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Title of Thesis : Preconcentration and Flame Ionization Method  
for Measurement of Non-Methane Organic  
Compounds in Ambient Air and Statistical  
Analysis of Experimental Data

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Master of Science in Environmental Science,  
1988

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#### ABSTRACT

A fast and reliable method for the determination of non-methane organic compounds (NMOC) in ambient air has been developed. Samples are collected in SUMMA polished stainless steel canisters using a sampling system with a critical orifice as flowrate controller. Analysis of NMOC in the atmosphere via a canister is carried out by cryogenic preconcentration and a direct flame ionization detection method (PDFID). This system is sensitive and provides accurate measurement of ambient NMOC concentration even if the concentration is as low as 0.1 ppm carbon. The performance of the method was characterized using 19 pairs of canister samples and tested by statistical analysis.

PRECONCENTRATION AND DIRECT FLAME IONIZATION METHOD FOR  
MEASUREMENT OF NON-METHANE ORGANIC COMPOUNDS IN AMBIENT AIR  
AND STATISTICAL ANALYSIS OF EXPERIMENTAL DATA

Lianyi Zuo

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  
1988

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## I. INTRODUCTION:

### 1. Determination of NMOC

The primary and secondary air quality standard for hydrocarbons promulgated by the U.S. Environmental Protection Agency is  $100 \mu\text{g}/\text{m}^3$  (0.24 ppm) not to be exceeded more than once a year. The established standard is not based on harmful health effects caused by hydrocarbons. Rather, it has been established as a requirement in order to limit ozone / oxidant concentrations to  $160 \mu\text{g}/\text{m}^3$  (0.08 ppm) as a maximum 1-hour concentration not to be exceeded more than once a year. These hydrocarbons are primary precursors of atmospheric ozone and other oxidants, which in turn give rise to photochemical smog.

A hydrocarbon air quality standard in excess of  $100 \mu\text{g}/\text{m}^3$  has significance only in cases associated with an ozone/oxidant concentration of greater than  $160 \mu\text{g}/\text{m}^3$ . The development of an adequate air quality strategy for ozone/oxidant control requires knowledge of the appropriate relationships between content of hydrocarbon in ambient air and the ozone/oxidant concentration levels. Such relationships are required throughout the entire concentration ranges of concern in regions of air quality.

A number of photochemical dispersion models have been developed to describe the quantitative relationships between the ambient concentration of NMOC and other compounds (e.g.  $\text{NO}_x$ ) and the concentration of ozone [1]. In order to get a reliable conclusion with these models and analyzing the photochemical reactivities of NMOC, accurate data on ambient NMOC concentration are required.

For this purpose, A.P. Altshuller et al.[2] developed a method to measure NMOC. In this method, atmospheric samples are collected in 70-80 liter volume Tedlar bags by means of an automatic time sequential sampler. Methane is determined by using a modified flame ionization analyzer with an activated carbon precolumn to hold hydrocarbons other than methane. Total hydrocarbons are measured with a second flame ionization analyzer. The amount of NMOC is obtained by subtraction. The problem associated with this method is the breakthrough of methane in the charcoal bed. Disadvantages of the sampling technique include sample degradation in the bag, added risk of contamination from the bags, permeation of compounds into or out of the bags, difficulty in cleaning the bags, and possible bag leaks.

In 1974 J.C. Cooper et al [3] developed NMOC determination using cryogenic separation. A tube at 77°K is used to trap heavy hydrocarbons, so that the processed air only contains CH<sub>4</sub>. The amount of CH<sub>4</sub> is determined by gas chromatography with flame ionization detector (FID). The amount of the total organic carbon is also obtained by determination of unprocessed ambient air sample by FID. The NMOC level is also obtained by subtraction. Apparently this method overcomes the problem of CH<sub>4</sub> breakthrough in charcoal beds.

In 1977, J.N. Driscoll [4] reported monitoring atmospheric non-methane hydrocarbons using photoionization. He pointed out that the relative sensitivity of the method to hydrocarbons was similar to FID but there was no response to CH<sub>4</sub>. This allows a

direct measurement of NMOC and thus avoids the subtraction in the other two methods.

In 1980, D.E. Burch [5] developed a monitor to measure continuously the concentration of NMOC in ambient air. The monitor consists of a pump and manifold system along with two basic instruments -- a CH<sub>4</sub> monitor and a FID. The CH<sub>4</sub> monitor, which employs gas-filter correlation techniques, uses the IR absorption characteristics of CH<sub>4</sub> to measure its concentration. The concentration of the total hydrocarbons including CH<sub>4</sub> is measured by FID. The concentration of NMOC is then found by subtraction of the concentration of methane from the total concentration of hydrocarbon .

Currently, commercial continuous NMOC analyzers [6] are used to measure the concentration of NMOC. However these analyzers have been shown to be unreliable, particularly at concentrations below about 0.5 ppm carbon due to a variety of instrumental problems. These problems include the indirect, subtractive nature of the measurement process employed [7,8,9,10], non-uniform per-carbon response for different compounds due to interference of oxygen [9,10], inadequate sensitivity [7,8] and interference from water vapor [1].

Another common method to measure the concentration of NMOC is GC speciation [11]. This method provides much more accurate and reliable measurement. Utilizing cryogenic preconcentration followed by GC separation and flame ionization detection (FID), the technique provides quantitative, identified, species concentrations of the C<sub>2</sub> to C<sub>10</sub> compounds typically observed in

ambient air [10]. NMOC measurement may be obtained by summing the individual species concentrations. The cryogenic sample preconcentration greatly increases the sensitivity of the method because it effectively minimizes interference from methane and oxygen, allowing direct measurement of various organic species with little variation in the per-carbon response for most compounds of interest. However the GC speciation method requires sophisticated analytical equipment, a skilled operator, and a long term analysis, that makes the measurement expensive. Moreover, individual species concentrations are not necessary for model using non-methane total carbon.

This work describes a simplified cryogenic preconcentration - direct flame ionization detection (PDFID) method for the measurement of ambient NMOC based on the experimental method of EPA [12]. PDFID is sensitive and provides accurate measurement of ambient NMOC level even as low as 0.1 ppm carbon. Furthermore, the sampling system provides a reliable integrated 24 hour air sample for analysis. The performance of the method (reliability of sampling system, stability of sample stored in canister and precision of the method, etc.) is characterized based on 19 pairs of canister samples and verified using statistical analysis.

## 2. Statistical analysis of experimental data

When an experimenter has only a few data to report, he is unlikely to confuse his readers if he just lists them. But as the number of data point grows, a simple list becomes less and less meaningful and much of the additional information associated with



the greater number of data will not be appreciated. As the complexity of the data increases, however, it becomes more and more difficult to arrive at a reliable conclusion by unaided judgment. In such case use of statistical analysis becomes necessary. By use of statistical methods, it is possible to improve the quality of an experimenter's work by enabling him:

(1) to present his results in the simplest and clearest way,

(2) to extract the maximum amount of information from a given set of experiments,

(3) to draw the right conclusions despite the variability present in the data,

(4) to determine the most economic way of designing a set of experiments in order to obtain the required information.

Statistical analysis is widely used to measure the variance of experimental data in chemical analysis. And the other important use of the method is to justify the rationality for a designed procedure by using statistical hypothesis. In this paper statistical methods are used to process the experimental data to determine:

(1) whether the sample can be stable during one week.

(2) whether the sampling system can provide reliable samples.

(3) how good the precision of our experiment is.

(4) whether the difference between two parallel canisters depends on the concentration of NMOC of the sample or on the operation time of the sampling system.

Analysis of the foregoing questions suggests that statistical method is really a powerful tool in processing experimental data.

## II METHOD DESCRIPTION

### A. Sampling System

Figure 1 illustrates the flow scheme of the sampling system employed in this study. The critical orifice consists of two parallel 33 gauge needles. The system provides almost constant flowrate to fill two 6-liter SUMMA polished canisters from vacuum to 15 PSIG ( 2 atm ) over a 24 hour period. The volume of collected air in one canister is about 12 liters at standard pressure.

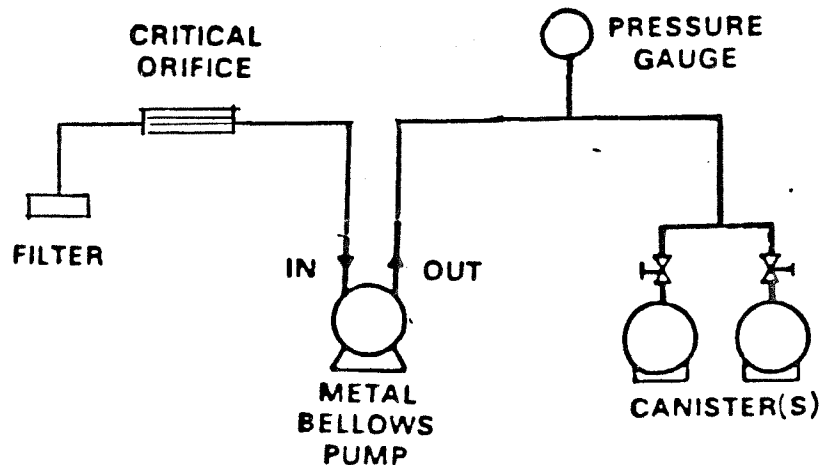


Figure 1. Sampling system for the collection of 24-hour integrated field sample

## B. Analysis System

### 1. Summary of analysis operation

Figure 2 shows a schematic diagram of the basic analytical apparatus. Major components include a sample volume metering system, a six-port gas valve, a cryogenic preconcentration trap, Varian 3700 GC and an integrator-recorder system.

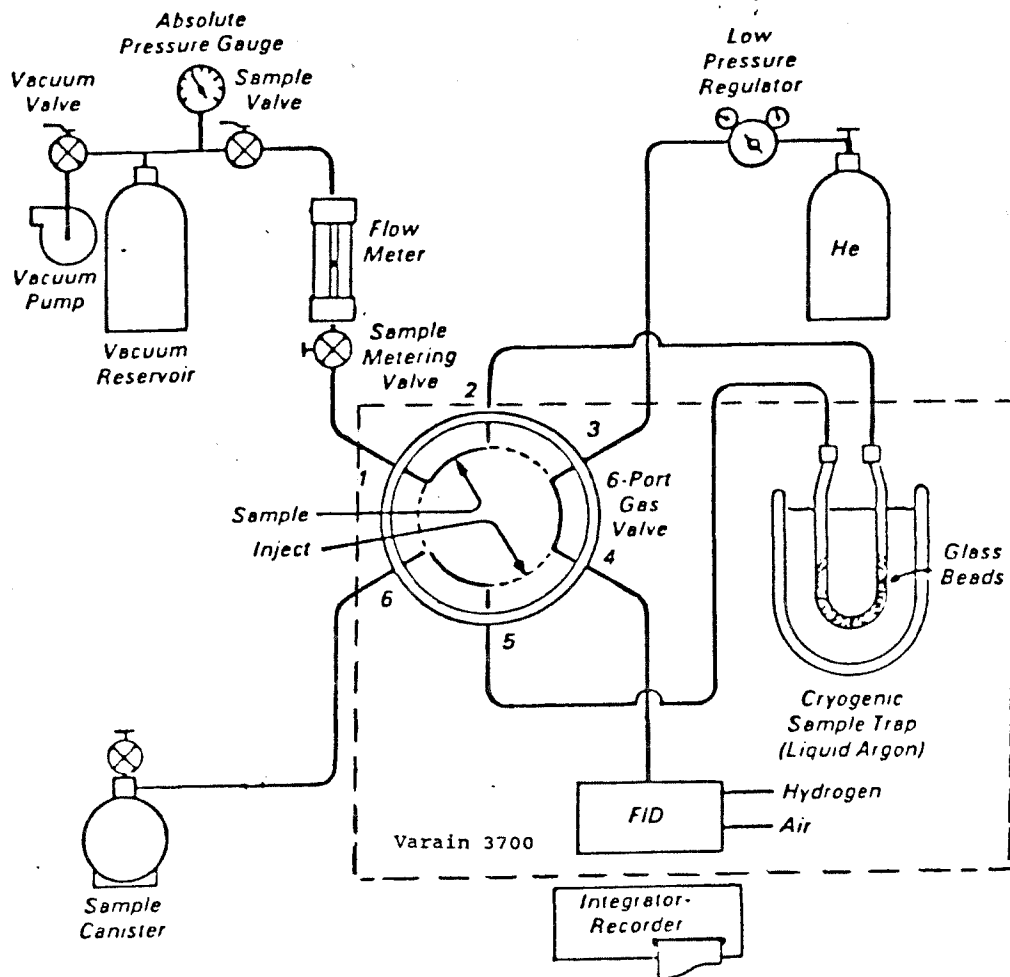


Figure 2. Schematic diagram of analysis system

At first the pressure in the vacuum reservoir is reduced to a known selected absolute pressure setting. When the 6-port valve is put in the sample (trapping) position, the sample valve is opened, air sample is drawn through the trap, which is immersed in liquid argon. When the hand of the absolute pressure gauge reaches the second selected reading, the sample valve is shut off. The volume of air passing through the trap is measured by the pressure increase in the reservoir. The trap condenses NMOC while permitting permanent gases and methane to pass through. During the trapping mode, helium carrier gas passes through the 6-port valve directly to the FID.

Following the trapping mode, the 6-port valve is switched to the inject position, where the helium carrier gas flows in a direction opposite to the previous sample flow through the trap, and passes to the FID. The cryogenic bath of the trap is then removed, and the trap is heated to approximately 90°C using the GC oven. Organic compounds collected in the trap revaporize and are carried into the FID by the carrier gas. The resulting peaks are integrated and calculated as ppm carbon by means of an NMOC calibration curve. The NMOC calibration curve was prepared previously by using a propane-in-air concentration standard. Use of the same precise reservoir pressure reading for each trapping cycle results in a constant sample volume and allows calibration of the system with known concentration standards without quantitatively measuring the actual sample volume.

## 2. Experimental Conditions

a. Carrier gas flowrate: Two carrier gas flowrates were tested ( 20 ml/min and 30 ml/min ). It was found that using the lower flow rate of helium led to a wider range of linear correlation between the NMOC concentration in the sample and relative GC peak area ( Fig.3 and 4). Therefore the following operating conditions were selected.

He: 20 ml/min.

Air: 300 ml/min

H<sub>2</sub>: 30 ml/min.

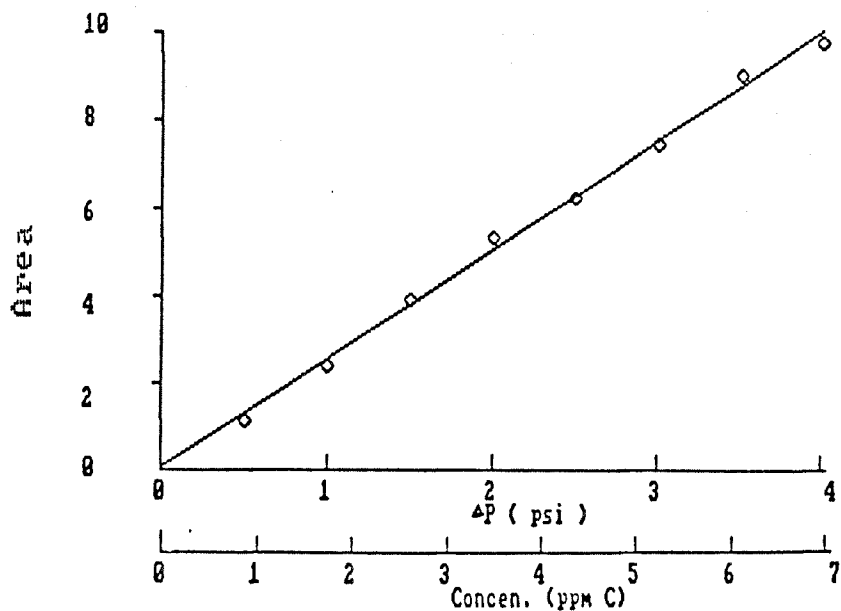


Figure 3. Calibration curve of propane standard when carrier gas flowrate is 20 ml/min

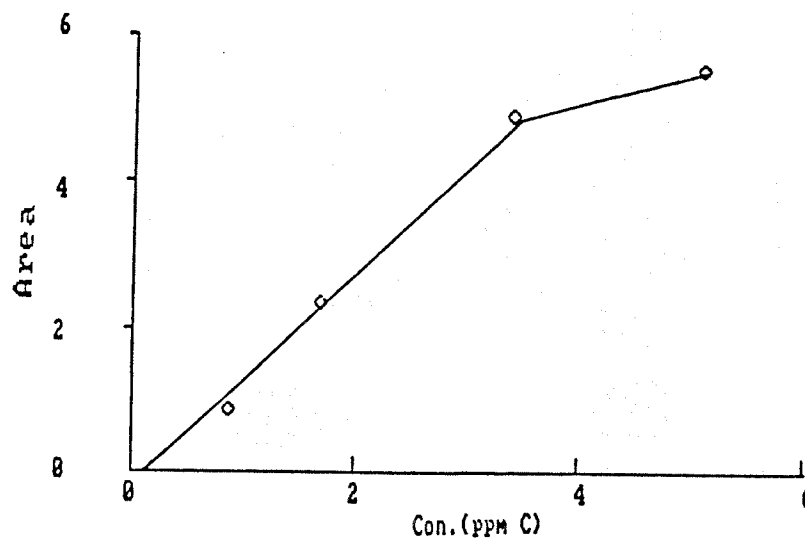


Figure 4. Calibration curve of propane standard when carrier gas flowrate is 30 ml/min

b. GC oven temperature: When running the propane standard, the Dewar flask of liquid argon was removed. The oven temperature was kept at about 40° C until the first peak appeared. Then the oven temperature was rapidly increased to 90° C. When running air samples, however, the oven temperature was increased immediately after removing the Dewar flask. Therefore there was a little difference in the conditions for running standard and air sample. The reasons for this arrangement were:

(a) In running propane bigger area was obtained when the oven temperature was kept at 40° C first, and then raised rapidly to 90° C .(Table 1)

Table 1 Effect of oven temperature in making calibration curve

Δp of reservoir (psi)	GC Area	
	1*	2*
2	3.511	5.691

1\* increase oven temperature immediately after removal of Dewar flask.

2\* increase oven temperature after appearance of the first peak.

(b) In running air sample, it was found that the first peak on chromatogram was small and of odd shape when the same conditions as those for propane were used, and the results were not reproducible. But if the oven temperature was increased immediately after removal of the Dewar, better peak shape and better repeatability of results were obtained ( Table 2 ).

Table 2 Effect of oven temperature when running air sample

ΔP of reservoir (psi)	GC Area	
	1*	2*
6.00	0.112	2.300
6.00	0.698	2.340
6.00	0.633	2.323

1\* keep the oven temperature at 40°C until the first peak appears.

2\* increase oven temperature immediately after the removal of Dewar.

### 3. Cryogenic sample trap

Figure 5 shows the dimensions of the cryogenic sampler. It is fabricated from 1/8" o.d. chromatographic grade stainless steel tubing to the approximate dimensions shown. The center 7 cm of the trap was packed with 60/80 mesh glass beads. Both ends of the tubing were plugged with glass wool. The glass beads and glass wool were dimethyl-dichlorosilane treated.

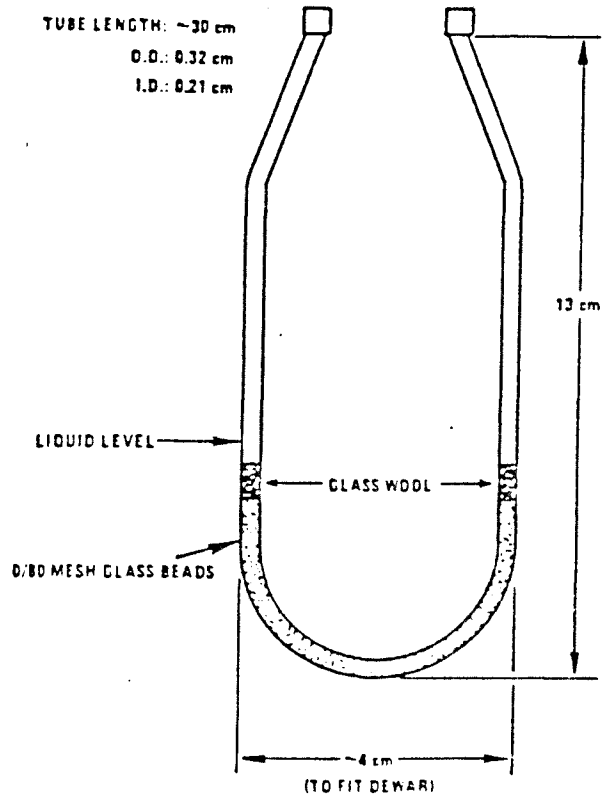


Figure 5. Cryogenic sample trap dimensions

## III EXPERIMENTAL DATA AND RESULTS

### A. Preparation of Calibration Curve and the Range of Determination

In the experiment, 3.4 ppm of propane in zero air was used as standard. Good calibration curves were obtained when reservoir



pressure differences ranged from 0.5 psi to 4 psi (i.e. concentration of carbon from 0.8 to 6.8 ppm) (Fig.3). The amount of carbon for each pressure difference is calculated based on the equation:

$$\text{PPM} * \text{GMW}/24.45 = \text{mg}/\text{m}^3 \quad (1)$$

where GMW = gram molecular weight

The concentration of propane in standard :

$$C_{\text{pro}} = 3.4 \text{ ppm}$$

The concentration of carbon in standard :

$$C_{\text{carb}} = 3.4 * 3 = 10.2 \text{ ppm}$$

The amount of carbon in one milliliter :

$$\begin{aligned} C &= 10.2 * 12 / 24.45 \text{ mg}/\text{m}^3 \\ &= 5.006 * 10^{-3} \text{ ug}/\text{ml} \end{aligned} \quad (2)$$

The volume of gas taken can be calculated by

$$V_s = \frac{\Delta P * V_r}{P_s}$$

Where

$V_s$  = Volume of gas taken (ml)

$\Delta P$  = Pressure difference measured by gauge (psi)

$V_r$  = Volume of vacuum reservoir (1200 ml)

$P_s$  = Standard pressure (14.7 psi)

In our case, the volume of gas taken for each distinct pressure difference could be calculated using the following equation

$$\begin{aligned} V_s &= (\Delta P * V_r) / P_s = \Delta P * 1200\text{ml} / 14.7 \\ &= 81.63 * \Delta P \text{ ml} \end{aligned} \quad (3)$$

The amount of carbon for distinct pressure difference using 3.4 ppm propane standard could be calculated as follows by use of Eq

(2) and (3)

$$\begin{aligned}C_w &= C * V_s = 5.006 * 10^{-3} \text{ ug/ml} * 81.63 * \Delta P \text{ ml} \\ &= 0.4086 * \Delta P \text{ ug}\end{aligned}\tag{4}$$

In all experiments, the pressure difference in the vacuum reservoir for air samples was kept at 6 psi ( The pressure in vacuum reservoir was from 0.5 psi to 6.5 psi ). Thus based on the calculation of Eq (3), the volume of gas taken for air samples was always

$$V_s = 81.63 * \Delta P \text{ ml} = 81.63 * 6 \text{ ml} = 489.8 \text{ ml}$$

Therefore, when 0.5 psi of pressure difference was taken from the propane standard, its carbon amount was equal to 0.2043 ug carbon, as computed from Eq (4). If the amount of carbon was placed in 489.8 ml of air sample, the corresponding carbon concentration was 0.8498 ppm. The calculation procedure is as follows:

$$\Delta P = 0.5 \text{ psi}$$

$$C_w = 0.4086 * \Delta P \text{ ug} = 0.2043 \text{ ug}$$

the concentration of carbon as  $\text{mg/m}^3$  unit in the gas should be

$$\begin{aligned}A \text{ mg/m}^3 &= C_w \text{ ug}/489.8 \text{ ml} = 0.2043 \text{ ug}/489.8 \text{ ml} \\ &= 4.171 * 10^{-4} \text{ ug/ml} \\ &= 4.171 * 10^{-4} * 1000 \text{ mg/m}^3 \\ &= 0.4171 \text{ mg/m}^3\end{aligned}$$

Using Eq (1), the concentration of carbon as ppm unit in the gas should be

$$\begin{aligned}
C_{\text{ppm}} &= ( A ) / ( \text{GMW}_{\text{carb}} / 24.45 ) \\
&= 24.45 / 12 * A \text{ ppm C} \\
&= 2.0375 * 0.417 \text{ ppm C} \\
&= 0.8498 \text{ ppm C}
\end{aligned}$$

The concentration of carbon for a pressure difference of 3.4 ppm propane standard corresponding in 489.8 ml of gas taken can be computed in the same way and the data are presented in Table 3.

Table 3 Concentration of carbon for distinct pressure difference

$\Delta P$ (psi)	C <sub>w</sub> (ug)	V <sub>air</sub> (ml)	A		C (ppm)
			ug/ml	mg/m <sup>3</sup>	
0.5	0.2043	489.8	4.171 x 10 <sup>-4</sup>	0.4171	0.8498
1.0	0.4086	"	8.342 x 10 <sup>-4</sup>	0.8342	1.6996
1.5	0.6129	"	1.2679 x 10 <sup>-3</sup>	1.2679	2.5870
2.0	0.8172	"	1.6684 x 10 <sup>-3</sup>	1.6684	3.3994
2.5	1.0215	"	2.0855 x 10 <sup>-3</sup>	2.0855	4.2492
3.0	1.2258	"	2.5026 x 10 <sup>-3</sup>	2.5026	5.0990
3.5	1.4301	"	2.9198 x 10 <sup>-3</sup>	2.9198	5.9491
4.0	1.6344	"	3.3369 x 10 <sup>-3</sup>	3.3369	6.7989

Figure 3 shows that the range of determination of NMOC is from 0 ppm C to 7 ppm C, the correlation coefficient for the calibration curve is 0.99873 and the line almost passes through the origin. Therefore, the calibration curve is good for determination of NMOC in air samples.

#### B. Interference of Moisture in the Determination of NMOC

According to USEPA's report [12], the moisture causes a definite positive shift in the FID baseline. This shift started

as soon as the trap was warmed up. The amount of the baseline shift seemed to be constant for different levels of humidity, but the duration of the shift varied in a manner roughly proportional to the total moisture content. The EPA group solved this problem by setting reasonable parameters for the integrator. ( Fig. 6 )

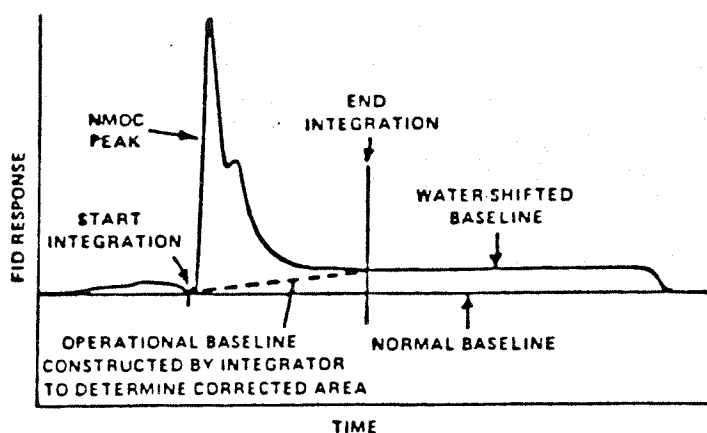
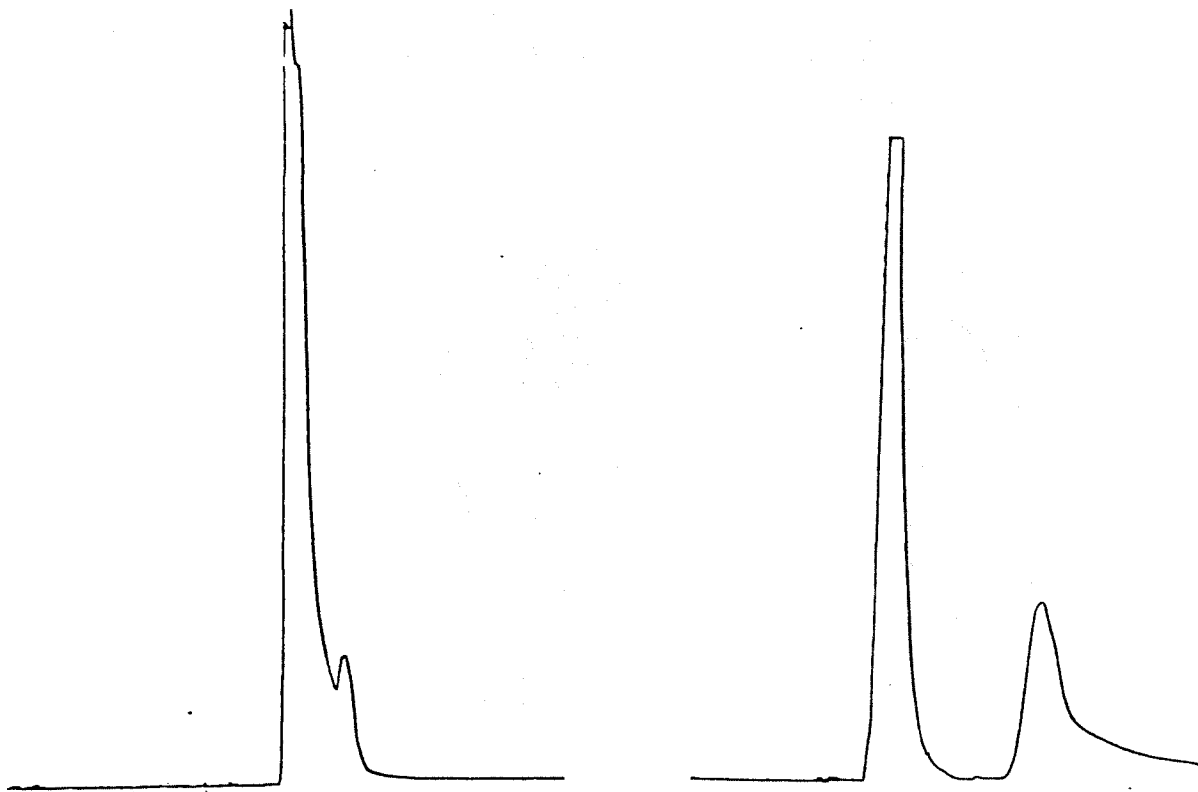


Figure 6. Technique used to minimize water interference by EPA

In our experiment dry propane standards was passed through water then analyzed by GC to prove moisture interference. It was found that another peak appeared after the propane peak ( Fig 7 ), but this peak did not affect the area of the propane peak (Table 4 ).



(a) Chromatogram of dry propane

(b) Chromatogram of wet propane

Figure 7. Chromatogram of dry and wet propane

Table 4 Comparison of areas of dry and wet propanes by GC

$\Delta p$ (psi)	Area wet propane	Area dry propane
4	37664	37822
4	37527	37567
4	36799	37482
average	37330	37624
relative error	0.8%	

For air samples, the same baseline drift mentioned by EPA( Fig. 8 ) appeared. The same remedial procedure was followed.

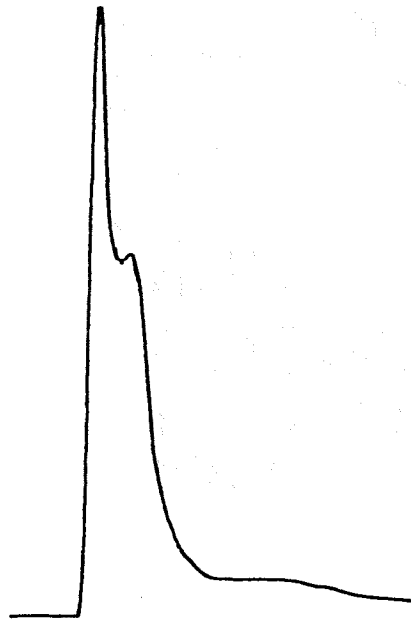


Figure 8. Chromatogram of air sample

### C. Analysis Reproducibility

Appendix I lists the results for 19 pairs of canister samples. These samples were taken on the roof of Tiernan Hall at N.J.I.T. The NMOC concentration in these samples ranges from 0.1 to 0.8 ppm C. Statistical analysis of the data gives a relative standard deviation of less than  $\pm 4\%$  for almost all individual

canisters. The relative standard deviation for a pair of parallel canisters is in about the same range as that for a single canister.

#### D. Sample stability

Oliver et al [13]. have studied the integrity of trace level volatile organic compounds in ambient air stored in SUMMA polished canisters by analyzing ambient air containing added known concentrations of 15 VOCs at <2 ppb. They pointed out that the relative standard deviation of concentrations of most VOCs in each canister set was  $\pm 10\%$  or less during the storage periods. For the 7-day tests, the mean change in concentration per day was within  $\pm 3.2\%$ . Therefore, these canisters appear to be suitable for the alternative sampling technique.

Appendix II tabulates analysis data of ambient air samples during 7 day storage period. Statistical analysis of the data shows that the relative standard deviation for the whole storage period is about  $\pm 4\%$ . Because the deviation is in the range of the relative standard deviation of the analysis reproducibility, the sample stored in the SUMMA polished canister is deemed stable during one week.

#### IV STATISTICAL ANALYSIS

##### A. Time Delay Test

In order to save liquid argon, analysis of the samples was carried out in a weekly batch. Thus, it is necessary to know whether the sample is stable or not during a week. For this purpose, the following experiment was designed. After the samples were taken, they were analyzed within 24 hrs. Then the canisters were placed aside for one week, and analyzed again. If the samples are stable during the week, almost the same result should be obtained for the second analysis. It means that the difference between the first and the second analyses should be zero. This is a statistical test for two samples, one from each of two populations. It should be known whether the means of the two populations are equal or not. In this case, pairing observation hypothesis [14] could be used.

Table 5 was obtained from Appendix II.

Table 5 Data observed on pairs of individuals  
for time delay test

	Pair No (i)			
	1	2	3	4
first	0.242	0.164	0.725	0.252
second	0.219	0.160	0.717	0.266
difference ( $d_i$ )	0.023	0.004	0.008	-0.014



statistical analysis:

$$\sum d_i = 0.021 \quad \sum d_i^2 = 0.000805$$

$$\bar{d} = \sum d_i / N = 0.021/4 = 0.00525$$

$$s_d^2 = \frac{\sum d_i^2 - (\sum d_i)^2/N}{N-1}$$

$$= \frac{0.000805 - (0.021)^2/4}{4-1}$$

$$= \frac{0.000805 - 0.000110}{3}$$

$$= 0.000695/3 = 0.000231$$

$$s_d = 0.000231 = 0.0152$$

Hypothesis :  $H_0 : \mu_1 = \mu_2$

$H_1 : \mu_1 \neq \mu_2$

Let  $\alpha = 0.05$  and use two tailed test

$$\text{Statistic: } t_s = \frac{\bar{d} - 0}{s_d/N^{1/2}} = \frac{0.00525}{0.0152/4^{1/2}}$$

$$= 0.6907$$

Assuming that the populations have normal distributions, then this statistic has a t distribution with  $4-1 = 3$  degrees of freedom. The critical value is  $t_{0.975}(3) = 3.182$  or  $t_{0.025}(3) = -3.182$  [16]. The hypothesis will be rejected if  $t < -3.182$  or  $t > 3.182$ . But the t from our test is between the two critical values. So the hypothesis  $H_0 : \mu_1 = \mu_2$  can not be rejected. The conclusion is that this experiment does not demonstrate any difference between the first analysis and the second analysis at 95% confidence level. In other words, the

samples are stable during a week, so analysis of the samples can be done in weekly batches.

#### B. Reliability of Sampling System

In order to get reasonable results, it must be known whether the sampling system provides a representative sample at a single site. For this purpose, two canister samples at a single site were simultaneously taken using the sampling system and analyzed under the same GC conditions. If these samples are really representative of the atmosphere, the mean ( $\bar{X}_1$ ) of the first canister sample should be equal to the mean ( $\bar{X}_2$ ) of the second canister sample. In this case, the hypothesis that  $\mu_1 - \mu_2 = 0$  should be tested. The statistic  $\bar{X}_1 - \bar{X}_2$  will be used and the hypothesis will be rejected if the difference is significantly far from zero. The pairing observation hypothesis [14] must still be used to justify the hypothesis. Results from Appendix I are presented in Table 6.

Table 6 Data observed on pairs of individuals for reliability of sampling system

pairNo.(i)	first	second	difference (d <sub>i</sub> )
1	0.295	0.268	+0.027
2	0.165	0.150	+0.015
3	0.158	0.164	-0.006
4	0.159	0.192	-0.033
5	0.382	0.344	+0.038
6	0.498	0.513	-0.015
7	0.209	0.221	-0.012
8	0.252	0.260	-0.008
9	0.348	0.363	-0.015
10	0.482	0.494	-0.012
11	0.126	0.141	-0.015
12	0.205	0.170	-0.035
13	0.385	0.353	+0.032
14	0.215	0.238	-0.023
15	0.160	0.156	+0.004
16	0.214	0.179	+0.035
17	0.564	0.654	-0.090
18	0.525	0.504	+0.021
19	0.457	0.469	-0.012

Statistical analysis:

$$\sum d_i = -0.034$$

$$\sum d_i^2 = 0.0172$$

$$\bar{d} = \sum d_i / N = -0.034 / 19 = -0.00179$$

$$s_d^2 = \frac{\sum d_i^2 - (\sum d_i)^2 / N}{N - 1}$$

$$= \frac{0.0172 - (-0.034)^2 / 19}{19 - 1}$$

$$= \frac{0.0172 - 0.00006}{18} = 0.000952$$

$$s_d = 0.000952^{1/2} = 0.0308$$

Hypothesis  $H_0 : \mu_1 = \mu_2$

$H_1 : \mu_1 \neq \mu_2$

degrees of freedom:  $19 - 1 = 18$

Let  $\alpha = 0.05$  and use two tailed test

$$\begin{aligned} \text{Statistic: } t &= \frac{\bar{d} - 0}{S_d/n^{1/2}} = \frac{-0.00179}{0.0308/19^{1/2}} \\ &= -0.253 \end{aligned}$$

Assuming that the populations have normal distributions, then the statistic has a t distribution with 18 degrees of freedom. The statistic value is  $t_{0.975}(18) = 2.101$  or  $t_{0.025}(18) = -2.101$ . [16]. The hypothesis will be rejected if  $t < -2.101$  or  $t > 2.101$ . But the t from the calibration is between the two critical values, so the hypothesis could not be rejected. The conclusion is that the samples in the two canisters taken simultaneously at a single site are the same. The sampling system can give us reliable samples with 95% confidence level.

#### C. Overall Precision of Our Method (Including Sampling System and Analysis System)

In the above analysis the hypothesis  $H_0 : \mu_1 = \mu_2$  was tested. If the hypothesis is true, the differences  $X_{1i} - X_{2i}$  will come from a set of numbers with a mean of 0. The sampling distribution of  $\bar{X}_1 - \bar{X}_2$  is, for large sample sizes, approximately normal. Based on this, test for overall precision through comparison of our data and the EPA data can be done. Assuming that our sample size and the EPA sample size are large enough, the distribution of  $\bar{X}_1 - \bar{X}_2$  in the data sets is normal. To

compare the overall precisions of the EPA and our own experiment, the variance of distribution of their data must be tested by using the hypothesis concerning two variances [15]. If our experiment has the same variance as the EPA experiment,  $\sigma_1^2 = \sigma_2^2$  must result. To test this hypothesis, the difference of each observed pair will first be computed and then the ratio of the difference variances,  $F = S_1^2/S_2^2$ , will be calculated. The hypothesis will be rejected if the observed value F is unusually large or unusually small. Percentiles of the F distribution can be used to define the critical range [17].

It is well known that large variance implies bad precision. In our experiment, it means that distribution of  $\bar{X}_1 - \bar{X}_2$  is not concentrated near zero, i.e. some of the absolute values of the difference are rather large. If this is so, the reliability of our sampling system or the accuracy of our analysis system must be doubted. Because a standard whose composition is almost the same as that of air cannot be obtained, the accuracy of our analysis system has only been tested with the propane standard. So if the hypothesis concerning two variances for the both data will be tested, the information about the overall precision of the two methods will be obtained.

Corresponding EPA data are from Appendix III. The data from NJIT are obtained from the above test.

EPA	NJIT
$N_1 = 58$	$N_2 = 19$
$\bar{d}_1 = -0.026 \text{ ppm c}$	$\bar{d}_2 = - 0.00179 \text{ ppm C}$
$S_1 = 0.119 \text{ ppm C}$	$S_2 = 0.0308 \text{ ppm C}$

Statistical analysis:

Let  $\alpha = 0.05$  and use two tailed test.

$$\text{Hypothesis : } H_0 : \sigma_1^2 = \sigma_2^2$$

$$H_1 : \sigma_1^2 \neq \sigma_2^2$$

If  $S_1^2/S_2^2 < F_{\frac{1}{2}\alpha} ( N_1 - 1, N_2 - 1 )$  or

$$S_1^2/S_2^2 > F_{1-\frac{1}{2}\alpha} ( N_1 - 1, N_2 - 1 )$$

The hypothesis  $H_0 : \sigma_1^2 = \sigma_2^2$  will be rejected.

$$\text{Statistic: } S_1^2/S_2^2 = 0.119^2/0.0308^2 = 14.9$$

The critical value [17] is

$$F_{0.025} ( 57, 18 ) = .514 \quad \text{or}$$

$$F_{0.975} ( 57, 18 ) = 2.22$$

Because  $S_1^2/S_2^2 \gg F_{0.975} ( 57, 18 )$ , the hypothesis  $H_0 : \sigma_1^2 = \sigma_2^2$  is rejected. Our experiment and EPA experiment do not have the same variance. In addition, the value  $S_1^2/S_2^2$  is large. This information shows us that the variance in the EPA experiment is much larger than the variance in the NJIT experiment. So, the hypothesis test proves that the overall precision of the NJIT method is not the same as that of EPA. Actually the overall precision of the method in NJIT is better than that of EPA.

D. Dependence of the Difference between a Pair of Canisters on the MNOC Concentration in Sample

It is very unusual to get the same numbers in parallel analytical studies. In our experiment it is very clear that there is a difference between the analysis of the parallel canisters (Appendix I). But how can one know whether the difference depends on the concentration of the sample or not? The answer lies in the test for independence in regression analysis.

Table 7 comes from Appendix 1.

Table 7 Relationship between the difference in two parallel canisters and the concentration of NMOC of sample

Average Concentration (X) (ppm)	difference in the two canisters* (Y) (ppm)
0.134	0.015
0.156	0.015
0.158	0.004
0.161	0.006
0.176	0.033
0.188	0.035
0.196	0.035
0.215	0.012
0.226	0.023
0.256	0.008
0.282	0.027
0.356	0.015
0.363	0.038
0.369	0.032
0.463	0.012
0.488	0.012
0.506	0.015
0.514	0.021
0.609	0.090

\* absolute value

When the set of data is processed by linear regression analysis. A expression for the difference Y when X is given is

$$Y = A + B * X$$

where A and B are regression coefficients, Y is the difference in two parallel canisters, X is the average concentration of NMOC of the sample. If the difference in two parallel canisters is independent of the concentration of NMOC of sample, the difference must be the same whatever the concentration of NMOC in the sample is. So it implies that B = 0 in the above equation.

Hypothesis:  $H_0 : B = 0$

$H_0 : B \neq 0$

Degrees of freedom:  $19 - 2 = 17$

let  $\alpha = 0.5$  and use two tailed test.

Assuming that the distribution of Y for each X is normal with the same variance and with the same mean, the sampling distribution of this statistic is a t distribution with  $N - 2$  degrees of freedom. The hypothesis  $H_0 : B = 0$  will be rejected if  $t < t_{\frac{1}{2}\alpha}(N-2)$  or  $t > t_{1-\frac{1}{2}\alpha}(N-2)$ . In this case, degree of freedom is  $19 - 2 = 17$ . The critical value is  $t_{0.025}(17) = -2.11$  or  $t_{0.975}(17) = 2.11$  [16]. So the hypothesis will be rejected if the statistic t from the experimental data is smaller than -2.11 or larger than 2.11.

From Table 7, the following computation can be carried out

$$\sum X_i = 5.816$$

$$\sum Y_i = 0.448$$

$$\sum X_i Y_i = 0.159$$

$$\sum X_i^2 = 2.178$$

$$\sum Y_i^2 = 0.017254$$

$$S_{XY} = \sum X_i Y_i - \frac{(\sum X_i)(\sum Y_i)}{N} = 0.021$$

$$SSX = \sum X_i^2 - \frac{(\sum X_i)^2}{N} = 2.064$$

$$SSY = \sum Y_i^2 - \frac{(\sum Y_i)^2}{N} = 0.016345$$

$$S_x^2 = \frac{SSX}{N - 1} = 0.114661 \quad S_x = 0.338616$$



$$b = \frac{S_{XY}}{SSX} = 0.010198$$

$$SSR = b^2 * SSX = 0.000214$$

$$S_{YX}^2 = \frac{SSY - SSR}{N - 2} = 0.000948 \quad S_{YX} = 0.030804$$

$$\text{statistic: } t = \frac{b * S_x * (N-1)^{1/2}}{S_{YX}} = 0.476$$

Based on the calculation, the statistic t from the experimental data is equal to 0.476. It is between the two critical values, so the hypothesis  $H_0 : B = 0$  can not be rejected. The statistical test proved that the difference in two parallel canisters is independent of the concentration of the sample with 95% confidence.

#### E. Dependence of the Difference between a pair of Canisters on the Operation Time of Sampling System

As the running period of the sampling system increases, the sampling system may be contaminated. If this is so, the difference in two parallel canisters in the later periods of operation must be bigger than in the earlier periods. In this case, it must be hypothesized that the difference in two parallel canisters is independent of running time of the sampling system. The test for independence in regression must still be used.

Table 8 comes from Appendix I.

Table 8 difference in two parallel canisters during operation time

sampler running day (X)	difference in two canisters* (Y) (ppm)
1	0.027
2	0.015
3	0.006
4	0.033
5	0.038
6	0.015
7	0.012
8	0.008
9	0.015
10	0.012
11	0.015
12	0.035
13	0.032
14	0.023
15	0.004
16	0.035
17	0.090
18	0.021
19	0.012

\* absolute value

Hypothesis:  $H_0 : B = 0$

$H_0 : B \neq 0$

Degree of freedom:  $19 - 2 = 17$

let  $\alpha = 0.5$  and use two tailed test.

From Table 8 the following computation can be done.

$$\sum X_i = 190$$

$$\sum Y_i = 0.448$$

$$\sum X_i Y_i = 4.969$$

$$\sum X_i^2 = 2470$$

$$\sum Y_i^2 = 0.017254$$

$$S_{XY} = \sum X_i Y_i - \frac{(\sum X_i)(\sum Y_i)}{N} = 0.489$$

$$SSX = \sum X_i^2 - \frac{(\sum X_i)^2}{N} = 2340$$

$$SSY = \sum Y_i^2 - \frac{(\sum Y_i)^2}{N} = 0.016345$$

$$S_X^2 = \frac{SSX}{N - 1} = 130 \quad S_X = 11.40175$$

$$b = \frac{S_{XY}}{SSX} = 0.000208$$

$$SSR = b^2 * SSX = 0.000102$$

$$S_{YX}^2 = \frac{SSY - SSR}{N - 2} = 0.000955 \quad S_{YX} = 0.0309$$

$$\text{statistic: } t = \frac{b * S_X * (N-1)^{1/2}}{S_{YX}} = 0.327$$

The critical region is  $t_{0.025(17)} < -2.11$  or  $t_{0.975(17)} > 2.11$  [16]. But the statistic  $t$  from the experimental data is between these two figures, so the hypothesis  $H_0 : B = 0$  cannot be rejected. The conclusion is that the difference in two parallel canisters does not depend on the running time of sampling system with 95% confidence.

Notations:

$N$  : number of duplicate sample pairs ( observed times)

$d_i$ : difference for  $i^{\text{th}}$  sample pair (difference in  $i^{\text{th}}$  observation)

$\sum d_i$ : sum of difference in sample

$\bar{d}_i$ : mean of sum of difference in sample

$S_d$  or  $S$  : standard deviation of difference in sample

$S_d^2$  = variance of difference in sample

$\sigma$  : standard deviation of difference in population

$\sigma^2$ : variance of difference in population

## V. CONCLUSION AND DISCUSSION

Cryogenic preconcentration and direct flame ionization detection method is suitable for determination of non-methane organic compounds (NMOC). In the experiment two 33 gauge needles were used as critical orifice to allow 24-hour running of the sampling system at constant flow rate. So if a different gauge needle is used, the period of sampling can be controlled to get an integrated sample during that period. For example, EPA uses 30 gauge needle (2.54 cm) to take a sample in a three-hour period [12].

On the other hand, the canister sampling method provides an attractive feature in the analysis of volatile organic compounds (VOCs). Now, the most widely used sampling method for VOCs involves the use of various solid absorbents. Tenax is the most frequently used one. The primary advantage of this sampling approach is the large volume of air which can be sampled compared to cryogenic sampling. But the major disadvantage is that the range of VOCs which can be collected is limited due to the different absorbents [18]. Furthermore, analyte decomposition has been observed during absorption/thermal desorption on Tenax [19]. However, the primary advantages of canister sampling cryogenic trap technique are:

(1) a wide range of organic materials can be collected, avoiding contamination problems with absorbents.

(2) the sample is immediately available for analysis without further work,

(3) consistent recoveries are generally obtained.

The important limitation of the technique, however, is the condensation of large quantities of moisture. If the effect of moisture in the analysis can be eliminated, the technique will be a really reliable sampling method.

Statistical methods are powerful tools for treatment of experimental data. They are not only used to determine the dispersion of data, but more importantly, they are very useful in the analysis of experimental data, so that meaningful information can be extracted and accurate conclusions can be reached.

Appendix I The NMOC concentration in the sample

sampling time and condition	date for analysis	canister number	concentration			
			Con. (ppmC)	Ave.	sd.	%sd.
2/20 6:10 PM to 2/21 5:30 PM sunny	2/24/87	A	0.289 0.295 0.300	0.295	0.006	2.2%
		B	0.264 0.285 0.264 0.260			
		A+B		0.279	0.0093	3.3%
2/21 5:30 PM to 2/22 5:00 PM sunny 39°F humidity: 31%	2/24/87	A	0.166 0.164	0.165	0.0011	0.7%
		B	0.164 0.151 0.150			
		A+B		0.159	0.0010	0.6%
2/24 5:20 PM to 2/25 4:50 PM 32°F humidity: 34% sunny winds: NW-7	2/26/87	G	0.164 0.152 0.159 0.163	0.158	0.0084	5.3%
		H	0.164 0.166			
		G+H		0.161	0.0060	3.7%
2/25 4:50 PM to 2/26 4:20 PM 45°F sunny	2/27/87	E	0.157 0.166 0.155	0.159	0.0058	3.6%
		F	0.196 0.188			
		E+F		0.172	0.0057	3.3%

Appendix I ---- continue

sampling time and condition	date for analysis	canister number	concentration			
			Con. (ppmC)	Ave.	sd.	%sd.
2/26 6:00 PM to 2/27 5:30 PM	3/2/87	D	0.371 0.393	0.382	0.016	4.1%
2/27 5:30 PM		A	0.345 0.342	0.344	0.002	0.58%
sunny 47°F		D+A		0.363	0.011	3.1%
3/2 4:15 PM to 3/3 4:15 PM	3/4/87	E	0.495 0.501	0.498	0.0042	0.84%
47°F humidity: 36%		F	0.515 0.511	0.513	0.0028	0.54%
wind: NW-10		E+F		0.506	0.0063	0.70%
3/3 4:30 PM to 3/4 4:30 PM	3/5/87	B	0.204 0.215	0.209	0.0078	3.7%
snowing 47°F humidity: 35%		A	0.222 0.220	0.221	0.0014	.63%
wind: NW-10		A+B		0.215	0.0056	2.6%
3/4 5:00 PM to 3/5 5:00 PM	3/6/87	G	0.254 0.249	0.252	0.0035	1.4%
46°F humidity: 31%		D	0.264 0.257	0.260	0.0049	1.9%
		G+D		0.256	0.0042	1.7%

Appendix I ---- continue

sampling time and condition	date for analysis	canister number	concentration			
			Con. (ppmC)	Ave.	sd.	%sd.
3/6 6:15 PM to 3/7 6:00 PM	3/9/87	B	0.346 0.350	0.348	0.0028	0.8%
		A	0.372 0.354			
sunny 64°F humidity: 30%		B+A		0.356	0.0096	2.7%
3/7 6:00 PM to 3/8 6:30 PM	3/9/87	E	0.474 0.489	0.482	0.011	2.3%
		F	0.492 0.495			
sunny 64°F		E+F		0.488	0.0079	1.6%
3/9 6:15 PM to 3/10 6:00 PM	3/13/87	D	0.124 0.128	0.126	0.0028	2.2%
		H	0.142 0.140			
sunny				0.141	0.0014	1.0%
3/10 6:00 PM to 3/11	3/13/87	B	0.204 0.206	0.205	0.0014	0.7%
5:30 PM		A	0.167 0.173			
sunny 22°F humidity: < 30%		B+A		0.188	0.0031	1.7%



Appendix I ---- continue

sampling time and condition	date for analysis	canister number	concentration			
			Con. (ppmC)	Ave.	sd.	%sd.
3/11 5:30 PM to 3/12	3/13/87	E	0.386 0.385	0.385	0.0007	0.2%
5:30 PM snowing 33°F humidity: 30%		F	0.365 0.347 0.347			
		E+F	0.366			
3/20 5:15 PM to 3/21	3/25	A	0.234 0.200 0.211	0.215	0.017	8.0%
5:00 PM sprinkling 40°F humidity: 79% wind: N-6		B	0.228 0.248 0.239			
		A+B	0.226			
3/21 5:00 PM to 3/22	3/25	C	0.159 0.160	0.160	0.0007	0.44%
5:00 PM sunny 50°F humidity: 40 %		D	0.155 0.161 0.152			
		C+D	0.158			
3/22 5:00 PM to 3/23	3/25	E	0.214 0.214	0.214	0	0
5:00 PM sunny 55°F humidity: 40% wind: W-7		F	0.176 0.181			
		E+F	0.196			

Appendix I ---- continue

sampling time and condition	date for analysis	canister number	concentration			
			Con. (ppmC)	Ave.	sd.	%sd.
3/27 6:00 PM to	3/31	G	0.557 0.570	0.564	0.009	1.6%
3/28 6:00 PM		H	0.676 0.631			
sunny 58°F humidity: 27%		G+H		0.609	0.024	3.8%
3/28 6:00 PM to	3/31	A	0.521 0.529	0.525	0.0056	1.1%
3/29 6:00 PM		B	0.593 0.615			
sunny 60°F humidity: 30%		A+B		0.564	0.011	2.0%
3/29 6:00 PM to	3/31	C	0.448 0.466	0.457	0.013	2.8%
3/30 6:00 PM		D	0.460 0.478			
raining 40°F humidity: 70%		C+D		0.463	0.013	2.8%

\* the standard deviation for two canisters together is pooled standard deviation

$$s_p^2 = \frac{(N_1-1)S_1^2 + (N_2-1)S_2^2 + \dots + (N_k-1)S_k^2}{N_1 + N_2 + N_3 + \dots + N_k - k}$$

Appendix II Sample stability

canister number	date for analysis	concentration			
		Con. (ppm C)	Ave.	sd.	%sd.
1#	2/10	0.247	0.242	0.006	2.6%
		0.238			
	2/13	0.236	0.246	0.014	5.7%
		0.256			
2/16	0.225	0.219	0.0085	3.8%	
	0.213				
	total		0.236	0.010	4.3%
H	2/26	0.163	0.164	0.0015	0.9%
		0.164			
		0.166			
	2/27	0.151	0.155	0.0042	2.7%
		0.157			
	3/2	0.164	0.164		
3/5	0.163	0.160	0.0049	3.1%	
	0.156				
	total		0.160	0.0034	2.1%
C	3/2	0.725	0.725	0.0007	0.05%
		0.726			
	3/7	0.706	0.717	0.015	2.1%
		0.728			
	total		0.721	0.011	1.5%
G	3/5	0.254	0.252	0.0035	1.4%
		0.249			
	3/13	0.271	0.266	0.0064	2.4%
		0.262			
	total		0.259	0.0052	2.0%

\* The standard deviation for total value is computed using pooled standard deviation

Appendix III Data from EPA

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$$N_1 = 58$$

$$\bar{d}_1 = -0.026 \text{ ppm C}$$

$$S_1 = 0.119 \text{ ppm C}$$

---

This table comes from reference(20), EPA assessed the overall precision of their method based on the differences between the analyses of 58 pairs of duplicate samples collected simultaneously in duplicate paired canisters. therefore this overall precision assessment included both analytical variability and variability contributed by collection and storage of the air samples in the canisters.

### Appendix IV

Calculation of statistic t for test of dependency of difference between a pair of canisters on the NMOC concentration of sample

X conc	day	canist 1	canist 2	Y difference	X*Y	X*X	Y*Y
0.134	11	0.141	0.126	0.015	0.00201	0.017956	0.000225
0.156	2	0.165	0.15	0.015	0.00234	0.024336	0.000225
0.158	15	0.16	0.156	0.004	0.000632	0.024964	0.000016
0.161	3	0.164	0.158	0.006	0.000966	0.025921	0.000036
0.176	4	0.192	0.159	0.033	0.005808	0.030976	0.001089
0.188	12	0.205	0.17	0.035	0.00658	0.035344	0.001225
0.196	16	0.214	0.179	0.035	0.00686	0.038416	0.001225
0.215	7	0.221	0.209	0.012	0.00258	0.046225	0.000144
0.226	14	0.238	0.215	0.023	0.005198	0.051076	0.000529
0.256	8	0.26	0.252	0.008	0.002048	0.065536	0.000064
0.282	1	0.295	0.268	0.027	0.007614	0.079524	0.000729
0.356	9	0.363	0.348	0.015	0.00534	0.126736	0.000225
0.363	5	0.382	0.344	0.038	0.013794	0.131769	0.001444
0.369	13	0.385	0.353	0.032	0.011808	0.136161	0.001024
0.463	19	0.469	0.457	0.012	0.005556	0.214369	0.000144
0.488	10	0.494	0.482	0.012	0.005856	0.238144	0.000144
0.506	6	0.513	0.498	0.015	0.00759	0.256036	0.000225
0.514	18	0.525	0.504	0.021	0.010794	0.264196	0.000441
0.609	17	0.654	0.564	0.09	0.05481	0.370881	0.0081

SUM X  
5.816

SUM Y    SUM X\*Y    SUM X\*X    SUM Y\*Y  
0.448    0.158184    2.178566    0.017254

SXY= SUM X\*Y-SUM X\*SUM Y/ N  
0.021048

SSX=SUM X\*X - SUM X\*X/N  
2.063904

SSY = SUM Y\*Y -SUM Y\*Y/N  
0.016345

SQUARE Sx= SSX/(N-1)                    square root Sx  
0.114661                                    0.338616

b= SXY/SSX  
0.010198

SSR= square b \* SSX  
0.000214

squareSyx=(SSY-SSR)/(N-2)            square root Syx  
0.000948                                    0.030804

t= b\*Sx \* square root(N-1)/Sy.x  
0.475635

## Appendix V

Calculation of statistic t for test of dependency of difference in two parallel canisters on operation time of samping system

X day	conc	canist 1	canist 2	Y diffrence	X*Y	X*X	Y*Y
1	0.282	0.295	0.268	0.027	0.027	1	0.000729
2	0.156	0.165	0.15	0.015	0.03	4	0.000225
3	0.161	0.164	0.158	0.006	0.018	9	0.000036
4	0.176	0.192	0.159	0.033	0.132	16	0.001089
5	0.363	0.382	0.344	0.038	0.19	25	0.001444
6	0.506	0.513	0.498	0.015	0.09	36	0.000225
7	0.215	0.221	0.209	0.012	0.084	49	0.000144
8	0.256	0.26	0.252	0.008	0.064	64	0.000064
9	0.356	0.363	0.348	0.015	0.135	81	0.000225
10	0.488	0.494	0.482	0.012	0.12	100	0.000144
11	0.134	0.141	0.126	0.015	0.165	121	0.000225
12	0.188	0.205	0.17	0.035	0.42	144	0.001225
13	0.369	0.385	0.353	0.032	0.416	169	0.001024
14	0.226	0.238	0.215	0.023	0.322	196	0.000529
15	0.158	0.16	0.156	0.004	0.06	225	0.000016
16	0.196	0.214	0.179	0.035	0.56	256	0.001225
17	0.609	0.654	0.564	0.09	1.53	289	0.0081
18	0.514	0.525	0.504	0.021	0.378	324	0.000441
19	0.463	0.469	0.457	0.012	0.228	361	0.000144

SUN X		SUM Y	SUM X*Y	SUM X*X	SUM Y*Y
190		0.448	4.969	2470	0.017254

SXY= SUM X\*Y-SUM X\*SUM Y/ N  
0.489

SSX=SUM X\*X - SUM X\*X/N  
2340

SSY = SUM Y\*Y -SUM Y\*Y/N  
0.016345

SQUARE Sx= SSX/(N-1)	square root Sx
130	11.40175

b= SXY/SSX  
0.000208

SSR= square b \* SSX  
0.000102

squareSyx=(SSY-SSR)/(N-2)	square root Syx
0.000955	0.030911

t= b\*Sx \* square root(N-1)/Sy.x  
0.327026

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