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## Gas chromatographic method for determination of 28 volatile organic compounds emitted from a sewerage plant

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## ABSTRACT

Title of Thesis: GAS CHROMATOGRAPHIC METHOD FOR DETERMINATION OF 28 VOLATILE ORGANIC COMPOUNDS EMITTED FROM A SEWERAGE PLANT

Yeming Sun, Master of Science, Environmental Science Department, 1991

Thesis directed by: Dr. Barbara B. Kebbekus Professor

In this study, 28 volatile organic compounds (VOCs) emitted from the Linden Roselle Sewerage Authority Plant (LRSA) were monitored. The determination by gas chromatography (GC) is presented. This work emphasizes the collection of whole air samples, using a canister-based sampling system with cryogenic concentration. An appropriate temperature program was selected to obtain the best sample separation. The procedure for the identification of 28 standard gas mixture was achieved by comparing the chromatograms of sample with those of the specific groups of target compounds, as well as by comparing the sample with the results from GC Mass spectrometric analysis. Because of the high humidity of the air samples collected above the surface of the water, the polar compounds tend to deposit on the wall of the canister, the transfer lines and the capillary column of GC. Both the canister cleaning method and the temperature program of GC were improved. A quality assurance protocol for the analytical system was set up and the minimum detection limits have also been determined.

2) GAS CHROMATOGRAPHIC METHOD FOR  
DETERMINATION OF 28 VOLATILE ORGANIC  
COMPOUNDS EMITTED FROM A SEWERAGE PLANT

by  
1) Yeming Sun

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

1991

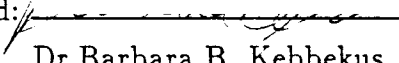
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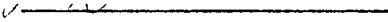
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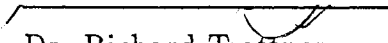
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**To My Grandparents**



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# Chapter 1

## Introduction

### 1.1 Sampling Collection Method

Volatile organic compounds (VOCs) are emitted into the atmosphere from a variety of sources. Many of these compounds have toxic or carcinogenic properties. Over the past two decades, increasing numbers of trace organic compounds have been identified in the atmosphere and water in order to determine their impact on human health. The work to be accomplished in this study is the determination of the fate of 28 VOC emissions at the Linden Roselle Sewerage Authority Plant (LRSA). The fraction of influent VOCs in LRSA actually destroyed in the treatment, and the final fate of those which are not, is being studied. An analytical methodology for the measurement of VOCs present in the air above each process of the plant is being developed. Both air and water samples are collected and analyzed in order to determine the particular changes in the influent composition which lead to odor episodes at the facilities. The canister-based sampling system is used for the analysis of the air samples. Since these air

samples typically occur in low concentration, the identification and the quantitation of the accurate trace levels of VOCs in ambient air requires complicated instrumentation.

The sampling techniques commonly used for air samples fall into following categories:

1. The first of technique combines the collection and concentration steps in the field by selectively trapping the organic compounds on a solid sorbent[1,2]. The analyte is recovered from the sorbent by extraction with solvents[3,4] or, more commonly for trace analysis, by desorption at elevated temperatures with a purge of inert gas[1,5,6]. Several sorbents have been used for this purpose.

Carbon adsorbents, which are less polar than inorganic adsorbents, are widely used and effectively remove organic compounds from the air[7]. There are three defects in this technique:

- (a) The strong adsorption on carbon adsorbents causes losses of VOCs such as benzene and toluene in thermal desorption recovery.
- (b) The dilution of the sample when solvents are used for desorption from charcoal results in a low sensitivity.
- (c) The extraction solvents, such as carbon disulfide, are extremely toxic and may present a potential health hazard.

Other sorbents are inorganic adsorbents which include silica gel, alumina, florisil and molecular sieves[8]. These compounds are more polar than the organic polymeric adsorbents and collect polar VOCs efficiently. The limitation is that rapid adsorption of water and deac-

tive the adsorbents.

Porous polymer adsorbents such as Tenax GC[9] have been successfully employed for sampling organic compounds from ambient air. The trapped organic compounds are heated and desorbed by connecting the collection tube to the analytical column in the inlet or the column oven of the gas chromatography. The advantages of this technique are that the entire concentrated air sample is allowed to go into the gas chromatograph. The limitations of this method are the inability to capture highly volatile materials[9], sample breakthrough and incomplete desorption.

2. The other approaches to collection of the whole sample are the use of flexible, inert bags[10,11,12], evacuated glass bulbs and electropolished stainless steel canisters[13,14]. These grab samples are either analyzed directly or are concentrated cryogenically before being injected into the gas chromatograph.

To avoid the cost, inconvenience and difficulty of field analysis, field samples are collected in stainless steel canisters and returned to a central laboratory for analysis. The interior surfaces of these stainless steel canisters are passivated using the Summa Passivation process[15], in which a pure chrome-nickel oxide layer is coated on the inner metal surface, increasing the stability and the storage interval of many organic compounds[15]. Various sample integrity studies of gas stored in Summa polished stainless steel canisters have been conducted in other laboratories. Harsch (1980) reported stability of

a number of halocarbons stored in canisters at parts per trillion by volume levels[16]. Westberg et al (1984) reported stability of parts per billion by volume levels of benzene and toluene in canisters, but observed losses of o-xylene[17]. The stainless steel canisters are not subject to sample permeation or photo-induced chemical effects. They can be reused after a simple clean-up procedure. The desorption efficiency of the target organic compounds is not a problem for canister collection. It is note that Tenax is particularly poor at trapping polar compounds, which we are studying in this project, but canister-based system is superior to Tenax at trapping most polar VOCs. Another advantage of Summa canister is that the analysis of canister sample can be repeated by using the remainder of the sample left in the canister. Thus, stainless steel canisters were chosen for use in this project. It has been demonstrated that the canister are less likely to bias the sample[18].

## 1.2 Preconcentration of the Collection

Since the target VOCs in ambient air occur in low concentration, it is necessary to concentrate the compounds prior to analysis. Several techniques have been well established which include cyogenic trapping, liquid impingers and pre-concentration on solid adsorbents[19,20].

Cryogenic trapping is a more attractive alternative than adsorption and impinger collection. It is particularly suitable for analysis of highly volatile compounds.



The advantages of this technique are:

- (a) A wide range of organic materials can be collected.
- (b) Contamination problems with adsorbents and other collection media are avoided.
- (c) Consistent recoveries are generally obtained.

N-propanol cooled by liquid nitrogen into a slush at a temperature about  $-110^{\circ}\text{C}$  was used for the cryogenic trap. The advantage of using this trap instead of liquid argon is that the  $-110^{\circ}\text{C}$  trap allows carbon dioxide and C1 to C3 hydrocarbons to pass through while capturing most of the organic vapors of interest from ambient air. This method gives the highest separation efficiency[21].

### **1.3 Procedure for Target VOCs**

Waste water is treated by Linden Sewerage Authority Plant every day. The sources are mainly municipal waste water and from local chemical companies. There are many kinds of volatile organic compounds contained in the waste water. Most of them were previously evaluated for animal and human carcinogenicity [25], and some are classified as hazardous substances, or hazardous waste materials (Table 1.1). In order to determine the particular changes in the influent composition which lead to odor episodes at the facility and to determine the ultimate fate of the VOCs, the project consists of sampling and analysis of both air and water samples taken from different sites in LRSA as well as theoretical calculations and the integration of the calculation

with the experimental data. The work that has been accomplished in this paper includes the collection of the whole air samples by using canister-based sampling system with cryogenic concentration. A temperature program was optimised to obtain the best sample separation. The identification of 28 target VOCs (Table 1.2) was achieved by comparing the chromatograms with different specific groups of volatile organic compounds. The identification of VOCs by GC-Mass Spectrometry was also a useful and reliable method. Because of the high humidity of the air samples collected above the surface of the water, the polar compounds are likely to deposit on the inner wall of the canister, the transfer lines of the analytical system and the capillary gas chromatography column. Both the canister cleaning method and the temperature program of the GC have been improved. The quality assurance protocol of the analytical system and the minimum detection limits have also been studied.

Table 1.1: Toxicity Data for the 28 Target Volatile Organic Compounds

No	Compound Name	Carcinogen (EPA)	Hazardous Substance (EPA)	Hazardous waste (EPA)	Priority Toxics (EPA)
1	MeOH	-	-	-	-
2	EtOH	-	-	-	-
3	ACN	-	-	+	-
4	Ace	-	-	+	-
5	IPA	-	-	-	-
6	Ether	-	-	-	-
7	MeCl <sub>2</sub>	+	-	+	+
8	CS <sub>2</sub>	-	+	+	-
9	Clform	+/animal	+	+	+
10	EtAcet	-	-	+	-
11	EtCl <sub>2</sub>	+	+	+	+
12	111-TCE	-	-	+	+
13	n-ButOH	-	-	+	-
14	Bz	+	+	+	+
15	CCl <sub>4</sub>	+/animal	+	+	+
16	Tric	+/animal	+	+	+
17	MIBK	-	-	+	-
18	Pyr	-	-	+	-
19	Tol	-	+	+	+
20	ClBz	-	+	+	+
21	EtBz	-	+	-	+
22	m-X	-	+	+	-
23	p-X	-	+	+	-
24	o-X	-	+	+	-
25	1,2-DiClBz	-	+	+	+
26	DMF	-	-	+	-
27	ELG	-	-	-	-
28	MEK	-	-	-	-

Table 1.2: List of 28 Target Volatile Organic Compounds

No	Compound Name	Abbre. Name	Conc (ppm)	MW	BP (C)
1	Methanol	MeOH	0.96	32.04	64.96
2	Ethanol	EtOH	0.67	46.07	78.50
3	Acetonitrile	ACN	0.75	41.05	81.60
4	Acetone	Ace	0.52	58.03	56.20
5	Isopropanol	IPA	0.51	60.11	82.40
6	Diethyl Ether	Ether	0.37	74.12	34.51
7	Methylene Chloride	MeCl <sub>2</sub>	0.62	84.00	40.10
8	Carbon Disulfide	CS <sub>2</sub>	0.67	76.14	46.30
9	Chloroform	CLform	0.79	119.50	61.20
10	Ethyl Acetate	EtAcet	0.29	88.11	77.10
11	1,2-Dichloroethane	EtCl <sub>2</sub>	0.47	99.00	83.50
12	1,1,1-Trichloroethane	111-TCE	0.39	133.40	74.10
13	n-Butanol	ButOH	0.43	74.12	117.25
14	Benzene	Bz	0.44	78.10	80.10
15	Carbon Tetrachloride	CCl <sub>4</sub>	0.41	153.80	76.70
16	Trichloroethylene	Tric	0.38	131.40	86.70
17	Methyl Isobutyl Ketone	MIBK	0.31	100.16	116.85
18	Pyridine	Pyr	0.48	79.10	115.20
19	Toluene	tol	0.37	92.00	110.70
20	Chlorobenzene	ClBz	0.38	112.56	132.00
21	Ethyl Benzene	EtBz	0.32	106.17	136.20
22	m-Xylene	m-X	0.32	106.17	139.10
23	p-Xylene	p-X	0.32	106.17	144.40
24	o-xylene	o-X	0.32	106.17	138.35
25	1,2-Dichlorobenzene	1,2-DiClBz	0.29	147.01	180.50
26	Diethyl Formamide	DMF	0.51	73.10	153.00
27	Ethylene Glycol	EG	0.69	62.07	198.00
28	Methyl Ethyl Ketone	MEK	0.43	87.12	152.00

## Chapter 2

# Experimental Methods

### 2.1 Method Descriptions

#### 1. Sample Collection

In this project, cleaned and evacuated 6 liter Summa polished stainless steel canisters, supplied by Scientific Instrumentation Specialists, Moscow, Idaho, were used for air sample collection. Five sampling points were selected in the sewerage plant (Figure 2.1):

(a) Two canister samples in the screen house: one connected with an 1/4" ID and 1.5m long inlet tube was lowered down into the inflow pit. The sample was taken by opening the valve of the evacuated canister and allowing it to fill under the atmospheric pressure differential over a span of 5-10 minutes, then closing the valve. The final pressure of the canister was about 0.9 atm. In order to determine the total outflow of vapors from this area, another canister sample, without the inlet tube, was collected in the center of the room. The method was as same as the above one. Airflow measurements were also made each time at the entrances of the air ducts ventilating the room.

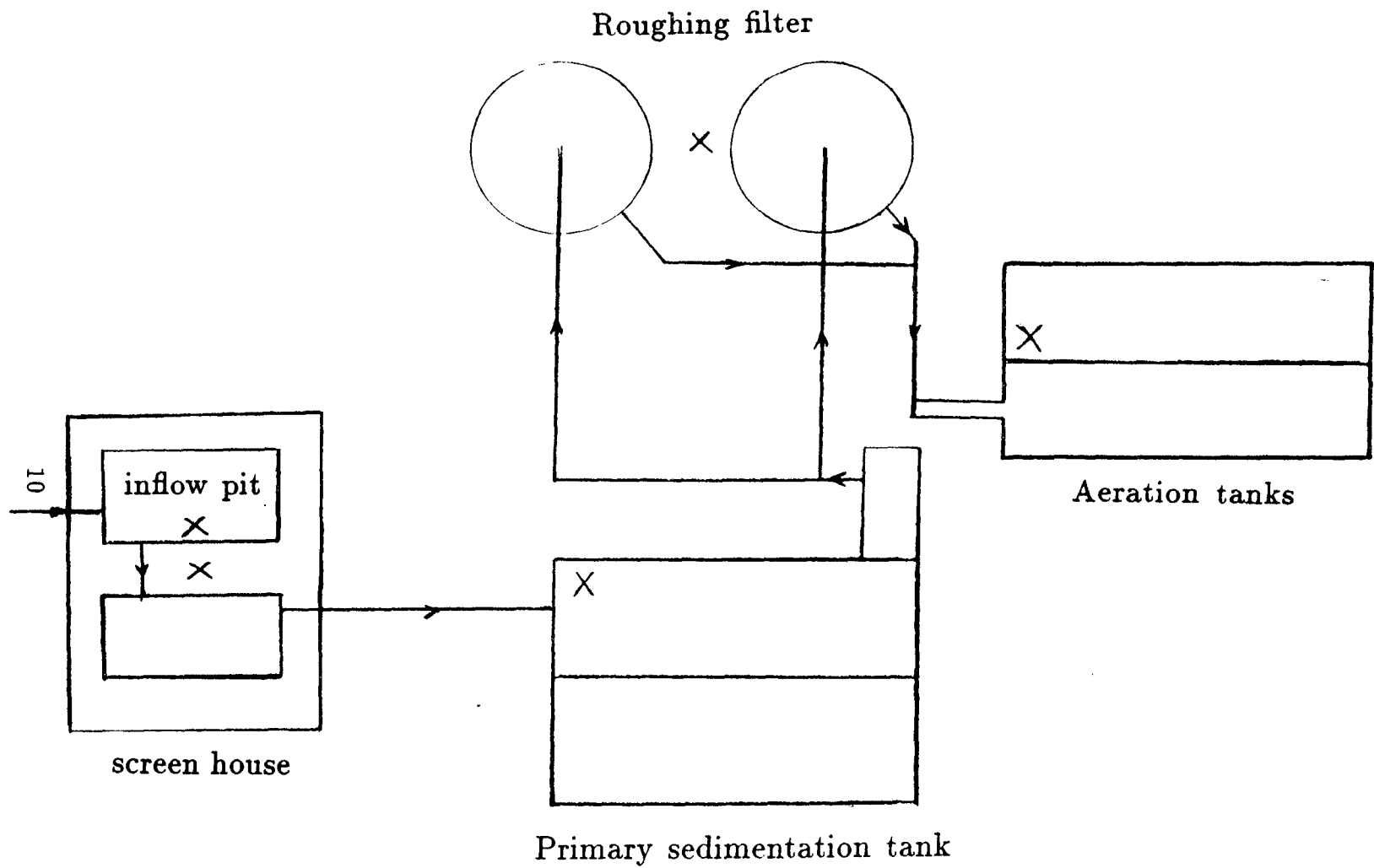


Figure 2.1 Air Sampling Points in Linden Roselle Authority Sewerage Plant

(b) Primary sedimentation tank: to collect an air sample which is in close contact with water surface, with as little influence of the prevailing breeze as possible, a draft-shield sampler was constructed (Figure 2.2). It consists of a large steel cylinder with open ends. The internal volume is about 10 liters. The cylinder is supported by a harness and pole, so that it can be lowered onto the surface of the water. The stainless inlet tube which is connected to the evacuated canister is situated near the center of the cylinder. Samples were collected in a period of 5 to 10 minutes.

(c) Roughing filter: since this point is the one at which there is the greatest interchange of volatile material between the air and water, it is the most important point for sampling. A canister without the inlet tube is placed between the centers of the two tricking filters at a level with the top of the filters. The collection method was the same as (a). Both wind speed and direction were measured during the sample collection time.

(d) Aeration tanks: the sampling showed that some substantial amount of the target volatile organic compounds remained in the water at this point. The same sampler used in (b) was employed. Since the pool is subject to air bubbling through it, a longer collection time was used to avoid biasing the sample. A system which may have random variation in concentration at the surface over a short time period requires that sampling be integrated over a sufficient amount of time to allow these short-term variations to be averaged.

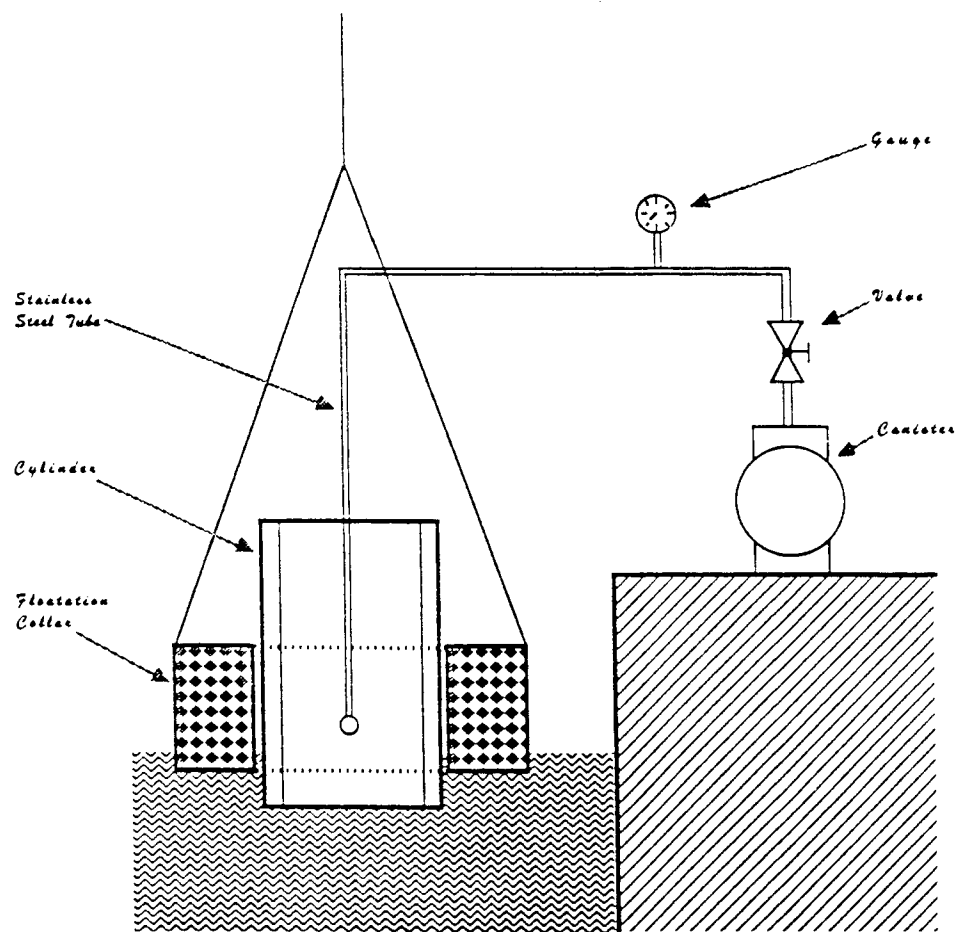


Figure 2.2 The Draft-shield Sampler



## 2. Analytical Apparatus

A Varian 3700 GC was used for sample analysis (Figure 2.3). The liquid injection system was replaced by a gas sampling and cryogenic focusing manifold which consists of a gas sampling valve A (Figure 2.3), having a 2ml volume sample loop. The gas sampling valve A is held at 120°C and all the exposed lines, through which the sample or standard gas mixture pass are heated with flexible tape to 60°C. Valve B is connected to a glass bead filled cryogenic trap made from 1/8" stainless steel tubing, 15cm in length. A second cold trap is made of the first coil of the capillary column immersed in liquid nitrogen, for sample focusing before final injection. A 1.2 liter ballast cylinder with a high precision pressure gauge is used to measure the sample volume. A vacuum line connected to a vacuum pump evacuates the sample, loop and cryogenic trap prior to filling to a measured pressure with sample. In order to achieve the highest possible resolution, a capillary column is used, which is a 50 meter crosslinked methyl silicone capillary column, 0.2mmID, bonded film thickness of 0.5 $\mu$ m, supplied by Hewlett Packard. Samples were run with helium carrier gas at a flow rate of 2.0ml/min..

The gas chromatography operation conditions were:

\* H<sub>2</sub>: 30ml/min. .... FID

\* He: 2ml/min. .... Column



\* N<sub>2</sub>: 28ml/min. .... Make up of the capillary column effluent

\* N<sub>2</sub>: 27ml/min. .... Make up of the splitter ECD effluent

\* Air: 300ml/min. .... FID

The gas chromatograph is run in an effluent split mode between an Electron Capture Detector (ECD) and a Flame Ionization Detector (FID). The standard ID of splitter channels is about 0.012". The split ratio is varied by inserting wires of various diameters into one channel. A 0.00815" ID stainless steel wire, supplied by Hamilton Co., is inserted in the ECD channel, which gives an effluent split ratio of 10:1[20]. FID receives 90% of the total column flow and ECD receives 10% of the flow. Thus, the 2ml/min capillary effluent, plus 28ml/min nitrogen make-up gas which is used for preventing peak broadening in both detectors, is split between the FID and ECD. The 3ml/min effluent from the splitter, plus 27ml/min nitrogen make-up gas, goes to the ECD detector. The signal from the ECD is very useful in identifying the peaks, since it shows only the halogenated compounds. Both ECD and FID detector signals are integrated and the sample concentrations are calculated by Chromatochart-PC, an integration system supplied by Interactive Microware Inc.

The optimized temperature program for analysis of 28 VOCs:

\* Temperature program

Initial T= 30°C, hold 8 min.

Rises at a rate of 6°C/min.

Final T= 210°C, hold 15 min.

### 3. Sample Analysis Operation Procedures

(a) Because of the relatively high concentration of the sample, it is necessary to close the valve of the 1.2 liter ballast cylinder to minimize the volume of sample. The volume of the reduced sample measurement system is 130ml.

(b) Turn valve A and B to the solid line position (left). Helium gas is allowed to flow into the column at 2ml/min. (This helium is kept passing through the column to protect it).

(c) The canister with air sample is heated to about 40°C, and the sample injection tubing is heated to 100°C. The tubing is flushed by 130ml of air sample and then evacuated by opening V4.

(d) Adjust the cryogenic trap between  $-110^{\circ}\text{C}$  to  $-120^{\circ}\text{C}$  by adding liquid nitrogen to n-propanol contained in a small Dewar flask and measuring temperature with thermocouple. Place the Dewar flask over the glass bead filled tubing and hold for about 8 minutes to cool it down between  $-110^{\circ}\text{C}$  to  $-120^{\circ}\text{C}$ . At this temperature, the target compounds are condensed while a large fraction of the carbon dioxide is not.

(e) Open the canister valve and V5 to let the sample pass through the first cryo-trap and into 130ml volume. Read the pressure P from pressure gauge. The volume of air sample injected is calculated by

the equation:

$$V_o = \frac{\Delta P V_r}{P_o} \quad (2.1)$$

Where:

$V_o$  = Volume of sample in normal pressure

$P_o$  = Normal pressure, 1atm=14.7psig

$\Delta P$  = Pressure change read from pressure gauge

$V_r$  = Volume of 0.13 liter

(f) Close V5 after injecting the desired volume. Place the focusing cold trap into liquid nitrogen, forming cryogenic trap 2, and replace the first cyogenic trap with a hot water bath, temperature around 90°C, allowing the condensed volatile compounds to vaporize. Switch valve B to dotted line position (right), and allow the carrier gas to transfer the sample to the focusing trap 2 which is cooled to -196°C by liquid nitrogen. Eight to ten minutes are required for the complete transfer.

(g) After the sample is transferred into focusing trap, the cryogenic trap 2 is replaced by a 95°C hot water bath for 8 minutes.

(h) The hot water is removed and GC oven temperature program is started. The program begins at 30°C, holds for 8 minutes, then rises at a rate of 6°C/min. to a final temperature of 210°C. Figure 2.4 shows the typical chromatogram of volatile organic compounds in ambient air from FID and ECD detectors respectively.

(i) To reduce variability, three replicate sequential analyses were made on each sample and averaged. Figure 2.4 shown a typical sample

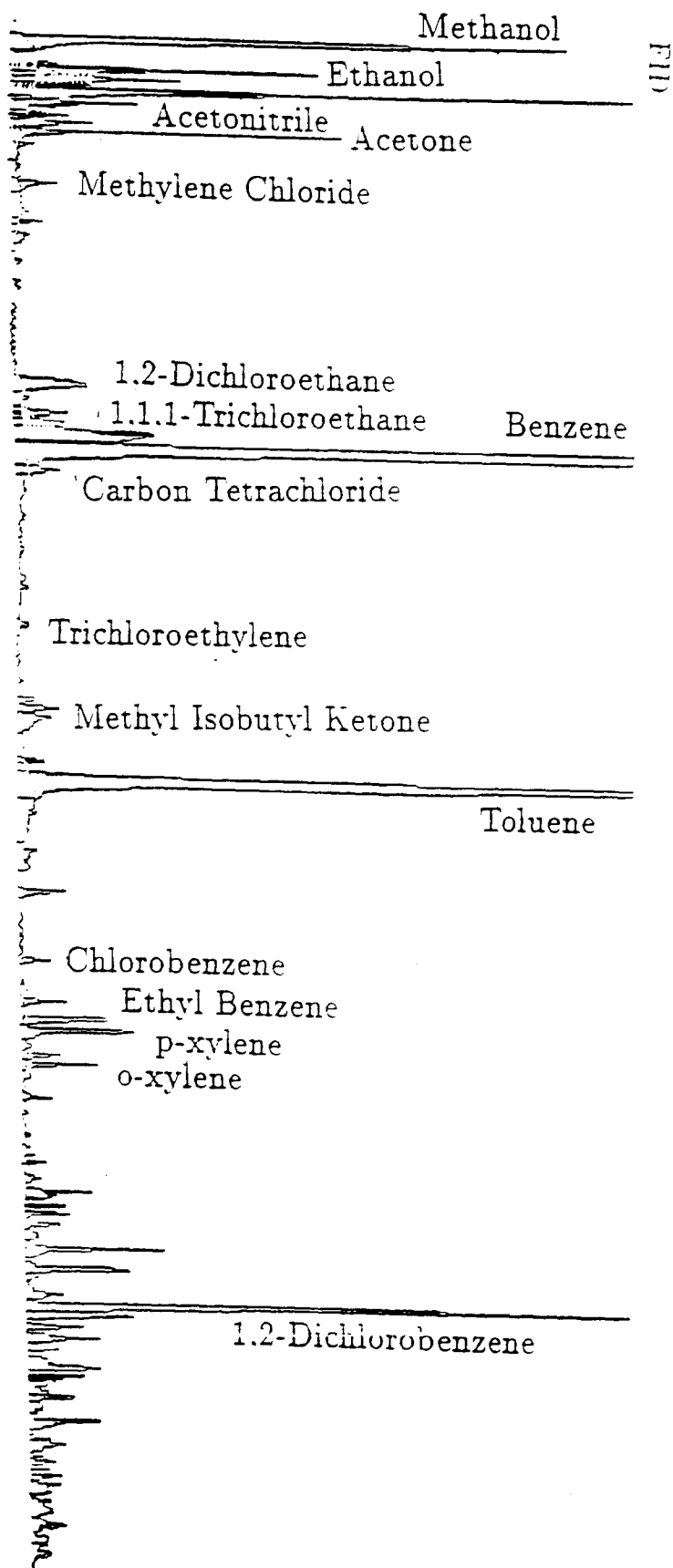


Figure 2.4 Chromatogram of Typical Sample

chromatograph.

(j) After all analyses have been performed, the canister was flushed, re-evacuated, and was ready for additional samples.

#### 4. Calibration Method

The standard gas was prepared from a mixture of 28 VOCs chosen to be representative of the possible contaminants in a field (Listed in Table 1.1). The compounds were injected into an evacuated and cleaned 12 liter stainless steel canister and pressurized with zero grade helium. The compounds were quantitated in the mixture by gas chromatograph (Figure 2.5), comparing them to a purchased standard gravimetrically prepared and analyzed by Alphagaz (Table 2.1 and Figure 2.6), Morrisville, PA. Calibration is carried out in the following steps:

1) The operating procedure for the Alphagaz standard:

(a) With the same GC operating conditions, the canister is replaced by a cylinder of compressed nitrogen. The standard gas cylinder is connected with the inlet of the sampling valve A.

(b) After the loop is flushed, the standard gas mixture is passed through a 2ml volume loop at 1atm, 165°C.

(c) Then the gas sample valve A is switched to the dotted line position (left).

(d) V5 is opened, allowing nitrogen to pass through the 2ml loop, carrying the standard gas through the glass bead filled trap to the 1.2 liter cylinder.

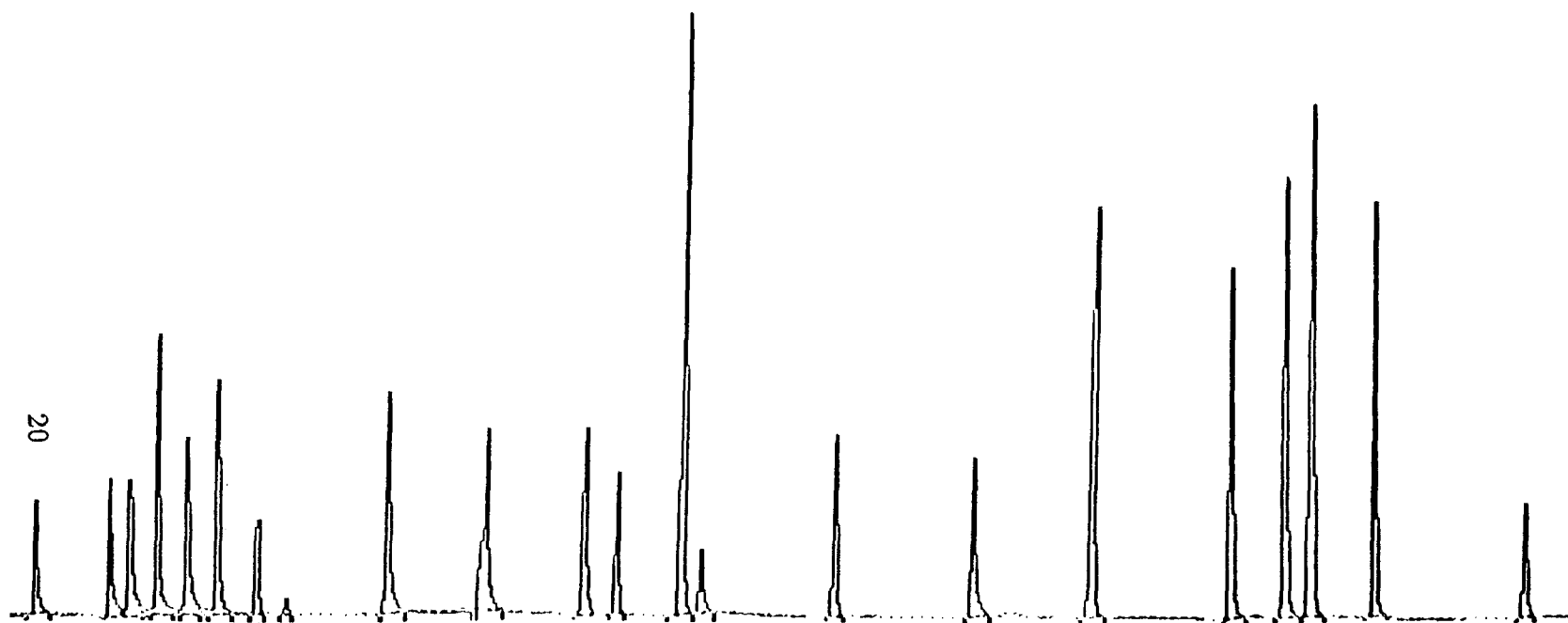


Figure 2.5 Chromatogram of Standard Gas Mixture (in-lab)



Table 2.1 Composition of Alphagaz Standard Gas

<u>COMPONENT</u>	<u>CONCENTRATION</u>
1,2-Dichlorobenzene	2.0 ppm
N,N-Dimethylformamide	4.7 ppm
n-Butanol	5.0 ppm
Methyl isobutyl ketone	4.9 ppm
p-Xylene	2.1 ppm
Ethylbenzene	1.9 ppm
Chlorobenzene	2.0 ppm
2-Methoxyethanol	5.1 ppm
Toluene	2.0 ppm
Isopropanol	4.9 ppm
Ethanol	4.8 ppm
Trichloroethylene	2.0 ppm
1,2-Dichloroethane	2.2 ppm
Benzene	2.0 ppm
Acetonitrile	4.8 ppm
Ethyl acetate	5.0 ppm
Methyl ethyl ketone	4.9 ppm
Carbon tetrachloride	2.0 ppm
Methanol	4.9 ppm
1,1,1-Trichloroethane	2.0 ppm
Chloroform	2.0 ppm
Acetone	4.9 ppm
1,1-Dichloroethane	1.9 ppm
Methylene chloride	1.9 ppm
Diethyl ether	4.9 ppm
Nitrogen	Balance

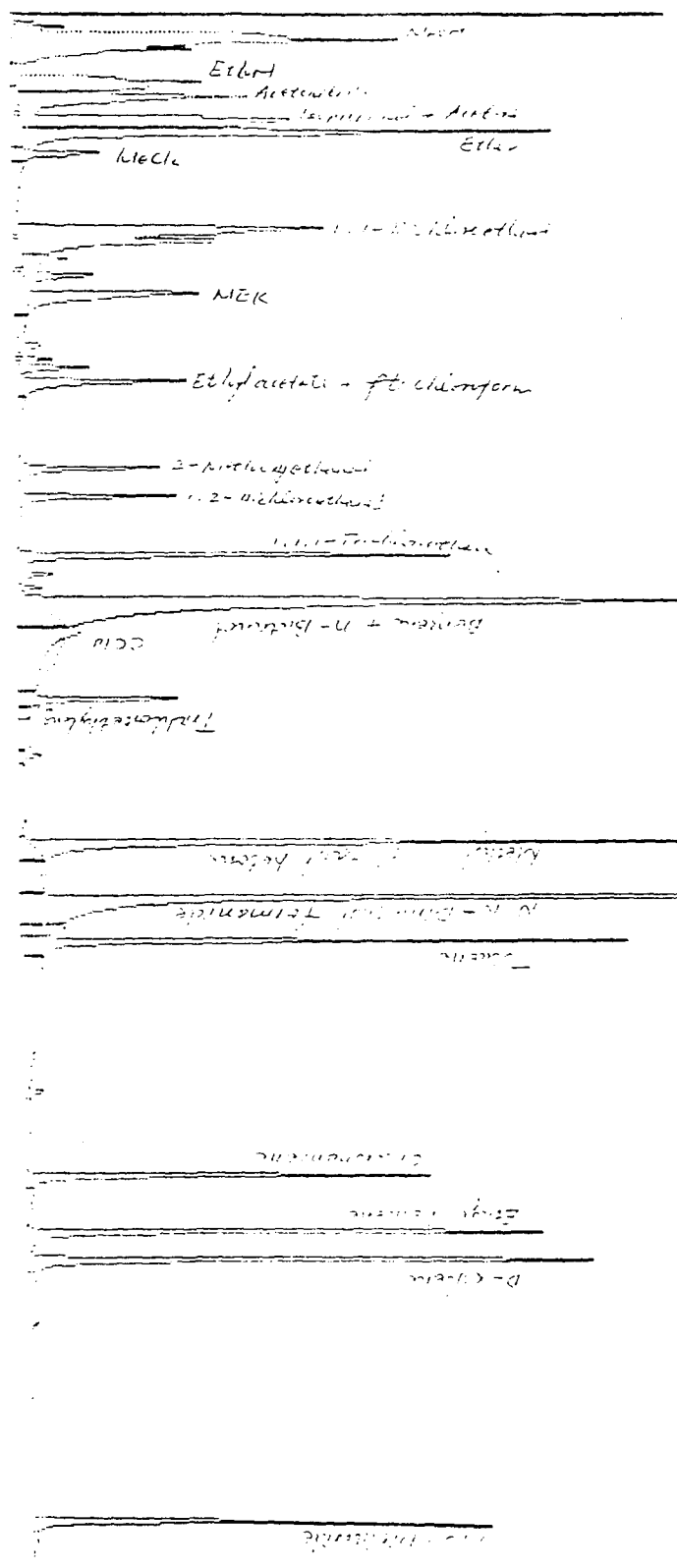


Figure 2.6 Chromatogram of Purchased Standard Gas Mixture

(e) The VOCs in standard are condensed in the cooled trap and transferred to the column in the same manner as the sample. Figure 2.5 and Figure 2.6 shows the standard gas chromatograms derived from FID.

(f) The calculation of sample concentration from peak area and standard concentration is derived as follows:

Volume of standard gas loop is 2ml, temperature is 165°C (438°K), pressure is 1atm.

$$V_{std} = \frac{2ml \times 273^{\circ}K}{438^{\circ}K} = 1.25ml \quad (2.2)$$

Where:

$V_{std}$  = Total volume of standard gas injected  
at 273°K, 1atm.

$$C_{i,sam} = \frac{A_{i,sam} V_{std} C_{std}}{A_{i,std} V_{sam}} \quad (2.3)$$

Where:

$C_{i,std}$  = Concentration of compound i in standard

$C_{i,sam}$  = Concentration of compound i in sample

$A_{i,std}$  = Peak area of compound i in standard

$A_{i,sam}$  = Peak area of compound i in sample

$V_{std}$  = Total volume of standard gas injected

$V_{sam}$  = Total volume of sample air injected

## 2) Procedure for use of in-laboratory standard mixture

The in-laboratory standard mixture was injected into cryogenic trap 1 using the same procedure as is used for sample analysis. Calculation of sample concentration from peak area and standard concentration is derived as following:

$$C_{i,std} = \frac{A_{i,samp}P_{std}C_{i,std}}{A_{i,std}P_{samp}} \quad (2.4)$$

Where:

$C_{i,std}$ = Concentration of compound i in standard

$C_{i,sam}$ = Concentration of compound i in sample

$A_{i,std}$ = Peak area of compound i in standard

$A_{i,sam}$ = Peak area of compound i in sample

$P_{std}$ = The pressure of standard gas read from the gauge

$P_{sam}$ = The pressure of sample read from the gauge

3)The comparison of the Alphagaz standard with the in-laboratory standard mixture results are discussed in Chapter 3.

## 2.2 Canister Cleaning Procedure

1. Connect canister to the vacuum manifold as shown in Figure 2.7.
2. Heat canister to about 40°C, open the vacuum shut-off valve V3 and evacuate to -30mmHg for 5 min.
3. Close the vacuum shut-off valve V3, open zero air supply valve V1 to pressurize canister with zero grade air to about 30 psig.

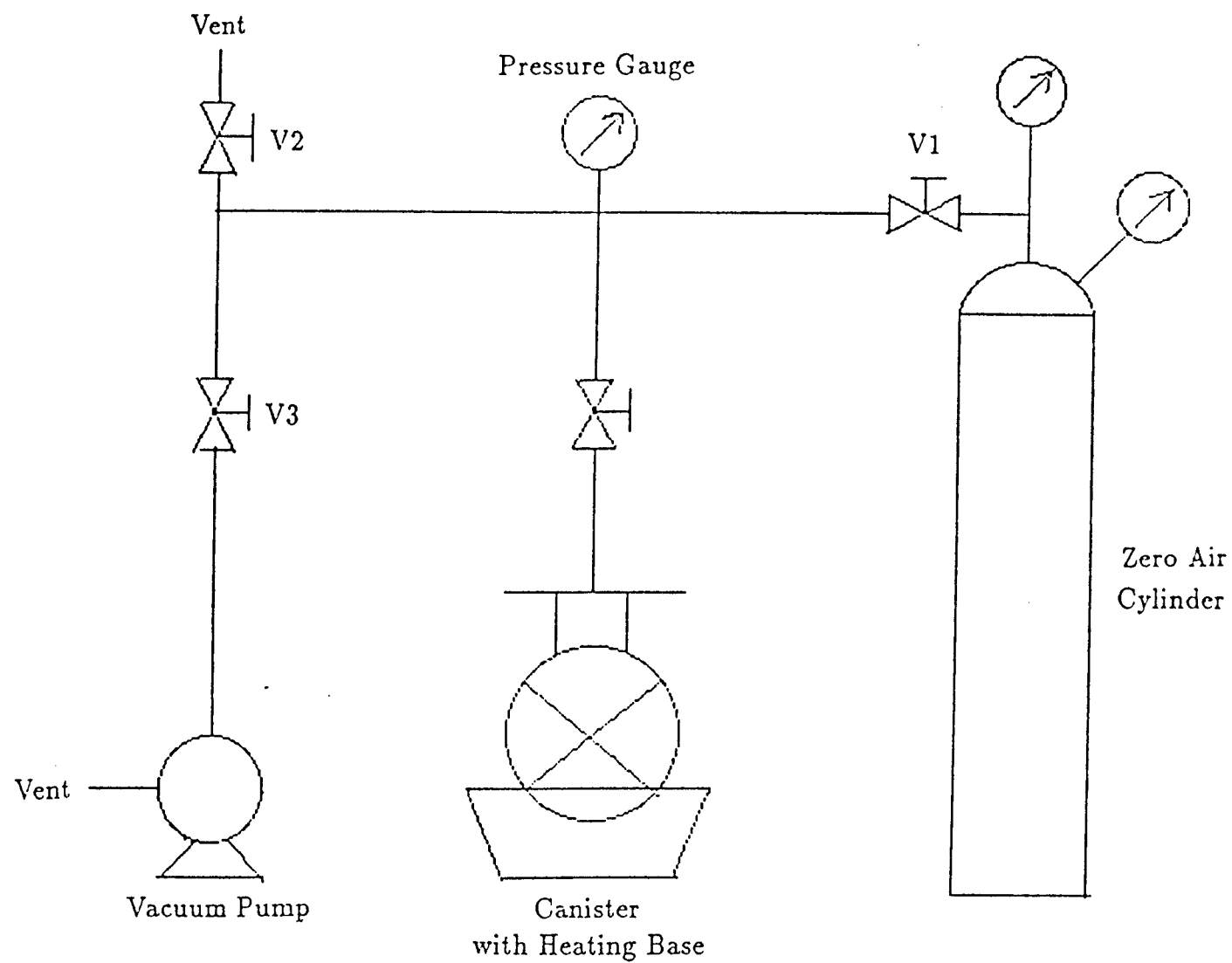


Figure 2.7: Canister Cleaning System

4. Close zero air valve V1, open the vent valve V2 to allow the air to vent out until the pressure is a little higher than atmospheric pressure to prevent the contamination by leaks. Then close V2.
5. Repeat step (b) to (d) several times until the blank analysis is satisfactory as indicated below (Figure 2.8).
6. Blank test: fill the canister with zero grade air to about 25psig and analyze the contents by the same procedure as was used for the samples. The result should be compared with the direct analysis of zero air, and show no significant difference.

## **2.3 Method of Identifying 28 VOCs**

In order to assure the accuracy of analyzing target VOCs, one of the most important procedures is the determination of the retention time for each component in the standard mixtures. The approaches to the identification of the VOCs have been done by the following method:

1. The comparison of standard compounds with subgroups of target compounds:
  - (a) The target 28 VOCs were divided into 7 groups according to their boiling points, polarities, and their molecular weights (See Table 2.2).

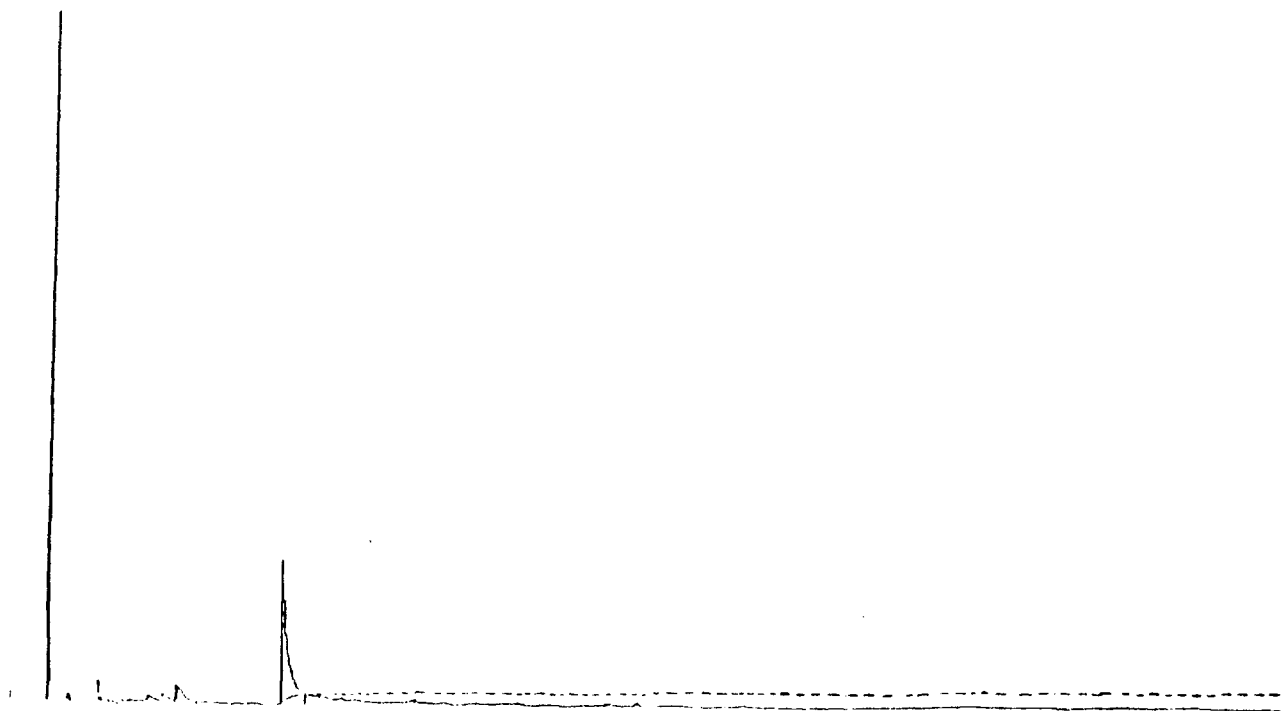


Figure 2.8 Chromatogram of Canister Blank Testing

**Table 2.2 The specific Subroups of Target VOCs**

Group 1	Group 2
Methanol	Diethyl Ether
Ethanol	Acetone
Isopropanol	Ethyl Acetate
n-Butanol	Acetonitrile
Ethylene Glycol	Pyridine
Group 3	Group 4
Methyl Isobutyl Ketone	Methylene Chloride
Methyl Ethyl Ketone	1,2-Dichloroethane
Dimethyl Formamide	Chlorobenzene
	1,2-Dichlorobenzene
Group 5	Group 6
Carbon Disulfide	o-xylene
Carbon Tetrachloride	m-xylene
Benzene	Ethyl Benzene
p-xylene	Toluene
Group 7	
Chloroform	
Trichloroethylene	
1,1,1-Trichloroethane	



- (b) The compounds of each group were mixed and the mixture of compounds was injected into a cleaned evacuated canister.
- (c) Each group of compounds was analyzed by gas chromatograph. The method is the same as the sample analysis.
- (d) The chromatogram of the standard gas mixture was compared with each group of specific compounds, matching retention times.

## 2. Comparing gas chromatography with GC/MS:

One of the advantages of GC/MS is its capability of accurate identification of compounds. During this project, the GC/MS was used for identifying components in air samples. The result was compared with the gas chromatograms of the air samples (Figure 2.9; Figure 2.10).

## 2.4 Detection Limit for Stainless Steel Canister Method

Questions relating to levels of detection are central in environmental assessments and investigations. It is important for the user of the data to have complete and accurate information regarding the quality of the measurement data obtained. The objectives of field studies require that the measurement methods be capable of detecting very low concentrations of volatile organic chemicals (e.g., ppb). It is essential that the methods used not

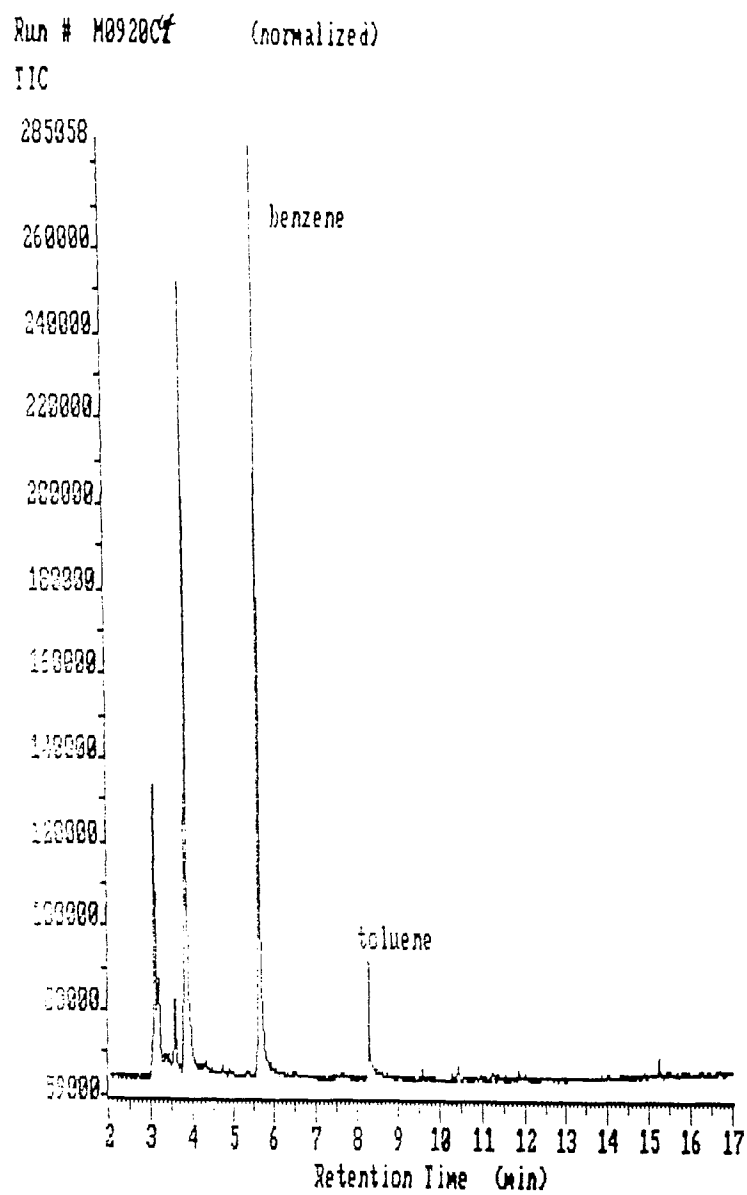


Figure 2.9 Sample 1 GC/MS Chromatogram

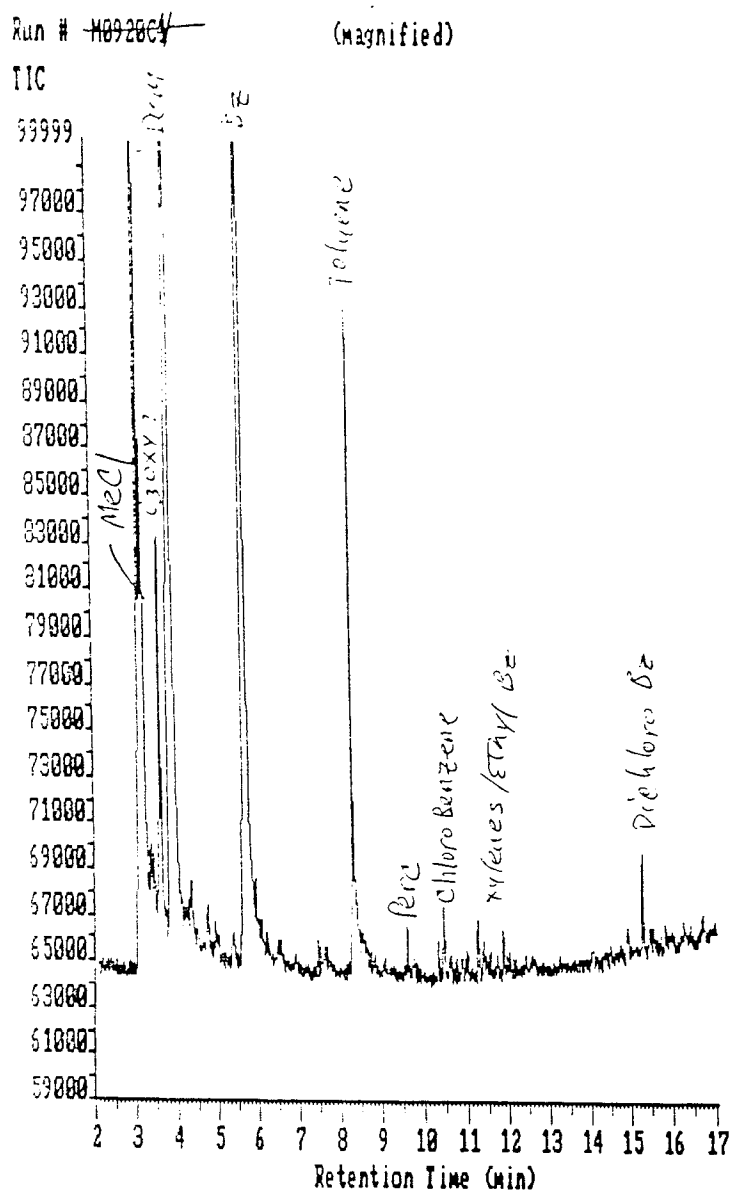


Figure 2.10 Sample 2 GC/MS Chromatogram

give false indications of their absence. The analytical methodology used in this work is outlined in EPA Compendium Method TO14.[24]

(a) A standard mixture of 28 VOCs with normal concentrations from 0.29ppm to 0.94ppm is used in various stages of this study.

(b) The standard mixture is diluted in a 12 liter Summa canister by zero grade air. The theoretical concentration of each analyte is in the range of 1.0 to 3.2ppb with the exception of the polar compounds that are on the order of 10 to 32ppb.

(c) Analyze the diluted standard mixture by GC. The operating procedure is as same as that used for as samples. The 1.2 liter ballast volume is used in the procedure. The injection volume of the standard gas mixture is 35ml. Under this volume, the operating procedure is repeated 7 times.

(d) Calculate the minimum detection limit by following formula:

$$DL = \frac{50 \times C}{A} \quad (2.5)$$

Where:

$C$ = The concentration of each VOC.

$A$ = The integrated area of each VOC.

50= The minimum integration peak area.

(f) Inject 70ml and 140ml of the diluted standard gas respectively. The operating procedures are as same as (c). For each inject

volume, each procedure should be repeated more than 3 times.

(g) Another 28 component VOC standard gas mixture was prepared with concentration near the limit of detection. This standard gas mixture was run at the maximum injection volume, 140ml. The method was repeated 3 times. The standard deviation of the results was calculated.

## Chapter 3

# Results and Discussion

### 3.1 Quality Assurance for the Analytical Method

All the gases used in analytical process described in Chapter 2 are zero grade, supplied by Liquid Carbonic Specialty Gas Corporation.

#### 1 Analytical Reproducibility Testing of Field Samples

To study the analytical reproducibility of the system, air samples in canisters were collected from Linden Roselle Sewerage Authority plant, New Jersey, from August 22 to November 1, 1990 and analyzed by the method described above. Each sample was analyzed at least three times. The mean value, standard deviation and the relative standard deviation were calculated by the following formula:

$$c = \frac{\sum C_i}{n} \quad (3.1)$$

Where:

$c$  = Volume of sample at normal pressure

$\sum C_i$  = Normal pressure, 1atm=14.7psig

$n$  = Pressure change read from pressure gauge

$$SD = \sqrt{\frac{\sum C_i^2 - \frac{1}{n} \sum C_i^2}{n - 1}} \quad (3.2)$$

$$RSD = \frac{SD}{C} \times 100 \quad (3.3)$$

One set of data for air samples taken from screen house influent is presented in Table 3.1.

Since different kinds of chemical compounds come into the influent of waste water, the components and the concentration of air samples varies on each day. The concentrations of each targeted VOC in air samples range from 0.01ppm to 19ppm. Non-polar compounds show a better reproducibility (relative standard deviation less than 35%) than that of polar compounds (relative standard deviation less than 50%), for polar compounds have a tendency to deposit on the inner wall of canister, transfer lines and capillary column which may effect on the reproducibility. Another possibility is that more polar chemicals are adsorbed by water under high relative humidity which may reduce the polar compound concentration level. Water may also cause the glass bead filled trap to be plugged by ice, which could reduce the injection volume of the sample.

Although benzene and carbon tetrachloride are non-polar compounds, it is shown that both compounds have fairly high relative standard deviation (relative standard deviation of benzene less than 35%; carbon tetrachloride less than 65%). This may be caused by

Table 3.1 The Reproducibility Data For Air Samples

No	Compound Name	Sample Number					
		1		2		3	
		Conc.	RSD%	Conc	RSD%	Conc.	RSD%
1	MeOH	0.2496	48.0	2.8911	48.0	2.6300	43.0
2	EtOH	0.0172	10.0	1.2123	23.0	-	-
3	ACN	0.0110	16.0	0.1444	15.0	0.7100	18.0
4	Ace	0.0582	44.0	8.3914	43.0	4.0900	39.0
5	IPA	-	-	-	-	-	-
6	Ether	-	-	-	-	7.2200	43.0
7	MeCl <sub>2</sub>	-	-	-	-	-	-
8	CS <sub>2</sub>	-	-	-	-	-	-
9	Clform	-	-	-	-	-	-
10	EtAcet	-	-	-	-	-	-
11	EtCl <sub>2</sub>	-	-	0.2300	56.0	-	-
12	111-TCE	-	-	-	-	-	-
13	n-ButOH	-	-	-	-	-	-
14	Bz	1.2500	32.0	18.700	30.0	18.410	31.0
15	CCl <sub>4</sub>	0.0100	100	0.0800	61.0	0.2300	61.0
16	Tric	-	-	0.1600	44.0	-	-
17	MIBK	0.0100	16.0	-	-	-	-
18	Pyr	-	-	-	-	-	-
19	Tol	1.0300	20.0	3.8900	23.0	0.4100	20.0
20	ClBz	-	-	0.1800	22.0	0.5500	16.0
21	EtBz	0.0100	3.0	0.0300	33.0	0.0600	17.0
22	m-X	-	-	-	-	-	-
23	p-X	0.0100	1.0	0.1100	18.0	0.2000	5.0
24	o-X	-	-	0.0700	14.0	0.130	8.0
25	1,2-DiClBz	0.0900	7.7	0.3800	8.0	0.5700	7.8
26	DMF	-	-	-	-	-	-
27	ELG	-	-	-	-	-	-
28	MEK	-	-	-	-	-	-



Table 3.1 The Reproducibility Data For Air Samples(continued)

No	Compound Name	Sample Number					
		4		5		6	
		Conc.	RSD%	Conc	RSD%	Conc.	RSD%
1	MeOH	0.6700	43.0	0.6387	3.0	1.1345	3.4
2	EtOH	-	-	-	-	0.6994	6.7
3	ACN	0.9200	12.0	0.0948	6.0	0.8925	6.4
4	Ace	1.8100	39.0	0.3859	3.0	0.3332	2.4
5	IPA	-	-	-	-	-	-
6	Ether	17.08	44.0	-	-	-	-
7	MeCl2	-	-	3.5013	4.0	8.4419	4.4
8	CS2	-	-	0.1633	7.0	0.0572	8.0
9	Clform	-	-	-	-	-	-
10	EtAcet	-	-	-	-	-	-
11	EtCl2	-	-	-	-	-	-
12	111-TCE	-	-	-	-	-	-
13	n-ButOH	-	-	-	-	-	-
14	Bz	17.650	31.0	2.0956	0.4	2.7877	3.0
15	CCl4	0.0800	63.0	1.0208	5.0	-	-
16	Tric	-	-	-	-	0.0352	7.0
17	MIBK	-	-	-	-	-	-
18	Pyr	-	-	-	-	-	-
19	Tol	0.5400	22.0	0.2410	2.0	4.8649	3.0
20	ClBz	9.1700	13.0	4.8014	2.0	0.5657	2.0
21	EtBz	0.1300	15.0	0.1344	6.0	0.0233	9.0
22	m-X	-	-	-	-	-	-
23	p-X	0.1600	6.0	0.1076	4.0	0.0277	5.0
24	o-X	0.1300	0.0	0.0499	8.0	0.0384	5.0
25	1,2-DiClBz	1.5500	7.8	0.3418	5.0	0.1971	20.0
26	DMF	-	-	-	-	-	-
27	ELG	-	-	-	-	-	-
28	MEK	-	-	-	-	-	-

n-butanol. N-butanol is not be separated from benzene and carbon tetrachloride under the current temperature program, using the non-polar capillary column. Since n-butanol is a polar compound, it is not well retained by the non-polar capillary column even though it has higher boiling point (BP 117°C) than that of benzene (BP 80°C) and of carbon tetrachloride (BP 74°C), however, n-butanol has as same molecular weight as benzene.

## 2 The Reproducibility of In-lab Standard Gas Mixture

The reproducibility data of the standard mixture is shown in Table 3.3. The relative standard deviation of most compounds is less than 20%. It is shown that the standard gas mixture has a better reproducibility than that of field samples, since the field samples have high relative humidity. This may have some effect on both peak sharpness and area as mentioned before. Also, field samples contain many more compounds, which can cause some interferences.

Polar compounds also have a higher relative standard deviation (RSD less than 45%) even in the dry standard because they are easier to deposit on the walls of GC sampling system.

## 3 Canister Blank Testing

Canister blanks can be analyzed by VOC analytical methods after cleaning the canisters. The individual compounds present in the blank can be identified by comparison with the chromatogram of the standard. Table 3.4 shows the results of blank test on three canisters. The peaks are not the target VOC and the average blank peak area

Table 3.3 The Reproducibility Data of Standard Gas Mixture

No	Compound Name	1		2		3	
		Area	RSD	Area	RSD	Area	RSD
1	MeOH	2141.3	43.0	2634.0	20.2	296.0	15.2
2	EtOH	2564.3	10.0	2131.8	31.7	707.0	34.6
3	ACN	2831.3	3.0	3543.7	17.0	872.7	30.2
4	Ace	1325.7	39.3	1753.0	0.1	340.7	34.0
5	IPA	685.7	25.0	3233.2	17.4	1135.7	14.1
6	Ether	364.3	42.4	1464.2	9.4	511.7	7.4
7	MeCl <sub>2</sub>	3646.0	10.2	567.3	30.6	278.0	33.2
8	CS <sub>2</sub>	1768.7	6.2	1805.3	8.5	577.7	12.7
9	Clform	1409.0	10.2	832.7	10.2	313.0	13.3
10	EtAcet	0.0	0.0	1464.3	26.3	428.0	12.3
11	EtCl <sub>2</sub>	1113.7	22.3	2090.8	9.6	699.3	7.2
12	111-TCE	1093.6	13.4	1451.4	14.4	527.7	15.0
13	n-ButOH	0.0	0.0	0.0	0.0	0.0	0.0
14	Bz	3364.0	17.5	5836.1	9.6	2007.7	2.3
15	CCl <sub>4</sub>	1043.3	38.0	479.3	12.9	191	18.6
16	Tric	925.3	17.0	1614.6	16.4	596.3	2.7
17	MIBK	1122.7	41.7	1654.0	5.4	380.3	26.2
18	Pyr	0.0	0.0	0.0	0.0	0.0	0.0
19	Tol	2298	19.2	3795.0	15.0	1349.7	2.1
20	ClBz	1845	13.3	2535.0	18.1	820.0	15.6
21	EtBz	2467.7	8.5	3091.7	16.7	1168.7	5.3
22	m-X	0.0	0.0	0.0	0.0	0.0	0.0
23	p-X	3255.0	2.1	3923.7	16.8	1524.0	6.8
24	o-X	2172.3	2.8	2790.6	24.2	1016.3	10.4
25	1,2-DiClBz	1844.0	19.7	2284.0	18.6	504.0	53.3
26	DMF	0.0	0.0	0.0	0.0	0.0	0.0
27	ELG	0.0	0.0	0.0	0.0	0.0	0.0
28	MEK	0.0	0.0	0.0	0.0	0.0	0.0

is only 0.29% of the typical sample area.

Table 3.4 Canister Blank Testing Results

Canister	Total Peak Area of Blank	Total Peak Area of Sample	Blank% ----- Sample
1	1194	181403	0.66
2	262	78710	0.08
3	272	134428	0.14
Average			0.29

## 3.2 Discussion of Standard Identification

In order to assure the accuracy of analyzing target VOCs, the identification of the standard gas mixture is the key step in analysis work.

By comparing the gas chromatogram of both the divided specific group VOCs and the Alphagaz standard gas mixture, 23 volatile organic compounds were totally identified. A few VOCs are missing from the standard gas chromatogram (Table 3.5).

N-butanol could not be separated from benzene and carbon tetrachloride in the standard gas mixture. Although the boiling point of n-butanol (117°C) is much higher than that of benzene (80°C) and of carbon tetrachloride (74°C), the non-polar capillary column can not hold n-butanol for a longer period of time. Since the molecular weight of benzene and n-butanol are similar (MW of benzene is 78; MW of n-butanol is 74), both of them give almost the same retention time

Table 3.5 Retention Time of 28 Target VOCs

No	Compound Name	Retention			Time(sec)	
		1	2	3	Average	SD
1	MeOH	209.5	201.1	202.5	204.4	4.5
2	EtOH	218.2	212.1	213.9	214.7	3.1
3	ACN	241.4	226.3	225.0	230.9	9.1
4	Ace	257.4	237.2	239.1	244.5	11.2
5	IPA	259.0	253.2	254.9	255.7	3.0
6	Ether	277.5	264.8	266.2	269.5	7.0
7	MeCl <sub>2</sub>	317.2	302.8	302.5	307.5	8.4
8	CS <sub>2</sub>	361.3	352.1	353.4	355.6	5.0
9	Clform	414.3	411.8	413.7	413.3	1.3
10	EtAcet	-	-	-	422.2	-
11	EtCl <sub>2</sub>	487.6	475.7	477.6	480.3	6.4
12	111-TCE	512.9	501.6	502.7	505.7	6.2
13	n-ButOH	-	-	-	-	-
14	Bz	558.3	548.3	548.2	551.6	5.8
15	CCl <sub>4</sub>	572.2	576.9	574.8	574.6	2.4
16	Tric	662.7	655.7	654.8	657.7	4.3
17	MIBK	758.0	752.4	751.4	753.9	3.6
18	Pyr	-	-	-	-	-
19	Tol	825.5	821.4	820.4	822.4	2.5
20	ClBz	975.9	973.2	972.4	973.8	1.8
21	EtBz	1010.3	1007.9	1007.0	1008.4	1.7
22	m-X	-	-	-	-	-
23	p-X	1026.5	1024.4	1023.8	1024.9	1.4
24	o-X	1061.1	1061.3	1060.6	1061.7	0.4
25	1,2-DiClBz	1265.6	1264.5	1264.0	1264.7	0.8
26	DMF	-	-	-	-	-
27	ELG	-	-	-	-	-
28	MEK	-	-	-	-	-

(Table 3.5). When only a mixture equal in quantity of benzene and n-butanol in a cleaned canister was analyzed, the separation of both compounds was obtained (Figure 3.1), but the peak area of n-butanol is smaller than that of benzene, for FID is less sensitive to n-butanol than to benzene.

Pyridine and methyl isobutyl ketone are also not separated because the boiling point of the two compounds are too close (BP of pyridine is 115.2°C; BP of methyl isobutyl ketone is 116.58°C).

Ethyl glycol can not be detected in the air because its vapor pressure is too low. Dimethyl formamide and methyl ethyl ketone can be identified in the purchased standard gas mixture, however, the peaks of both compounds disappeared from the in-lab standard gas mixture after it was kept for several months.

To achieve a better separation, one suggested method is to utilize a GC with subambient temperature capability, using a temperature program (−30°C to 210°C). Another approach to use a more polar capillary column to obtain better results on polar compounds.

The GC/MS showed that tetrachloroethylene exists in the sample. Since the standard gas mixtures prepared for this project lack this chemical, a standard gas mixture contained 12 VOCs (Figure 3.2) was used for calibration of these compounds.

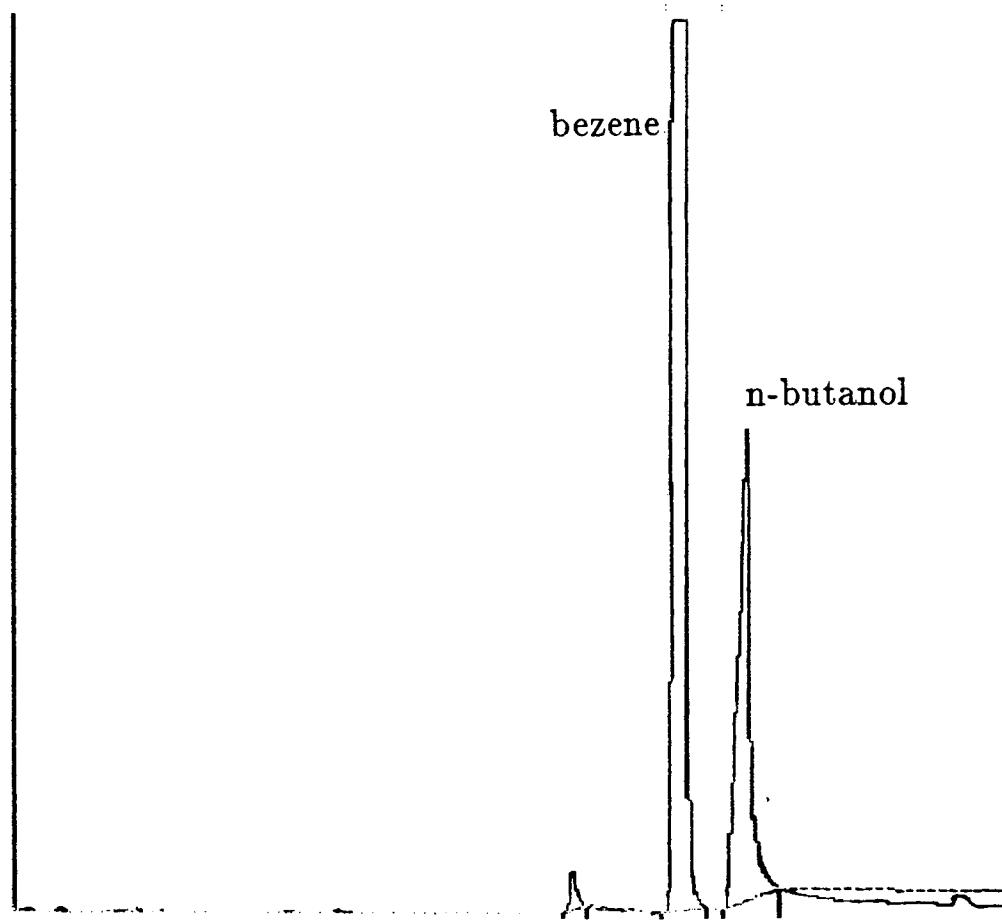
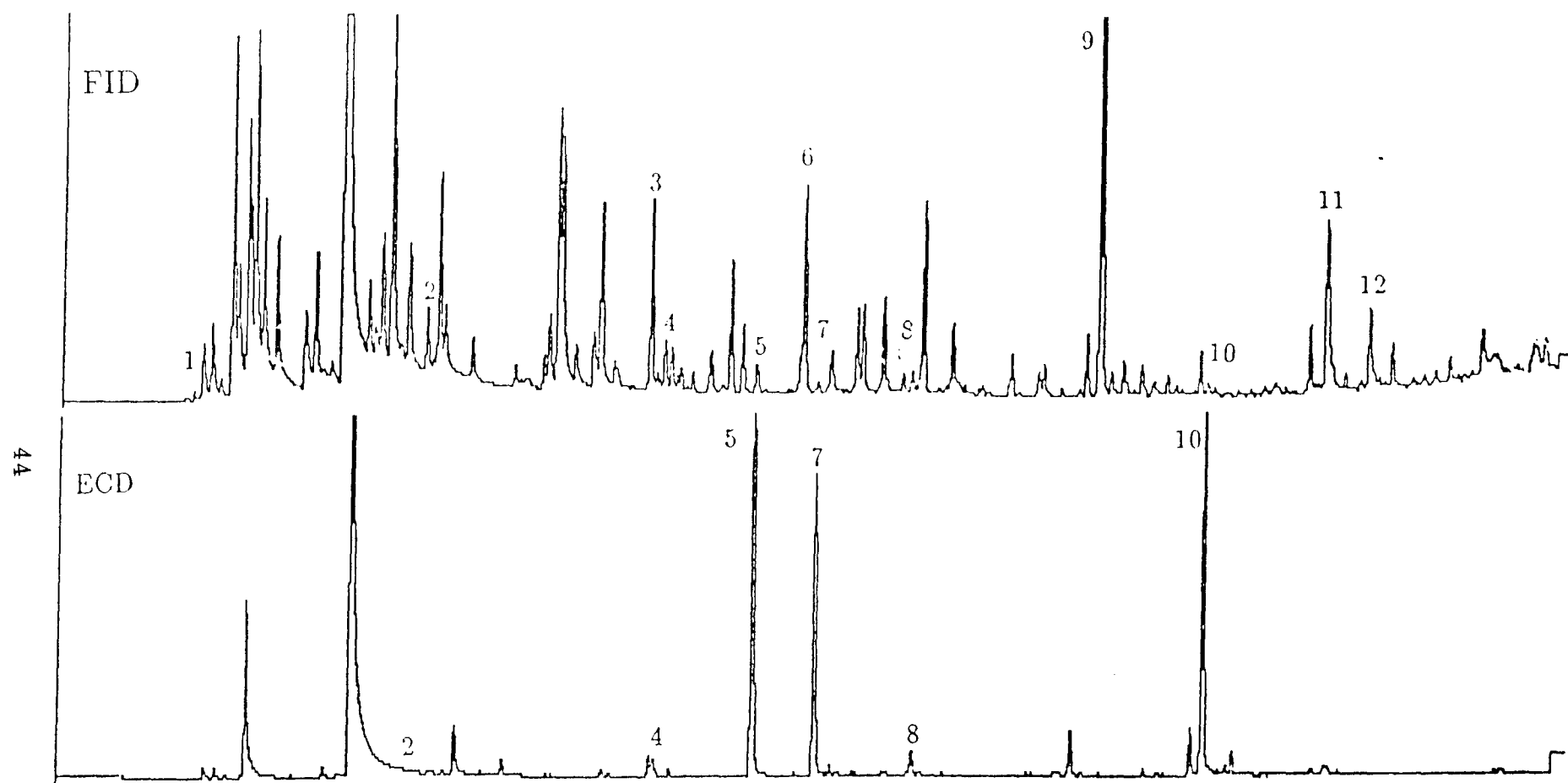


Figure 3.1 Chromatogram of Benzene and n-Butanol



1 - MECL, 2 - DCM, 3 - C6, 4 - CFOR, 5 - 1,1,1, 6 - BZ,  
7 - CCL<sub>4</sub>, 8 - TRIC, 9 - TOL, 10 - PERC, 11 - p, m-X, 12 - o-X

Figure 3.2 Chromatogram of Twelve Standard Gas



### 3.3 Discussion of Detection Limit

Table 3.6 contains a compilation of all the available detection limit data. Values for some compounds were not determined. Certain compounds such as n- butanol, carbon tetrachloride can not be totally separated from benzene on FID. Pyridine and methyl isobutyl ketone are also not able to be separated from each other.

It is shown that FID is sensitive to all the compounds. The detection limit range for non-polar compounds is from 0.18 to 0.39ppbv. Since the analysis of polar compounds, such as methanol and acetone was not as reproducible as the non-polar compounds, the detection limit range of these compounds is higher than that of non-polar compounds (range from 0.5ppbv to 3.68ppbv).

FID shows lower sensitivity to chlorinated volatile organic compounds although they are non-polar chemicals (range from 0.52 to 1.39ppbv). Chloroform shows a much higher detection limit from FID (16.5ppbv), for it is difficult for ethyl acetate to be completely separated from chloroform. This may have an effect on the integration peak area.

Table 3.7 contains the minimum detection limit, compared with the standard deviations of the diluted standard gas mixture injection volume (70ml; 140ml). It shows that the two sets of standard deviations are less than the minimum detection limit, thus, the minimum detection limit was verified.

Table 3.6 Detection Limit Data

No	Compound	Detect Limit (ppbv)	S.D. n=7
1	Methanol	0.82	0.24
2	Ethanol	0.61	0.20
3	Acetonitrile	0.50	0.12
4	Acetone	0.63	0.20
5	Isopropanol	0.50	0.26
6	Diethyl Ether	0.64	0.19
7	Methylene Chloride	1.25	0.38
8	Carbon Disulfide	1.39	0.26
9	Chloroform	16.51	4.25
10	Ethyl Acetone	3.68	1.36
11	1,2-Dichloroethane	0.62	0.11
12	1,1,1-Trichloroethane	0.52	0.14
13	n-Butanol	-	-
14	Benzene	0.20	0.06
15	Carbon Tetrachloride	-	-
16	Trichloroethylene	0.58	0.07
17	Methyl Isobutyl Ketone	1.70	0.47
18	Pyridine	-	-
19	Toluene	0.21	0.04
20	Chlorobenzene	0.39	0.06
21	Ethyl Benzene	0.22	0.04
22	m-Xylene	0.18	0.03
23	p-Xylene	-	-
24	o-xylene	0.26	0.05
25	1,2-Dichlorobenzene	0.79	0.09
26	Diethyl Formamide	-	-
27	Ethylene Glycol	-	-
28	Methyl Ethyl Ketone	-	-

Table 3.7 The Comparison of Detection Limit  
and the Standard Deviation

No	Compound	DL (ppbv)	V:70ml SD(n=7)	V:140ml SD(n=3)
1	Methanol	0.82	0.17	0.07
2	Ethanol	0.61	0.31	0.17
3	Acetonitrile	0.50	0.15	0.13
4	Acetone	0.63	0.02	0.01
5	Isopropanol	0.50	0.17	0.04
6	Diethyl Ether	0.64	0.21	0.08
7	Methylene Chloride	1.25	0.33	0.17
8	Carbon Disulfide	1.39	0.19	0.12
9	Chloroform	16.51	0.79	1.87
10	Ethyl Acetone	3.68	0.43	0.16
11	1,2-Dichloroethane	0.62	0.12	0.10
12	1,1,1-Trichloroethane	0.52	0.13	0.11
13	n-Butanol	-	-	-
14	Benzene	0.20	0.02	0.04
15	Carbon Tetrachloride	-	-	-
16	Trichloroethylene	0.58	0.07	0.06
17	Methyl Isobutyl Ketone	1.70	0.22	0.05
18	Pyridine	-	-	-
19	Toluene	0.21	0.01	0.01
20	Chlorobenzene	0.39	0.04	0.04
21	Ethyl Benzene	0.22	0.02	0.02
22	m-Xylene	-	-	-
23	p-Xylene	0.18	0.02	0.02
24	o-xylene	0.26	0.01	0.01
25	1,2-Dichlorobenzene	0.79	0.01	0.01
26	Diethyl Formamide	-	-	-
27	Ethylene Glycol	-	-	-
28	Methyl Ethyl Ketone	-	-	-

Table 3.8 The Comparison of Minimum Concentration  
of Standard and the Detection Limit (140ml)

No	Compound	DL (ppbv)	Min Conc (ppbv)	A	SD
1	Methanol	0.82	0.80	122	50.6
2	Ethanol	0.61	0.56	828	22.3
3	Acetonitrile	0.50	0.63	103	57
4	Acetone	0.63	0.43	142	18
5	Isopropanol	0.50	0.43	907	226
6	Diethyl Ether	0.64	0.64	349	20.5
7	Methylene Chloride	1.25	2.10	104	18.2
8	Carbon Disulfide	1.39	2.30	265	31.3
9	Chloroform	16.51	22.00	266	135
10	Ethyl Acetone	3.68	10.00	689	123
11	1,2-Dichloroethane	0.62	1.60	191	43
12	1,1,1-Trichloroethane	0.52	1.30	129	8.3
13	n-Butanol	-	-	-	-
14	Benzene	0.20	0.37	121	9.5
15	Carbon Tetrachloride	-	-	-	-
16	Trichloroethylene	0.58	0.64	167	13.1
17	Methyl Isobutyl Ketone	1.70	10.00	1327	189
18	Pyridine	-	-	-	-
19	Toluene	0.21	0.31	128	3.6
20	Chlorobenzene	0.39	0.32	66	2.1
21	Ethyl Benzene	0.22	0.27	60	1.5
22	m-Xylene	-	-	-	-
23	p-Xylene	0.18	0.27	76	2.6
24	o-xylene	0.26	0.27	50.3	1.5
25	1,2-Dichlorobenzene	0.79	11.00	268	43.5
26	Diethyl Formamide	-	-	-	-
27	Ethylene Glycol	-	-	-	-
28	Methyl Ethyl Ketone	-	-	-	-

Table 3.8 shows a series of data obtained from making a standard gas mixture in which the concentration range was similar to the minimum detection limit.

### **3.4 Water Effect on Canister Collection**

Water content is a significant factor in the quality of the data. When ambient air samples are collected in internally polished stainless steel canisters, the volatile organics are concentrated for gas chromatographic analysis by cryogenic trapping. The glass bead filled tubing can be plugged by ice during the sample condensation process if the sample contains too much water. Then the amount of sample injected will be limited. Meanwhile, the baseline will shift and the separation efficiency will be largely reduced. Water in samples may also cause sample error as compounds dissolve in the water. This happens more easily to polar compounds. The deleterious effects of water can be seen in the fact that the precision of replicate samples with high humidity is significantly worse than that of samples taken on less humid days [22]. Water content not only affects the analytical process but also the canister cleaning and storage process. Large amounts of water in samples can cause compounds, especially polar chemicals to deposit on the inner wall of canisters, making cleaning difficult. The method to improve the deleterious effect of water is described as following:

1. To change the temperature program

One method of overcoming the effect of water on the precision of

replicate samples is to change the temperature program. Instead of keeping the GC oven temperature at 210°C for 8 minutes, 15 minutes are needed. The advantage is that the column is cleaned more thoroughly by the carrier gas, helium, since more VOCs volatilize from water at a higher temperature, better reproducibility can be obtained. The disadvantage is time-consumption. The problem of the glass bead filled trap being plugged by ice can only be resolved by keeping the amount of sample small. Further research and experimental data are needed to resolve this problem.

## 2. Discussion of canister cleaning method

Based on the canister cleaning procedure described in chapter 2 (recommended by EPA method TO-12)[23], the canister cleanup efficiency is basically affected by purge gas purity, number of cleaning cycles, time of evacuation, pressure and canister temperature, which can be expressed as:

$$C = f(g, n, t, p, T) \quad (3.4)$$

Where:

C= Concentration of contaminants left in canister

g= Purity of purge gas

n= Numbers of cleaning cycle

t= Time of evacuating in each cleaning cycle

P= Canister pressure

T= Temperature of canister during cleaning

In the cleaning process, zero grade air was used as the purging gas.

To avoid the leakage, 5 to 10 minutes of evacuating step instead of 1 hour suggested by EPA method TO-12 was used. It was reported that the concentrations of all 12 target VOCs dropped below minimum detection limit after 1 to 2 cycles, three cleaning cycles are sufficient[22]. However, a series of high relative humidity air samples were collected in the LRSA project, and the polar chemicals depositing on the wall of canister made cleaning procedure difficult. As a result, 5 to 6 cleaning cycles were needed. The canister blank testing was performed (see Table 3.4 and Figure 3.1). Raising the temperature of the canister during cleaning the procedure may also be helpful, for at higher temperature, it is easier for VOCs to volatilize from the water or to desorb from the wall of the canister.

## Chapter 4

### Conclusion

The method of gas chromatographic determination of trace volatile organic compounds collected in canisters under relative high humidity has been studied, and provides an attractive alternative in VOC analysis as a sampling method. The analytical system is sensitive and provides an accurate measurement of VOC concentration. For non-polar compounds the minimum detection limit could be achieved as low as 0.18ppb while the polar compound detection limit is 0.5ppb.

Since air samples were collected directly without using a sampling train, such as pump and filter, the sampling system carry-over contamination is minimized. Twenty-three VOCs are totally separated and the reproducibility of polar compounds and non-polar compounds are less than 65%, 35% respectively.

Although there are many advantages of canister collection, the humidity contained in canister is an unsolved problem. It reduces the volume of sample which may be injected into the column, makes the baseline shift and effects on the separation efficiency. Since water



contained in canister causes polar compounds to deposit on the wall, more cleaning cycles are needed. This could cause time-consumption. All of these problems should be considered in future study.

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