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An improved method of gas chromatographic determination of trace organic vapors in ambient air collected in canisters

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ABSTRACT

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Name of Candidate: Yong-jin Shen
Master of Science in Environmental Engineering,
1988

Thesis and Abstract Approved: 5/9/88
Dr. B. Kebbekus Date
Assistant Chairperson
Department of Chemical Engineering, Chemistry

An improved method for analysis and quantitation of volatile organic compounds in ambient air has been developed. Samples are collected in evacuated SUMMA polished stainless steel canisters using a sampling flow apparatus with a critical orifice as flowrate controller. Analysis of VOCs in the collected air is carried out by cryogenically concentrating the sample, then thermally transfering it onto the head of a capillary column in a gas chromatograph. The column effluent is measured by a parallel flame ionization detector (FID), and electron capture detector (ECD). The problems associating with quantitative transfer of the sample to the initial cryofocusing loop and with injection of the sample to the capillary column (2nd cryofocusing step) created by the relatively high levels of carbon dioxide and moisture in these samples have been evaluated and minimized by optimizing the temperature of the cryogenic trap. The analytical system

is sensitive and provides an accurate measurement of VOC concentration in ambient air even if the concentration is as low as 0.02 ppb by volume. The performance of this method was tested during the Northeastern New Jersey - Staten Island, Urban Air Toxics Assessment Project.

AN IMPROVED METHOD OF GAS CHROMATOGRAPHIC DETERMINATION OF TRACE ORGANIC VAPORS IN AMBIENT AIR COLLECTED IN CANISTERS

Yong-jin Shen

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 Engineering
1988

APPROVAL SHEET

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I. INTRODUCTION

Volatile organic compounds (VOCs) are emitted into the atmosphere from a variety of sources including industrial and commercial facilities, hazardous waste storage facilities, and automobile exhausts. Many of these compounds are toxic, hence knowledge of the levels of such materials in the ambient atmosphere is required in order to determine human health impacts.

The U.S. Environmental Protection Agency (EPA) is currently developing analytical methodology for the measurement of volatile organic compounds present in ambient air. Since these compounds typically occur in great numbers yet individually in low concentrations (often less than 1 ppb by volume) [1, 2], their identification and quantitation become a non-trivial task. In most cases the samples are first collected by some convenient means such as on solid adsorbents, or in specially prepared canisters or polymeric bags, and transported to the appropriate analytical instrumentation.

In order to select optimal sampling techniques for a given compound or qroup of compounds one must consider the important properties of the compounds of interest having an effect on the sampling process. Compounds which are predominantly in the gas phase at ambient temperature and pressure are generally sampled by passing the air sample through a filtration device to remove particulate material prior to capture of the gasous components. The sampling techniques commonly used for gas phase components are summarized as following [3]:

(1). Solid adsorbents
    a. Organic Polymers (Tenax, XAD-2)
    b. Inorganics Materials (Silica gel, Florisil)
    c. Carbon (Activated Carbon, Carbon Molecular Sieves)
(2). Cryogenic trapping
(3). Impingers
(4). Whole air collection (Canisters, Glass bulbs)
(5). Derivatization techniques

In selected cases, direct analysis of the filtered gas stream is possible, circumventing the need for the collection process. This situation is rare in ambient air monitoring for toxic organics because the low concentrations generally make preconcentration of the sample a necessity.

Solid adsorbents such as Tenax GC and XAD-2 [4] are the media most commonly employed for sampling gas phase organics. The primary advantage of this sampling approach is that little water is collected in sampling process and that a large volume of air which can be sampled relative to other techniques such as impingers or cryogenic sampling. A major disadvantage of these materials is their inability to capture highly volatile materials (e.g., vinyl chloride) as well as certain polar materials (e.g., methanol, acetone) [4]. Sample breakthrough, incomplete desorption, and accurate quantitating collection and recovery are also the problems with this method.

Inorganic adsorbents include silica gel, alumina, florisil, and molecular sieves. These materials are considerably more polar than the organic polymeric adsorbents, leading to the efficient collection of polar materials. Unfortunately, water is also efficiently captured leading to rapid deactivation of the adsorbents [5].

Carbon adsorbents are relatively nonpolar, compared to the inorganic adsorbents and hence water adsorption is a less significant problem, although the problem may still prevent analysis in certain applications. The carbon based materials tend to exhibit much stronger adsorption properties than organic polymeric adsorbents, hence allowing efficient collection of volatile materials such as vinyl chloride. However, the strong adsorption on carbon adsorbents can be a disadvantage in cases where recovery by thermal desorption of less volatile materials such as benzene or toluene is desired because of the excessive temperatures required (e.g., $400^{o}C$) [6].

The collection of atmospheric organics by condensation in a cryogenic trap is an attractive alternative to adsorption or impinger collection. The primary advantages of this technique include:

(1). A wide range of organic materials can be collected.

(2). Contamination problems with adsorbents and other collection media are avoided.

(3). The sample is immediately available for analysis without further workup.

(4). Consistent recoveries are generally obtained. But disadvantage is that cryo mechanism in field is needed and awkward.

However, an important limitation of the technique is condensation of large quantities of moisture and carbon dioxide, and lesser amounts of certain reactive gases (SO2, NOx, etc.). The principles of cryogenic sampling are described in Stern's Air Pollution series [7].

Whole air collection:

Collection of whole air samples using evacuated glass bulbs, stainless steel canisters, or similar devices is probably the simplest sampling approach, and can be useful in many situations. An obvious limitation of this approach is that the sample components of interest may be adsorbed or decomposed through interaction with the container walls. At very high analyte levels (e.g., several ppm) condensation may be a problem. Consequently, this approach is most useful for relatively stable, volatile compounds such as hydrocarbons and chlorinated hydrocarbons with boiling points less than 150^{o}C. However certain compounds within these classes pose storage stability problems (e.g., carbon tetrachloride interacts with stainless steel surfaces and is lost) [8]. Preconditioning surfaces (e.g., formation of an oxide coating) or selection of alternate container materials can circumvent these problems in many cases [8]. In all cases, the container must be flushed with zero grade nitrogen or clean air prior to sampling in order to remove trace contaminants.

Canister-based sampling systems for toxic volatile organic compounds have been developed by the Environmental Monitoring Systems Laboratory (EMSL), US EPA. The most frequently used solid sorbent, Tenax GC, has been shown empirically to give results that are difficult to interpret [9, 10]. Use of the canister sampling systems for toxic VOCs has evolved as an extension of use of canisters for halocarbon and hydrocarbon analysis. The canister-based samplers have the following advantages as compared to solid sorbent cartridges:

(1). Canister pressure can be used as an indicator of correct sampler operation.

(2). No thermal desorption is required.

(3). Multiple analysis can be performed from canister.

(4). Artifact problems related to the storage of enhanced trace gas concentrations, to thermal decomposition of the sorbent, to memory effects in in the sorbent and to the effect of thermal desorption on the target compound concentration are not present.

(5). The evacuated canisters can be used for sampling without need for electricity [11].

In many cases none of the available screening techniques will be suitable to accomplish a given monitoring objective, and, hence, a more sophisticated analytical approach will be required. GC is by far the most widely employed technique in ambient air monitoring of toxic organic compounds. The sensitivity, specificity, and versatility of GC, coupled with the relatively volatile nature of most compounds in ambient air, make this a very attractive technique [12].

The accurate identification and quantitation of the many trace level volatile organic compounds in ambient air generally requires preconcentration of analytes to enhance instrument sensitivity. In this laboratory, preconcentration is accomplished by passing whole air through a cryogenic trap. The sample is then thermally desorbed onto a capillary column GC using flame ionization detector (FID), electron capture detector (ECD), and/or mass selective detector (MSD). The methodology has been described elsewhere [13, 14, 15, 16].

Carbon dioxide and moisture-related problems can be alleviated by various methods. The simplest method is to reduce sampling volume, but this also reduces sensitivity. Other techniques involve predrying the sample with various desiccants; however these desiccants can affect sample integrity by adsorbing or outgassing some compounds. Also, desiccants are inconvenient to use because they require periodic replacement or reconditioning [17, 18, 19]. The large amount of carbon dioxide in ambient air (0.3% by volume) is a more significant problem than moisture since CO_2

is much more volatile and can cause GC peak spreading. The VOC analytical method described in this work is designed to eliminate the effect of CO_2 on the GC operation, and carry out the ambient air analysis without use of a sample predryer.

II. METHOD DESCRIPTION

A. Sampling apparatus

1. Sample collection system

The canister-based sampling system for toxic volatile organic compounds (VOCs) has been developed by the Environmental Monitoring System Laboratory (EMSL), US EPA [20, 21] as a possible alternative to collection on solid sorbents. The sampling system is shown in Figure 1. Air enters the system through a glass microfiber filter, which prevents particulates from being drawn into the system. A cylindrical aluminum hood surrounds the inlet to shield it from precipitation. The air then passes through a critical orifice which serves as a flow rate control device. A stainless steel, metal bellows pump, model MB-151, supplied by Metal Bellows Company, Sharon, MA, pressurizes the air into the 6 liter, internally polished stainless steel canister, supplied by Demaray Scientific Instruments, Ltd., Pullman, WA, The canister is fitted with a compression fitting for disconnecting it from the sampling system, and a noncontaminating valve. A pressure gauge installed between the pump and canister allows reading of the final canister pressure, and is also used for checking the system for leaks before starting sampling.

One significant problem is the difficulty of maintaining a constant, low flow rate of air sample into the canister as the canister pressure rises from 0 psia to 15 psig during the desired 24 hour collection period. Since the air sample must pass through any flow control device used, it must be of a simple, non-contaminating design. A low flow mechanical control Model 2-2413 was purchased from Supelco, Bellefonte, PA, Model 202 Ls/As flow controller with optional digital dial, supplied by VICI Condyne, Pasadena, CA, were installed between the sampling system filter and inlet of the pump. Either of these easily hold a flow of about 8 ml/min for 24 hours without discernable change in flow. But the blank tests showed that there was significant contamination coming from both of these flow controllers. The blank was done by filling the clean canister, through the flow controller, with zero grade air over a period of 24 hours. When this air was analyzed, there was a significant contamination. An attempt was made to clean these flow controllers by purging with

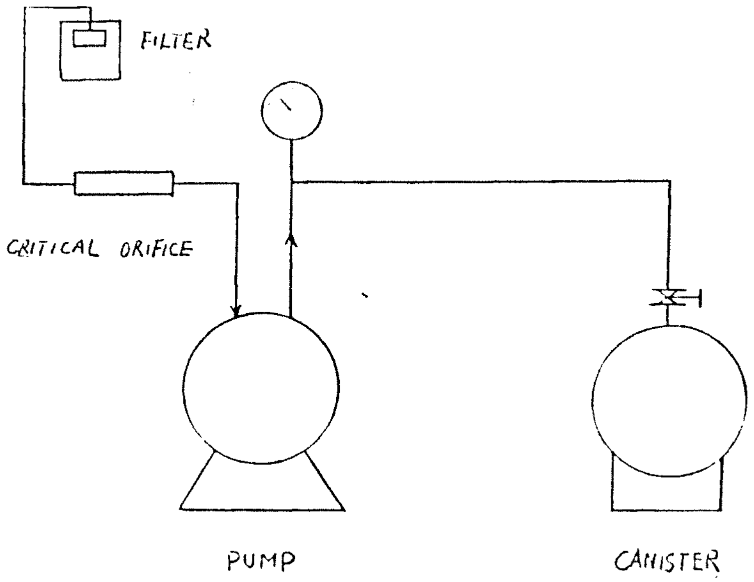

Figure 1. Sampling system for the collection of 24 hours integrated field sample

nitrogen keeping the temperature at 30^{o}C, for 72 hours. The contamination was decreased, but never reached an acceptable level. Both controllers have polymeric diaphrams. Also, there was a concern that the flow controller might adsorb material of interest from the sample.

Using stainless steel hypodermic needles of 30, 31, 32, and 33 gauge, 2.54 cm long, as critical orifice, a constant flow rate with a little drop when the canister reaches the high pressure was readily maintained. Figure 2. shows the performance of these 30 to 33 gauge needle orifices, relating the flow rate to the canister pressure. Also, Table 1. indicates that each different gauge needle gives a different

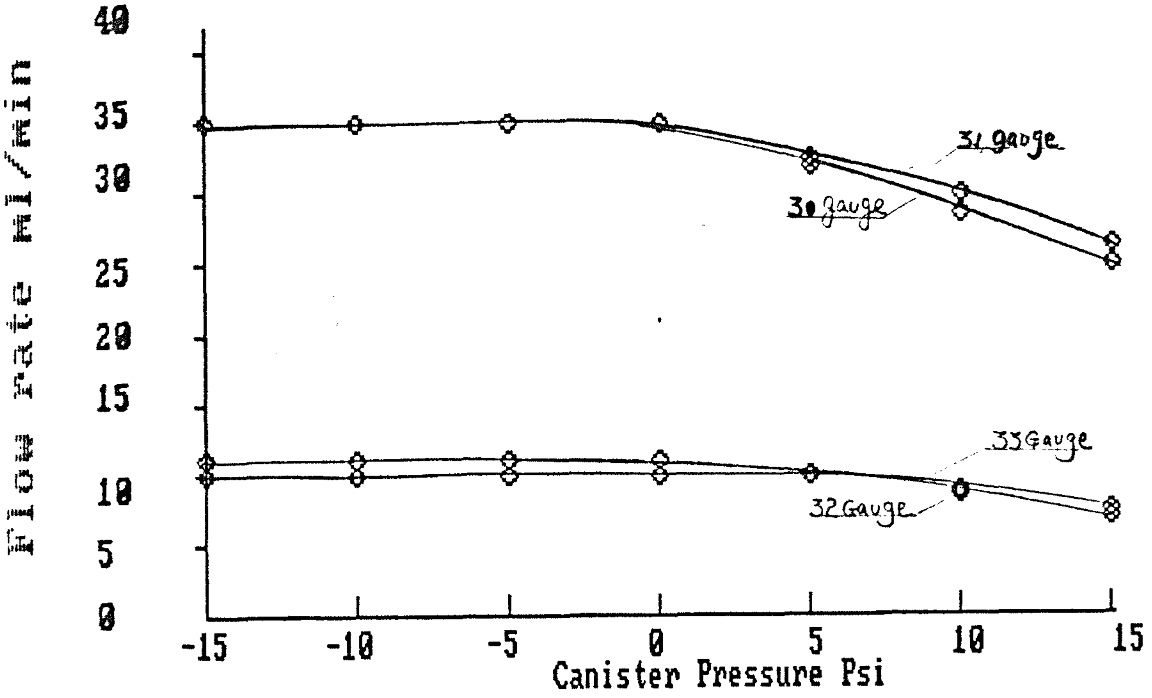

Figure 2. Sample flow rate into a canister as the canister pressure rises, for different gauge needle as a critical orifice

Table 1. performance of 30 - 33 gauge needle relating flow rate to the canister pressure

Pressure (psi)	Flow rate (ml/min)			
	30 gauge	31 gauge	32 gauge	33 gauge
-15	35	35	11	10
-10	35	35	11	10
-5	35	35	11	10
0	35	35	11	10
+5	32	32.5	10	10
+10	28.5	30	8.5	9
+15	25	26.5	7	7.5

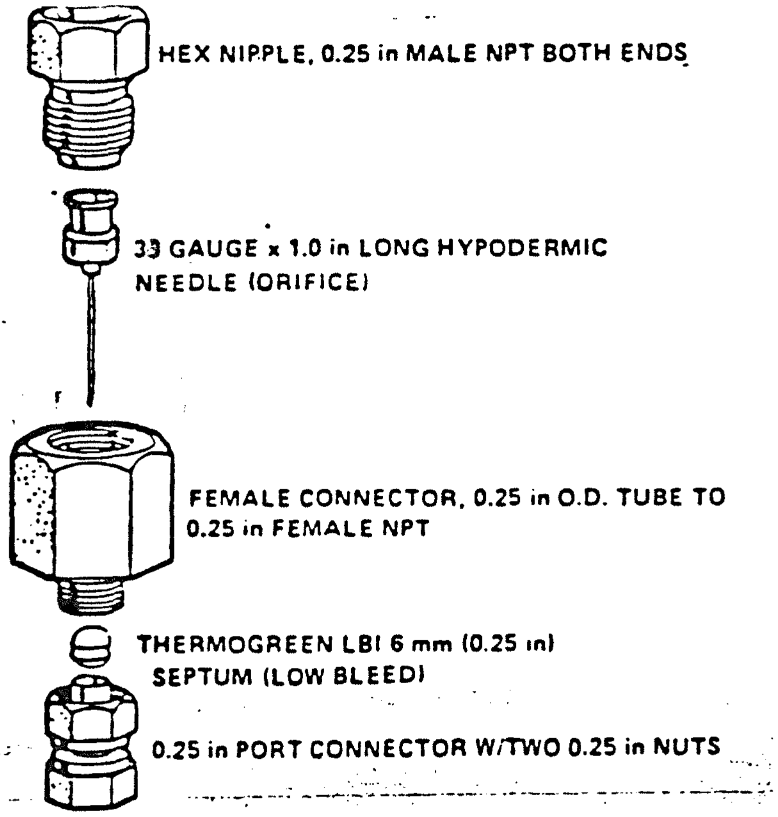

Figure 3. 33 gauge needle assembly for air sample inlet flow control

flow rate range, which can be utilized to using the time needed for filling the canisters from 0 psia to 15 psig. The 33 gauge needle was chosen as a critical orifice, since it gave an ideal flow for collection of 24 hour samples. Figure 3. shows the 33 gauge hypodermic needle assembly for sample inlet flow control. Assuming that 33 gauge has averaged flow rate 9 ml/min, about 12 liters air sample can be collected in 24 hours.

2. Procedure for air sample collection (Figure 1.)

(1). Remove cap from canister top, and leave it in the top ring of the canister for storage, connect canister inlet to sampler inlet tube.

(2). Turn on the pump. The pressure gauge will read > 15 psig if the pump is working and there are no leaks. If

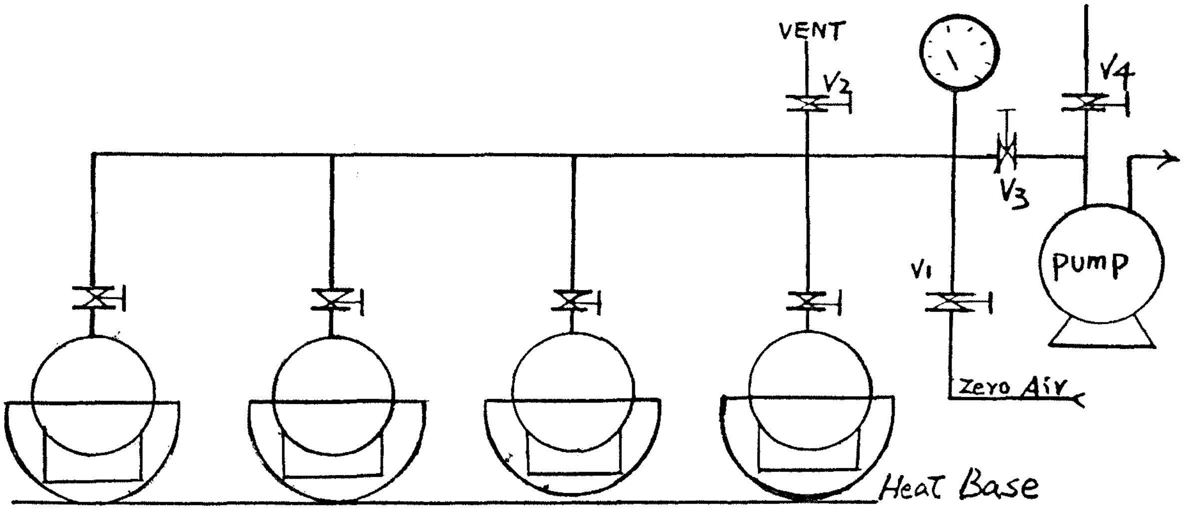

Figure 4. Canister cleaning apparatus

pressure is good, open canister valve. Record start time and canister identification.

(3). Read and record gauge pressure and time. Close the canister valve, turn the pump off, disconnect the canister, and replace the sealing cap on it.

3. Canister cleaning procedure

(1). Connect canisters to the vacuum manifold as shown in Figure 4.

(2). Heat the canisters to 35°C, open the vacuum shut-off valve (V3) and evacuate the canister to less than 1mm for 1 hour.

(3). Close the vacuum shut-off valve (V3), open the zero air valve (V1) to pressurize the canisters with zero air to about 35 psig (240 KPa).

(4). Close the zero air valve (V1), open the vent valve (V2) to allow the canisters to vent down to atmospheric pressure, then close the vent valve (V2).

(5). Repeat steps (2) to (4) two additional times.

(6). Fill the canister with zero air about 15 psig and analyze the contents as a blank check of the canisters and of the cleanup system and procedure, using the NMOC method. A blank test should be performed on each of the canisters until the cleanup system and procedure are proven to be reliable. Any canister that does not test clean (compared to direct analysis of zero air) after repeated cleaning should not be used.

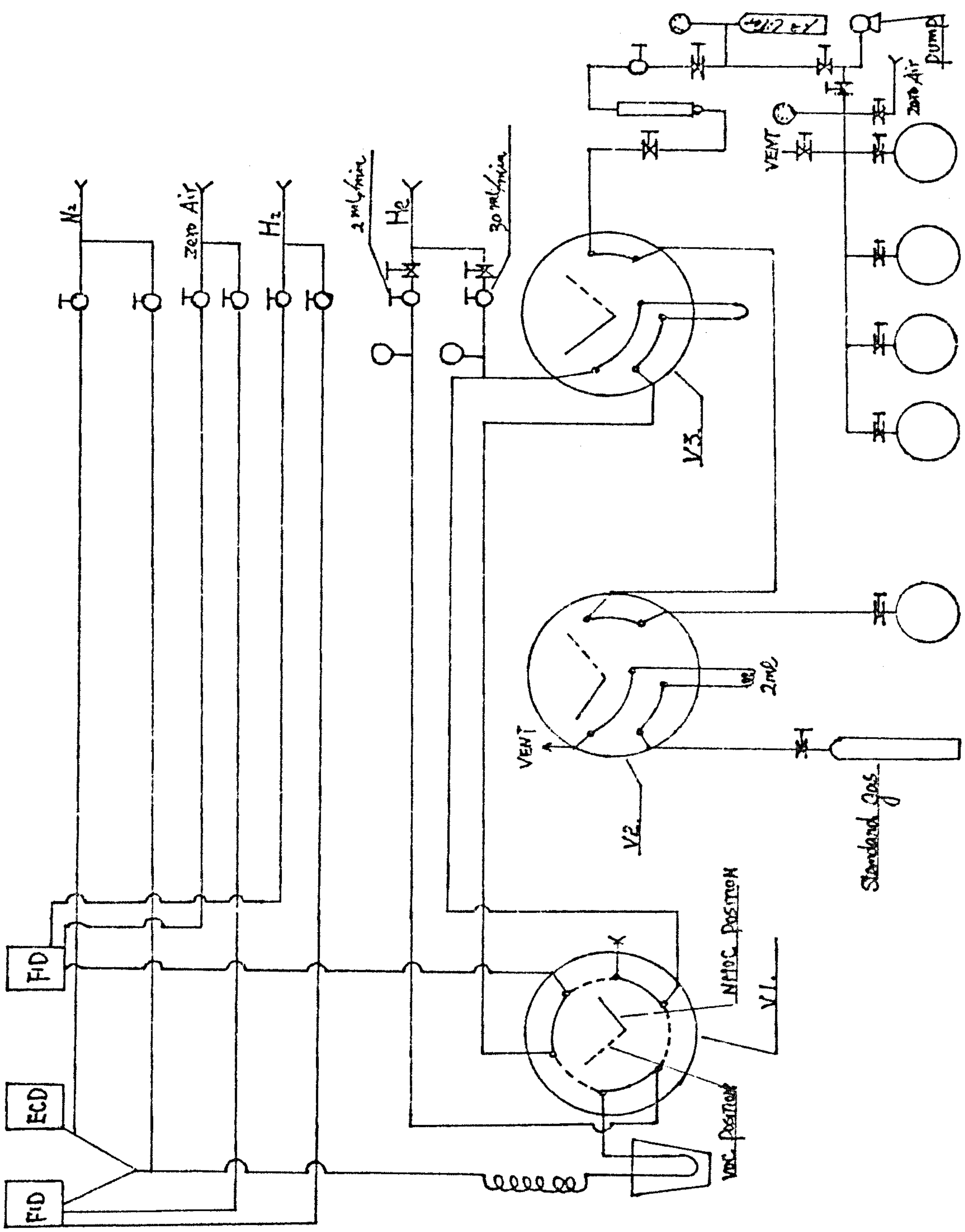

Figure 5. Analytical apparatus for NMOC and VOC method

B. Analytical apparatus and methods

The NMOC and VOC analyzer was constructed from a Varian 3700 gas chromatograph as shown in Figure 5. The system includes one electron capture detector (ECD) and two flame ionization detectors (FID). NMOC are quantitated by one FID and VOCs by the other FID and the ECD. Other major components include three six-port valves, a 2 ml standard gas loop, a sample volume measurement system, and a 60/80 mesh glass bead cryogenically trap.

1. NMOC analysis for canister blank testing and measurement of non-methane total organic carbon in air samples (Figure 6.)

FID Gas flows:

H_2 : 30 ml/min
He : 30 ml/min (pass trap)
Air: 300 ml/min

Six-port valve 1. (NMOC and VOCs method selection valve) should be rotated to the solid line position (right). Valve 2. (the standard/sample selection valve) should be rotated to the solid line position (left), and the helium valve should be set to allow the flow of 30 ml/min. Another 2 ml/min helium should always pass through capillary column to maintain the column quality while the oven temperature above 90°C. The volume of sample injected is measured by first evacuating the 1.2 liter ballast tank to below 1 mm pressure. Then, the valve 3. is switched to the dotted line position (right), and the sample is allowed to flow through a liquid argon (-186^{o}C) cooled glass microbead trap into the ballast tank, where the pressure is monitored by a Wallace and Tiernan high accuracy pressure gauge (model 61D-1A-0030). The flow rate is controlled by a mechanical flow regulator in the line after the trap, to insure a constant flow rate of about 100 ml/min. When the ballast tank pressure reaches to 6 psi, after 5 minutes, valve 3. is switched to the solid line position (left), flow of helium at 30 ml/min will pass through the trap and carry the organic compounds to the FID. The liquid argon container is removed and the GC oven turned on, allowing the trap to heat to 95^{o}C. The canister blank test is also carried out by this method before sending canister out for collection of air sample.

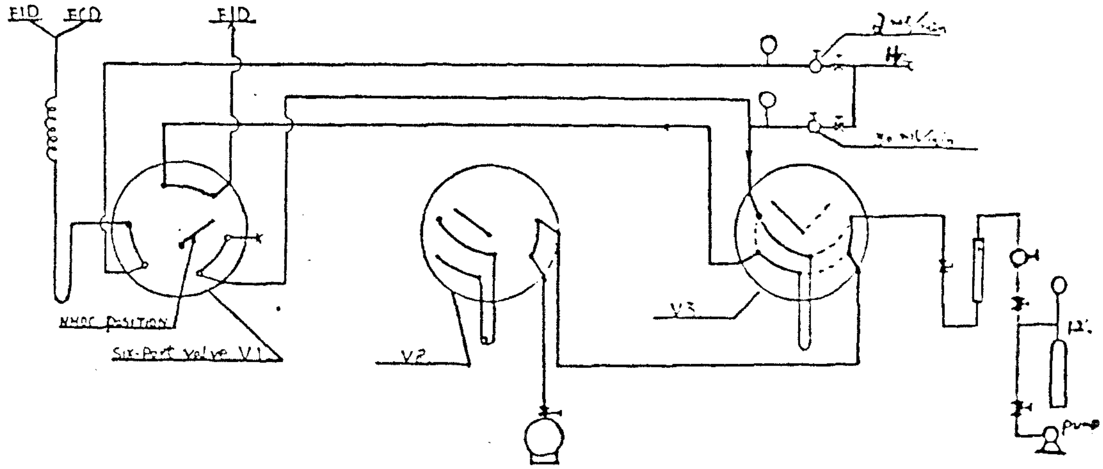

Figure 6. NMOC analysis chart

The volume of air sample injected is calculated by:

$$V_s = \frac{\triangle P \; V_r}{P_s}$$

V_s = Volume of air sample injected (liter)

$\triangle P$ = Pressure difference measured by high accuracy gauge (psi)

V_r = Volume of vacuum ballast tank (1.2 l)

P_s = Standard pressure (14.7 psi)

2. VOC analysis for air samples in canisters (figure 7.)

GC operating condition:

H_2 : 30 ml/min --- FID

He : 2 ml/min --- column

N_2 : 28 ml/min (make up of the capillary column effluent)

N_2 : 27 ml/min (make up of the spliter ECD effluent)

Air: 300 ml/min --- FID

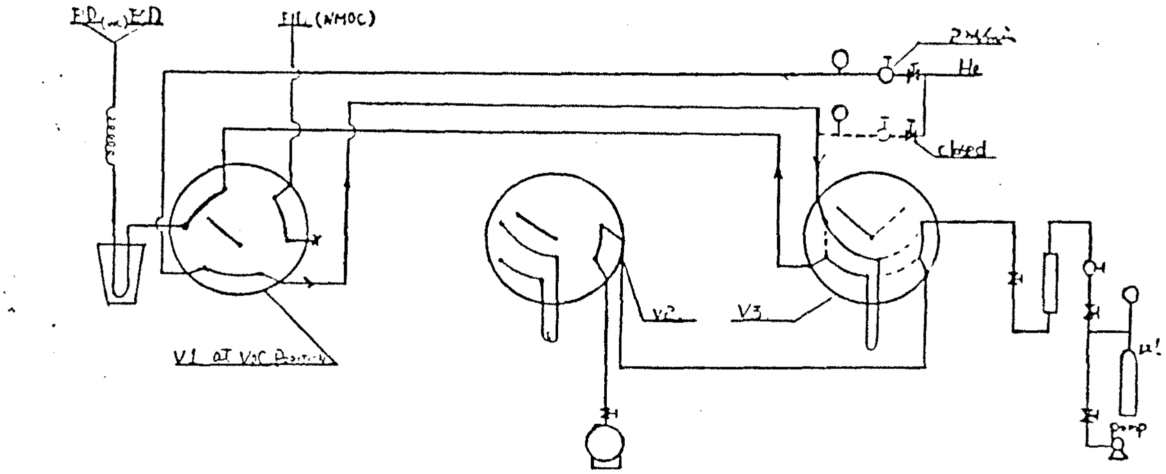

FIgure 7. VOCs analysis chart

Oven temperature program:

Initial t = 35°C, hold for 5 minutes then rise at a rate of 6°C/min to a final temperature of 195°C.

Operating procedure:

(1). the 30 ml/min helium valve is kept closed, with valves 1. and 2. turned to the solid line position (left). Only 2 ml/min helium is allowed to flow into the column.

(2). The canister is heated to 35°C, the sample injection tubing to 100°C, and the tubing is flushed by 0.5 liter of air sample.

(3). The glass microbead trap is cooled to -186°C by inserting it into the liquid argon container. The ballast tank is evacuated to below 1 mm pressure. Valve 3. is switched to the dotted line position (right) and the shut-off valve is turned on at the same time to inject about 0.65 liter air sample. The volume of air sample injected is also calculated by the equation:

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

(4). Placing the head of first coil of the column into a small insulated container of liquid nitrogen, switch valve 3. to the solid line position (left), and replace the liquid argon by 95°C water bath, allowing the condensed volatile organic compounds vaporize and be transferred to the head of the column. The transfer time is 6-8 minutes.

(5). After the sample is transferred into the focusing trap, the head of first coil is heated by placing it into a

95°C water bath. Then the bath is removed and GC oven is allowed to temperature program. The program begins at 35°C, holds for 5 minutes then rises at a rate of 6°C/min to a final temperature of 195°C. The column used is a 50 meter methyl silicone bonded fused silica column, 0.2 mm ID, with a film thickness of 5 um, suupplied by Hewlett Packard. The 2 ml/min capillary effluent, plus 28 ml/min nitrogen make-up gas, is split between a FID and an ECD detector. 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 insrted in the ECD channel, which gives an effluent split ratio of 10:1. The 3 ml/min effluent from the

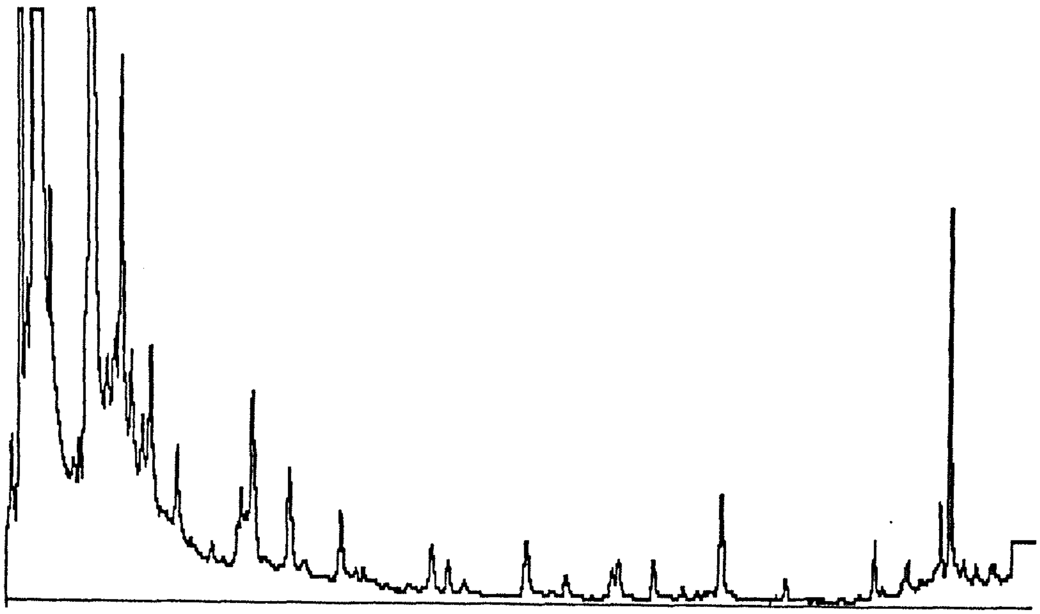

Figure 8. VOCs analysis chromatogram for air sample

splitter, plus 27 ml/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. Figure 7. shows the VOCs analysis system. Figure 8. showns a typical chromatogram of the volatile organic compounds in ambient air.

3. Standard gas for calibration

With the same GC operating conditions, the canister is replaced by a tank of compressed nitrogen. After the loop is flushed, a standard gas mixture is passed through a 2 ml volume loop at 1 atm, 100^{o}C. Six-port valve 3. is switched to the dotted line position (right). Then valve 2. is also switched to the dotted line position (right), allowing

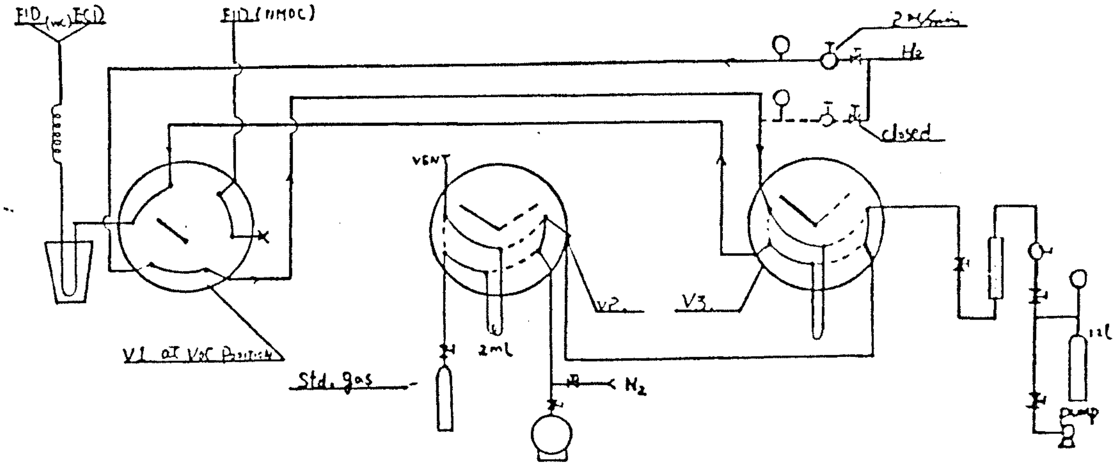

Figure 9. Standard gas analysis Chart

nitrogen to pass through the 2 ml loop, carrying the standard gas through the glass bead trap to the ballast tank. The VOCs in the standard gas will be condensed in the cooled trap, and transferred to the column in the same manner as the sample. Figure 9. shows the diagram of the system for standard analysis. Figure 10. showns the standard gas chromatogram.

The standard gas is prepared from a mixture of target compounds listed in Table 2. The compounds are injected into an evacuated and cleaned 13 liter stainless steel cylinder, and cylinder is pressurized with zero grade helium. The compounds were then quantified in the mixture by gas chromatography, comparing them to NBS traceable standards. The analysis of the standard was done by Alphagaz, Edison, NJ.

Table 2. The standard of targeted VOC for calibration

Name	Formula		M.W.	ppm
1. Chloromethane	CH_3Cl	MECL	50.5	2.98
2. Methlene Chloride	CH_2Cl_2	DCM	85	11.86
3. Hexane	C_6H_{14}	C_6	86	7.54
4. Chloroform	$CHCl_3$	CFOR	119.5	12.66
5. 1,1,1-Trichloroethane	$C_2H_3Cl_3$	1.1.1*	133.4	7.89
6. Benzene	C_6H_6	Bz	78.1	9.50
7. Carbon Tetrachloride	CCl_4	CCl_4	153.82	10.15
8. Trichloroethlene	C_2HCl_3	TRIC	131.4	9.15
9. Toluene	C_7H_8	TOL	92.1	9.05
10. Tetrachloroethylene	C_2Cl_4	PERC*	165.8	6.49
11. m and p-Xylene	C_6H_{14}	PMX	106.17	3.51
12. o-Xylene	C_6H_{14}	OX	106.17	4.46

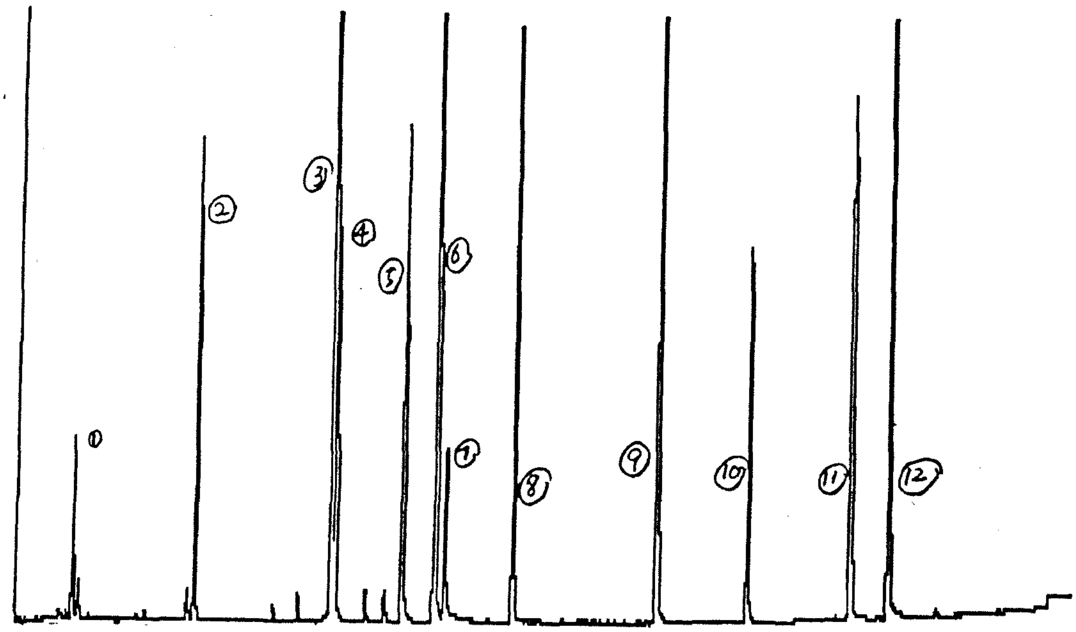

Figure 10. Standard gas analysis chromatogram

The equation for the calculation of the sample concentration from the area and standard concentration is derived as follows:

Sample loop = 2 ml, at $100^{o}C$ $(373^{o}K)$, pressure = 1 atm.

Total amount of standard gas injected:

$$n = \frac{PV}{RT} = \frac{1 \times 0.002}{0.082 \times 373} = 6.5 \times 10^{-5} \text{ moles}$$

Benzene in injected standard gas:

$$n_{Bz} = 6.5 \times 10^{-5} \times 9.5 \times 10^{-6} = 6.2 \times 10^{-10} \text{ moles}$$

(1). Sample Benzene (ppb)

$$= \frac{\text{Area}_{\text{sample}} \times 6.2 \times 10^{-10}\ (\text{moles}) \times 24.5\ (\text{l})}{} \times 10^{9}$$

$$\text{Area}_{\text{Bz Std.}} \times V_{\text{sample}} \text{ (l)} \times 1 \text{ (mol)}$$

$$= 15.2 \times \frac{\text{Area}_{\text{sample}}}{\text{Area}_{\text{Bz Std.}} \times V_{\text{sample}}} \text{ (ppb)}$$

(2). Sample Benzene (ppb)

$$= \frac{A_{\text{sample}} \times 9.5 \times 10^{-6} \times V_{\text{std.}} \text{(ml)} \times 10^{-3} \text{ (l/ml)} \times 10^{9}}{V_{\text{sample}} \times \text{Area}_{\text{Bz Std.}}}$$

$$= 9.5 \times \frac{\text{Area}_{\text{sample}} \times V_{\text{Std.}} \text{ (ml)}}{V_{\text{sample}} \times \text{Area}_{\text{Bz Std.}}} \text{ (ppb)}$$

(1) = (2)

$$15.2 \frac{\text{Area}_{\text{sample}}}{\text{Area}_{\text{Bz Std.}} \times V_{\text{sample}}} = 9.5 \frac{\text{Area}_{\text{sample}} \times V_{\text{Std.}} \text{ (ml)}}{\text{Area}_{\text{Bz Std.}} \times V_{\text{sample}}}$$

$V_{\text{Std.}} = 1.6$ ml

Equation of sample concentration in air:

$$= \frac{\text{Area}_{\text{sample}} \times \text{Std. (ppm)} \times 10^{-6} \times V_{\text{Std.}} \text{ (ml)} \times 10^{-3}}{\text{Area}_{\text{Std.}} \times V_{\text{sample}} \text{ (l)}} \times 10^{9}$$

$$= \frac{\text{Area}_{\text{sample}} \times \text{Std. (ppm)} \times 1.6}{\text{Area}_{\text{Std.}} \times V_{\text{sample}}} \text{ (ppb)}$$

4. Analysis of a spiked sample

To assist in peak identification, spiking of an air sample is sometimes useful. The canister sample, after being once analyzed, is run again after standard has been added. Spiking is done in the same way as the standard gas analysis, only the nitrogen is replaced by the air sample from the canister. The procedure of analysis is same as for a standard. The air

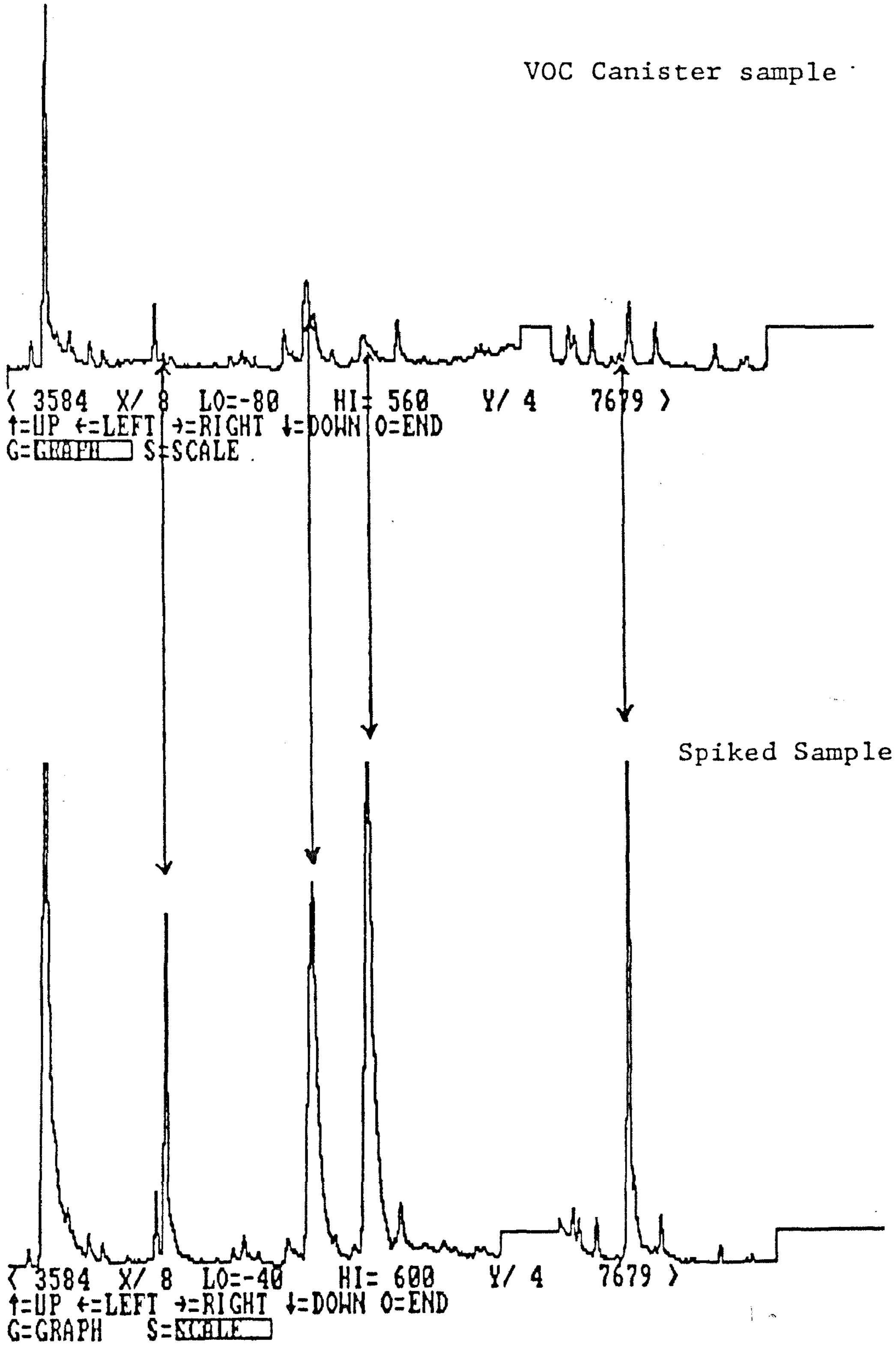

Figure 11. Comparison with the original and spiked peaks

sample carries a measured volume of standard gas from the loop, through the cooled glass bead trap, to the evacuated ballast tank. The volatile organic compounds in the standard gas and air sample are condensed in the trap, transferred to the first coil of the column cooled in liquid nitrgen container, and injected onto the column. Figure 11. indicates the identification of peaks and compares the original and spiked samples.

III. EFFECT OF MOISTURE ON VOCs ANALYSIS

When the canister is used as an air sample collector, the amount of moisture in the air depends on the ambient temperature, and relative humidity. Figure 12. indicates a drifting baseline during VOC analysis because the head of first coil of the column was not heated after removing the liquid nitrogen container. The possibility of ice plugging the capillary column or the glass bead trap and stopping or altering the flow is of concern, since a carrier flow variation or temporary stoppage will cause variability in the retention times and decrease the resolution of the column. If

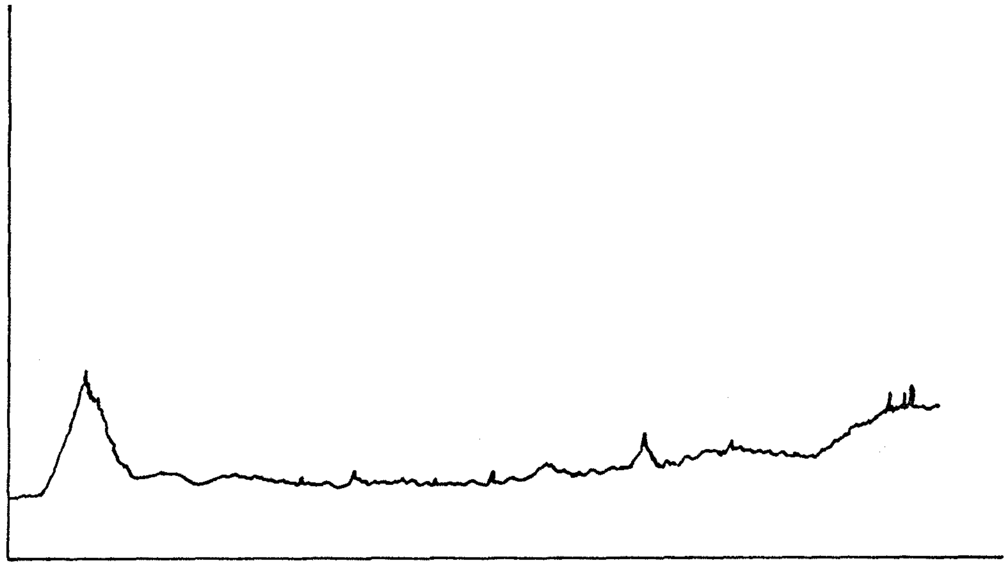

Figure 12. Shifted baseline during VOC analysis

the glass bead trap was plugged, it would be obvious that there was a problem, because the pressure in the ballast tank would cease to rise. However, if the first coil of the column becomes plugged before all the sample had been transferred, then a portion of the sample would not be focused, and would emerge as such low intensity, broad peaks as to be lost in the baseline.

The amount of water present in the column from various samples can be estimated. Assume the ambient temperature to be 25°C, and relative humidity 50%. The amount of moisture in 1 liter of air is calculated, using a psychrometric chart (Properties of air and water-vapor mixtures from 32° to 600°F) in appendix I, and table of density of dry air, density of water in appendix II [22].

$T = 25^{o}C = 77^{o}F$, relative humidity = 50%

From psychrometric chart, dew point = 65°F

Pounds water/lb dry air = 0.01 g/g dry air

From appendix B. $t = 25^{o}C$, $H = 76$ cm

$$\text{Density of dry air} = \frac{0.001293}{1 + 0.00367t} \times \frac{H}{76}$$

$$= 0.001185 \text{ g/ml}$$

$$\text{g } H_2O/\text{l dry air} = 0.01 \text{ (g } H_2O) \times 0.001185 \text{ (ml}^{-1} \text{ dry air)}$$

$$= 1.185 \times 10^{-5} \text{ g } H_2O/\text{ml dry air}$$

$$= 11.85 \text{ mg } H_2O/\text{l dry air}$$

For VOC analysis, about 0.5 liter air sample is injected, which contains about 5.93 mg water at the above conditions.

The density of ice = 0.917 g/cm^3

$$\text{The volume of ice} = \frac{5.93 \text{ mg}}{0.917 \text{ g/cm}^3} = 6.46 \times 10^{-3} \text{ cm}^3$$

The capillary column has 0.021 cm ID, and approximately a 20 cm length of first coil of the column is submerged in the liquid nitrogen container. The internal volume of column in liquid nitrogen is 6.9×10^{-3} cm^3. A 1/8" OD. stainless steel tube filled 60/80 glass beads has 0.2159 cm ID., 15.24 cm (6") length in the liquid argon bath, the inside volume is 0.5579 cm^3.

The bulk density of 60/80 glass beads = 1.4888 g/cm^3

The real density of 60/80 glass beads = 2.3821 g/cm^3

The volume of air in the loop = Vloop - Vglass beads

$$= 0.5579 - \frac{0.5579 \times 1.4888}{2.3821} = 0.2094 \text{ cm}^3$$

The inside volume of air is much more greater than the volume of the first coil of the capillary column. Therefore, it is more likely that the column, rather than the trap will be plugged. Also, when the sample is injected, the pressure in the ballast tank did not cease to rise, indicating that the problem is not in the glass trap.

In order to solve this problem, a mechanical flow controller was purchased from Supelco, and used as the helium carrier gas flow controller, replacing the pressure controller. Because the pressure controller was adjusted to about 30 psi, if the system is plugged, the 2 ml/min helium flow will be reduced, even stopped. A flow controller can maintain a constant flow rate at 2 ml/min, with the same head pressure. When valve 3. is at solid line position (left) side, as shown in Figure 7., 2 ml/min of helium passes through the glass bead trap, carrying the vaporized organic compounds and water to the cooled first coil of the capillary column. If the column is plugged, the pressure gauge will rise above 30 psi. Several experiments showed that the pressure gauge always stayed at 30 psi, which means the ice did not plug in the column, but only condensed on the inside the wall of capillary column, and still allowed the helium to pass through. When the focusing trap was allowed to heat to the oven temperature with no added heating, the sample volatilized slowly, broadening the peaks and giving poor separation. When a hot water bath was used to rapidly heat the trap, the organic compounds, including water vaporized quickly enough to achieve good separation. Over 60 experiments using this method shows that with control of the injected sample volume, one can get good separation, even during high humidity summer sampling.

IV. REPRODUCIBILITY AND QUALITY ASSURANCE TESTING

A. Analytical reproducibility testing

To study the analytical reproducibility of the system, air samples in canisters were collected from Carteret, NJ, Newark, NJ, and Staten Island, NY, and a synthetic sample was prepared for us by the EPA EMSL Lab at Research Triangle Park, NC, and analyzed by the method described above. The concentrations of each of the targeted VOC in these samples range from 0.02 to 10 ppbv. The mean concentrations of VOC in the different canisters, with their standard deviations are listed in table 3.

Table 3. Mean concentration and standard deviation of VOC in different canisters

	10/21(SI) n = 2		10/22(SI) n = 2		10/29(TPa) n = 2		10/29(TPb) n = 3		3/10(Ct) n =5	
No.	mean	Sd.	mean	Sd.	mean	Sd.	mean	Sd.	mean	Sd.
1	0.07	0.00	0.44	0.56	0.00	0.00	0.00	0.00	0.00	0.00
2	0.07	0.00	0.04	0.01	0.00	0.00	0.00	0.00	0.33	0.03
3	0.67	0.10	0.53	0.43	0.00	0.00	0.00	0.00	0.45	0.30
4	0.03	0.00	0.03	0.00	0.13	0.00	4.96	0.00	0.35	0.08
5	0.07	0.00	0.06	0.03	2.62	0.88	2.88	1.59	0.26	0.12
6	1.06	0.19	0.99	0.15	2.97	1.00	3.72	2.45	1.10	0.08
7	0.06	0.00	0.06	0.00	3.94	0.00	5.81	4.85	0.43	0.12
8	0.04	0.00	0.03	0.00	3.51	1.88	3.64	1.49	0.06	0.08
9	4.82	0.74	3.61	0.02	2.49	0.53	3.26	1.40	8.75	1.16
10	0.05	0.00	0.03	0.00	3.84	2.60	3.97	0.86	0.14	0.01
11	0.29	0.10	0.02	0.00	0.00	0.00	0.00	0.00	4.75	0.00
12	0.22	0.00	0.42	0.05	3.66	0.28	5.49	1.58	1.20	0.01
Average		0.09		0.10		0.57		0.92		0.16

The average of concentration: $\bar{X} = \dfrac{\Sigma_n X_i}{n}$

Standard deviation: $sd^2 = \dfrac{\Sigma X_i^2 - (\Sigma X_i)^2/N}{N - 1}$

$$sd. = \left[\frac{\Sigma X_i^2 - (\Sigma X_i)^2/N}{N - 1} \right]^{0.5}$$

B. Determination of analytical accuracy

Because the VOC measurements encompass an unspecified mixture of various organic compounds, absolute accuracy is not readily determined. The quality control of sample for evaluating analytical performance should include the canister blank, spiked samples, and comparison with the other VOC analytical method.

1. Canister blank testing

Canister blanks can be analyzed by NMOC or VOC analytical methods, after cleaning the canisters, the total organic compounds in the canister can be checked by the NMOC method, which only takes 5 minutes. While the individual compounds present in the blank, can be identified by the VOC method, i. e., by comparison with the chromatogram of the standard. Table 4 shows the results of blank tests on three canisters, done by VOC analysis. The peaks are not the targeted VOC, and the average blank peak area is only 0.12% of the typical sample area, and the standard deviation is 0.035%.

Table 4. Canister blank quality accuracy

Canister	Total peak area of blank	Total peak area of sample	$\frac{\text{Blank}}{\text{Sample}}$ %
1	65	45600	0.14%
2	30	36222	0.08%
3	45	31057	0.14%
		Average	0.12%
		Sd.	0.035%

2. Analysis of spiked sample in canister

The QA testing for unknown spiked sample in canisters was prepared by Environmental Monitoring Systems Laboratory, U.S. EPA Research Triangle Park, NC, on Oct. 29, 87, and was analyzed by the non-predryer VOC analytical method. Table 5 indicates the average concentration of each organic compound in the canister, comparing the analytical results with the prepared concentration as supplied by EPA.

Table 5. Canister QA sample for VOC method comparison (NJIT)

Compound	Prepared ppb A & B	Reported ppb A	Sd.	Diff%	Reported ppb B	Sd.	Diff%
Cfor	5.2	-	-	-	5.0	0.14	-3.8
1.1.1*	3.7	2.6	0.77	-30	2.9	0.56	-22
Bz	5.5	3.0	1.76	-45	3.7	1.27	-33
CCl4	4.2	3.9	0.21	-7.1	5.8	1.13	38
TriC	5.1	3.5	1.13	-31	3.6	1.06	-29
Tol	3.7	2.5	0.84	-32	3.3	0.28	-11
PerC*	4.2	3.8	0.28	-9.5	4.0	0.14	-4.8
Ox	3.9	3.7	0.14	-5.1	5.5	1.13	41
Average			0.73	22.8		0.71	22.8

The average of the average difference %

= (22.8 + 22.8)/2 = 22.8%

The average of the average standard deviation:

Sd. = (0.73 + 0.71)/2 = 0.72 ppb

3. Comparative testing for samples from Tenax adsorbent cartridge and canister

Samples were collected simultanously on tenax traps and in canisters. The Tenax sample was thermally desorbed, transfered to a 10 ml volume cylinder, which is cooled to -60°C, and pressurized to 60 psi. The standard gas tank is replaced by the sample cylinder as shown in the Fiure 13., the vent port of V2. is connected to the vaccum system including the pressure gauge and shut-off valve. The 2 ml

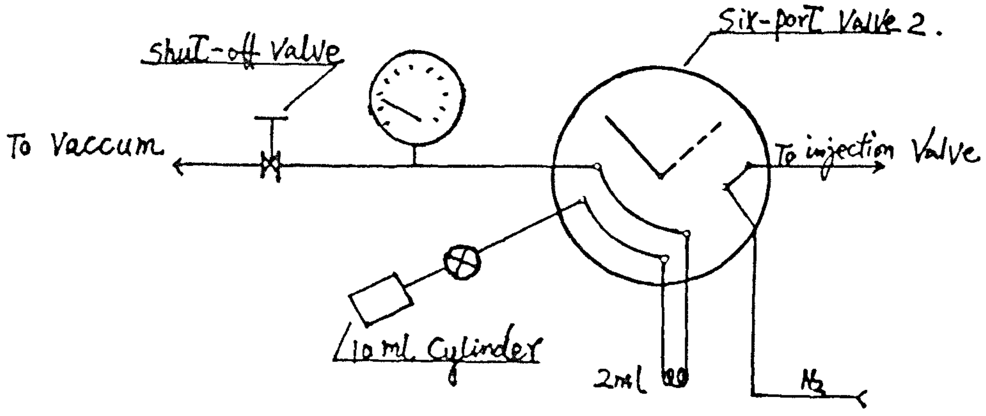

Figure 13. 10 ml cylinder connected with six-port valve 2. chart

loop is evacuated to below 1 mm pressure, closing the shut-off valve, then the sample is injected by turning on the valve of sample cylinder. After the pressure of 2 ml loop rises to the desired pressure, the valve of the cylinder is closed, and V2. is switched to the dotted line position, allowing the nitrogen to pass through the 2 ml loop following the procedure of VOC analysis. Table 6 lists the comparison of VOC concentration in the ambient air, collected by the canister and the Tenax trap.

Table 6. Comparison of VOC concentration in the canister and Tenax trap

	Canister	Tenax				
Compound	ppb (a)	ppb (b)	ppb (c)	Sd.(1)	Sd.(2)	Sd.(3)
MeCl	0.07	0.09	0.86	0.01	0.54	0.45
DCM	0.09	0.12	2.29	0.02	1.53	1.26
C6	1.25	2.67	2.08	1.00	0.41	0.71
CFor	0.10	0.23	2.28	0.09	1.50	1.22
1.1.1*	0.08	0.06	0.68	0.01	0.43	0.35
Bz	1.47	2.32	2.44	0.60	0.08	0.52
CCl4	0.16	0.12	0.00	0.03	0.08	0.08
TriC	0.80	0.06	0.53	0.52	0.33	0.37
Tol	3.86	6.22	6.70	1.66	0.34	1.52
PerC*	0.09	0.12	1.12	0.02	0.70	0.58
PMX	0.79	1.55	0.87	0.53	0.48	0.42
OX	0.02	0.47	0.74	0.31	0.19	0.36
			Average	0.40	0.55	0.65

Air sample was collected in Carteret NJ on 10/12/87.

ppb (a) --- air sample was collected by canister and analyzed by VOC method.

ppb(b)--- air sample was collected by tenax trap, transfered to 10 ml cylinder, and analyzed by VOC method.

ppb (c) --- air sample was collected by tenax trap, transfered to 10 ml cylinder, analyzed on another GC.

Sd. (1) --- the standard deviation between (a) and (b).

Sd. (2) --- the standard deviation between (b) and (c).

Sd. (3) --- the standard deviation between (a), (b), and (c).

The equation for the calculation of the air sample concentration from the Tenax trap is derived as follows:

10 ml cylinder: $V_c = 10$ ml

$P_c = 60$ psi $= 4$ atm

$T_c = -60^{o}C = 213^{o}K$

At normal condition: $P_n = 1$ atm, $T_n = 25^{o}C = 298^{o}K$.

$$V_{n1} = \frac{P_c \times V_c \times T_n}{T_c \times P_n} = \frac{4 \times 10 \times 298}{213 \times 1} = 56 \text{ ml}$$

Sample loop condition: $V_s = 2$ ml, $T_s = 100^{o}C = 373^{o}K$,

$P_{s1} = 0$ psi, assume $P_{s2} = 14$ psi.

$$V_{n2} = \frac{P_{s2} \times V_s \times T_n}{T_s \times P_n} = \frac{14 \times 2 \times 298}{373 \times 14.7} = 1.52 \text{ ml}$$

$$\frac{V_{n2}}{V_{n1}} = \frac{1.52}{56} = 0.027$$

The volume of air passed through to the Tenax trap was:

$V_t = n\ 1,$

the volume of air sample which was injected into the GC:

$V_{sample} = n\ 1 \times V_{n2}/V_{n1}$ (liter)

Sample concentration in the air

$$= \frac{\text{Area}_{sample} \times \text{Std.(ppm)} \times V_{std.}\text{(ml)}}{\text{Area}_{Std.} \times V_{sample}}$$

$$= \frac{\text{Area}_{sample} \times \text{Std.(ppm)} \times 1.6}{\text{Area}_{Std.} \times V_{sample}} \text{ (ppb)}$$

V. NAFION TUBE TESTING AND EFFECT OF CARBON DIOXIDE ON VOC ANALYSIS

A. Testing of Nafion sample dryer

Because the concentration of volatile organic compounds in the ambient air is on the trace level (0 - 15 ppbv), preconcentration is accomplished by passing the whole air sample through a cooled glass bead trap as described above. The injected volume of sample has to be adjusted depending on the ambient temperature, and relative humidity. In summer time sampling, if the temperature is over 30°C, and relative humidity is over 75%, only 0.5 liter of air sample can be injected. If the temperature is down to 25°C, and relative humidity is below 50%, 0.7 liter of sample volume can be injected. In order to increase the detector sensitivity, the sample volume has to be increased. Nafion tube dryers can utilize a hygroscopic, ion exchange membrane in a continuous drying process to selectively remove water vapor from mixed gas streams. The membrane is a proprietary extrudible polymer in tubular form. A single dessicant tube is fabricated in a shell and tube configuration and sealed into an impermeable shell which has openings adjacent to the sample inlet and product outlet (Figure 15.). If a wet gas stream flows through the tubes and a countercurrent dry gas stream purges the shell, water vapor molecules are transferred though the wall of the tubing [23]. Perma pure dryers (MD-125-12F, MD-125-48F) were purchased from Perma-Pure, Farmingdale, NJ. The dryer was cleaned by purging with nitrogen at 40 ml/min, both inside and outside tube, keeping the temperature at 80°C, for 96 hours. Blank testing indicates that the contamination in the dryer tube was reduced to an acceptable level after 4 days of cleaning. Then, the dryer was connected between the canister and the injection tube, keeping the dryer at room temperature (25 - 28°C), as suggested by the Perma-Pure and EPA [24, 25], the sample flow rate is set at 80 ml/min, and the nitrogen purging flow rate at 300 ml/min. After sample injection, the dryer was cleaned and purged of adsorbed water by passing nitrogen through the inside tube at 80 ml/mim, heating to 80°C, then cooling to room temperature before the next experiment.

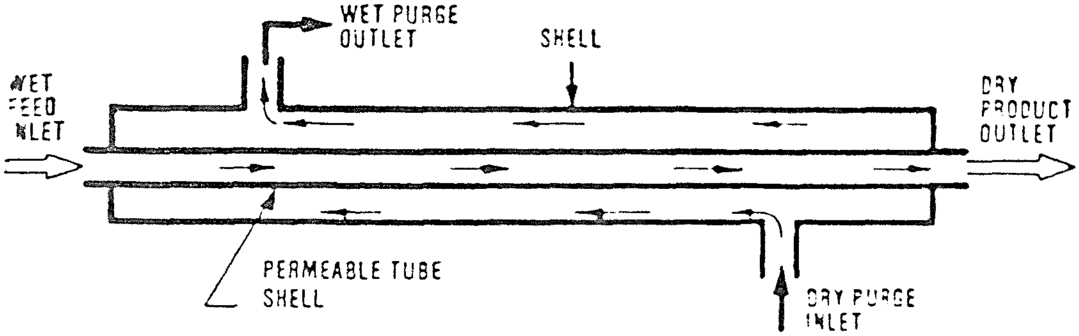

Figure 14. Dryer performance chart

Several experiments showed that there is still a large peak in the chromatogram where the C_1 to C_3 hydrocarbons elute (Figure 15.), even larger than that found when the sample dryer was not used. There are two possible explanations. Either organic compounds were desorbed from the dryer while the air sample was being injected, or more water was being injected, due to the increased the volume of sample, if the dryer does not work. To gain insight into the cause of this problem, a sample from a canister was analyzed by mass spectrometer. The result indicated that there is a large amount of carbon dioxide in the sample as shown in Figure 16. and 17. Therefore, the presence of carbon dioxide becomes a major problem in this analytical method.

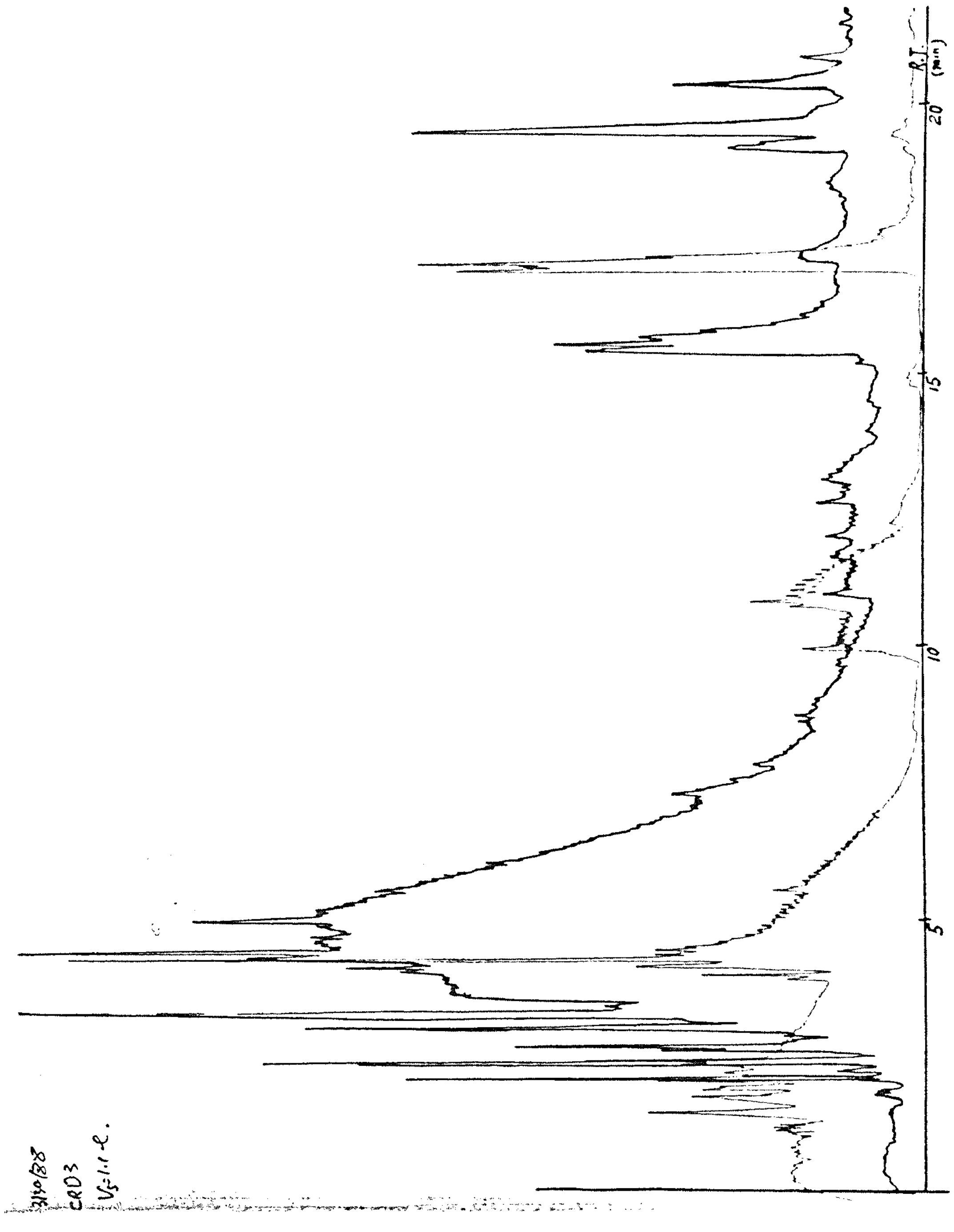

Figure 15. Air saple passes through dryer

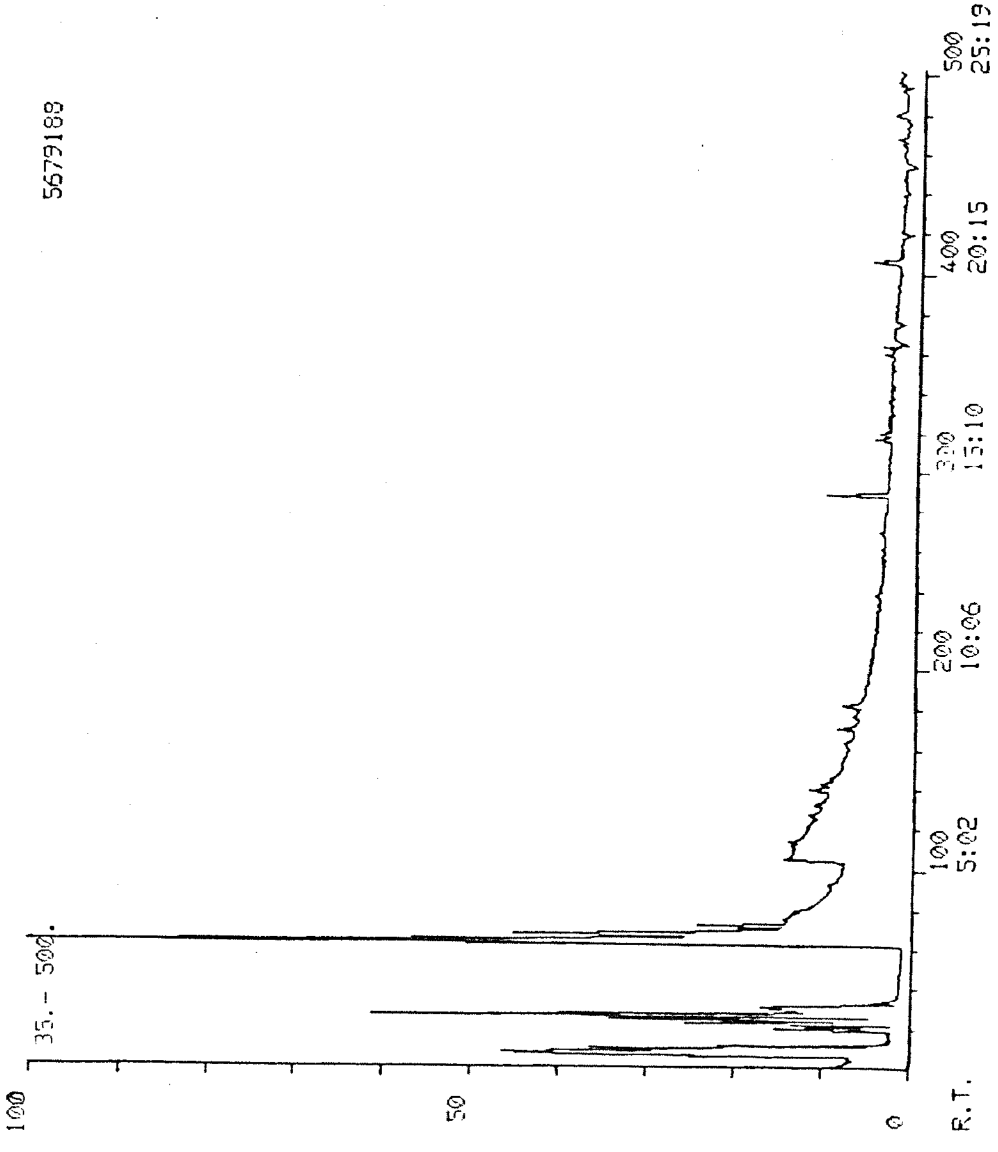

Figure 16. MS chromatogram of sample in canister

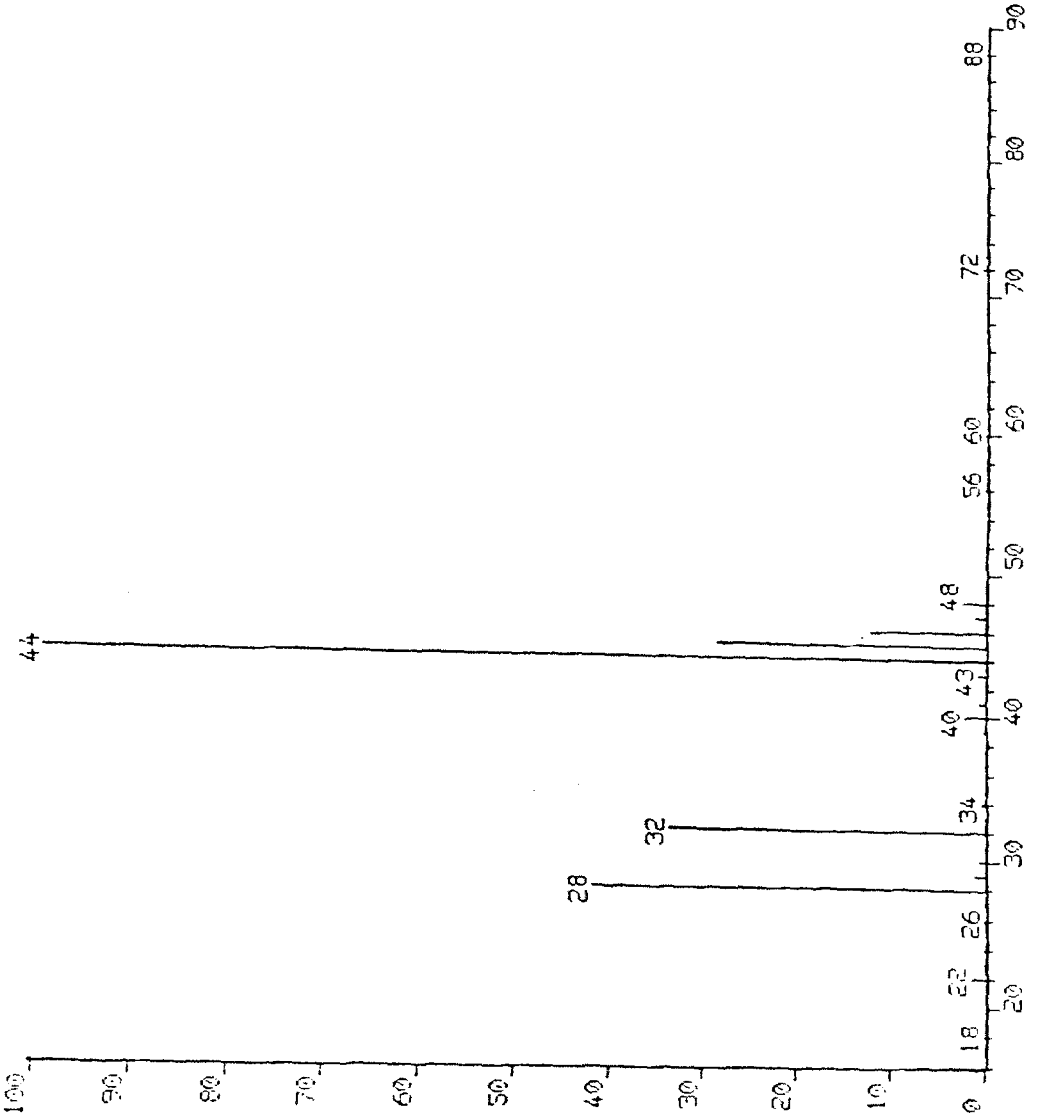

Figure 17. MS chart of peak at RT = 3:09 min
of Figure 16. sample

B. Effect of carbon dioxide on VOC analysis

Carbon dioxide exists in air at a concentration of 0.03% by volume, or 0.0474% by weght [24].

Assuming that 0.5 liter air sample is injected,

the volume of CO_2 = 500 ml X 0.03% = 0.15 ml

Also, from the air temperature at the time of sampling, and the relative humidity, the volume of water in the sample can be calculated.

Assuming T = 25°C, relative humidity = 50%.

From chapter III, the volume of liquid water in 0.5 liter

$$= 5.93 \times 10^{-3} \text{ g} \times 1 \text{ ml/g} = 5.93 \times 10^{-3} \text{ ml}$$

$$\frac{\text{Volume of gaseous } CO_2}{\text{Volume of liquid } H_2O} = \frac{0.15}{5.93 \times 10^{-3}} = 25.3$$

From chapter III, 0.5 liter air weight about 0.53 g.

The moles of carbon dioxide in 0.5 liter air

$$= \frac{0.53 \text{ g} \times 0.0474\%}{48 \text{ g/mol}} = 5.2 \times 10^{-6} \text{ mole } CO_2$$

The melting point of carbon dioxide is -78.5°C [26]. When the air sample is allowed to pass through a liquid argon (-186°C) cooled glass bead trap, the organic compounds, moisture, and carbon dioxide are condensed in the trap and are transferred to the liquid nitrogen cooled first coil of the capillary column. After the liquid nitrogen container is replaced by the hot water bath, the organic compounds, along with the moisture and carbon dioxide are volatilized rapidly. Because the carbon dioxide has the lower boiling point (-37°C) [24] than water (100^{o}C), it rapidly expands to a volume of 0.15 ml again, which is 25 times of the volume of liquid water, spreading out the narrow focused band of compounds in the first coil of the column. The water, on the other hand, is less volatile than most of the compounds and evaporates slowly, causing less disruption to the band of sample.

An attempt was made to remove the carbon dioxide from the sample in second focusing trap by putting the first coil of the column into a cooled iso-propanol bath (-60^{o}C) instead of liquid nitrogen bath. Figure 18. indicates that, while the carbon dioxide escaped, the lighter organic compounds including benzene, were also not condensed in the focusing trap during the transfer period. The heavier compounds eluting later than benzene, however, are focused very well, as is demostrated on the chromatographic chart.

From the gas equilibrium chart in appendix III [27], under 0.005 atm partial pressure, and a temperature of -130^{o}C condition, gaseous carbon dioxide will be converted to solid. Because n-propanol has the melting point temperature of -127^{o}C, it is convenient to prepare a bath of -105 to -115^{o}C by mixing it with liquid nitrgen. Then the light volatile organic compounds, including chloromethane, can be condensed in the glass bead trap, without freezing the carbon dioxide, by using a -110^{o}C bath of n-propanol slush.

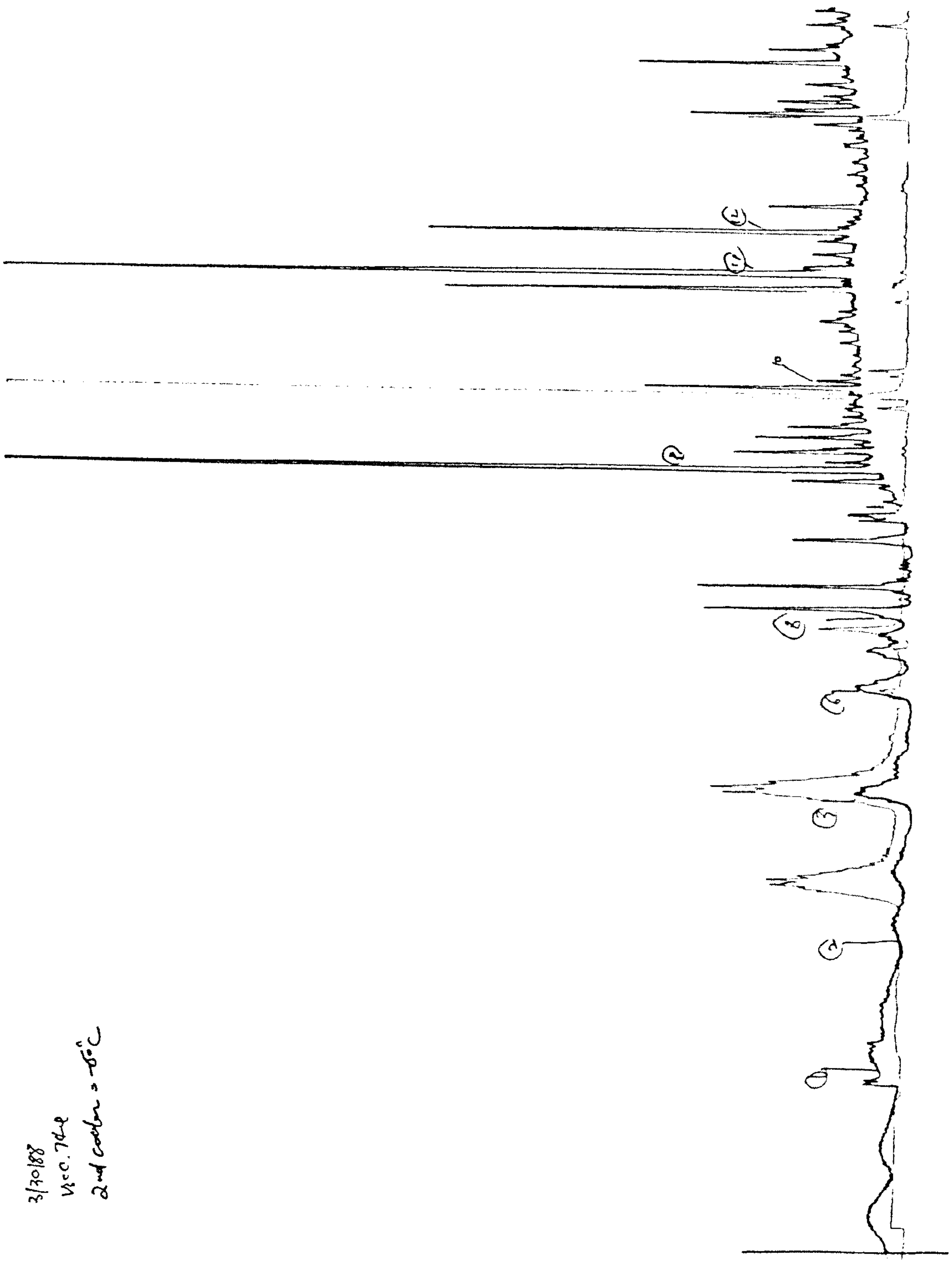

Figure 18. Using iso-propanol coolant (-60°C) on second trap

CRF1

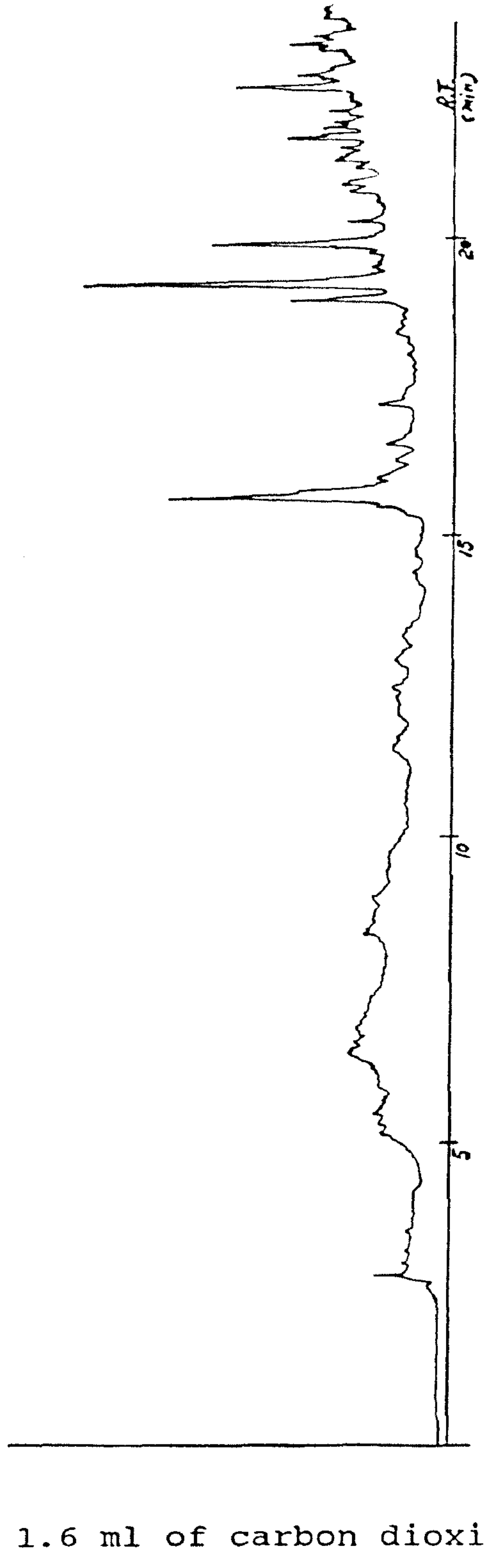

Figure 19. Sample spiked with 1.6 ml of carbon dioxide using liquid argon coolant

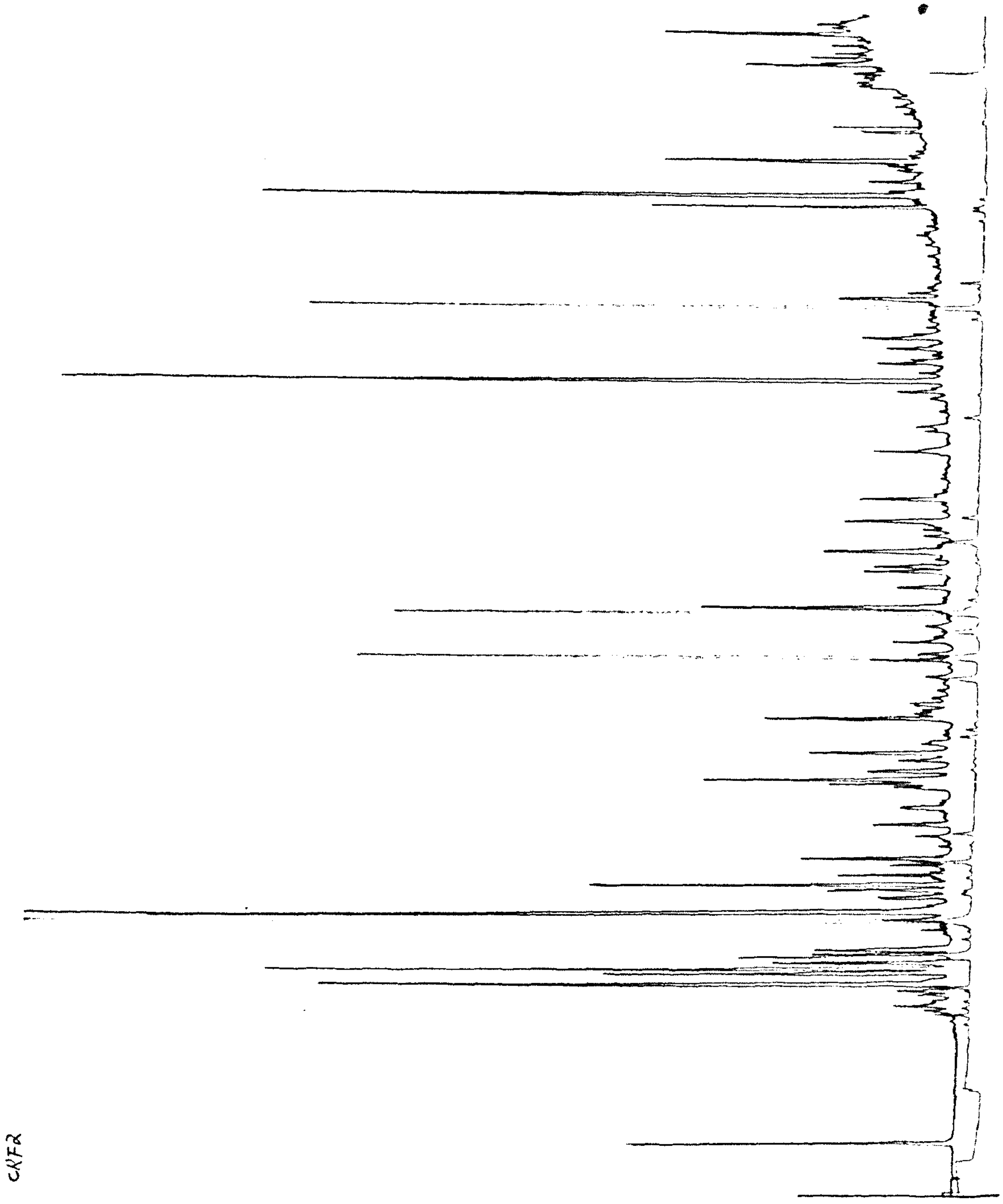

Figure 20. Sample spiked with 1.6 ml of carbon dioxide using n-propanol cold bath

1. Comparison testing of sample spiked with carbon dioxide

The effect of carbon dioxide on VOCs analysis can be shown by using different temperature coolant baths on the glass bead trap. The comparison testing of air sample spiked with carbon dioxde are based upon the analytical procedure of VOC standard gas, and spiked sample analysis (chapter II B.3 and 4). The standard gas tank is replaced by carbon dioxide tank, measuring the carbon dioxide in a 2 ml loop, and following the procedure of the spiked sample analysis. In the first experiment, the glass bead trap is cooled in liquid argon (-186°C). In the second experiment, the glass bead trap is cooled in a n-propanol (-110°C) bath. Figures 19. and 20. show that there is a significant difference between the two experiments. In the first case (Figure 19.), the chromatographic base line is shifted by the added carbon dioxide, and the peaks are wider, giving poorer resolution. Figure 20. shows the extremely good separation, with sharp peaks because the carbon dioxide did not condense in the -100°C trap.

2. Collecting ability of targeted VOC testing

If a higher temerature trap is to be used, it is necessary to show that the target compounds are quantitatively trapped. 1.44 ml of the standard gas mixture, containing no carbon dioxide is run using the liquid argon cooled trap as described in chapter II B.3. This is compared with the same standard, trapped in the n-propanol bath at -108°C. The results are shown in Table 7. There is no significant loss by using n-propanol coolant.

Table 7. Comparison of trapping efficiency at two temperatures

Compound	Test 1 -108°C	Test 2 -186°C	Diff. 2 - 1	Diff.% (2 - 1)/2
1. MECl	635	853	228	26.7
2. DCM	2613	2540	-73	-2.8
3. C_6	10456	9736	-720	-7.4
4. CFOR	2427	2338	-89	-3.8
5. 1.1.1*	1913	2377	464	19.5
6. BZ	12082	12791	709	5.5
7. CCL_4	1094	1158	64	5.5
8. TRIC	3787	4231	444	10.5
9. TOL	12467	12259	-208	-1.7
10. PERC*	2626	2617	-9	-0.3
11 PMX	7146	7278	102	1.4
12. OX	10217	10544	327	3.1
			Average	7.35

3. Reproducibility testing

An air sample, collected at Newark, NJ. on 3/28 - 3/29/88, was subjected six replicate analyses, using the n-propanol -106 to - 110°C trap. The data is listed in Table 8, and 9. and Figure 21. shows the VOC chromatogram. We conclude here that the -106 to -110°C traps collect the VOCs effectively.

Sampling date: 3/28 - 3/29/88

Sampling site: Newark

Canister ID: E

Table 8. Peak areas for six replicates

	Std. 1.6ml	NEE1 0.861	NEE2 0.861	NEE3 0.821	NEE4 0.821	NEE5 0.861	NEE6 0.861
1. MECl	635	24	24	43	31	35	46
2. DCM	2613	225	240	268	233	248	228
3. C6	10456	513	636	618	587	687	732
4. CFOR	2427	97	109	98	71	102	94
5. 1.1.1*	1913	186	252	233	280	250	172
6. BZ	12082	678	876	777	740	862	857
7. CCl4	1094	53	55	27	48	44	66
8. TRIC	3787	153	108	79	67	70	98
9. TOL	12467	3492	3638	3241	3232	3625	3543
10. PERC*	2626	93	92	85	88	107	87
11. PMX	7146	1359	1383	1202	1201	1356	1348
12. OX	10217	514	542	442	431	551	541

Table 9. Concentration of six replicates

	NEE1 ppb	NEE2 ppb	NEE3 ppb	NEE4 ppb	NEE5 ppb	NEE6 ppb	mean ppb	S.D. ppb	RSD %
1.	0.19	0.19	0.36	0.26	0.28	0.36	0.27	0.076	28.2
2.	1.72	1.83	2.15	1.87	1.89	1.74	1.87	0.154	8.2
3.	0.62	0.77	0.79	0.75	0.83	0.89	0.78	0.083	10.6
4.	0.85	0.96	0.90	0.63	0.89	0.82	0.84	0.104	12.4
5.	1.29	1.75	1.70	2.04	1.73	1.19	1.62	0.290	17.9
6.	0.90	1.16	1.08	1.03	1.14	1.13	1.07	0.089	8.2
7.	0.83	0.86	0.44	0.79	0.69	1.03	0.77	0.180	23.2
8.	0.62	0.44	0.34	0.29	0.28	0.40	0.40	0.126	31.5
9.	4.26	4.44	4.15	4.14	4.42	4.32	4.29	0.129	3.0
10.	0.39	0.38	0.37	0.38	0.44	0.36	0.39	0.028	7.1
11.	1.12	1.14	1.04	1.04	1.12	1.11	1.10	0.043	3.9
12.	0.38	0.40	0.34	0.33	0.40	0.40	0.38	0.032	8.4

Average S.D. 0.111

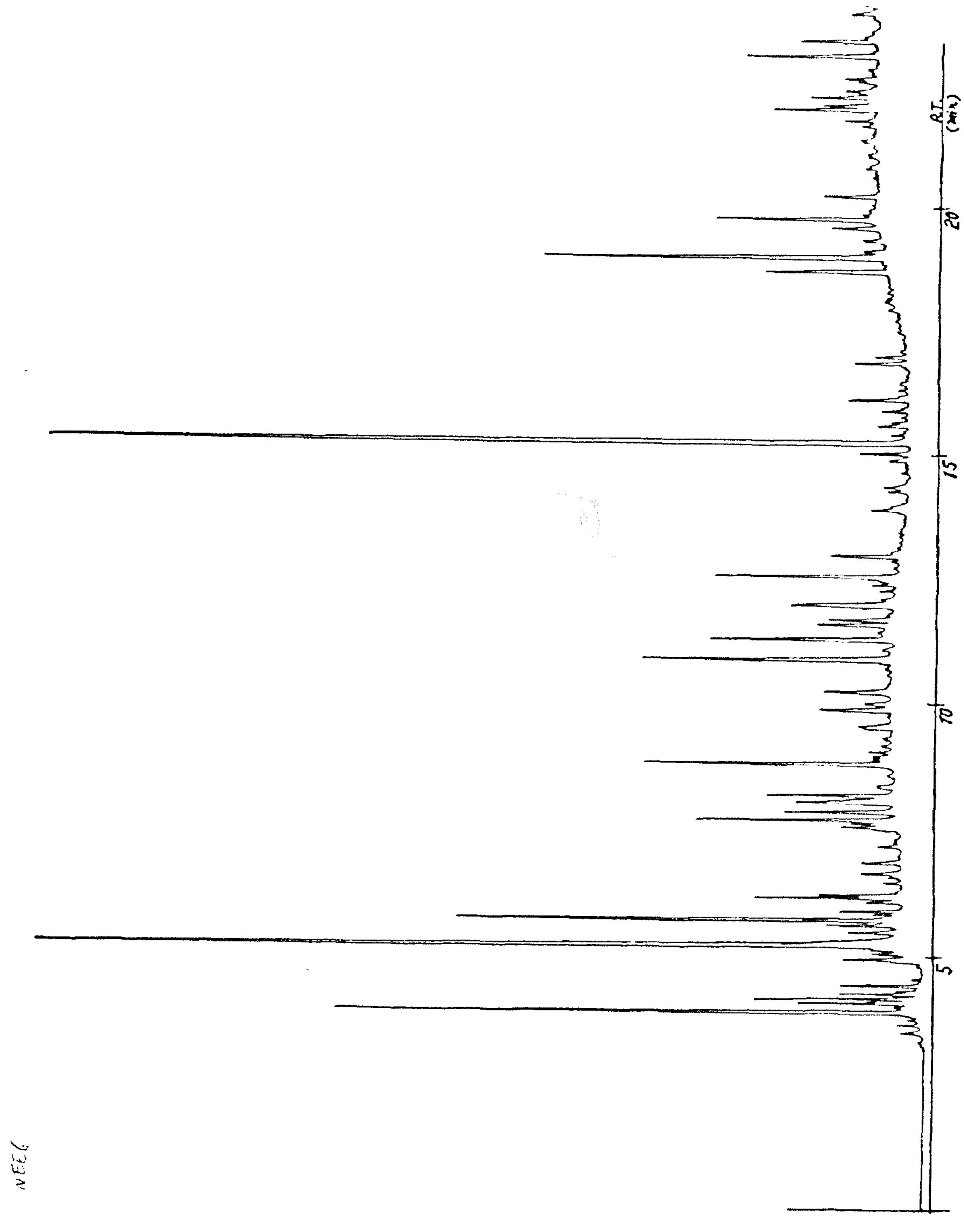

Figure 21. VOC chromatogram using n-propanol coolant

VI. CONCLUSION AND DISCUSSION

The method of gas chromatographic determination of trace volatile organic compounds in ambient air collected in canisters has been studied, and provides an attractive alternative in VOC analysis (compounds of B.P. below 150^{o}C) as a sampling method. The analytical system is sensitive and provides an accurate measurement of VOC concentration in ambient air for concentrations as low as 0.02 ppb by volume. The deleterious effects of carbon dioxide and moisture on VOCs analysis from canister samples has been identified and eliminated. When the sample is concentrated in a trap cooled in n-propanol cold bath (-110^{o}C), the volume of air sample which can be injected is as large as 1.5 liters, and use of a dryer is not needed.

Because the whole air sample can be collected in canister, accurate characterization of volatile organic compounds in the atomsphere sampling, ambient air or any sampled area can be accurately determined. However the air sample is stored after passage through a sampling system, each component of the sampling train (stainless steel tubing, pump, and gauge, etc.) must always be clean. Solid sorbent tubes, on the other hand, are usually the first element in the sampling system. Some contamination was found in the sampling train after it had been used for two years; example a toluene blank of 1 ppb was found, and a deposit of fine particulate was evident on the inner walls. One suggestion is that a 12 liter canister can be used without pump and gauge. The air would enter the evacuated canister only through a filter and a critical orifice, and the stainless steel tube would be made as short as possible, thus, the contamination could be reduced.

APPENDIX I

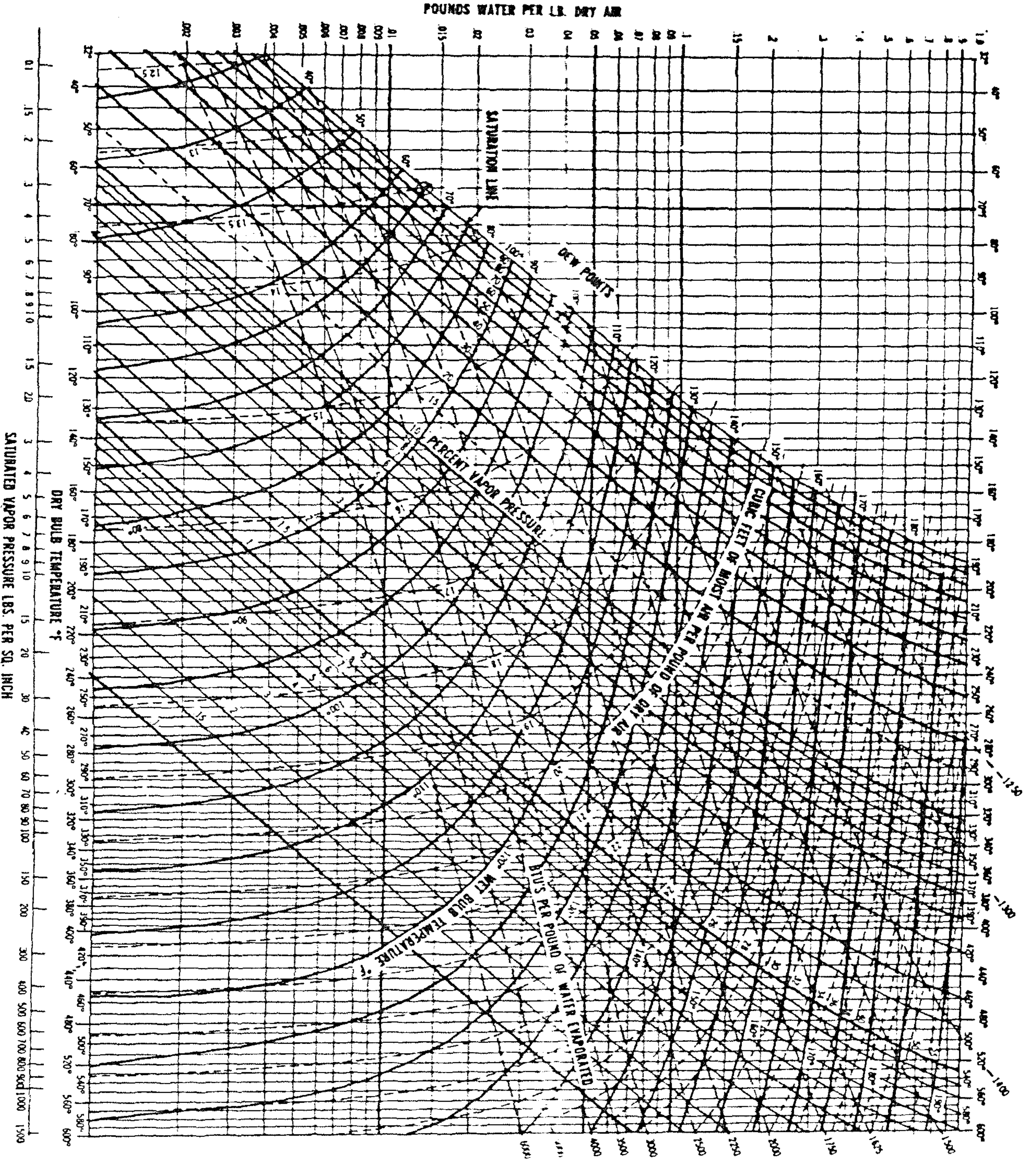

Fig. 20-11. Psychrometric chart. Properties of air and water-vapor mixtures from 32° to 600°F. *(Proctor & Schwartz, Inc.)*

APPENDIX II

DENSITY OF DRY AIR

AT THE TEMPERATURE t, AND UNDER THE PRESSURE H CM OF MERCURY THE DENSITY OF AIR

$$= \frac{0.001293}{1+0.00367\,t}\,\frac{H}{76}.$$

Units of this table are grams per milliliter
(From Miller's Laboratory Physics, Ginn & Co., publishers, by permission.)

t	Pressure H in Centimeters					
	72.0	73.0	74.0	75.0	76.0	77.0
°						
10	0.001182	0.001198	0.001215	0.001231	0.001247	0.001264
11	178	193	210	227	243	259
12	173	190	206	222	239	255
13	169	186	202	218	234	251
14	165	181	198	214	230	246
15	0.001161	0.001177	0.001193	0.001210	0.001226	0.001242
16	157	173	189	205	221	238
17	153	169	185	201	217	233
18	149	165	181	197	213	229
19	145	161	177	193	209	225
20	0.001141	0.001157	0.001173	0.001189	0.001205	0.001221
21	137	153	169	185	201	216
22	134	149	165	181	197	212
23	130	145	161	177	193	208
24	126	142	157	173	189	204
25	0.001122	0.001138	0.001153	0.001169	0.001185	0.001200
26	118	134	149	165	181	196
27	115	130	146	161	177	192
28	111	126	142	157	173	188
29	107	123	138	153	169	184
30	0.001104	0.001119	0.001134	0.001150	0.001165	0.001180

Proportional Parts	
	17
cm	
0.1	2
0.2	3
0.3	5
0.4	7
0.5	8
0.6	10
0.7	12
0.8	14
0.9	15
	16
cm	
0.1	2
0.2	3
0.3	5
0.4	6
0.5	8
0.6	10
0.7	11
0.8	13
0.9	14
	15
cm	
0.1	1
0.2	3
0.3	4
0.4	6
0.5	7
0.6	9
0.7	10
0.8	12
0.9	13

DENSITY OF WATER

The temperature of maximum density for pure water, free from air = 3.98C (277.13K)

t, °C	d, gm/ml	t, °C	d, gm/ml
0	0.99987	40	0.99224
3.98	1.00000	45	0.99025
5	0.99999	50	0.98807
10	0.99973	55	0.98573
15	0.99913	60	0.98324
18	0.99862	65	0.98059
20	0.99823	70	0.97781
25	0.99707	75	0.97489
30	0.99567	80	0.97183
35	0.99406	85	0.96865
38	0.99299	90	0.96534
		95	0.96192
		100	0.95838

APPENDIX III

THERMODYNAMIC PROPERTIES

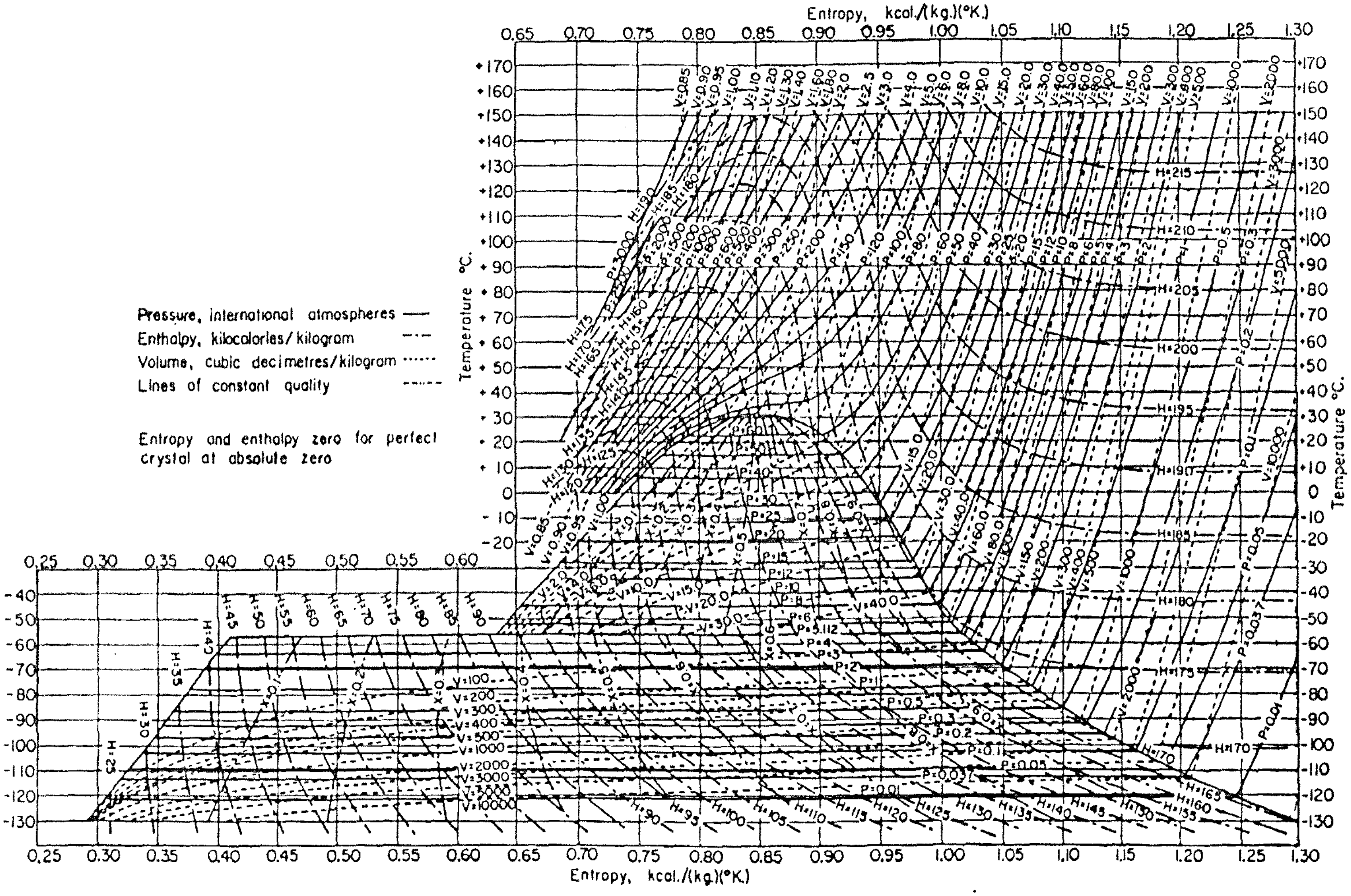

Fig. 3-19. Temperature-entropy diagram for carbon dioxide. [*From "Thermodynamic Functions of Gases," vol. 1, Butterworth, London, 1956. Copyright material. Reprinted by permission of the authors and publishers. A wall-sized reproduction of this diagram is obtainable from Butterworth & Co. (Canada), Ltd.*] .

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