so close to it that they may result in interference. Third, perchloroethylene is poorly separated in a two peak set. Again, the same result as for chloroform may be expected. Fourth, 1,1,1-trichloroethane and carbon tetrachloride seem to show good separation.

(2) In the chromatogram of the air samples, no shoulder exists for chloroform and only one peak stands at the retention time of perchloroethylene, indicating significant hydrocarbon interference and lack of good quantitation for this chlorocarbon.

(3) If one assumes that no co-elution occurs, when 5 peaks of chloro compounds (4, 5, 7, 8, 10) are picked by simply matching with the standard chromatogram, their ratios of FID vs ECD response should approximate those of standard gas. Table 12 lists the comparison of ratios. If the ratio for the spiked sample is much greater than that of the standard, it demonstrates that co-elution is occurring. Peak 5 has the least co-elution, peaks 7 and 8 have about 54 and 44% interference, respectively, and peaks 2,4 and 10 have even more interference. As for DCM, it is difficult to quantitate due to described co-elution as well as its relatively insensitive ECD response compared to the other chloro compounds.

(4) This study indicates that the ECD is a preferred and more accurate method to quantitate the chloro compounds, since its good linear response in the appropriate concentration range has been mentioned earlier.

B. Breakthrough Study of Target Compounds

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Concerning the sampling system, the flow rates of current air sampling are set approximately at 5 and 10

ml/min in each sampler. The air volumes of low and high flow rate total up to 7 and 14 liters, respectively. The sampling traps, as mentioned, are packed with 7 cm long bed of 350 mg Tenax-TA. To understand the breakthrough problem under field conditions, both front and backup traps were put in series when sampling at both Elizabeth and Carteret on Sep. 30, 1988. The results are described as below:

(1) Due to the interference of hydrocarbons with chloro compound, the concentrations of the following chlorocompounds, chloroform, 1,1,1-trichloroethane, carbon tetrachloride, trichloroethylene and perchloroethylene, are obtained by ECD peak response, where there is no response from HC's. The concentrations of all other compounds are directly obtained by FID peak response. The methyl chloride and dichloromethane do not have good sensitivity on the ECD detector and the peaks from FID detector may have background interference from hydrocarbons.

(2) Table 13 and 14 show that the air concentrations of front and backup tubes at high and low flow rates sampled in Carteret and Elizabeth on September 1988. Table 15 and 16 shows the average concentration percentage being trapped by both front and backup traps in each site. As shown in Table 15 and 16, breakthrough percentage of each compound is within 10% except for the light compounds, Methyl chloride and Dichloromethane. As for the term of relative average error(R.A.E), it explains the agreement between
high and low flow rates. Again MeCl and DCM show larger values of R.A.E. Poor agreement is due to poor adsorption for these light compounds.

(3) The results indicate that the current sampling conditions are acceptable for the required quantitation of this project.

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V. Quality Control and Assurance

A. Reproducibility of Spiked Tenax

In this experiment, we spiked 8 Tenax blank traps with known quantities of standard and then desorbed them into the analytical system. The result of 8 replicates is shown in Table 17. The quantity of spike is approximately equivalent to the ppb level in ambient air. The reproducibility can be noted by the relative dispersion value(i.e., CV), which is indicative of the spread in a set of observations. As shown in Table 17, the coefficients of variation of target compounds are within 10 %, excluding MeCl due to its very low breakthrough volume, described before.

B. Bias experiment audited by EPA

There are two different types of errors that may be present in statistical measurements, namely, systematic errors and random errors. Systematic errors (or bias), as the term implies, caused a measurement to be incorrect in some systematic way. These are errors involved in the procedures of a statistical investigation and may occur after the processes of collection and analysis. Reproducibility experiments can demonstrate the performance of spiked Tenax and the analytical system. However, it cannot assure that precise quantitation has been achieved

because bias can be introduced by the standard gas mixture or other factors.

The Environmental Monitoring Systems Laboratory of EPA loaded four cleaned Tenax traps with known standards, including one background trap. The result of audit is presented in Table 18, which records spiked and reported amount of the compounds, and Table 19 shows the bias percentage. Among those compounds, the bias of CCl4, Tol and Perc range from +30 to +60 %, while that of Bz and Tric range up approximately to +20 %, and the others are within +/- 10 %.

C. Agreement Between High and Low Flow Tenax Samples

The agreement of high vs low flow traps was statistically analyzed by employing the data generated from Carteret (March 4 December 29, 1988) and Elizabeth (June 14 ~ December 29 1988). A useful aid in studying the agreement between high and low is to plot a scatter diagram of paired point data. This allows visual examination of the extent to which the data follow the ideal line (slope=1); it roughly gives an understanding of (1)whether breakthrough or inefficient adsorption occurs ; (2) how much agreement is achieved; and (3) abnormal discrepancies in the data. Figure 9-1 through 9-22 present scatter diagrams for a given compound and site. From visual examination, the paired points for most of the diagrams are

below the ideal line, it indicates that larger values of air concentrations result from the low flow tube. To further understand the strength of the linear relationship and the difference between the two flows, that is, how well the two flows are correlated and how well the regression slopes approach the ideal line, we calculated the coefficients of determination (R squared) and the slope by linear regression analyses, as summarized in Table 20. To assure data quality, both large values of correlation coefficients and slopes near unity are preferred. As a general principle, if an absolute value of R is larger than 0.7 (if R squared is larger than 0.49), there is significant correlation. As shown in Table 20, all R squared values are larger than 0.49, which demonstrates that one of the two requirements is statisfied. From the slope column, the values larger than 0.9 are those compounds of C6, Bz, Tric, and Tol in Carteret, and CCl4, Tric in Elizabeth. the others are between 0.70 and 0.90 except for MeCl in both sites and CCl4 in Carteret. Further comparing the slopes, half of the paired slopes are close to each other excluding those of C6, Bz, 1,1,1, CCl4 and Tol.

Because all the slope values except Bz in Carteret are smaller than 1, and air concentration is determined by the two factors of weight/volume of target compound and total sampling air volume, it indicates that either

breakthrough or system bias has been involved. However, as discused earlier, the safe sampling flow rate has been assured in the breakthrough study. Should it happen, the reason may be that Tenax has gradually deteriorated from frequent re-use. Therefore, the system bias, excluding the less dominant bias from analytical system as has been described, may be contributed by the factor of total sampling air volume, which subsequently may lead to bias resulting from flow-rate calibration curve of a rotameter calibrated at room temperature.

Another way to study the agreement can be obtained by computing the mean of relative average error (M.R.A.E) and its standard deviation. The lower the mean is, the higher precision and agreement are acheived. Table 21 shows the M.R.A.E of each compound sampled during a long time series mentioned above. As may be seen, it seems that the precisions of hydrocarbons, especially those in Carteret, are better than chloro compounds, which were generated by ECD response. To determine the precision of entire system, the two M.R.A.E columns in Table 19 were averaged, giving the 14.54% +/- 8.49%.

D. Results of Staten Island Interlaboratory

Comparison Study

This study -- "Shootout" #2 of SI/NJ UATP -- was held July 25 ~ 29 1988 at Susan Wagner High School, Staten

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Island, New York. Duplicate Tenax samplers were employed to collect air samples at low and high flow rates. The precision, in terms of R.A.E between high and low flow by each compound, of air data generated by NJIT was calculated in Table 22. Again the precision of entire system, as noted in the preceding section, was obtained from a six measurements of data in this study and the calculated value is 19.18% +/- 11.29%.

The interlaboratory data evaluation[10], released by SI/NJ UATAP Management/Steering Committee meeting February 8 1989, was digested in Table 23. The results show the % difference and its absolute value from the mean for all compounds/all organizations. The shootout data allowed the following conclusions:

(1) most organizations [CSI, NJSDEC, PEI, EPA/RTP, NJIT Tenax] has results within +/-40% (NJIT: -15.67 %) of the mean, as measured by difference from the mean;

(2) precision, as measured by absolute value of the differences from the mean, was within 45% (NJIT: 25.33%) for the organizations measured above;

(3) greatest factor responsible for variation of results was the organization performing analysis, not sampling method;

(4) there was a high correlation between the results of the performance evaluation samples (i.e., bias audit by EPA) and the results of the "shootout".

VI. Statistical Analysis of Ambient Air Data

A. Concentrations Trend of Target Compounds

The ambient air data generated was based on a weekly time series of VOC collection and analyses and it is a set of analytical measurements arranged in chronolgical order. In general, the raw weekly data contains trends of cyclical and weekly variations as well as other irregular factors. In this section, our interest is centered on the two elements of the trends or cycles. A practical method [11] has been employed to obtain a series of moving averages that smooth, but still illustrate roughly the trend and cycle components. These are computed using the following procedures: the first moving average figure contains the first four weekly data. Then the first weekly data point is dropped, and the second through fifth weekly figures are averaged. The computation proceeds this way until the last moving average is calculated, containing the last four weekly data of the original series. In the actual calculation an adjustment was made in order to center the moving average figures so their timing corresponds to that of the original data.

The moving averages along with the original raw data points have been plotted in Figure 10-1 through 10-16 by site and given target compound. As may be expected by

visual examination, the moving average, which runs through the original data, can be observed to follow the cyclical fluctuations. If the series were long enough, we would be able to see how the moving average describe long term trend movements as well. To further visually compare the relationship between compounds in each site, we combine the curves of several target compounds moving averages and present them in Figure 11-1 through 11-4.

In summary, the concentration levels of the moving averages in this geogrphical area of Carteret and Elizabeth can be divided into four groups. Among them, one includes the highest level target compound of 5 ppb of Tol; the second group, near 2 ppb, are Bz, C6 and pmX; the third group such as 1,1,1 is near 1 ppb; and the group of lowest level, which is near 0.5 ppb, are CCl4, Perc, and oX. The trend of the moving average for most compounds in Carteret site can be roughly described as follows: First, an upward movement occurred in early April, this gradually increased to a maximum point in early June. After early June, there was one-month downward trend with a valley point in early July. Again, two months of upward trend happened through July and August. After maximum point in late August, a stable level was maintained from early October till early November, then moved upward to another peak in early December. It seems that Perc and oX moved steadly along the level of the moving average of 0.5 ppb. For the Elizabeth

site characterized from June 14 to December 29 1988, the same trends occurred with a little difference for C6, which had a peak at mid August ahead of the others.

B. Site Relationship of Target Compounds

The comparison of moving average between sites for a given compound was shown in Figure 12-1 through 12-8. In general, there is no significant difference between sites for any given compound, however, several deviations are described. As a generality, there was a obvious distinction between sites in that the Perc level (moving average) in Elizabeth was always larger than that in Carteret. For the other compounds, the higher levels occurred in Elizabeth between June and late August or early September (summer time); then higher level were observed in Carteret between late August or early September and mid/late November(autumn). The higher levels in Elizabeth again appeared between mid/late November and late December. The oscillations seem to be associated with the change of seasonal weather condition (i.e., from hot weather to mild then cold).

VII. Conclusion

1. This paper describs the aspects of Tenax sampling of ambient VOCs - methylchloride, dichlomethane, hexane, chloroform, 1,1,1-trichloroethane, benzene, carbon tetrachloride, trichloroethylene, benzene, carbon perchloroethylene, p,m-xylene and o-xylene. It covers the analytical method - Tekmar Automatic Thermal Desorber and capillary GC system with a FID as well as an ECD, and statistical air data analysis. A whole series of quality assurance procedures have been established and experiments performed to evaluate the precision of sample collection and analysis.

2. By parallel field sampling at 5 and 10 ml/min of intake flow with 350 mg Tenax adsorbent, it is assured that no breakthrough of target compounds except methylchloride will occur.

3. Comparison of a direct sample injection into GC (no Tekmar) with indirect injection into GC(with Tekmar), shows percent differences ranging from -6.44 to 1.71, and indicates that satisfactory performance of the Tekmar desorber has been achieved under the selected conditions of time, temperature and system flow.

4. Due to co-elution of chloro compounds with atmospheric HC's as well as high linear responses of both FID and ECD, it is shown that the ECD is clearly preferred

to more accurately quantitate the chlorocarbons, while hydrocarbons are quantitated by FID.

5. The adsorption/desorption efficiencies of Tenax using spiked samples are shown to be between 95 and 125 % for all target compounds with the exception of methylchloride (17 % only). Reproducibilities of analysis on spiked Tenax, in terms of the dispersion with 8 replicates for all target compounds, are within 12 %, except for methylchloride (29.26 %).

6. It is difficult to quantitate both methylchloride and dichloromethane, due to the former's very low breakthrough volume on Tenax, and the latter's relatively insensitivity on the ECD in addition to co-elution of other HC's in the background.

7. The entire system precision, as measured by the mean of relative average error for all target compounds, averages 15% with a standard deviation of 8%. The precision is within 148 for most compounds except carbon tetrachloride (21%) for the Elizabeth site, while, for Carteret , trichloroethylene was quantitated with the precision of 26%, 1,1,1-trichloroethane, perchloroethylene and carbon tetrachloride approximate to 20% and the other compounds are within 9%. As menthioned above, the analytical method performs at higher precision for hydrocarbons than for chlorocarbons.

8. The measured concentrations of moving average,

during a time period in the area of Carteret and Elizabeth, are divided into four levels : (1) 5 ppb for toluene; (2) 2 ppb for benzene, hexane, and p,m-xylene; (3) 1 ppb for 1,1,1-trichloroethane; and (4) 0.5 ppb for carbon tetrachloride, perchloroethylene and o-xylene. In general, the concentrations of hydrocarbons are higher than chlorocarbons. As for the site relationship for a given compound, there appears to exist oscillations in concentration levels which alternate when the seasonal weather conditions change.

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at the

| | | | Date | | • | | |
|----------|---------|---------|---------|--------|---------|-------|-------|
| Compound | 1 | | | | | Avg | C.V |
| | 2/15/88 | 2/19/88 | 2/24/88 | 3/5/88 | 3/10/88 | | 010 |
| 1. MeCL | 1203 | 1216 | 1202 | 1266 | 1252 | 1228 | 2.40 |
| 2. DCM | 2895 | 2959 | 3065 | 3127 | 3116 | 3032 | 3.35 |
| 3. C6 | 13572 | 14112 | 14520 | 14206 | 13994 | 14081 | 2.45 |
| 4. CFor | 2724 | 3037 | 2859 | 2880 | 3167 | 2933 | 5.84 |
| 5. 1,1,1 | 4802 | 4950 | 5623 | 5243 | 5439 | 5211 | 6.49 |
| 6. Bz | 17785 | 18842 | 19064 | 19382 | 19110 | 18837 | 3.28 |
| 7. CCL4 | 1947 | 2271 | 2523 | 2454 | 2516 | 2342 | 10.38 |
| 8. Tric | 6097 | 6023 | 6957 | 6487 | 6603 | 6433 | 5.96 |
| 9. Tol | 18990 | 20525 | 21333 | 19872 | 21231 | 20390 | 4.81 |
| 10. Perc | : 3993 | 4489 | 5216 | 4246 | 4568 | 4502 | 10.17 |
| 11. pmX | 11470 | 11996 | 12716 | 11680 | 13258 | 12224 | 6.10 |
| 12. oX | 17224 | 17671 | 18380 | 16902 | 19950 | 18025 | 6.71 |

Table 1 Peak Area Of Standard Gas Mixture By Method 1 * (2 ml, 1 atm, 170°C)

Note : C.V = Coefficient of Variation

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* --- Run through desorber and GC (Cryo-1 and 2)

| | | | | Date | | | | |
|-----|--------|----------------------|--------|--------|---------|---------|---------|--------|
| Coi | mpound | 1 <u></u> 1/30/88 | 2/3/88 | 2/9/88 | 2/15/88 | 2/21/88 | 2/27/88 | 3/4/88 |
| ī. | MeCL | 1295 | 1299 | 1324 | 1317 | 1280 | 1289 | 1270 |
| 2. | DCM | 3237 | 3173 | 3226 | 3301 | 3180 | 3214 | 3129 |
| 3. | C6 | 15952 | 15892 | 15906 | 15988 | 15548 | 14911 | 15228 |
| 4. | CFor | 3153 | 3049 | 3197 | 3200 | 3214 | 3801 | 3347 |
| 5. | 1,1,1 | 5609 | 5627 | 5546 | 5668 | 5420 | 5593 | 5450 |
| 6. | Bz | 20856 | 20454 | 20887 | 20873 | 20265 | 20183 | 1991 |
| 7. | CCL4 | 2708 | 2607 | 2703 | 2594 | 2801 | 2688 | 2652 |
| 8. | Tric | 6867 | 6730 | 7021 | 6952 | 6728 | 6746 | 6597 |
| 9. | Tol | 22634 | 21711 | 22578 | 22598 | 22704 | 22446 | 21838 |
| 10 | . Perc | 4793 | 4580 | 4822 | 4920 | 4761 | 4781 | 4647 |
| 11 | . pmX | 13964 | 12860 | 14025 | 13959 | 14368 | 14026 | 13340 |
| 12 | . oX | 20227 | 18183 | 20360 | 20216 | 20371 | 20378 | 18575 |

Table 2 Peak Area Of Standard Gas Mixture By Method 3 * (2 ml, 1 atm, 140°C)

| Compound | Date | Avg | c.v |
|----------|-------|--------------|---------|
| | 10/00 | | 6 |
| 1. MeCL | 1279 | 1295 | 1.37 |
| 2. DCM | 3210 | 3209 | 1.58 |
| 3. C6 | 15405 | 15604 | 2.55 |
| 4. CFor | 3340 | 3288 | 6.96 |
| 5. 1,1,1 | 5474 | 5548 | 1.64 |
| 6. Bz | 20125 | 20444 | 1.88 |
| 7. CCL4 | 2730 | 2685 | 2.51 |
| 8. Tric | 6757 | 6800 | 2.02 |
| 9. Tol | 22412 | 22365 | 1.69 |
| 10. Perc | 4798 | 4763 | 2.21 |
| 11. pmX | 14118 | 13833 | 3.53 |
| 12. oX | 20102 | 19802 | 4.49 |
| Note : * | dire | ct injection | into GC |
| | (Cry | o-2 only) | |

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| Compound | Avera | qe | difference |
|----------|-------------------|-------|------------|
| | Method 1 Method 3 | | 8 ' |
| 1. MeCL | 1228 | 1207 | 1.71 |
| 2. DCM | 3032 | 2991 | 1.37 |
| 3. C6 | 14081 | 14547 | -3.21 |
| 4. CFor | 2933 | 3065 | -4.29 |
| 5. 1,1,1 | 5211 | 5173 | 0.75 |
| 6. Bz | 18837 | 19060 | -1.17 |
| 7. CCL4 | 2342 | 2504 | -6.44 |
| 8. Tric | 6433 | 6339 | 1.48 |
| 9. Tol | 20390 | 20851 | -2.21 |
| 10. Perc | 4502 | 4440 | 1.40 |
| 11. pmX | 12224 | 12896 | -5.21 |
| 12. oX | 18025 | 18461 | -2.36 |
| | | | |

Table 3 Percentage Difference Between Method 1 and 3

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Note : * --- corrected value by a temp. factor of 413/443

Table 4 Weight Detected On Various Transfer Line Temp., ng

| Cor | nound | 9 Mar - 2000 - 20 Mar 20 Mar 20 Mar - 2000 - 2 - 2000 - 2 | | Transfer | line te | mperatur | e, C | | |
|-----|-------|---|--------|----------|---------|----------|--------|-------|--------|
| | pound | 60 | 80 | 90 | 100 | 120 | 150 | 180 | 210 |
| ī. | MeCL | 8.42 | 8.66 | 8.80 | 8.94 | 9.04 | 8.92 | 8.96 | 8.75 |
| 2. | DCM | 60.41 | 56.88 | 56.00 | 59.75 | 58.83 | 55.58 | 57.58 | 56.85 |
| 3. | C6 | 35.50 | 37.49 | 37.51 | 38.42 | 34.26 | 37.55 | 38.36 | 37.86 |
| 4. | CFor | 101.10 | 94.05 | 94.68 | 92.47 | 94.78 | 93.90 | 94.17 | 90.02 |
| 5. | 1,1,1 | 69.23 | 68.80 | 67.92 | 69.14 | 69.18 | 67.49 | 69.17 | 66.82 |
| 6. | Bz | 43.78 | 43.33 | 42.92 | 44.38 | 45.25 | 43.78 | 44.36 | 43.03 |
| 7. | CCL4 | 106.41 | 100.08 | 116.59 | 110.76 | 96.69 | 101.89 | 99.85 | 101.80 |
| 8. | Tric | 69.72 | 69.04 | 67.30 | 69.19 | 72.84 | 70.61 | 66.52 | 71.27 |
| 9. | Tol | 45.48 | 47.08 | 47.57 | 48.22 | 49.71 | 48.25 | 48.59 | 48.21 |
| 10. | Perc | 60.03 | 61.75 | 61.33 | 62.75 | 64.77 | 63.78 | 63.38 | 62.94 |
| 11. | pmX | 2.67 | 17.54 | 17.44 | 19.48 | 21.78 | 21.03 | 21.51 | 20.65 |
| 12. | οX | 0.87 | 22.00 | 19.43 | 23.90 | 26.91 | 27.44 | 26.84 | 26.46 |
| | | | | | | | | | |

| | No. of Avg Re. Eff. | C.V |
|----------|---------------------|-------|
| Compound | replicate % | 20 |
| 1. MECL | 8 20.88 | 28.99 |
| 2. DCM | 8 103.66 | 6.64 |
| 3 C6 | 8 99.58 | 2.42 |
| 4. CFOR | 8 99.01 | 7.56 |
| 5. 1,1,1 | 8 97.73 | 4.80 |
| 6. Bz | 8 108.15 | 3.09 |
| 7. CC14 | 8 103.63 | 9.81 |
| 8. Tric | 8 96.30 | 7.61 |
| 9. Tol | 8 105.40 | 4.08 |
| 10. Perc | 8 120.87 | 6.11 |
| 11. PMX | 8 112.38 | 11.81 |
| 12. OX | 8 112.70 | 8.10 |
| | | |

Table 5 Recovery Efficiencies By Analytical System

Table 6 Reproducibility Comparison of GC Detector Response

| | | C | 2V |
|------|--------------|-----------------------|------------------------|
| | Compound | FID (7 replicates) | ECD (11 replicates) |
| 1. | MECL | 0.98% | |
| 2. | DCM | 1.93% | |
| 3. | C6 | 2.04% | |
| 1. 8 | CFOR | 2.938 | 9.12% |
| 5. | 1,1,1 | 2.91% | 16.72% |
| 5. | Bz | 2.478 | |
| 7. | CCL4 | 5.33% | 12.83% |
| 3. | TRIC | 2.75% | 12.95% |
| э. | Tol | 2.418 | |
| 10 | Perc | 4.80% | 6.65% |
| 11 | PMX | 9.75% | |
| 12 | OX | 8.96% | |

| | and the set of the set of the state of the | | Peak area | of FID | | ine printer and in the second states |
|----|--|-------|-----------|--------|------|--------------------------------------|
| | Compound | 28" | 20" | 10" | 5" | 2" |
| 1. | MECL | 1140 | 837 | 448 | 284 | 178 |
| 2. | DCM | 3599 | 2332 | 1124 | 563 | 302 |
| 3. | C6 | 13228 | 9212 | 4441 | 2759 | 1619 |
| 4. | CFOR | 3656 | 2270 | 1072 | 594 | 371 |
| 5. | 1,1,1 | 4843 | 3217 | 1543 | 987 | 571 |
| 6. | Bz | 24574 | 15433 | 7250 | 4346 | 2510 |
| 7. | CCL4 | 2104 | 1304 | 563 | 406 | 194 |
| 8. | TRIC | 9625 | 5544 | 2448 | 1360 | 772 |
| 9. | Tol | 36656 | 21286 | 9208 | 5076 | 2846 |
| 10 | Perc | 9421 | 5372 | 2282 | 1264 | 654 |
| 11 | PMX | 33999 | 19954 | 8438 | 4608 | 2510 |
| 12 | OX | 50818 | 30057 | 13349 | 7184 | 4008 |

| Table | 7 | Experimental | Data On | FID versus | ECD Response |
|-------|---|--------------------------------|---------|-------------------|--------------|
| | | Undr Differen Standards (2m | t Press | ure (in-Hg) C) | Loading of |

| | |] | Peak area o | of ECD | | |
|----|----------|-------|-------------|---|------|------|
| | Compound | 28" | 20" | 10" | 5" | 2" |
| 1. | MECL | | | and a second statement of the | | |
| 2. | DCM | 166 | 140 | | | |
| 3. | C6 | | | | | |
| 4. | CFOR | 1686 | 1296 | 884 | 522 | 288 |
| 5. | 1,1,1 | 1610 | 1284 | 587 | 355 | 166 |
| 6. | Bz | | | | | |
| 7. | CCL4 | 16784 | 12214 | 5554 | 3434 | 1715 |
| 8. | TRIC | 1998 | 1578 | 896 | 497 | 317 |
| 9. | Tol | | | | | |
| 10 | Perc | 19992 | 14555 | 6823 | 3298 | 1862 |
| 11 | PMX | | | | | |
| 12 | OX | | | | | |

| | | No of | R sq | uared | ng |
|----|----------|--------------|------|-------|--------------|
| | Compound | observations | FID | ECD | range |
| 1. | MECL | 5 | 1.00 | | 1.26~8.09 |
| 2. | DCM | 5 | 0.99 | | 6.03~71.91 |
| 3. | C6 | 5 | 1.00 | | 4.58~37.79 |
| 4. | CFOR | 5 | 0.98 | 0.99 | 11.07~109.05 |
| 5. | 1,1,1 | 5 | 0.99 | 0.99 | 7.22~61.25 |
| 6. | Bz | 5 | 0.99 | | 6.04~59.12 |
| 7. | CCL4 | 5 | 0.98 | 1.00 | 8.10~87.87 |
| 8. | TRIC | 5 | 0.97 | 1.00 | 10.07~125.56 |
| 9. | Tol | 5 | 0.97 | | 7.91~101.91 |
| 10 | Perc | 5 | 0.97 | 1.00 | 11.16~160.82 |
| 11 | PMX | 5 | 0.98 | | 6.25 84.47 |
| 12 | OX | 5 | 0.98 | | 8.69~110.21 |
| | | | | | |

Table 8 Linearity Comparison of GC Detector By Response vs Pressure Loading

Table 9 Parameters of The Standard Gas Mixture

| | Standa | ard | Conc. | M.W | B.P | M.P |
|--------|----------|-------|-------|--------|-------|-------|
| | Compou | und | ppm | g | С | С |
| 1. | MECL | | 2.98 | 50.50 | -23.7 | -97.7 |
| 2. | DCM | | 11.86 | 84.00 | 40.1 | -96.7 |
| 3. | C6 | | 7.54 | 86.00 | 68.8 | -95.3 |
| 4. | CFOR | | 12.66 | 119.50 | 61.2 | -63.5 |
| 5. | 1,1,1 | | 7.89 | 133.40 | 75.0 | -30.6 |
| 6. | Bz | | 9.50 | 78.10 | 80.1 | 5.5 |
| 7. | CCL4 | | 10.15 | 153.80 | 76.7 | -22.6 |
| 8. | TRIC | | 9.15 | 131.40 | 86.7 | -73.0 |
| 9. | Tol | | 9.05 | 92.00 | 110.7 | -95.0 |
| 10 | Perc | | 6.49 | 165.80 | 121.0 | -19.0 |
| 11 | PMX | | 3.51 | 106.17 | 138.8 | * |
| 12 | ох | | 4.46 | 106.17 | 144.0 | 0.1 |
| Note : | p-Xylene | -25.2 | c | | | |
| | o-Xylene | -47.9 | С | | | |
| | | | | | | |

| Trap I.D. | | | | | | | | |
|-----------|-------|-------|-------|-------|-------|------|--|--|
| Compound | T-307 | T-502 | T-507 | T-309 | avg | C.V | | |
| 1. MECL | 16 | 16 | 9 | 26 | 16.9 | 36.0 | | |
| 2. DCM | 109 | 94 | 95 | 106 | 101.1 | 6.4 | | |
| 3 C6 | 104 | 97 | 96 | 102 | 100.0 | 3.3 | | |
| 4. CFOR | 110 | 97 | 98 | 101 | 101.6 | 5.0 | | |
| 5. 1,1,1 | 103 | 101 | 101 | 103 | 102.1 | 1.2 | | |
| 6. Bz | 108 | 105 | 103 | 110 | 106.8 | 2.5 | | |
| 7. CC14 | 90 | 98 | 97 | 94 | 95.0 | 3.5 | | |
| 8. Tric | 103 | 101 | 102 | 106 | 103.2 | 1.8 | | |
| 9. Tol | 108 | 109 | 109 | 111 | 109.3 | 1.1 | | |
| 10. Perc | 130 | 120 | 118 | 130 | 124.5 | 4.5 | | |
| 11. PMX | 98 | 128 | 129 | 130 | 121.1 | 11.0 | | |
| 12. OX | 104 | 121 | 125 | 126 | 119.1 | 7.4 | | |

Table 10 Experiment Data of Adsorbates Adsorption/Desorption Adsorption/Desorption Efficiencies, %

Breakthrough Compounds, %

| C | Compound T307 | | T-502 | T-507 | T-309 | Avg |
|----|---------------|----|-------|-------|-------|------|
| ī. | MECL | 98 | 99 | 101 | 100 | 99.6 |
| 2. | DCM | 0 | 0 | 0 | 0 | 0.0 |
| 3 | C6 | 0 | 0 | 0 | 0 | 0.0 |
| 4. | CFOR | 0 | 0 | 0 | 0 | 0.0 |
| 5. | 1,1,1 | 0 | 0 | 0 | 0 | 0.0 |
| 6. | Bz | 3 | 3 | 5 | 3 | 3.2 |
| 7. | CC14 | 0 | 0 | 0 | 0 | 0.0 |
| 8. | Tric | 0 | 0 | 0 | 0 | 0.0 |
| 9. | Tol | 1 | 0 | 2 | 1 | 0.9 |
| 10 | . Perc | 0 | 3 | 5 | 3 | 2.8 |
| 11 | . PMX | 0 | 1 | 5 | 1 | 1.7 |
| 12 | . ox | 0 | 0 | 3 | 0 | 0.9 |

9 F.

| | No. of Replicate | | Purge- | out Perce | nt |
|----------|---------------------|----------|--------|-----------|---------|
| | | 4.8 ml | /min * | 9.8 ml | /min ** |
| Compound | | Avg | S.D | Avg | S.D |
| 1. MECL | 3 | 97 | 0.7 | 95 | 1.8 |
| 2. DCM | 3 | 100 | 0.0 | 100 | 0.0 |
| 3 C6 | 3 | 15 | 4.6 | 57 | 7.4 |
| 4. CFOR | 3 | 54 | 16.2 | 100 | 0.0 |
| 5. 1,1,1 | 3 | 23 | 5.9 | 56 | 4.6 |
| 6. Bz | 3 | 18 | 2.3 | 37 | 7.1 |
| 7. CC14 | 3 | 19 | 5.4 | 59 | 6.0 |
| 8. Tric | 3 | 5 | 1.1 | 18 | 4.7 |
| 9. Tol | 3 | 5 | 0.9 | 2 | 0.8 |
| 10. Perc | 3 | -9 | 0.9 | -14 | 4.3 |
| 11. PMX | 3 | 13 | 0.6 | 11 | 1.7 |
| 12. OX | 3 | 7 | 0.4 | 3 | 1.7 |
| Note : * | Total Flo | w = 7.01 | 1 | | |

Table 11 Purge -out Percentage of Various Purge Flow Rate

** --- Total Flow = 14.27 1

Table 12 Ratio Comparison of FID vs ECD Response

| | | Standard | Gas | - | Spiked A | ir Samp | l ratio factor |
|----------|-------|----------|--------|--------|----------|---------|-------------------|
| Compoun | FID | ECD | F/E(1) | FID | ECD | F/E(2) | (2)/(1) |
| 1. MECL | 1176 | 70 | 16.80 | 830 | | | |
| 2. DCM | 2789 | 129 | 21.62 | 7166 | 155 | 46.23 | 2.14 |
| 3 C6 | 12634 | | | 41351 | | | |
| 4. CFOR | 2833 | 1310 | 2.16 | 9379 | 1327 | 7.07 | 3.27 |
| 5. 1,1,1 | 4514 | 1404 | 3.22 | 15060 | 4720 | 3.19 | 0.99 |
| 6. Bz | 17491 | | | 66340 | | | |
| 7. CC14 | 1850 | 13435 | 0.14 | 3663 | 17243 | 0.21 | 1.54 |
| 8. Tric | 5265 | 1107 | 4.76 | 8867 | 1297 | 6.84 | 1.44 |
| 9. Tol | 17486 | | | 191320 | | | |
| 10. Perc | 3660 | 6406 | 0.57 | 15789 | 9603 | 1.64 | 2.88 |
| 11. PMX | 9708 | | | 101400 | | | |
| 12. OX | 13977 | | | 51714 | | | |

Note : | --- Pick up peak by the same retention time as the standard gas

Table 13 Concentrations From Front and Backup Tenax Tubes At High and Low Flow Rates Total Flow : High -- 15.05 1 (10.59 ml/min) Low -- 7.7 1 (5.42ml/min) (Carteret Site: 9/30/88, ppb)

| | | Fron | t | Bacl | kup | Blank |
|----|----------|------|------|------|------|-------|
| | Compound | Low | High | Low | High | |
| 1. | MECL | 0.29 | 0.13 | 0.36 | 0.19 | 0.07 |
| 2. | DCM | 7.35 | 3.03 | 1.29 | 4.46 | 0.00 |
| 3. | C6 | 1.35 | 1.36 | 0.02 | 0.01 | 0.00 |
| 4. | CFOR | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 5. | 1,1,1 | 1.23 | 1.26 | 0.00 | 0.00 | 0.00 |
| 6. | Bz | 1.94 | 1.85 | 0.17 | 0.10 | 0.19 |
| 7. | CCL4 | 0.09 | 0.09 | 0.00 | 0.00 | 0.00 |
| 8. | TRIC | 0.05 | 0.07 | 0.00 | 0.00 | 0.00 |
| 9. | Tol | 9.84 | 8.88 | 0.08 | 0.13 | 0.04 |
| 10 | Perc | 0.13 | 0.17 | 0.00 | 0.00 | 0.00 |
| 11 | PMX | 2.45 | 2.37 | 0.02 | 0.03 | 0.02 |
| 12 | ox | 0.81 | 0.77 | 0.00 | 0.02 | 0.00 |

Table 14 Concentrations From Front and Backup Tenax Tubes At High and Low Flow Rates Total Flow : High -- 12.93 1 (9.26 ml/min) Low -- 6.14 1 (4.4 ml/min) (Elizabeth Site: 9/30/88, ppb)

| | | Fron | t | Bacl | kup | Blank |
|----|----------|------|------|------|------|-------|
| | Compound | Low | High | Low | High | |
| 1. | MECL | 0.37 | 0.14 | 0.27 | 0.32 | 0.07 |
| 2. | DCM | 9.90 | 5.75 | 1.38 | 3.48 | 0.00 |
| 3. | C6 | 2.17 | 1.96 | 0.02 | 0.01 | 0.00 |
| 4. | CFOR | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 5. | 1,1,1 | 0.80 | 0.80 | 0.00 | 0.00 | 0.00 |
| 6. | Bz | 2.23 | 1.97 | 0.25 | 0.17 | 0.19 |
| 7. | CCL4 | 0.09 | 0.07 | 0.00 | 0.00 | 0.00 |
| 8. | TRIC | 0.07 | 0.07 | 0.00 | 0.00 | 0.00 |
| 9. | т61 | 7.27 | 6.65 | 0.09 | 0.07 | 0.04 |
| 10 | Perc | 0.16 | 0.15 | 0.00 | 0.00 | 0.00 |
| 11 | PMX | 3.01 | 2.81 | 0.06 | 0.05 | 0.02 |
| 12 | OX | 0.85 | 0.82 | 0.01 | 0.03 | 0.00 |

| | | From | nt,8 | Backup, % | |
|----|----------|------|-------|-----------|-------|
| | Compound | Avg | R.A.E | Avg | R.A.E |
| 1. | MECL | 43 | 38 | 57 | 31 |
| 2. | DCM | 64 | 42 | 36 | 55 |
| 3. | C6 | 99 | 0 | 1 | 20 |
| 4. | CFOR | | | | |
| 5. | 1,1,1 | 100 | 1 | 0 | |
| 6. | Bz | 93 | 2 | 7 | 25 |
| 7. | CCL4 | 100 | 2 | 0 | |
| 8. | TRIC | 100 | 16 | 0 | |
| 9. | Tol | 99 | 5 | 1 | 26 |
| 10 | Perc | 100 | 14 | 0 | |
| 11 | PMX | 99 | 2 | 1 | 37 |
| 12 | OX | 99 | 3 | 1 | 100 |

| Table 15 | Average | Concen | tration | Percent | of | Front | and |
|----------|----------|--------|---------|-----------|------|-------|-----|
| | Backup T | ubes (| Cartere | et, 9/30/ | (88) | | |

Note : R.A.E --- Relative Average Error

| Table 16 | 16 | Average Concentration Percent of Front and | d |
|----------|----|--|---|
| | | Backup Tubes (Elizabeth, 9/30/88) | |

| | | Fro | nt, % | Backup, % | | |
|----|----------|-----|-------|-----------|-------|--|
| | Compound | Avg | R.A.E | Avg | R.A.E | |
| 1. | MECL | 46 | 45 | 54 | 8 | |
| 2. | DCM | 76 | 26 | 24 | 43 | |
| 3. | C6 | 99 | 5 | 1 | 26 | |
| 4. | CFOR | | | | | |
| 5. | 1,1,1 | 100 | 0 | 0 | | |
| 6. | Bz | 91 | 6 | 9 | 19 | |
| 7. | CCL4 | 100 | 11 | 0 | | |
| 8. | TRIC | 100 | 1 | 0 | | |
| 9. | Tol | 99 | 4 | 1 | e | |
| 10 | Perc | 100 | 1 | 0 | | |
| 11 | PMX | 98 | 3 | 2 | 12 | |
| 12 | OX | 97 | 2 | 3 | 54 | |

Note : R.A.E --- Relative Average Error

| | No. of | Avg | S.D | C.V |
|----------|-----------|-------|------|-------|
| Compound | replicate | ng | ng | 90 |
| 1. MECL | 8 | 1.74 | 0.51 | 29.26 |
| 2. DCM | 8 | 57.80 | 3.97 | 6.87 |
| 3 C6 | 8 | 35.71 | 0.85 | 2.38 |
| 4. CFOR | 8 | 82.83 | 6.13 | 7.40 |
| 5. 1,1,1 | 8 | 56.91 | 2.44 | 4.28 |
| 5. Bz | 8 | 44.38 | 1.49 | 3.36 |
| 7. CC14 | 8 | 89.51 | 9.22 | 10.30 |
| B. Tric | 8 | 64.01 | 4.53 | 7.08 |
| 9. Tol | 8 | 48.52 | 1.74 | 3.58 |
| 10. Perc | 8 | 71.92 | 4.22 | 5.86 |
| L1. PMX | 8 | 23.15 | 2.65 | 11.42 |
| 12. OX | 8 | 29.50 | 2.27 | 7.69 |

Table 17 Reproducibility of Spiked Tenax

Table 18Audit Sample Results for Staten Island Study
(Tenax Tubes)

| | | Spiked, no | 3 |] | Reported, ng | | | |
|-----------|----------|-------------|----------|------------|--------------|-------|--|--|
| Compound | T-103 | T-109 | T-110 | T-103 | T-109 | Ť-110 | | |
| MeC1 | | | | | | | | |
| CFor | 72 | 72 | 108 | 79 | 85 | 134 | | |
| 1,1,1 | 97 | 97 | 146 | 97 | 103 | 146 | | |
| CC14 | 116 | 116 | 174 | 163 | 167 | 246 | | |
| Bz | 128 | 128 | 192 | 155 | 155 | 226 | | |
| Tric | 142 | 142 | 213 | 175 | 176 | 256 | | |
| Tol | 147 | 147 | 220 | 233 | 234 | 341 | | |
| Perc | 118 | 118 | 177 | 155 | 162 | 230 | | |
| pmX | | | | | | | | |
| οX | 128 | 128 | 192 | 118 | 118 | 177 | | |
| Tenax-118 | (Tenax k | olank) : Ba | 2 ng, To | ol 2 ng, d | oX 3 ng | | | |

| | Bias. % | | | | |
|----------|---------|-------|-------|--|--|
| Compound | T-103 | T-109 | T-110 | | |
| MeCl | | | | | |
| CFor | 9.7 | 18 | 24 | | |
| 1,1,1 | 0 | 6.2 | C | | |
| CC14 | 40 | 44 | 41 | | |
| Bz | 21 | 21 | 18 | | |
| Tric | 23 | 24 | 20 | | |
| Tol | 58 | 59 | 55 | | |
| Perc | 31 | 37 | 30 | | |
| pmX | | | | | |
| οX | -7.8 | -7.8 | -7.8 | | |

Table 19[°] Percent Bias of Audit Results

Table 20Linear Regression Data of Ambient Air DataBy High vs Low Flow

| Compound | | Cartere | t | Elizabeth | | | |
|----------|------------------------|---|-------------------|--------------------------|-----------|-------|--|
| • | No of | R | R | | R | | |
| | Observation | n Squared | Slope | Observatio | n Squared | Slope | |
| MECL | 4 | 0.6 | 0.38 | 3 | 3 0.79 | 0.47 | |
| DCM | | e de la composición d | - | - | | | |
| C6 | 4 | 0.94 | 0.92 | 3 | 3 0.92 | 0.74 | |
| CFOR | 4 | 0.95 | 0.76 | 3 | 3 0.72 | 0.73 | |
| 1,1,1 | 49 | 0.59 | 0.51 | 3 | 3 0.75 | 0.82 | |
| Bz | 4 | 0.94 | 1.02 | 3 | 3 0.89 | 0.70 | |
| CCL4 | 49 | 0.71 | 0.45 | 3 | 3 0.95 | 0.93 | |
| TRIC | 49 | 0.89 | 0.95 | 3 | 3 0.92 | 0.94 | |
| Tol | 49 | 0.94 | 0.95 | 3 | 3 0.94 | 0.82 | |
| Perc | 49 | 0.86 | 0.78 | 3 | 3 0.94 | 0.81 | |
| PMX | 49 | 0.82 | 0.85 | 3 | 3 0.93 | 0.83 | |
| OX | 49 | 9 0.77 | 0.83 | 3 | 3 0.89 | 0.82 | |
| Note : | R Squared - Slope 2 | Coeff (axis, Lo (axis, H) | icient ow Flow | of Determi v Tube and | nation | | |

| - Antonio - Antonio - Antonio | Carteret | | | Elizab | | |
|-------------------------------|----------------------|--------------|----------|----------------------|--------------|----------|
| Compound | No of observation | M.R.A.E % | 5.D % | No of observation | M.R.A.E % | S.D % |
| MECL | 49 | 34.52 | 19.26 | 31 | 33.30 | 12.83 |
| DCM | 2 - 2010 | - | | | | - |
| C6 | 49 | 7.42 | 6.97 | 33 | 10.34 | 8.18 |
| CFOR | | - | - | | - | - |
| 1,1,1 | 49 | 19.98 | 24.02 | 33 | 13.85 | 15.67 |
| Bz | 49 | 8.96 | 7.96 | 33 | 9.51 | 5.38 |
| CCL4 | 48 | 20.24 | 24.25 | 33 | 9.56 | 8.86 |
| TRIC | 35 | 26.08 | 29.95 | 24 | 21.29 | 31.04 |
| Tol | 49 | 7.58 | 12.96 | 33 | 7.7 | 5.52 |
| Perc | 48 | 18.45 | 24.96 | 33 | 9.26 | 14.38 |
| PMX | 49 | 8.3 | 15.05 | 33 | 7.23 | 5.71 |
| OX | 49 | 8.9 | 12.8 | 33 | 8.35 | 6.12 |

Table 21 Precision of Ambient Air Data Carteret : March 4 ~ December 29 1988 Elizabeth : June 14 ~ Dec 29 1988

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Note : M.R.A.E --- Mean of Relative Average Error

Table 22Precision of Project "Shoot-out" #2 ---Staten Island Interlaboratory Comparison Stud

| Compound N | o of | M.R.A.E | S.D | | |
|------------|-----------|---------|-------|--|--|
| Obs | ervations | ક | 8 | | |
| 1. MECL | 6 | 37.75 | 8.17 | | |
| 2. DCM | 6 | 42.70 | 4.89 | | |
| 3 C6 | 6 | 15.92 | 9.71 | | |
| 4. CFOR | 6 | 29.36 | 12.28 | | |
| 5. 1,1,1 | 6 | 21.88 | 7.82 | | |
| 5. Bz | 6 | 14.36 | 8.15 | | |
| 7. CC14 | 6 | 20.14 | 12.79 | | |
| 3. Tric | 6 | 13.11 | 16.18 | | |
| 9. Tol | 6 | 6.23 | 4.81 | | |
| 10. Perc | 6 | 8.20 | 5.14 | | |
| L1. PMX | 6 | 9.54 | 6.19 | | |
| 12. OX | 6 | 11.00 | 7.32 | | |

Note : M.R.A.E --- Mean of Relative Average Error

Table 23Results of Staten IslandInterlaboratory Comparison Study

% Difference From The Mean for All Compounds/All Organizations

| | | NJIT | NYDEC Envirc-chem | NYDEC ATD-50 | CSI | UMDNJ | TEXAS A | SEPA/RTP |
|------|---|---------|----------------------|-----------------|---------|---------|---------|----------|
| | | Average | Average | Average | Average | Average | 2 Tube | 4 Tube |
| | | 2-Tubes | 2-Tubes | 2-Tubes | 2-Tubes | 2-Tubes | Average | Average |
| Day | 1 | -38.95 | -61.14 | N/S | -19.62 | 118.52 | -55.52 | -13.49 |
| Day | 2 | N/S | -9.11 | -11.52 | 11.23 | -24.19 | -210.99 | 39.77 |
| Day | 3 | -16.7 | -37.06 | -7.26 | -10.91 | -15.54 | -24.96 | II/S |
| Day | 4 | 8.65 | -32.85 | -30.78 | 13.06 | -5.01 | -8.92 | N/S |
| Avg. | | -15.67 | -35.04 | -16.52 | -1.56 | 18.45 | -75.10 | 13.14 |

Absolute Value Of The % Difference From The Mean for All Compounds/Organizations

| | | NJIT | NYDEC Enviro-chem | NYDEC ATD-50 | CSI | UMDNJ | TEXAS A | &EPA/RTP |
|------|---|--------------------|----------------------|--------------------|--------------------|--------------------|-------------------|-------------------|
| | | Average 2-Tubes | Average 2-Tubes | Average 2-Tubes | Average 2-Tubes | Average 2-Tubes | 2 Tube Average | 4 Tube Average |
| Day | 1 | 38.95 | 61.14 | N/S | 28.4 | 126.21 | 55.52 | 28.89 |
| Day | 2 | N/S | 24.05 | 23.54 | 36.71 | 67.28 | 210.99 | 58.2 |
| Day | 3 | 20.86 | 37.06 | 35.46 | 49.79 | 44.66 | 42.11 | N/S |
| Day | 4 | 16.17 | 32.86 | 43.39 | 62.62 | 37.81 | 24.66 | N/S |
| Avg. | | 25.33 | 38.78 | 34.13 | 44.38 | 68.99 | 83.32 | 43.55 |

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Figure 1 . : Analytical System Configuration













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9 . 8 (Sec= 969 X/Scale=2 Bottom= +0 Top= +5120 Y/Scale= 32 Sec= 1378) Select Mode (GST) & Action (1+++,End): Run 25 = _____ G=Graph____S=Scale T=Time 1=UP +=LEFT +=RIGHT +=DOHN End=END

FID Response ^ Figure 8 - 3 (Air Sample) ECD Response v

8 . (Sec= 969 X/Scale=2 Bottom= +0 Top= +1280 Y/Scale= 8 Sec= 1378) Select Mode (GSI) & Action (t++1,End): Run 26 = _____ G=Graph_ S=Scale T=Time t=UP t=LEFT +=RIGHT 4=DOHN End=END



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And the second second













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Figure 9 - 9 Correlation Between Hi & Lo Flow Tubes











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Figure 9 - 18 Correlation Between Hi & Lo Flow Tubes










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Avg conc., ppb









Figure 10 - 13 Concentration Trend of Tol



Figure 10 - 14 Concentration Trend of Perc



Figure 10 - 15 Concentration Trend of pmX



Figure 10 - 16 Concentration Trend of oX



Figure 11 - 1 Comparison of Moving Avg at Carteret



Figure 11 - 2 Comparison of Moving Avg at Carteret







Figure 12 - 1 Comparison of Moving Avg Between Sites



Figure 12 - 2 Comparison of Moving Avg Between Site



Figure 12 - 3 Comparison of Moving Avg Between Sites



Figure 12 - 4 Comparison of Moving Avg Between Site



Figure 12 - 5 Comparison of Moving Avg Between Sites



Figure 12 - 6 Comparison of Moving Avg Between Site



Figure 12 - 7 Comparison of Moving Avg Between Site

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Figure 12 - 8 Comparison of Moving Avg Between Sites

References:

1.

[1]. McClenny, William A., Joachim D. Pleil, Michael W. Holdren, and Richard N. Smith, Automated Cryogenic Preconcentration and Gas Chromatographic Determination of Volatile Organic Compounds in Air.

Analytical Chemistry, Vol 56, No. 14, Dec 1984.

[2]. Janak, J., J. Ruzickova, and J. Novak,

Effect of Water Vapor in The Quantitation of Trace Compounds Concentrated by Frontal Gas Chromatography on Tenax GC.

Journal of Chromatography 99 (1974) 689.

[3]. Pellizzari, E. D., R.E. Berkley, and J. McRae, Collection and Analysis of Trace Organic Vapor Pollutants in Ambient Atmosphere. The Performance of A Tenax GC Cartridge Sampler For Hazardous Vapors.

Analytical Letters 9 (1976) 45.

[4]. Holzer, G., H. Shanfield, A. Zlatkis, W. Bertsch, P. Juarez, H. Mayfield, and H.M. Liebich. Collection and Analysis of Trace Organic Emissions From Natural Source.

Journal of Chromatography 142 (1977) 755.

[5]. Black, M.S., W.R. Rehg, R.E. Sievers, and J. J. Brooks,

> Gas Chromatographic Technique for Compounds Class Analysis of Jet Engine Exhaust.

Journal of Chromatographic Science 12 (1974) 175.

[6]. Westendorf, R. G.,

An Instrument for Thermal Desorption of Adsorbent Traps.

American Laboratory, Dec. 1985.

[7]. Skoog, Douglas A.,

Principles of Instrumental Analysis, 3rd ed. New York: Holt, Rinehart and Winston, Inc., 1980.

[8]. Van Wijk, R.,

The use of Poly-para-2,6-diphenyl-phenlene Oxide as a Porous Polymer in Gas Chromatography. Journal of Chromatography Science 8 (1970) 418.

[9]. Jacerk Namiesnik, Liberto Torres, Edmund Kozlowski, and Jacques Mathieu,

> Evaluation of the Suitability of Selected Porous Polymers for Preconcentration of Volatile Organic Compounds.

Journal of Chromatography, 208 (1981) 239-252.

[10]. Proceedings of Management/Steering Committee Meeting, Staten Island/New Jersey Urban Air Toxics Assessment Project, Feb 8, 1989, NYC. [11]. Huntsberger, David V., D. James Croft, and Partrick Billingsley,

Statistical Inference For Management and Economics, 2nd ed.

Boston, Massachusetts : Allyn and Bacon, Inc., 1980.

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