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Atmospheric Hydrocarbon Analysis

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THESIS APPROVAL

The abstract and thesis of Dawei Han for the Master of Science in Chemistry

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AN ABSTRACT OF THE THESIS OF Dawei Han for the Master of Science
in Chemistry presented December 9 , 1993.

Title: Atmospheric Hydrocarbon Analysis

This treatise studied two correlated important issues in
atmospheric chemistry: real-time monitoring of ambient air and
removal mechanisms of atmospheric hydrocarbons. An analytical
system was designed for the purpose of identification and
measurement of sub-ppb level hydrocarbons of different reactivities
in air samples. This analytical system was then applied to a series of
smog-chamber studies which simulated the removal of reactive
hydrocarbons from the atmosphere by reaction with hydroxyl
radicals. Six representative atmospheric hydrocarbons (hexane,
octane, toluene, m-xylene, o-xylene and mesitylene) were selected
for these experiments. The experimental data indicated that the
decay of atmospheric hydrocarbons under laboratory conditions is
entirely due to reaction with hydroxyl radicals. The conclusion drawn
from a time-resolved plume study that aromatic molecules decay
much faster than could be accounted for solely by reaction with
hydroxyl radicals was not verified; this indicates a difference
between laboratory study and the study in the real atmosphere, and
some physical factors besides chemical mechanism might take a

more significant role in removing aromatics faster from the atmosphere.

ATMOSPHERIC HYDROCARBON ANALYSIS

by

DAWEI HAN

A thesis submitted in partial fulfillment of the
requirements for the degree of

MASTER OF SCIENCE
in
CHEMISTRY

Portland State University
1993

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CHAPTER I

INTRODUCTION

Atmospheric hydrocarbons (also called volatile organic compounds, VOCs) are important factors in tropospheric chemistry. Due to their high photochemical reactivity and complex photo oxidation mechanisms, many VOCs are relevant participants in the photochemical atmospheric reaction chains and cycles even if they are present in levels as low as a few ppb or even fractions of a ppb. Current control strategies depend on hydrocarbon abatement as the primary means of controlling photochemical air pollution (Singh, 1981). Information on hydrocarbon species present in ambient air is important to help pinpoint sources of emissions, as well as to provide data necessary for photochemical modeling studies. The relative composition of hydrocarbons in ambient air has been used as an indicator of different source contributions to the atmosphere . In addition, because VOCs differ in their ability to produce oxidants, a strategy based on the control of those VOCs that manifest themselves most strongly in smog formation would constitute a potentially superior technical approach that could also be cost-effective. (Singh, 1981)

It has been long considered that aromatic hydrocarbons are more reactive than aliphatic hydrocarbons, but the decay of both

aromatic and aliphatic hydrocarbons is entirely due to reaction with hydroxyl radicals. (Roberts, 1984; Singh, 1981) However, based on their time-resolved plume studies, N.J. Blake and his research fellows found out that aromatic hydrocarbons decay much faster than could be accounted for solely by reaction with hydroxyl radicals. They thus brought up the hypothesis that atmospheric removal processes other than reaction with hydroxyl radicals are occurring. The central objective of this treatise was to test this hypothesis by means of smog-chamber studies in the laboratory.

For the purpose of smog-chamber experiments, an analytical system was first devised which enables measurements to be made of many different atmospheric hydrocarbons, including alkanes, alkenes and aromatics. This system is mainly composed of three components: (1) an on-line continuous sampling device with cryogenic preconcentration; (2) GC/FID detection ; (3) a self-designed data processing software. This system was successful in monitoring the ambient air in the Portland metropolitan area.

A smog chamber was set up in the laboratory to simulate the removal reactions with hydroxyl radicals. Seven hydrocarbons including two aliphatic compounds (hexane and octane), and four aromatic compounds (mesitylene, toluene, m-xylene and o-xylene) were chosen for the smog-chamber experiments. The theoretical reaction rates derived solely from the reactions with hydroxyl radicals were checked against experimental data. It turned out that experimental reaction rate ratios were in fairly good agreement with those theoretical values. These results verified again that the

hydroxyl radical is the principal agent responsible for the destruction of both aliphatic and aromatic hydrocarbons under laboratory conditions. N. J. Blake's hypothesis was not confirmed under these conditions, which implied that in the real atmosphere there might be some factors other than chemical mechanism contributing to the removal process of atmospheric hydrocarbons.

CHAPTER I I

OVERVIEW OF VOLATILE ORGANIC COMPOUNDS

DEFINITION

The following definition of volatile organic compounds (VOCs) given by the US Environmental Protection Agency seems to be the best so far:

> A volatile organic compound (VOC) is any organic compound that, when released to the atmosphere, can remain long enough to participate in photochemical reactions. While there is no clear line of demarcation between volatile and non-volatile organics, the predominant fraction of the VOC burden are compounds which evaporate rapidly at ambient temperatures. Almost all organics which can be considered VOC have vapor pressures greater than 0.1 mm of Hg at standard conditions (20 °C and 760 mm Hg).

Furthermore, current preference is to exclude methane, where possible, from VOC emission estimates since it does not participate in photochemical reactions.

THE ROLE OF VOCS IN PHOTOCHEMICAL SMOG

Many of the VOCs play a critical role in the photochemical reactions resulting in the formation of photochemical smog, which is recognized as a severe environmental pollution. Photochemical smog formation is defined as the production of gaseous and aerosol products as a result of reactions between oxides of nitrogen,

hydrocarbon and oxygen in the air, under the influence of solar radiation (Demerjian, 1974). A complex range of substances, including ozone, aldehydes, hydrogen peroxide, peroxyacylnitrates, free radicals and particulate characterize the reaction products. The kinetic scheme describing the HC-NOx photo-oxidation is complex, and the complete description is outside the scope of this treatise. The primary step in ozone formation, however, is the photolysis of nitrogen dioxide as given in reaction (1), followed by reaction (2) and (3).

$$NO_2 + hv \xrightarrow{k_1} NO + O \quad (1)$$
$$O + O_2 \xrightarrow{k_2} O_3 \quad (2)$$
$$O_3 + NO \xrightarrow{k_3} NO_2 + O_2 \quad (3)$$
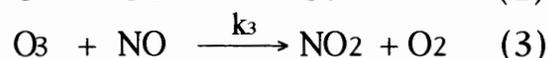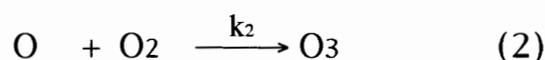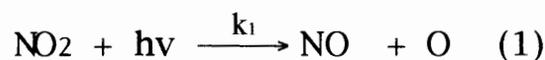
From these equations the photo-stationary state of O_3, which is often used as an index for photochemical smog formation is determined by equation (4):

$$[O_3] = (k_1 [NO_2]) / (k_3 [NO]) \quad (4)$$

Reactions (1)-(3) are termed the $NO/NO_2/O_3$ photostationary state (PSS). In the absence of hydrocarbon pollutants the NO_2 to NO ratio is such that significant build-up of ozone is not permitted.

However, in the presence of hydrocarbons ozone production occurs when the PSS is disturbed by reactions such as (5) and (6), which convert the NO into NO_2 rapidly, permitting the O_3 to build up.

$$CH_3O_2 + NO \longrightarrow NO_2 + CH_3O \quad (5)$$
$$HO_2 + NO \longrightarrow HO + NO_2 \quad (6)$$

Such reactions are mostly initiated by reactions of hydrocarbons with hydroxyl radicals and eventually lead to photochemical smog (Altwicker, 1990).

Numerous studies have been carried out on the effects of photochemical air pollution. The primary toxicological effects are increased susceptibility to infectious pulmonary disease; pulmonary and systemic biochemical changes; eye, nose and throat irritation; nausea and headaches; impairment of pulmonary function; structural changes in lung tissue; and chromosomal alterations of white blood cells (Calvert, 1976).

Photochemical smog can also affect plants in a visible manner, i.e. necrosis, bronzing, silvering, etc. of leaves, and in an initially less obvious manner, i.e. reduced yield and output. Apart from health effects and plant damage, photochemical smog also has an effect on some materials such as rubber, for which it accelerates the deterioration process (Calvert, 1976).

OTHER ROLES OF VOCS

In addition to their well-known role as precursors of photochemical smog, VOCs have been proposed as (1) significant contributors to the global budget of carbon monoxide (Rudolph, 1985), (2) carriers of reactive nitrogen through their oxidation products such as peroxyacetyl nitrate (Calvert, 1976), (3) possible sinks for Cl atoms in the troposphere and lower stratosphere (Rudolph, 1985), (4) tracers of atmospheric transport (Rudolph, 1985), (5) possible indicators of tropospheric HO radical

concentrations (Calvert, 1976; Singh, 1981, 1985, Roberts, 1984), (6) either directly or indirectly, contributors to the global budget of tropospheric ozone (Rudolph, 1985), and (7) a potentially important link in the global carbon cycle (Rudolph, 1985).

CHEMICAL SPECIES OF VOCS

There are more than 100 VOCs species emitted to the atmosphere from both natural and anthropogenic sources (Purdue, 1991). From available data on methane and terpene emissions, it is estimated that natural emissions of volatile organic compounds (VOCs) are one order of magnitude greater than anthropogenic emissions on worldwide basis (Rudolph, 1985). However, their contribution to the photochemical smog pollution problem is not believed to be significant because natural emissions are widely distributed over the entire globe and are largely composed of methane (at least 70 per cent) which is usually non-reactive photochemically.

THE REACTIVITY OF VOCS

The mixing ratios of VOCs may be as low as a few ppb or even down to a fraction of ppt over very remote areas. It is important to recognize that the highly reactive hydrocarbons do not need to be highly abundant. The atmospheric reaction chain of hydrocarbon oxidation starts mainly with the attack of an HO radical:

$$HC + HO \longrightarrow R + H_2O \quad (7)$$
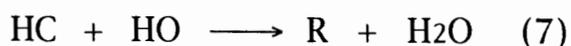
The conversion rate for a given hydrocarbon in the atmosphere then can be written as:

$$-\frac{d[HC]}{dt} = K_{HO}\,[HO]\,[HC] \qquad (8)$$

From this it is evident that for a comparison of the different hydrocarbons with respect to their participation in atmospheric chemistry we have to consider the reaction rate constants as well as the atmospheric concentrations of the individual hydrocarbons if we want to compare their atmospheric reaction rates.

The VOC pattern in the atmosphere is quite complex - even outside urban or industrialized areas (Hough, 1987). Engine exhaust, natural gas leakage, solvent evaporation, plant emissions, etc. contribute a large variety of different organic substances which can be observed at varying levels in the atmosphere. Due to this extremely complex pattern and very low atmospheric mixing ratios the measurement of most of these trace gases requires specially adapted techniques. The most suitable method is programable gas chromatography in connection with a preconcentration step. Chapter III will discuss this issue in detail.

THE ROLE OF HYDROXYL RADICALS

As shown by Eq. (7), the hydroxyl radical is regarded as the principal agent responsible for the destruction of the hydrocarbons in the atmosphere (Roberts, 1984; Singh,1981). In addition, VOCs may also be oxidized by ozone (via ozonation of non-aromatic carbon/carbon double bonds (Atkinson 1990). Based on an hydroxyl

density number of 6×10^5 molecules cm^{-3} (Roberts, 1984) and an ozone number density of 1.3×10^{12} (50 ppbv at 760 Torr, 0°C) the removal of hydrocarbons by reaction with HO radicals prevails over that of reaction with ozone by factors of approximately 500 -1000. It is thus reasonable to make the assumption that reaction with hydroxyl radicals accounts for most of the removal of hydrocarbons (Davis, 1975; Mckeen, 1990). The average hydroxyl radical concentration can be calculated as following:

$$HC \ + \ HO \ \longrightarrow \ R \ + \ H_2O \quad (7)$$
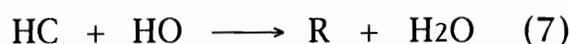
$$- \frac{d[HC]}{dt} = k_{HO} \, [HO] \, [HC] \quad (8)$$

$$dlnHC = k_{HO} \, [HO] \, dt \quad (9)$$

In the smog-chamber studies, the hydrocarbons have no new sources after the initial mixture preparation and share the same HO concentration during the removal process, hence we may get the following relationship between the ratios of hydrocarbon concentrations and the ratios of reaction rates:

$$\frac{dln \ HC1}{dln \ HC2} = \frac{K_{HO1}}{K_{HO2}} \quad (10)$$

Where HC1 and HC2 stand for different hydrocarbon species and k_{HO1} and k_{HO2} stand for their reaction rates, respectively. This expression is independent of reaction time and hydroxyl radical concentration (number density), and predicts that a log-log plot of one ratio vs.

another should give a straight line with a slope equal to the ratio of reaction rates.

This kind of relationship can be utilized to verify whether or not the reaction with hydroxyl radicals accounts for the sole reason for hydrocarbon removal. Based on this idea, smog-chamber studies simulating hydrocarbon removal can be carried out and the ratios of a series of decreasing hydrocarbon concentrations against another are then plotted. The resulting slope is supposed to be equal to the ratio of their reaction rates obtained from reactions with hydroxyl radicals. The detailed design and results of these smog-chamber experiments is presented later in this treatise.

CHAPTER III

VOC CHROMATOGRAPHIC MEASUREMENT ISSUES

TARGET VOCS

VOCs are typically in the C2 through C12 carbon range. Table I presents a list of typical VOCs in the order of their expected chromatographic elution from a J &W DB-1 dimethylsioxane capillary analytical column. Compounds with lower boiling points elute first on this particular analytical column , followed by the heavier molecular weight components with highest boiling points. Concentrations of target VOCs are calculated in units of parts per billion carbon (ppbC), which can be divided by the number of carbon atoms in that compound to estimate the concentrations of VOCs in parts per billion volume (ppbv).

GAS CHROMATOGRAPHY WITH FLAME IONIZATION DETECTION (GC/FID)

GC / FID is the recommended technique for monitoring VOCs in ambient air. The sensitivity, stability, dynamic range, and versatility of GC / FID systems make them extremely useful for measuring very low concentrations of VOCs in ambient air. The basic components of GC / FID systems applicable to these measurements are:

- The carrier gas supply and regulation system;

TABLE I

TARGET VOLATILE ORGANIC COMPOUNDS IN AMBIENT AIR

Acetylene	cis-2-Hexene
Ethylene	Methylcyclopentane
Ethane	2,4-Dimethylpentane
Propylene	Benzene
Propane	Cyclohexane
Isobutane	2-Methylhexane
1-Butene	2,3-Dimethylpentane
n-Butane	3-Methylhexane
trans-2-Butene	2,2,4-trimethylpentane
cis-2-Butene	n-Heptane
3-Methyl-1-Butene	Methylcyclohexane
Isopentane	2,3,4-Trimethylpentane
1-Pentene	Toluene
n-Pentane	2-Methylheptane
Isoprene	3-Methylheptane
trans-2-Pentene	n-Octane
cis-2-Pentene	Ethylbenzene
2-Methyl-2-Butene	p-Xylene
2,2-Dimethylbutane	Styrene
Cylcopentene	o-Xylene
4-Methyl-1-Pentene	n-Nonane
Cyclopentane	Isopropylbenzene
2,3,Dimethylbutane	n-Propylbenzene
2-Methylpentane	1,3,5-Trimethylbenzene
3-Methylpentane	1,2,4-Trimethylbenzene
2-Methyl-1-Pentene	Total NMOC
n-Hexane	
trans-2-Hexene	

- The sample concentration and injection system;
- The analytical or chromatographic separation column;
- The analytical column oven;
- The detection device; and
- the recording or integration device.

In the GC/FID technique, an air sample is taken from a canister

or directly from the ambient air, and passed through the sample concentration system (Kohno, 1991). The concentrated sample is then desorbed and injected onto the analytical column of the gas chromatograph. The VOCs are separated by taking advantage of each compounds distribution between the mobile phase (i.e., the carrier gas) and the stationary phase (i.e., the solid or liquid phase coating on the analytical column). The compounds then elute from the column and enter the detector. The time of elution, or retention time, aids in identification because it is a characteristic of each particular compound.

Typically, a sample taken from an urban environment contains more than100 detectable compounds in the C2 through C12 carbon range, that may be reasonably separated into quantifiable peaks. These compounds are generally present at concentrations varying from less than 0.1 ppbC to greater than 1000 ppbC with the typical concentration being 0.1 to 50 ppbC (Arnts, 1985). Detection of typical urban concentration levels generally requires that samples be concentrated cryogenically in order to selectively concentrate the compounds of interest and not the components of the sample that are not of interest (i.e., air). The retention characteristic of the analytical column must be determined for each target compound using pure compounds or a mixture of pure compounds diluted with inert gas.

Several non-specific but selective GC detectors are available for determining hydrocarbon compounds. The Flame Ionization Detector (FID) is the most widely used and universal GC detector. The FID

provides good sensitivity and uniform response based on the number of carbon atoms in the compound. The uniformity of response allows reasonable estimates of hydrocarbon compound concentration to be determined. This estimate of concentration is achieved by calibrating the FID response with a single representative compound (e.g., propane). The FID also has a broad linear dynamic range of response, allowing analysis of samples with concentrations ranging from nanogram (ng) to milligram (mg) quantities of hydrocarbons (Cox, 1982).

MOISTURE ISSUES

The effects of moisture should be considered in any monitoring program where ambient sample preconcentration is required to increase detection sensitivity. Cryogenic techniques are commonly used for sample preconcentration of C2 through C12 hydrocarbon. Collection of moisture in the cryogenic trap during sample preconcentration can cause several problems. These problems include retention time shifting of the earlier-eluting compounds, column deterioration, column plugging due to ice formation, FID flame extinction, and adverse effects on adsorbent concentration traps and some analytical detectors. If "cold spots" exist in the sample concentration or transfer system, water can collect and cause sample carryover of "ghost" peaks in subsequent sample analyses. This carryover may affect the data by causing chromatographic interferences which affect the resolution, identification, and quantitation of components of interest.

Moisture removal from the sample stream prior to sample concentration minimizes these problems and allows larger sample volumes to be concentrated, thus providing greater detection sensitivity.

Moisture can be removed from the air sample stream using a Perma-Pure® permeable membrane or equivalent drying device. The permeable membrane drying device generally consists of a copolymer of tetrafluoroethylene and fluorosil monomer that is coaxially mounted within a larger polymer or stainless steel tube. The sample stream is passed through the permeable membrane tube, allowing water to permeate through the walls into a dry nitrogen or air purge stream flowing through the annular space between the membrane and the outer tube. To improve drying efficiency and prevent memory effects, the dryer can periodically be cleaned using a procedure that involves heating (typically at 100 degrees centigrade for 20 minutes) and purging with dry N_2 or air.

ANALYTICAL SYSTEM CALIBRATION

It may be impractical and unnecessary to determine compound specific response factors for each of the VOCs, because the per Carbon response of the FID to these compounds is approximately equal. It is possible to measure each compound concentration in terms of ppbC using the relative response factor determined from the standard gas.

For a known, fixed sample volume, the concentration is proportional to the areas under the chromatographic peak. The area

is converted to ppbC using the following equation:

$$C_A \quad = \quad RF \; (AC)$$

Where:

RF	=	Response Factor
AC	=	Area Counts
C_A	=	Concentration (ppbC)

The response factor (RF) is an experimentally determined calibration constant (ppbC/area count), and is used for all compound concentration determinations.

COLUMN SELECTION

Column selection is primarily dictated by total sample analysis time and target compound resolution requirements. Other column selection factors to be considered include practical and cost considerations, such as the need to minimize cryogen consumption. Selecting columns that will provide the desired separation of the C2 through C4 hydrocarbons without cooling the column oven to sub-ambient temperatures will decrease cryogen consumption significantly.

Analyzing the full range of C2 through C12 hydrocarbon using a single analytical column may result in less than optimum separation characteristics for either the light or heavy hydrocarbons, depending on the analytical column chosen. For example, to improve resolution of the C2 through C4 hydrocarbons, a thick liquid phase column and sub-ambient column oven temperatures is desirable. However, the use of thick liquid-phase column results in less than optimum

resolution of the C5 through C12 hydrocarbons, and sub-ambient column oven temperatures result in increased cryogen consumption.

The heavy hydrocarbons (C5 - C12) maybe resolved using a 0.32 millimeter (mm) inside diameter (I. D.), 60 meter (m) J&W®DB-1 fused silica column with a 1-micron dimethylsiloxane coating. However, this column will not provide complete separation of the light hydrocarbons (C2 - C4) even at sub-ambient column oven temperatures. The DB-1 column has been historically and extensively used in ambient air applications. It can be used in conjunction with a 0.32 mm I. D., 50 m Chrompack® Porous Layer Open Tubular (PLOT) fused silica analytical column, with a 5-micron Al2O3/KCl coating. The PLOT column provides acceptable light hydrocarbon separation under the same column oven temperature program conditions used for the DB-1 column but does not provide complete separation of C9-C12 hydrocarbons. The PLOT analytical column is susceptible to moisture, which may cause peak retention times shifting and column deterioration; therefore, moisture must be removed from the sample using a permeable membrane dryer or other drying device (Purdue, 1991).

There are a large number of alternate column options that can be used for C2 through C12 analysis for single column approaches. The recommended manufacturer conditions, along with the carrier gas flow rates, must be evaluated and optimized in order to verify acceptable peak resolution prior to use.

The following columns are alternatives for single-column, light (C2 - C4) hydrocarbon separation and, in some cases, require sub-

ambient oven temperature conditions:

1. J&W DB-1 with a 5-micron dimethylsiloxane phase thickness, an internal diameter of 0.32 mm, and a length of 60 m. The recommended oven temperature program is -60 degrees centigrade (°C) for 2 minutes, to 180 °C at 8 °C per minute. The final oven temperature is maintained for 13 minutes for a total analytical run time of 45 minutes.

2. J&W GS-Q fused silica capillary column with an internal diameter of 0.53 mm and a length of 30 m. The recommended oven temperature is 40°C to 200°C at 4°C per minute. The final oven temperature is maintained for 5 minutes for a total analytical run time of 45 minutes.

The following columns are alternatives for single-column, heavy(C5 - C12) hydrocarbon separation and, in some cases, require sub-ambient oven temperature conditions:

1. Chrompack WCOT (Wall Coated Open Tubular) capillary fused silica column with a 5-micron CP-SIL 5CB dimethylsiloxane stationary phase thickness, an internal diameter of 0.32 mm, and a length of 50 m. The recommended oven temperature program is -20 °C for 5 minutes, to 200°C at 7°C per minutes. The final temperature is maintained for 9 minutes, which results in a total analytical run time of 40 minutes.

2. Restek RTx-502.2 capillary fused silica column with a 3-micron phase thickness, an internal diameter of 0.53 mm, and a length of 105 m. The recommended GC oven temperature program is 35°C for 10 minutes, to 200°C at 4°C per minutes. The final oven temperature is maintained for 7 minutes, which results in a total analytical run time of 58 minutes. This column is capable of separating the C4 through C12 hydrocarbons without the need for sub-ambient column oven temperatures.

VOC MEASUREMENT UNCERTAINTIES

Although a variety of VOC measurements have been performed, there are several uncertainties that remain unresolved. For example, in one atmospheric intercomparison study conducted in a remote area of the Pacific ocean, involving only light hydrocarbons, which were all analyzed using GC/FID, significant differences in hydrocarbon quantitation were evident (Rudolph, 1983). The following major weaknesses exist in present measurement capabilities.

Sampling:

(1) Possible destruction of species by reaction with O_3, NO_2 and / or artifact formation during sampling.

(2) Sample contamination and unrepresentative sampling.

Detection:

(1) Improper and incomplete identification of chromatographic peaks due to lack of GC-MS confirmation.

(2) Lack of chromatographic separation resulting in incorrectly identified and overlapping peaks.

(3) Lack of FID selectivity and sensitivity, and a clear need for more sensitive and specific detectors.

(4) Lack of continuous (slow and fast response) instrumentation

Calibration:

(1) Lack of uniformly available stable standards at low (ppb or ppt) concentrations.

(3) Wide use of carbon response with FID leading to errors in quantitation that may approach 10% for hydrocarbons.

Overall, the basic tools for measurements of VOCs are in hand,

but many improvements are necessary before uniformly reliable data can be obtained. The FID has undergone little change in the last two decades. Sample analysis is cumbersome and usually requires several hours from sample introduction to final tabulation. It is therefore difficult to acquire the temporal and spatial resolution required to adequately define the hydrocarbon distribution so that photochemical models of their effects on the chemistry of the atmosphere can be adequately tested. In addition, since there have been no instruments with the capability for fast continuous operation, it has been difficult to take advantage of micrometerological advances, such as eddy correlation, to measure hydrocarbon fluxes. There is a continuing need for more sensitive snd specific detectors, and for fast continuous instruments that can be used to measure fluxes of specific classes of hydrocarbons.

CHAPTER IV

THE DESIGN OF EXPERIMENTATION

SUMMARY OF METHOD

An analytical system was designed so that a whole air sample can be extracted directly from the ambient air and analyzed on site by the GC system.

The analysis requires drawing a fixed-volume portion of the sample air at a low flow rate through a glass-bead filled trap that is cooled to approximately -195° C with liquid nitrogen. The cryogenic trap simultaneously collects and concentrates the VOCs (either via condensation or adsorption) while allowing the methane, nitrogen, etc to pass through the trap without retention.

After the fixed-volume air sample has been drawn through the trap, a carrier gas flow is diverted to pass through the trap, in the opposite direction to the sample flow, and into an FID. When the residual air and methane have been flushed from the trap and the FID baseline restabilizes, the cryogen is removed and the temperature of the trap is raised to approximately 90°C.

The organic compounds previously collected in the trap revolatilize due to the increase in temperature and are carried into the FID, resulting in a response peak or peaks from the FID. The area of the peak or peaks is integrated, and the integrated value is

translated to concentration units via a previously-obtained calibration curve relating integrated peak areas with known concentrations of standard gases (ethane, propane, butane, pentane and hexane).

The schematic block diagram of the VOC analysis system is shown in Figure 1.

THE DESIGN OF SAMPLING UNIT

For direct ambient air sampling, the cryogenic trapping system draws the air sample directly from a pump-ventilated sample line. A general purpose laboratory pump was used. A Teflon sample inlet line was installed all the way up to the roof of Science Building II and the ambient air samples were drawn directly from the outside atmosphere into the analytical system.

Because Portland City is a " rain city", the humidity is often quite high, which may cause moisture interference to the analytical system. So two measures were adopted to moderate the effect of moisture: (1) Sampling in rainy weather was avoided; (2) A Perma-Pure® permable membrane drying device was used. The sample stream was passed through the permeable membrane tube, allowing water to permeate through the walls into a dry nitrogen purge stream flowing through the annular space between the membrane and the outer tube. To improve drying efficiency and prevent memory effects, the dryer was periodically cleaned using a procedure that involves heating.
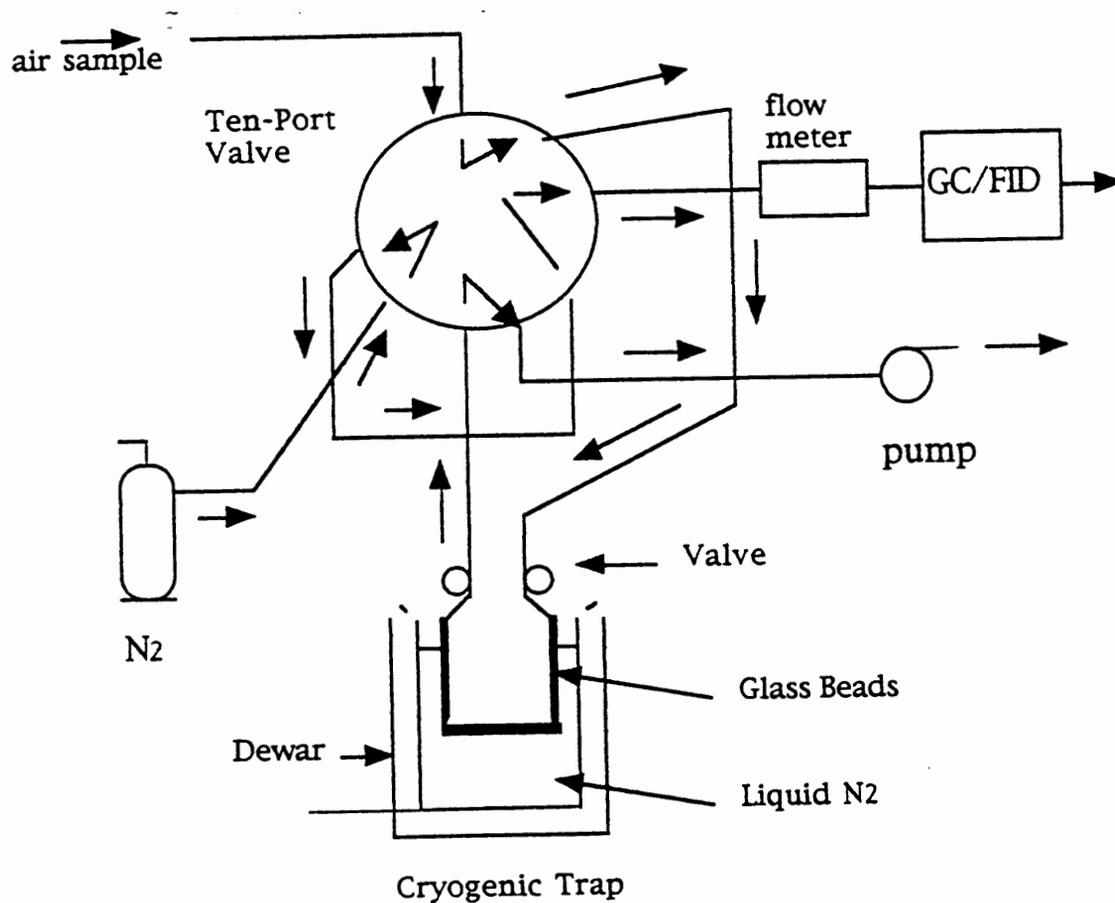
Figure 1 Schematic Diagram of the VOC analytical System (Sampling cycle)

THE DESIGN OF PRECONCENTRATION UNIT

The trap was carefully constructed from a single piece of chromatographic-grade stainless steel tubing (0.32 cm O..D., 0.21 cm I.D.) as shown in Figure 2 . The central portion of the trap (7-10 cm) was packed with 60/80 mesh glass beads, with small glass wool (dimethyldichlorosilane-treated) plugs to retain the beads. The trap fitted conveniently into the Dewar flask, and the arms were of an appropriate length to allow the beaded portion of the trap to be submerged below the level of liquid cryogen in the Dewar. The trap connected directly to the ten-port valve to minimize the line length between the trap and the FID. The trap was mounted to allow the Dewar to be slipped conveniently on and off the trap and also to facilitate heating of the trap.

The ten-port chromatographic valve (Valco) and as much of the interconnecting tubing as practical were wrapped with heating tape which was able to heat up to 80 °C-90 °C to minimize wall losses or adsorption/desorption in the connecting tubing.

A mug filled with boiling water was used to heat the trap to 80°C-90 °C in 1-2 minutes.

Oxygen may deteriorate the column interior surface and thus lead to noisy baseline and poor chromatographic resolution, so oxygen must not be concentrated by the trap when sampling (Purdue, 1991). This was accomplished by adjusting the needle valve mounted next to the trap to control the trap pressure at a low level so that the oxygen can not be condensed by liquid nitrogen. (Purdue, 1991). This was accomplished by adjusting the needle valve
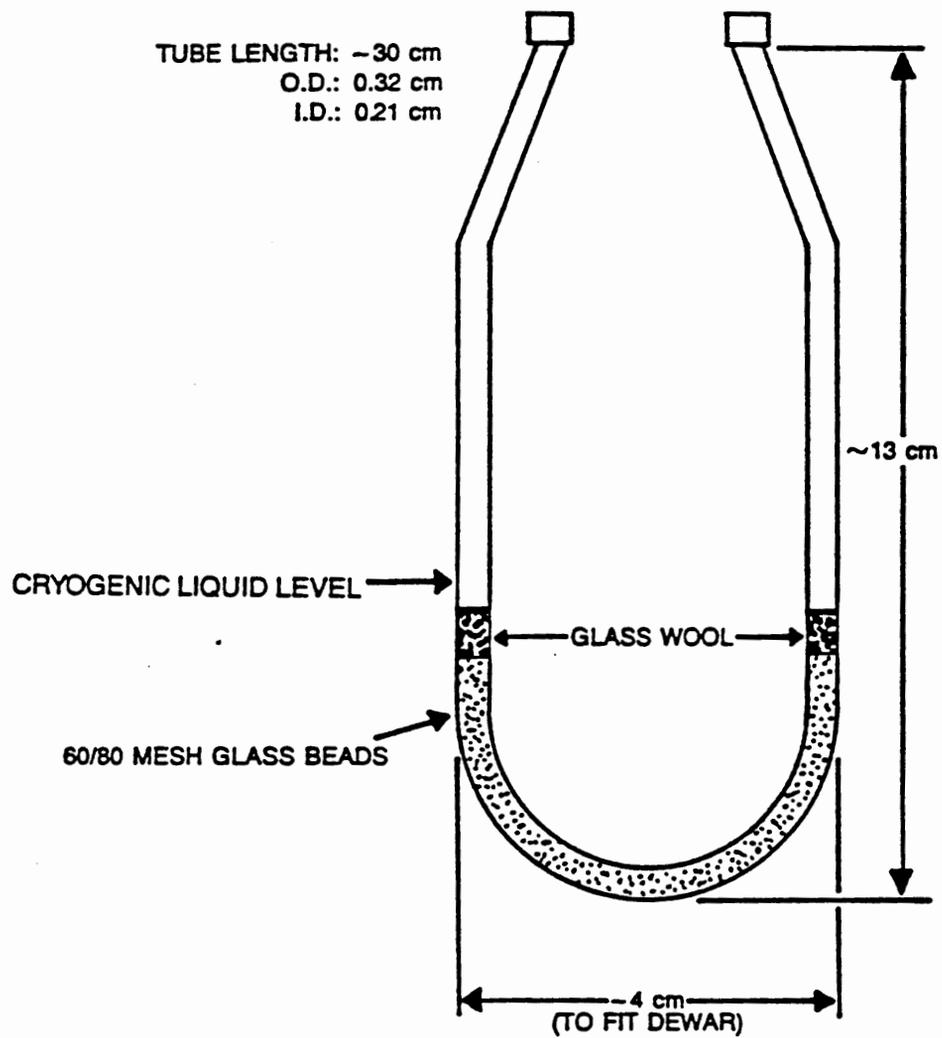
Figure 2 Cryogenic sample trap dimensions

mounted next to the trap to control the trap pressure at a low level so that the oxygen can not be condensed by liquid nitrogen.

An absolute pressure gauge was mounted next to the trap to monitor the pressure of the trap when sampling. Figure 3 shows the ideal trap pressure is about 0.7-0.8 atm.

GC CONDITIONS

In a flame ionization detector, the sample is injected into a hydrogen-rich flame where the organic vapors burn producing ionized molecular fragments. The resulting ion fragments are then collected and detected. The FID is a nearly universal detector. However, the detector response varies with the species of functional group in the organic compound in an oxygen atmosphere so helium was selected as the carrier gas to make the detector response nearly the same for all compounds. Thus, the historical short-coming of the FID involving varying detector response to different organic functional groups was minimized (McClenny, 1984).

Based on the discussion about column selection in Chapter II, a 0.546 millimeter (mm) inside diameter (I.D.), 30 meter (m) long J&W ®GS-Alumia column was chosen. Since the VOC analysis requires measurement of a range of compounds from C2 to C12, the superior efficiency of GS-Alumia provides complete resolution of typical, complex hydrocarbon mixtures including all C4 unsaturates, BTX' s and even decane in a single run. GS-alumina columns are fabricated using a highly automated "HRQ" coating process, which yields columns with remarkably reproducible performance. Another reason
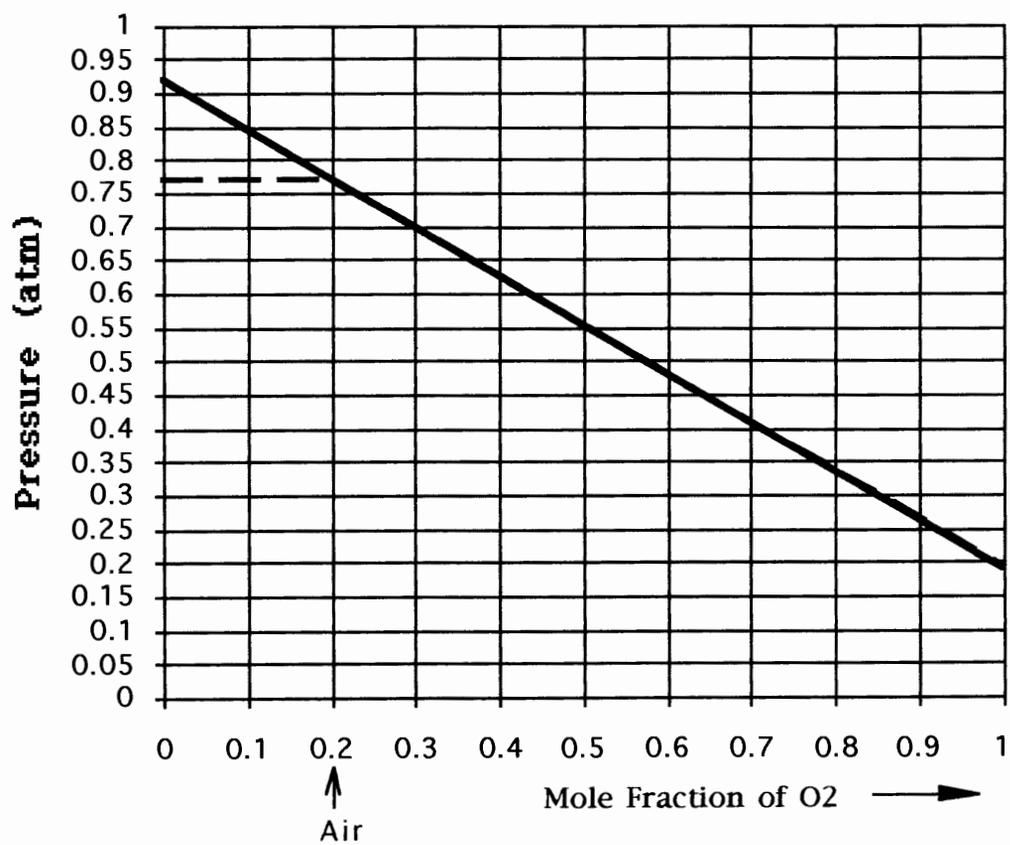
Figure 3 Vapor pressure of nitrogen/oxygen mixtures at 77.35 K
(Assuming Raoult's law)

for choosing the GS-Alumina column was that it was fairly cheap compared to other alternative columns. For example, it cost only one half as much a J&W DB-1 column .

Tremendous time was taken on the initial setup of the analytical system to determine optimum system operating conditions. Critical parameters include the sample collection flow rate and sampling time; flow rate and temperature for the sample concentration trap; oven temperature program parameters and flow rates for carrier gas and make-up gas, etc. These parameter are optimized by varying the operating conditions to achieve the best resolution of the target VOCs using pure component mixtures.

The optimal operating conditions are listed as follow:

Sample collection rate and time:	15 ml/min for 10 minutes
Total sample volume:	150 ml
Trap desorption temperature:	80-90 °C
Column:	J&W GS-Alumina, 0.546 mm x 30 m
Carrier gas flow rate plus make-up gas flow rate:	30 ml/min
GC oven initial temperature:	28°C
GC oven final temperature:	200°C
GC oven ramp rate:	28°C to 200°C at 3°C / minutes
GC oven final time:	5 minutes
Detector temperature:	250°C
Detector hydrogen flow-rate:	30 ml / min
Detector range:	11

Detector attenuation: 1

The GC system was calibrated in units of ppbC using Scott specialty gases. Based on the carbon response of the FID to the standard, a relative response factor (ppbC/area count) was determined. This factor was used to convert area counts from every peak in a chromatogram into concentration units. Figure 4 shows the separation of a 50ppb standard gas sample.

DATA ACQUISITION SYSTEM:

This research employed a PC-DOS personal computer with a set of data acquisition and integration software which was written by myself in TBasic language. This software was comprised of subroutines that perform data acquisition, peak integration, PC-GC interfacing and hard copy output. The program is attached in the Appendix of this treatise, and the flow-chart of the peak integration program is shown in Figure 5

VOC MEASUREMENT PROCEDURE

Before sample analysis, the analytical system was assembled (see Figure 1) and leak checked.

To leak check the analytical system, place the ten-port gas valve in the trapping position. Disconnect and cap the absolute pressure gauge. Insert a pressure gauge capable of recording up to 60 psig at the vacuum valve outlet.

Attach a valve and a zero air supply to the sample inlet port. Pressurize the system to about 50 psig (350 kpa) and close the valve.
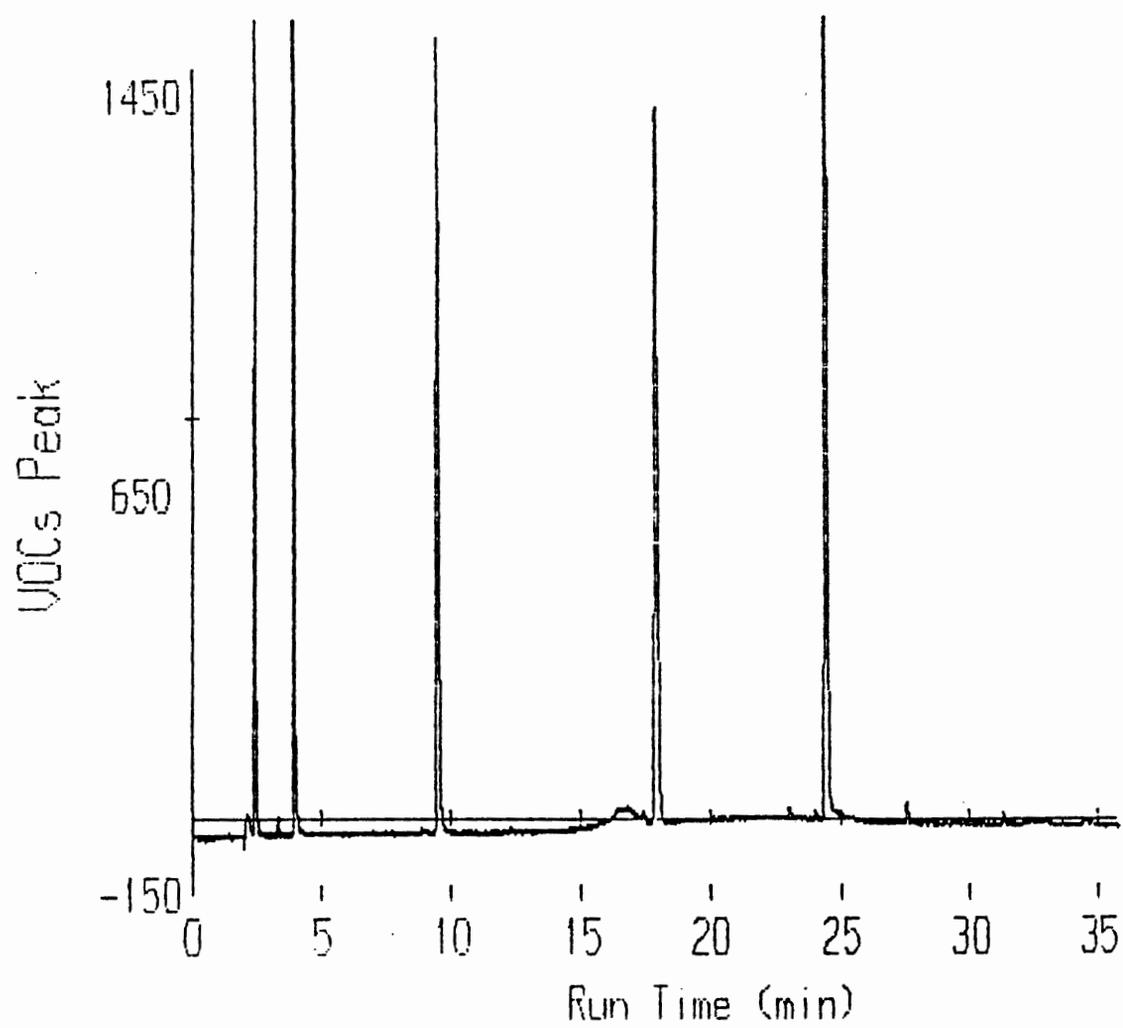
Figure 4 The separation of a 50ppb standard sample
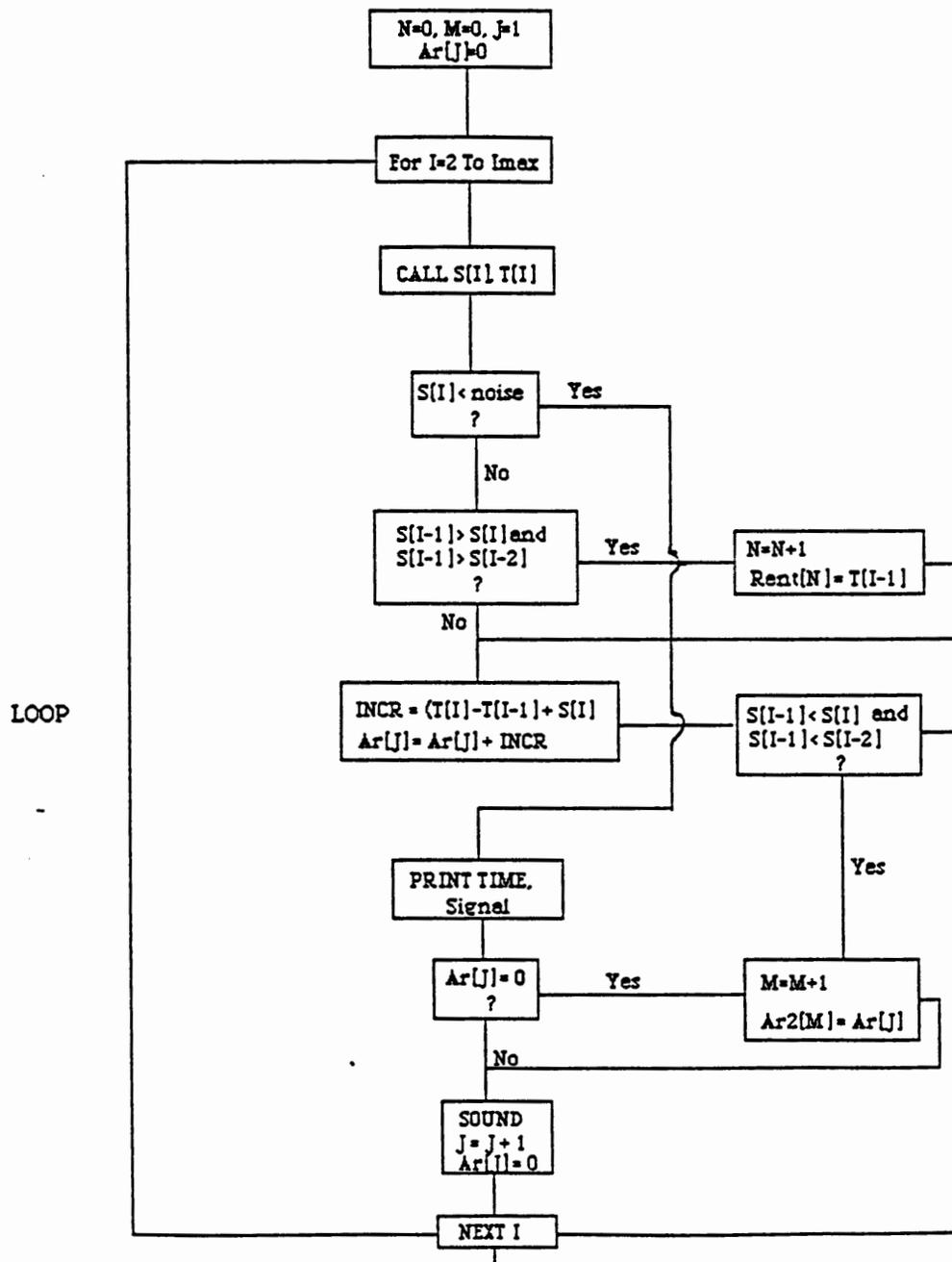
Figure 5 Flow chart of integration

Wait approximately 3 hours and re-check pressure. If the pressure did not vary more than ± 2 psig, the system is considered leak tight. If the system is leak free, de-pressurize and reconnect absolute pressure gauge.

After above steps, light the FID detector and allow the signal to stabilize.

Check and adjust the helium carrier pressure to provide the correct carrier flow rate and make-up flow rate for the system. Also check the FID hydrogen and burner air flow rates.

Place the ten-port valve in the sampling position, start the dry purge gas and turn on the vacuum pump to draw the ambient air for five minutes in order to eliminate the dead volume. In the meantime, submerge the trap in the cryogen. Allow a few minutes for the trap to cool completely (indicated when the cryogen stops boiling). The level of the cryogenic liquid should remain constant with respect to the trap and should completely cover the beaded portion of the trap.

Add a little cryogen or elevate the Dewar to raise the liquid level to point slightly higher (3-15 mm) than the initial level at the beginning of the trapping. This insures that organics do not bleed from the trap.

When the sampling time is over, turn on the heating tape, switch the ten-port valve to the inject position, start both GC and data acquisition program and replace the Dewar flask containing the cryogenic liquid with a mug of boiling water. The condensed organic of interest will be desorbed and carried into the column by helium gas. The chromatographic peaks will be continuously obtained by PC

and the results can be later on analyzed using integration program.

SMOG CHAMBER SETUP AND EXPERIMENTAL CONDITIONS

The smog chamber was made of Teflon film bag. It was tested for its ability to transmit Ultra-Violet (UV) radiation. The UV wave lengths that the proposed mechanism relied on are 254 nm (ozone photolysis to produce O (^{1}D)), and 310-400 nm (NO_2 photolysis to produce NO and O (X^3P)). The bag was then sealed onto a platform which held the inlet and sampling tubes.

The volume of the bag was calculated based on its geometric structure. It was approximately considered as a wedge structure and its volume was calculated to be about 130 liters. With this value, the amount of NO required to initiate the reactions can be calculated .

Six hydrocarbons were selected for the smog-chamber study: hexane, octane, mesitylene, toluene, m-xylene, and o-xylene. These hydrocarbons cover both aliphatic and aromatic compounds with different reactivitiy. In order to make these compounds have close initial concentrations , a mixture of them was first made up having same mole ratios. The initial equilibrium concentrations of these compounds in the bag ranged between one and a few hundred ppbv .

Six fluorescent light bulbs were installed around the bag to emit UV radiation required to produce hydroxyl radicals. NO/NO_2 are necessary elements for this purpose. The mechanism of this process is extremely complicated and is not going to be discussed in this treatise. One thing worthy of notice though, is that UV radiation

photolyzes ozone to produce the first excited state of the oxygen atom, $O(^1D)$:

$$O_3 + h\nu \longrightarrow O(^1D) + O_2 \quad (11)$$

$O(^1D)$ is a reactive atom which may also cause the destruction of hydrocarbons (O'Brien, 1992). In order to remove the effect of $O(^1D)$ and make hydroxyl radical the sole removal agent to the reaction of hydrocarbons, water was introduced into the bag:

$$O(^1D) + H_2O \longrightarrow 2HO \quad (12)$$

$O(^1D)$ is energetic enough to abstract a hydrogen atom from water and HO radicals are generated.

Another issue associated with smog chamber setup is to remove the obvious effect of dilution on the change of hydrocarbon concentrations. If the effect of dilution is too obvious it will cover up the removal effect of hydroxyl radicals. A good deal of experimental results were not satisfactory because of this. Eventually the problem was worked out pretty well and satisfactory experimental results were obtained showing insignificant effect of dilution. These results will be discussed in next chapter.

CHAPTER V

RESULTS AND DISCUSSION

MONITORING OF AMBIENT AIR IN PORTLAND DOWNTOWN AREA

The use of the self-designed analytical system containing cryogenic preconcentration and chromatography techniques described in Chapter IV permitted the analysis of up to twenty three individual hydrocarbons in ambient air. Figure 6 shows the analysis of an ambient air sample collected at 10pm on the roof of building Science II at Portland State University. The identification of each individual compound was achieved by spiking a standard gas sample with relevant compounds under the same experimental conditions and by comparing their retention times with experimental data. Although theoretically the employed J&W GS-Alumina megabore column is capable of separating VOC s from C1 to C10, in this example the heaviest compound observed is toluene because the upper limit detected in ambient air is defined by various factors such as desorption temperature and time of cryogenic trap, the volume of helium used for desorption , and the temperature of the valves, fittings and transfer lines in the sample path. Due to the complexity of ambient air, many identified analytes are unknown and most of them occur at later retention times in the less volatile range. Among those identified known analytes, alkanes hold the
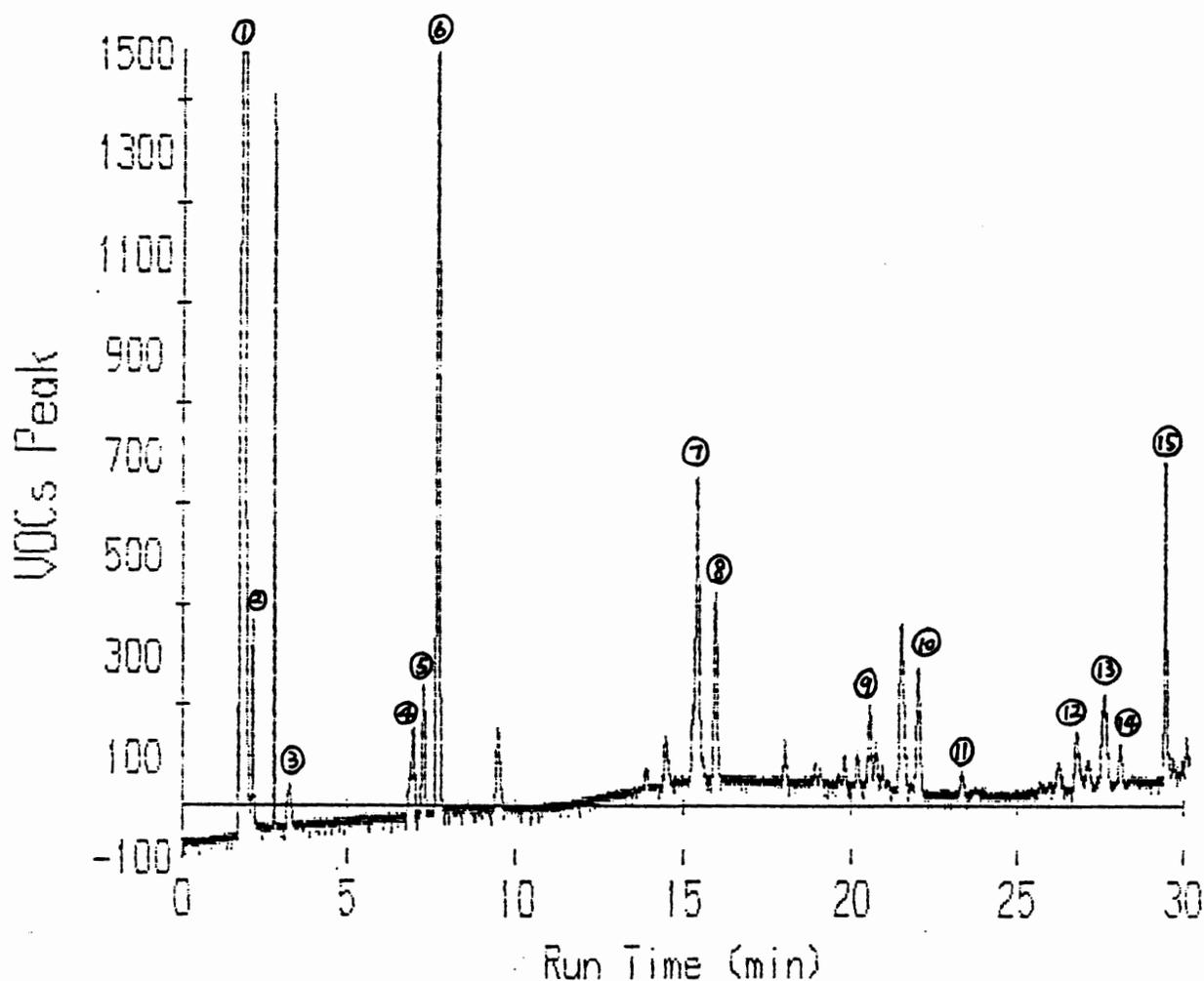
Figure 6 Separation of an ambient air sample on a 30m GS-Alumina megabore column, sample volume 200 ml. Temperature Program described in Section " GC Conditions " in Chapter IV. 1: Methane , 2: Ethane, 3: Propane, 4: Acetaldehyde, 5: i-Butane, 6: n-Butane, 7: i-Pentane, 8: n-Pentane, 9: Acetone, 10: n-Hexane, 11: cyclohexane, 12: 13: Benzene, 14: Octane, 15: Toluene.

largest percentage, which matches the ambient air pattern in the United States (Seila, 1989).

The quantitation of VOCs was accomplished in the way shown in Figure 4 in Chapter IV. Due to the limitations of the experimental conditions (i.e. gas calibration and integration software), the quantification of VOCs in ambient air was not a primary objective in this treatise.

The continuous monitoring of ambient air in Portland downtown area indicates that strong diurnal variation in the distribution of VOCs is present and is largely dictated by their reactivity and prevailing meteorology. Figure 7 shows the identification of ambient air sample collected at 2 PM and Figure 8 shows the diurnal behavior of toluene based on the approximate measurements. The minimum level of VOCs in the afternoon as the result of deep convective mixing and chemical loss by hydroxyl radicals was observed before (Singh ,1985). Due to the time limitation of this study, further detailed information on this diurnal variation was not obtained.

HYDROXYL RADICAL SCAVENGING OF VOCS

The smog-chamber study described in Chapter IV aimed at simulating the decay process of hydrocarbons under laboratory conditions. In the real atmosphere, however, the concentrations of atmospheric hydrocarbons declines due to the combination of complex factors, not only including chemical factors but also physical factors such as dilution. This study was designed in such a
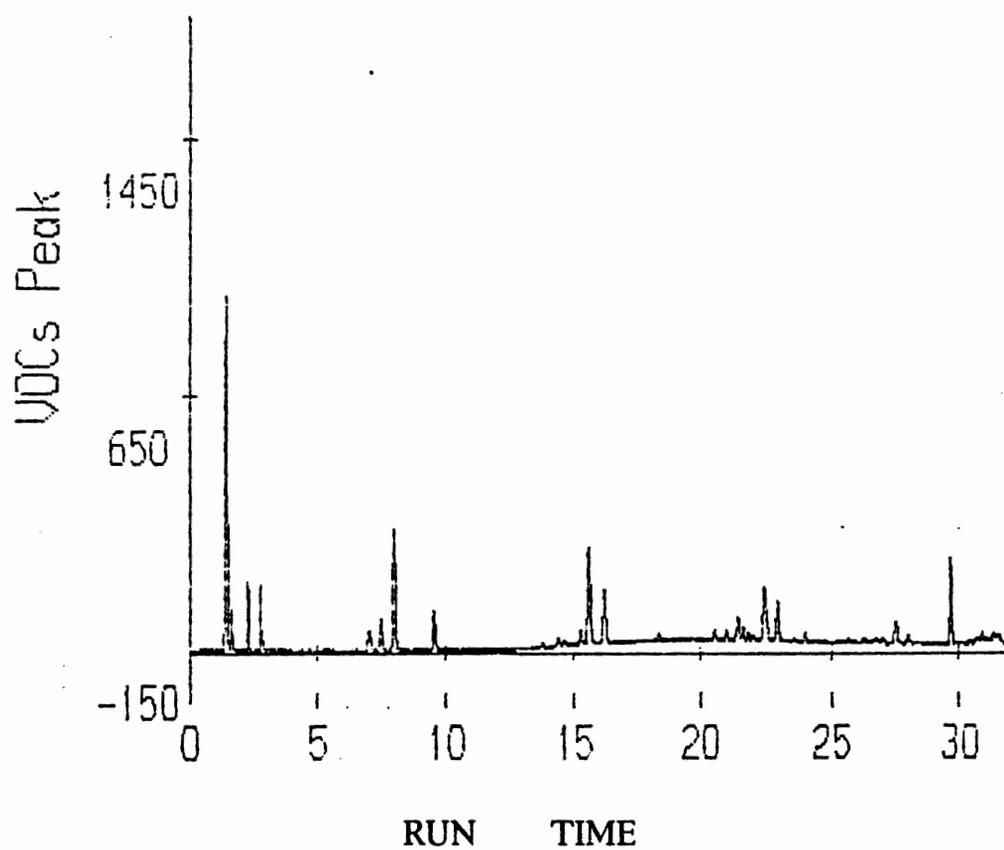
Figure 7 Separation of an ambient air sample at 2 pm.
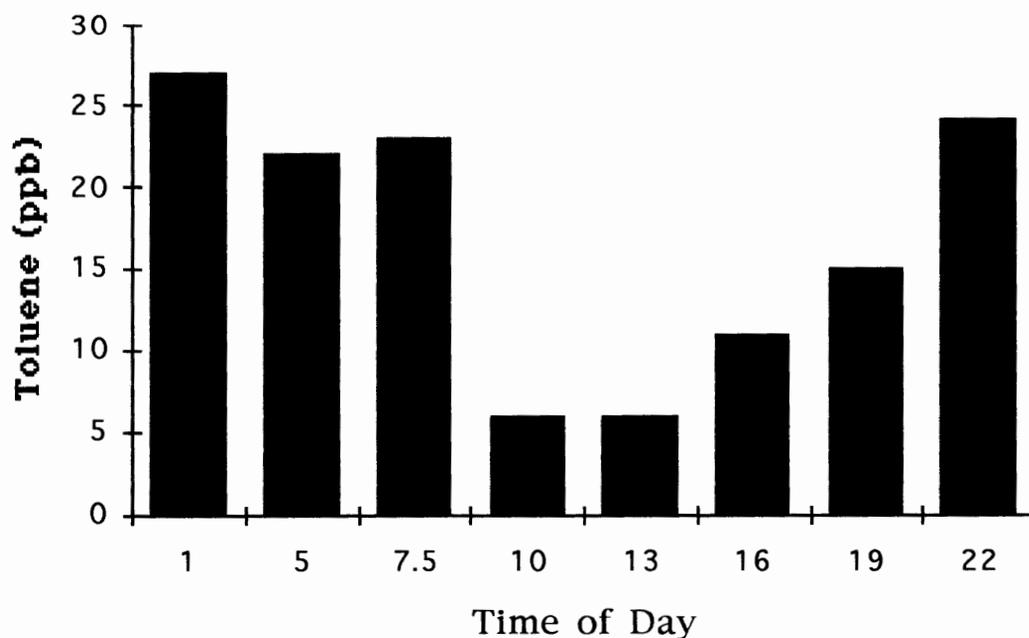
Figure 8 Diurnal behavior of toluene from the measurements at Portland State University, April 1993.

way that the reaction with hydroxyl radicals accounts for the sole cause of atmospheric hydrocarbon removal. Estimated rate constants for the reaction of hydroxyl radicals with hydrocarbons involved in this study are listed in Table II.

Based on the above assumption, the HO concentration during this process can be expressed by Equation (13):

$$dlnHCi = K_{HO} i \{HO\} \qquad (13)$$

Where HCi signifies certain species of hydrocarbons and K_{HO} is the second order rate constant of the reaction of HO with this species.

This assumption can be tested through the interrelationship between ratios of concentrations through the use of above expression

TABLE II

ABSOLUTE REACTION RATE CONSTANTS OF HYDROCARBONS WITH HO
(298 K)

Compound	$K_{HO} \times 10^{11} cm^{-3} s^{-1}$
Hexane	0.558
Octane	0.872
Mesitylene	5.48
Toluene	0.619
m-Xylene	2.45
o-Xylene	1.47

Source: Atkinson, 1986

for two different ratios (more than three different compounds) and dividing one by the other , the term [HO] is thus factored out and the following expression is obtained:

$$\frac{dlnHC_1}{dlnHC_2} = \frac{K_{HO1}}{K_{HO2}} \quad (14)$$

The resulting expression is independent of reaction time and HO concentrations and predicts that a log-log plot of one ratio vs. another should give a straight line with a slope equal to the ratio of reaction rates.

The smog-chamber experiments involving six hydrocarbons (hexane, octane, toluene, m-xylene, o-xylene, mestilyene) were carried out during several months and three solid sets of experimental data were processed based on the idea described

above. Figure 9 through Figure 13 are plots of octane : hexane, toluene : hexane, m-xylene : hexane, o-xylene ; hexane, and mestilyene : hexane, respectively. All three parallel results for the rest compounds are in fairly good agreement. The slopes of the correlation from the data are compared in Table III to those predicted by the rate constants. The agreement is on the same order of magnitude for each compound.

As mentioned early in this treatise, a published experimental result made by N. J. Blake (1993) and his research fellows speculated the presence of a chemical removal mechanism for aromatics additional to HO radical chemistry. They carried out a series of plume studies using a sampling and analytical system to collect time-resolved data over several hours on a large number of hydrocarbons. Hydroxyl concentrations were derived from the decay of both aliphatic and aromatic hydrocarbons in combination with kinetic data based on hydrocarbon reactions with HO radicals. They found out substantial differences in the HO radical concentration from a consideration of alkane decay and the decay of aromatic hydrocarbons in the plume. This systematic difference between values of HO concentration calculated from aliphatic and aromatics has been noted previously by Singh (1981) and by Robert (1984). If this hypothesis was true , the slopes of the log-log charts of aliphatic hydrocarbon against aromatic should not be equal to ratios of their reaction rates, which are derived simply from reaction with HO radicals. However, this was not confirmed by my study. This indicated the big difference between smog-chamber conditions and
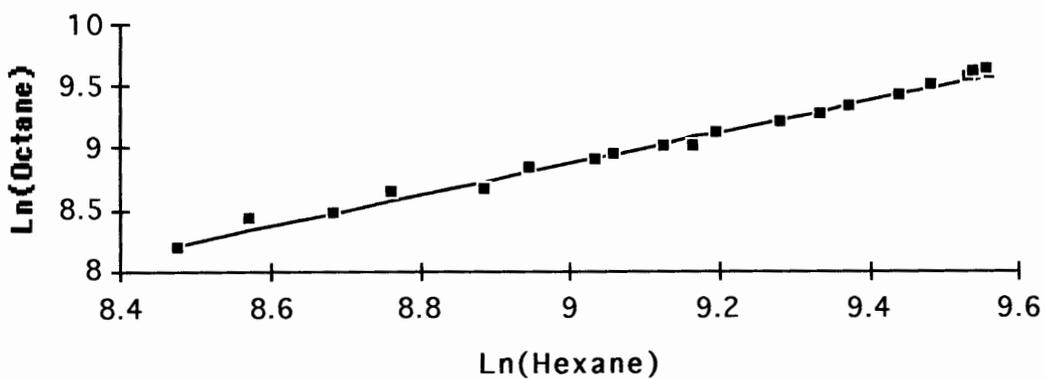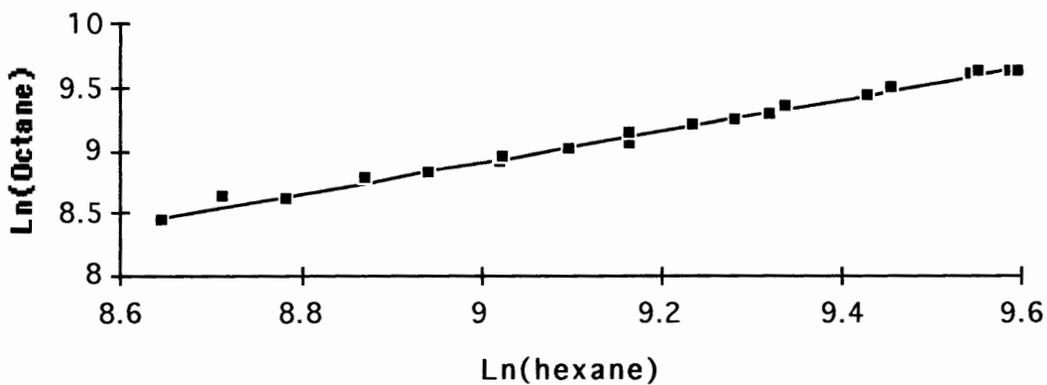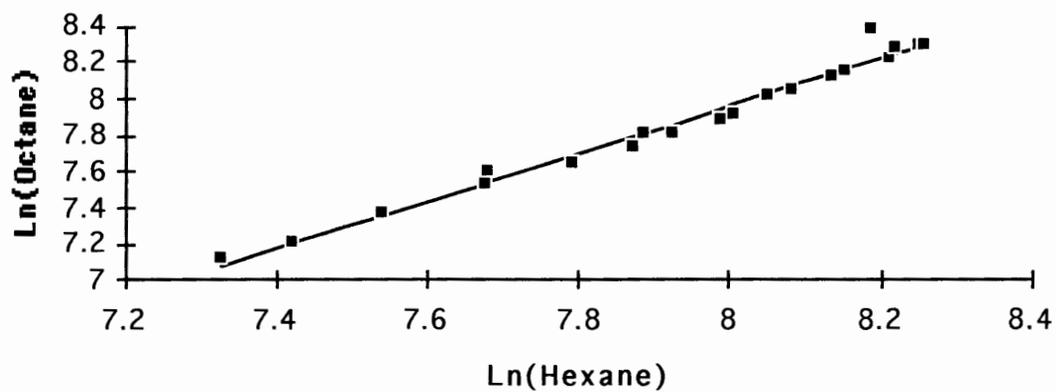
Figure 9 Concentration ratios of octane to hexane from three separate experiments.
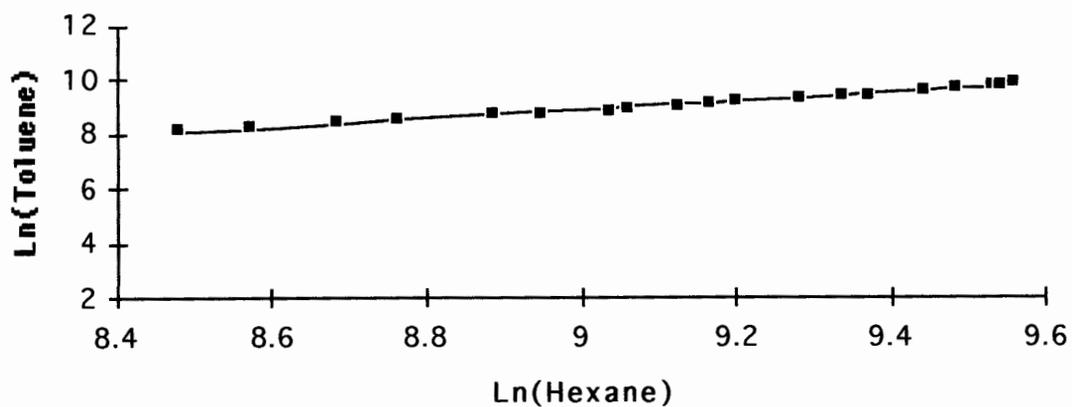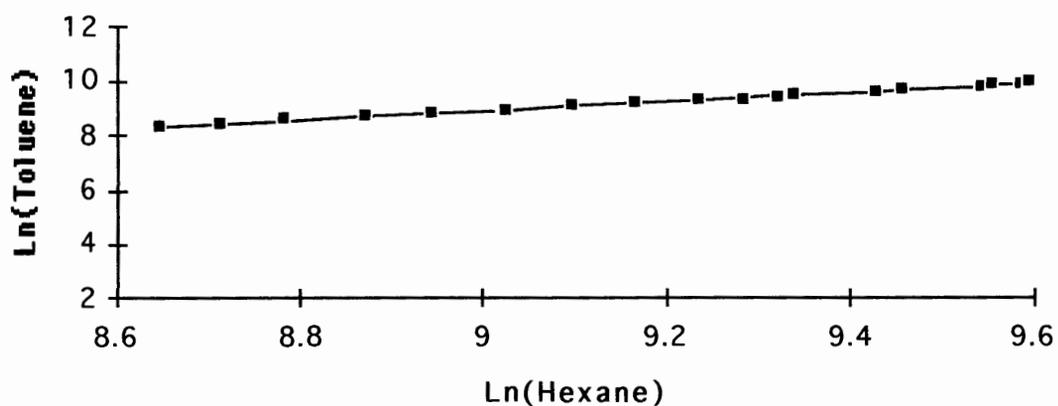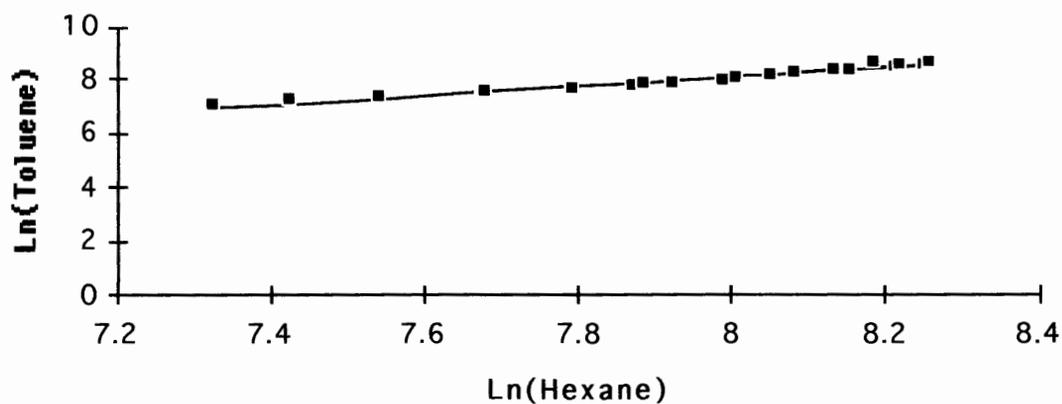
Figure 10 Concentration ratios of toluene to hexane from three separate experiments.
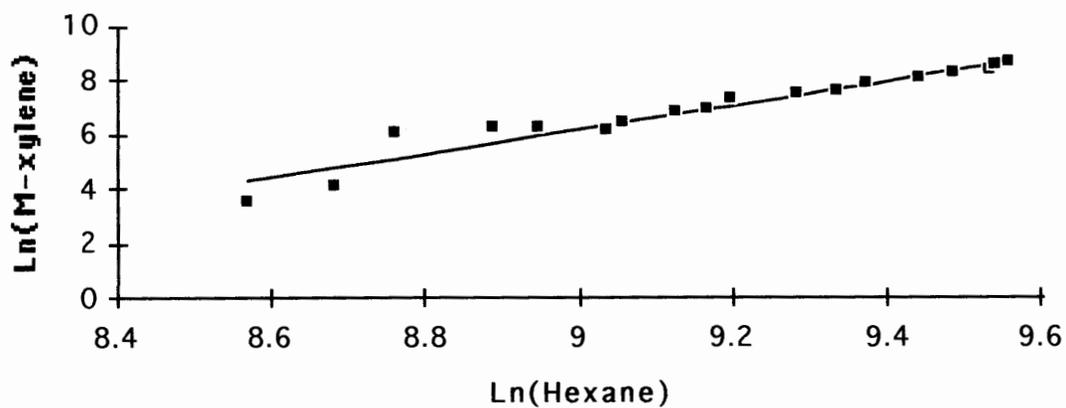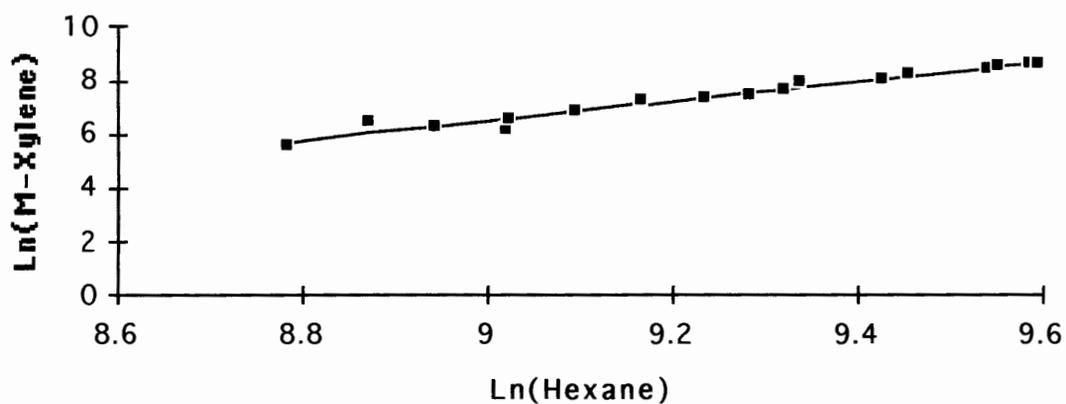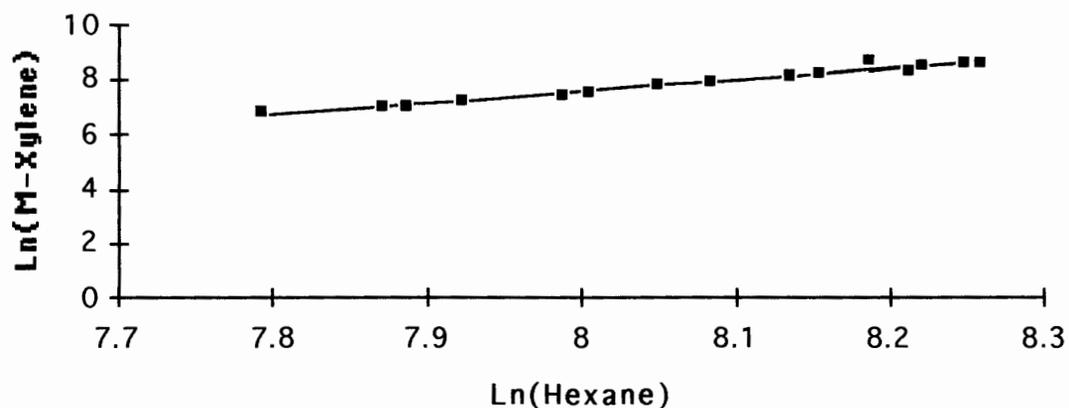
Figure 11 Concentration ratios of m-xylene to hexane from three separate experiments.
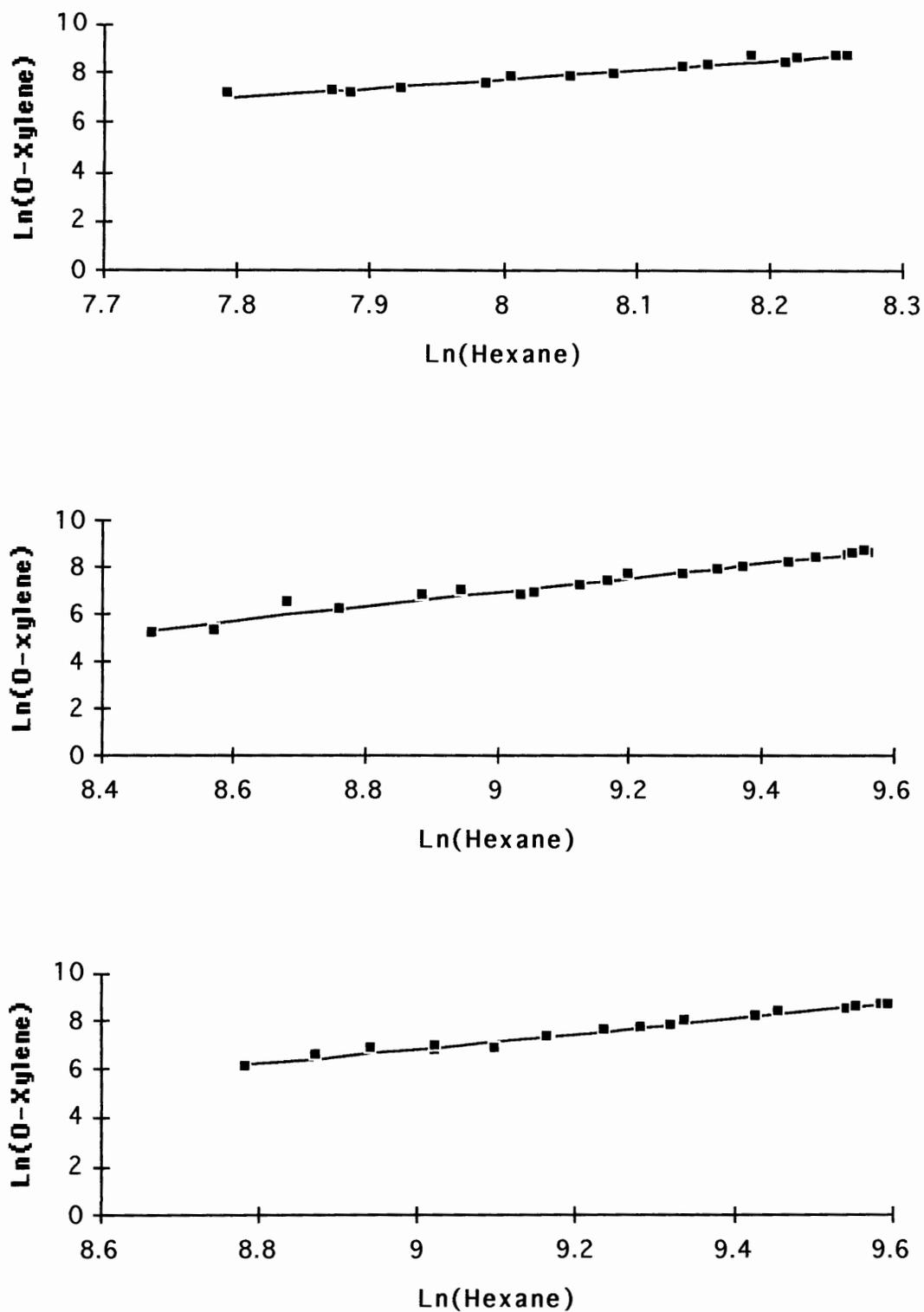
Figure 12 Concentration ratios of o-xylene to hexane from three separate experiments.
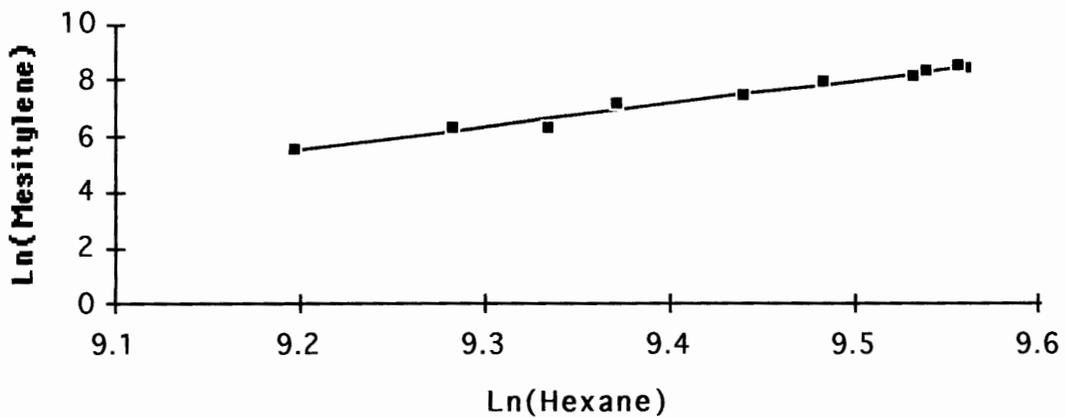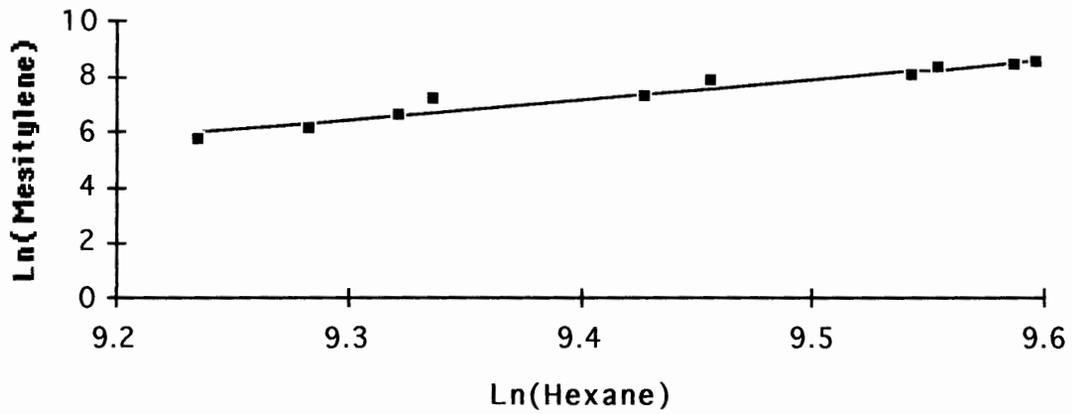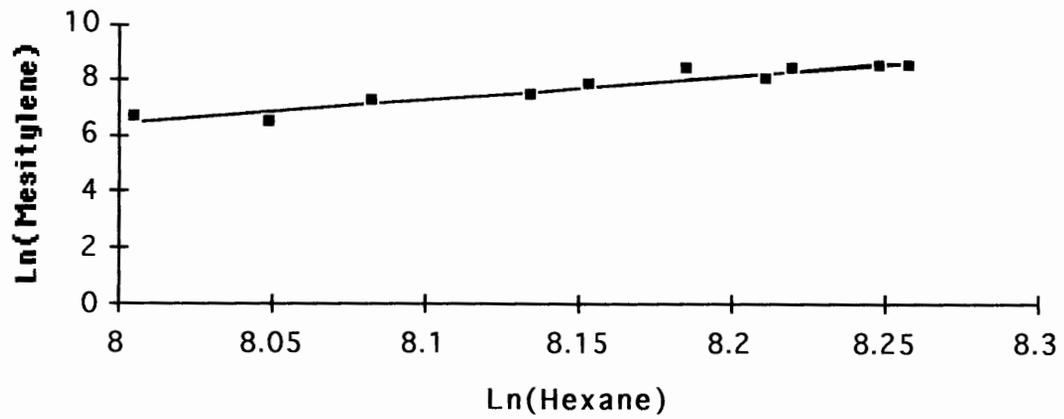
Figure 13 Concentration ratios of mesitylene to hexane from three separate experiments.

TABLE III

OBSERVED VS. PREDICTED SLOPES OF THE CORRELATION
OF HYDROCARBON RATIOS

Ratio	Trial Number	Slopes measured	Slopes from rate constants*
Octane : Hexane	1	1.298	1.547
	2	1.268	
	3	1.251	
	Average	1.272	28%**
	%RSD	1.870	
Toluene: Hexane	1	1.689	1.109
	2	1.624	
	3	1.677	
	Average	1.663	28%**
	%RSD	2.079	
m-Xylene : Hexane	1	4.218	4.391
	2	4.489	
	3	3.644	
	Average	4.117	32%**
	%RSD	10.480	
o-Xylene : Hexane	1	3.665	2.634
	2	3.026	
	3	3.185	
	Average	3.292	32%**
	%RSD	10.105	
Mesitylene : Hexane	1	8.602	9.821
	2	8.100	
	3	7.383	
	Average	8.028	26%**
	%RSD	7.631	

* Calculated based on data in Table II.

** The acceptable experimental error (Atkinson, 1986).

real atmosphere conditions because one thing in common in all those

previous results mentioned above is that all of those studies were carried out in the complex real atmosphere.

An explanation for it is that in the real atmosphere the transport properties of hydrocarbons and their chemical reactivity are related, such that shorter-lived hydrocarbons may be subject to more decay between measurement points and emission point than would be predicted from a simple flow analysis due to substantial vertical mixing within the planetary boundary layer increasing the effective path length during transit, although horizontal mixing out of the plume would produce the same effect. In addition, since compounds with faster HO reaction rates have shorter atmospheric lifetimes, the absolute concentrations of the reactive compounds decrease faster than for compounds with shorter HO reaction rates. Thus, sources of more reactive compounds along the transport path may contribute significantly to atmospheric conditions, making the final compound ratios high and therefore HO estimate low.

CONCLUSIONS

1. An analytical system has been devised which enables in-situ measurements of atmospheric hydrocarbons from C1 to C12, including alkane, alkene and aromatics. This system was successful in identifying VOCs in ambient air in Portland downtown area.

2. A series of smog-chamber experiments were carried out to simulate the removal mechanisms of hydrocarbons from the atmosphere. The method of correlation of compound ratios was employed to specifically verify the speculation brought up by recent

published study doubting that HO radical is the principal agent responsible for the destruction of the aromatic hydrocarbons in the atmosphere. This hypothesis was not confirmed by this treatise, indicating the substantial difference between the atmospheric studies made in the laboratories and in the real atmosphere. The reason could be associated with the complex physical pattern in the real world.

3. The method of correlation of compound ratios represents a powerful tool in the examination of chemical mechanism in the atmosphere. The potential of the use of changes in composition of hydrocarbons to the estimation of average HO concentration in the atmosphere was implied.

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APPENDIX

DATA ACQUISITION SOFTWARE IN TBASIC

```
1 ! Dawei Han 1993
4 SET GRAPH DEVICE | END
8 RUN 100 | END
12 RUN 4000 | END
16 RUN 8400 | END
20 RUN 8000 | END
24 RUN 2000 | END
28 RUN 3000 | END
32 RUN 7000 | END


100 CLE | Sfr$ = "15 ml/min" | st$ = "13 min" | Ite$ = "28 c" |
Iti$ = "5 min" | Prog$ = "28 C to 200 C  at 3 c/min" | Ft$ = "5
min"
120 INPUT PROMPT "PLEASE ENTER DATE(mm-dd--yy) : ":D$
130 PRINT "  "
140 INPUT PROMPT "PLEASE ENTER TIME(hr:min): ":T$
150 PRINT "  "
160 INPUT PROMPT "PLEASE ENTER ANALYST NAME: ":An$
170 PRINT "  "
180 INPUT PROMPT "PLEASE ENTER SAMPLING LOCATION: "
S1$
190 PRINT "  "
200 INPUT PROMPT "PLEASE ENTER THE DATA FILE: ":Df$
210 PRINT "  "
220 INPUT PROMPT "PLEASE ENTER THE REPORT FILE: ":Rf$
230 PRINT "  "
240 PRINT "PLEASE CHECK SAMPLING CONDITIONS:"
250 PRI "  (1)  sampling flow rate     ",Sfr$ | INP PRO " (y/n)?"
:C1$
260 IF C1$="n" THEN INPUT PROMPT "Please enter new
sampling flow rate:":Sfr$
270 PRI "  (2)  sampling time     ",St$ | INP PRO "     (y/n)?":C2$
```

280 IF C2$="n" THEN INPUT PROMPT "Please enter new
sampling time:":St$
290 PRINT " "
300 PRINT "PLEASE CHECK GC TEMPERATURE PROGRAM: "
310 PRI " (1) initial temperature ",Ite$ I INP PRO " (y/n)?"
:C3$
320 IF C3$="n" THEN INPUT PROMPT "Please enter new initial
temp :":Ite$
330 PRI " (2) initial holding time ",Iti$ I INP PRO " (y/n)?":
C4$
340 IF C4$="n" THEN INPUT PROMPT "Please enter new initial
time: ":Iti$
350 PRINT " (3) ",Prog$ I INPUT PROMPT " (y/n)?":C5$
360 IF C5$="n" THEN INPUT PROMPT "Please enter new
program: ":Prog$
370 CLEAR
380 PRI " (4) final holding time ",Ft$ I INP PRO "(y/n)?":
C6$:
390 IF C6$="n" THEN INPUT PROMPT "Please enter new final
time: ":Ft$

400 PRINT " "
410 INPUT PROMPT " PRESS KEY S TO START: ":C7$
420 IF C7$<>"S" THEN GOTO 100
430 SOUND "C"
440 GOTO 4000 ! END

600 SUB Das8
605   Dbas = 768
610   CALL S_OUT(Dbas+2,5) ! CH 5=gc
620   CALL S_OUT(Dbas+1,0)
630   CALL S_IN(Dbas+2) RETURN Stat
640   IF Stat>=128 THEN 630
650   Call S_IN(Dbas) RETURN Hb I CALL S_IN(Dbas+1)
RETURN Lb
660   ! Dt = Hb/16+Lb*16 I Dt = Dt*10/4096-5
662   Dt = Hb/16+Lb*16
670 END SUB
680 !   !!!
!!!
800 SUB Timenow

```
810    T$ = TIME
820    Hr$ = SEG$(T$,1,2) | Hr = VAL(Hr$)
830    Mn$ = SEG$(T$,4,2) | Mn = VAL(Mn$)
840    Se$ = SEG$(T$,7,4) | Se = VAL(se$)
850    Tn = 60*Hr+Mn+Se/60
860 END SUB
870 ! !!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!
!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!


2000 OPEN #1:Df$,"W"
2005 PRI #1:An$ | PRI #1:D$ | PRI #1:T$ | PRI #1:S1$ | PRI
#1:Df$ | PRI #1:Rf$ | PRI #1 :Sfr$ | PRI #1:St$ | PRI #1:Ite$ | PRI
#1:Iti$ | PRI #1:Prog$ | PRI #1:Ft$ | PRI #1:Imax | PRI #1:Tspanl
| PRI   #1:Tspan2 | PRI #1:I0
2010 FOR I = 1 TO Imax
2020     PRINT #1:S1[I]
2030 NEXT I
2031 FOR I = 1 To I0
2032     PRINT #1:S2[I]
2033 NEX I | CLO #1 | PRI "The data has been stored in file ";Df$
| INP Z$
2040 END
2041 PRINT #1:S1[I],S2[I]
2050 OPEN #2:Rf$,"W" | PRINT #2:N
2051 NEX I | CLO #1 | PRI "The data has been stored in file ";Df$
| INP Z$
2060 FOR L = 1 To N
2080     PRINT #2:L,Rent[L],Ar2[L]
2085 NEX L | CLO #2 | PRI "The data has been stored in file ";Df$
| INP Z$
2090 GOTO 5300 ! END
2100 ! !!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!
!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!


3000 INP PRO "Enter the data file that you want to open:":Df$ |
OPE#1:Df$,"r"
3003 DEC INTE Imax | Imax = 32000 | DEC INTE
I,N,M,J,I0,S1[Imax],L,S2[Imax]
3004 INP #1:An$ | INP #1:D$ | INP #1:T$ | INP #1:S1$ | INP
#1:Df$ | INP #1:Rf$ | INP #1:Sfr$ | INP #1:St$ | INP #1:Ite$ | INP
```

```
      #1:Iti$ I INP #1:Prog$ I INP #1:Ft$ I INP I #1:Imax I INP
      #1:Tspan1 I INP #1:TSPAN2 I INP #1:I0
3005  ! DIM T[Imax] ! ,S[Imax],Ar[200],Rent[200],Ar2[200]

3010  FOR I = 1 TO Imax
3020      INPUT #1:S1[I]
3030  NEXT I
3031  FOR I = 1 TO I0
3032      INPUT #1:S2[I]
3033  NEXT I I CLOSE #1 I PRINT "The data file has been
      opened." I END
3050  INP PRO "Enter the report file that you want to open:":Rf$
      I OPE #2:Rf$,"r" I INP #2:N
3055  ! DIM Rent[Imax],Ar2[Imax]
3060  FOR L = 1 TO N
3070      INPUT #2:L,Rent[L],Ar2[L]
3080  NEXT L
3090  CLOSE #2 I PRINT "The report has been opened."
3100  END
3110  ! !!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!
      !!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!

4000  CLE I DEC INTE Imax,I,I0 I Imax = 32000 I I0 = 2000 I DEC
      INTE S1[Imax],Hb,Lb,Dt,Stat,S2[Imax] ! ,S3[Imax],S4[Imax],
      S5[Imax]
4010  Xmin = 0 I Xmax = 12 I Xint = 2 I Ymin = -150 I Ymax =
      2500 I Yint = 500
4020  CALL Tg
4030  ! MOVE 0,0
4035  CALL Timenow I T0 = Tn
4040  FOR I = 1 TO Imax
4050      Dbas = 768
4060      CALL S_OUT(Dbas+2,5) ! CH 5=gc
4070      CALL S_OUT(Dbas+1,0)
4080      CALL S_IN(Dbas+2) RETURN Stat
4090      IF Stat>=128 THEN 4080
4100      CALL S_IN(Dbas) RETURN Hb I CALL S_IN(Dbas+1)
      RETURN Lb
4120      Dt = Hb/16+Lb*16 I S1[I] = Dt-1740
4130  NEXT I
```

```
4140 CAL Timenow I Tmax1 = Tn-T0 I Tspan1 = Tmax1/Imax I
PRI "Tspan1= ",Tspan1
4145 MOVE Tmax1,0
4150 FOR I = 1 TO I0 ! Imax
4160    CALL Das8 I S2[I] = Dt-1740 I CALL Timenow
4180    LINE Tn-T0,S2[I];
4190    PRINT AT 1,30:"   I    Time    Signal    "
4200    PRI AT 2,30:"                    " I PRI AT 2,30 USI
"(5d,5x, 2d.4d,5x,5d)":I,Tn-T0,S2[I]
4210 NEXT I
4220 CAL Timenow I Tmax2 = Tn-T0 I Tspan2 = (Tmax2-
Tmax1)/I0 I PRI "Tspan2= ",Tspan2
4550 PRINT "         THE    END    OF    RUN"
4560 SOUND "g" ! I INPUT PROMPT "Plot this experimental
data?(y/n)":C11$
4570 GOTO 8400 ! IF C11$="Y" THEN GOTO 9000
4580 END
4999 ! !!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!
!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!


5000 O = 32
5020 CLEAR
5030 PRI #O:"*************************************************
**************"
5040 PRI #O:" " I PRI #O:"             ANALYSIS    REPORT" I
PRI #O:" "
5050 PRI #O:"*************************************************
**************"
5060 PRI #O:"
             "
5070 PRINT #O:"Analyst Name:  ",An$,"Sampling Location:  ",S1$
5075 PRINT #O:"Date:  ",D$,"Time:  ",T$
5080 PRINT #O:"Data File:  ",Df$," Report File:  ",Rf$
5090 PRI #O:"
             "
5100 PRINT #O:"Sampling Conditions: "
5110 PRINT #O:"  (1)  sampling flow rate          ",Sfr$
5120 PRINT #O:"  (2)  sampling time              ",St$
5130 PRINT #O:"  "
5140 PRINT #O:"GC Conditions: "
5150 PRINT #O:"  (1)  initial temperature          ",Ite$
```

```
5160 PRINT #O:“  (2)  initial holding time              ”,Iti$
5170 PRINT #O:“  (3) ”,Prog$
5180 PRINT #O:“  (4)  final holding time               ”,Ft$
5190 PRI#O:“_____
_____ ”
5200 PRINT #O:“Analysis Results: ”
5210 PRINT #O:“  ” | PRINT #O:“  ” | INPUT D$ | CLEAR
5220 PRINT #O:“ Peakn Number   Retention Time  Peak Area”
5230 PRINT #O:“ --------------    --------------   ----------”
5240 FOR I = 1 TO N
5250   PRINT #O USING 5251:I,Rent[I],Ar2[I]
5251   IMAGE (6x,3d),(19x,2d.2d),(19x,7d.3d)
5260 NEXT I
5270 PRINT #O:“ ”
5280 PRI #O:“Total        ”;N,“  Peaks” | PRI #O:“*************
****************************************************” | PRI #O:“
  END   OF   REPORT”
5290 PRI #O:“***************************************************
**************”
5295 INP A ! INP PRO “Do you want to store the result
?(y/n)”:C10$ | IF C10$=“Y” THE GOT 2050
5300 ! INP PRO “Do you want to print the chromatogram and
report ?(y/n)”:C8$ | IF C8$=“Y” THE 5320 ELS 5340
5320 R = 1 | SET GRA DEV “IBMPRN” | GOS 8400 | COP | SET GRA
DEV | INP A$
5330 O = 2 | OPEN #O:“LPT1”,“W” | GOTO 5030 | CLOSE #O
5340 END
5350 PRINT “!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!”


6000 SUB Tg
6010   ! Xmin = 0.2 | Xmax = 0.5 | Xint = 0.1 | Ymin = -350 |
Ymax = 1500 | Yint = 200
6020   X1b$ = “Run Time (min)” | Y1b$ = “VOCs Peak ”
6030   Xran = Xmax-Xmin | Yran = Ymax-Ymin
6040   CLEAR | SET VIEWPORT 20,120,15,95
6050   SET WINDOW Xmin,Xmax,Ymin,Ymax
6060   SET CLIP OFF
6070   SET POI STY 0 | SET POI COL 15 | SET LIN STY 0 | SET
LIN COL 15
```

```
6080    SET TEXT COLOR 15 I SET TEXT STYLE -1 I SET TEXT
ANGLE 0
6090    Ysiz = (Ymax-Ymin)*0.04 I Xsiz = (Xmax-Xmin)/(Ymax-
Ymin)*0.5
6100    SET TEXT SIZE Ysiz,Xsiz I SET TEXT ALIGN 3,3
6110    AXIS Xint,Yint,Xmin,0
6120    AXIS Xint,0,Xmin,Ymin,-3,0 !
6130    FOR Xg = Xmin TO Xmax STE Xint I GOS 6200 I TEX AT
Xg,Ymin-Yran*0.05:I$ I NEX Xg
6140    FOR Xg = Ymin TO Ymax STE Yint I IF ABS(Xg)<2.E-16
THE Xg = 0 I GOS 6200 I TEX AT Xmin-Xran*0.05,Xg:I$ I NEX Xg
6150    IF X1b$< >" " THE I I$ = X1bs I GOS 6210 I X1b$ = I$ I
TEX AT (Xmin+Xmax)/2,Ymin-Yran*0.13:X1b$ I END IF
6160    IF Y1b$< >" " THE I I$ = Y1b$ I GOS 6210 I Y1b$ = I$ I
SET TEX ANG 90 I SET TEX SIZ Xran*0.04,Yran/Xran*0.8
6170    TEXT AT Xmin-Xran*0.15,(Ymin+Ymax)/2:Y1b$
6180    SET TEXT ANGLE 0 I SET TEXT SIZE Ysiz,Xsiz I END IF
6190 END SUB
6200 I$ = STR(Xg) I I$ = EDI(I$, "<") I FOR Ii = 1 TO LEN(I$) I Ii$
= SEG(I$,Ii,1) I IF Ii$="0" THE I$ = REP("0",Ii,1) I NEX Ii I RET
6210 I$ = EDI(I$, "<") I FOR Ii = 1 TO LEN(I$) I Ii$ = SEG(I$,Ii,1) I
IF Ii$="0" THE I$ = REP("0",Ii,1) I NEX Ii I RET
6220 ! !!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!
!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!
!!!!!!!!!!!!!
```

```
7000 CLE I DEC INTE Imax,I,Io I Imax = 32000 I Io = 32000 I
DEC INTE S1[Imax],Hb,Lb,Dt,Stat,S2[Imax]
7010 Xmin = 0 I Xmax = Io I Xint = 32000 I Ymin = -100 I Ymax
=2500 I Yint =500
7020 CALL Tg
7030 MOVE 0,0
7050 FOR I = 1 TO Io ! Imax
7070    Dbas = 768
7080    CALL_OUT(Dbas+2,5)
7090    CALL S_OUT(Dbas+1,0)
7100    CALL S_IN(Dbas+2) RETURN Stat
7110    IF Stat>=128 THEN 7100
7120    CALL S_IN(Dbas) RETURN Hb I CALL S_IN(Dbas+1)
RETURN Lb
7130    Dt = Hb/16+Lb*16 I S1[I] = Dt-1740
```

```
7135     LINE I,S1[I];
7136    PRINT AT 1,30:"i=",I,"s1[i]=",S1[I],"
7140 NEXT I | INIT | END


8000 Baseline = -30 | R = 0
8010 DECLARE INTEGER Ar,Ar2[100],N,M,J,L,P,Sval[100],En,B |
DIM Rent[100]
8015 Xmin = 0 | Xmax = 12 | Xint = 1 | Ymin = -150 | Ymax =
450 | Yint = 200
8020 CALL Tg
8025 MOVE 0,0
8030 Ar = 0 | N = 0 | M = 0 | An$ = "n" | First = 0 | Noise =
Basline+30 | En = Noise+1 | Pass = 0
8035 FOR I = 4000 TO Imax-1 ! 14=<i<=imax-14
8055     LINE I*Tspan1,S1[I];
8056    IF S1[I]>=Noise THEN 8060 ELSE 8057
8057    IF Noise-S1[I]<30 THEN 8058 ELSE 8059
| NEX P | Baseline = Summ/16 | Noise = Baseline+10 | Y = 0 | GOT
8145
8059    Y = 0 | GOTO 8145
8075     IF First=0 AND Ar=0 THEN 8076 ELSE 8085
8076    IF S1[I+100]>=S1[I] AND Ans$="n" THEN 8080 ELSE
8085
8080     First = 1 | SOU "C" | LIN I*Tspan1,0; |LIN I*Tspan1,S1[I];
| First = I*Tspan1 | N = N+1
8085     IF Ans$="Y" THEN 8115 | IF First=0 THEN 8115
8090     IF S1[I]=1495 AND S1[I+1]=S1[I] THEN 8115
8095     FOR L = 1 TO 120 | IF S1[I]>=S1[I+L] AND S1[I]>=S1[I-L]
THEN 8105
8100       L = 121 | NEXT L | GOTO 8115
8105 NEXT L
8110 Ans$ = "Y" | Rent[N] = I*Tspan1 | Sval[N] = S1[I] | SOUND
"e"
8115 Incr = (S1[I]+S1[I-1]-2*Baseline)/2*0.02
8120 Ar = Ar+Incr | IF Ans$="Y" AND 2290>S1[I] AND
S1[I]>Noise THE 8125 ELS 8165
8125 IF Sval[N]-S1[I]>70 THEN 8130 ELSE 8165
8130 FOR J = 1 TO 120 | IF S1[I]<=S1[I+J] AND S1[I]<=S1[I-J]
THEN 8140
8135    J = 121 | NEXT J | GOTO 8165
8140 NEXT J | IF J>=120 THEN Y = 1
```

8145 IF Ar< >0 AND First=1 AND Ans$="Y" THEN 8150 ELSE 8155

8150 M = M+1 | Ar2[M] = Ar | First = 0 | Ans$ = "n" | SOU "f" | LIN   I*Tspan1,0; | LIN I*Tspan1,S1[I]; | En = S1[I] ! | IF Pass=1 THE   STO

8160 Ar = 0 | GOTO 8170

8170 NEX I | GOT 5000

8359 Ar = 0

8360 FOR I = 1 TO I0

8365   LINE I*Tspan2+Imax*Tspan1,S2[I]; | IF S2[I]>=Noise THEN 8370 ELSE 8380

8370   Incr = (S2[I]+S2[I-1]-2*Baseline)/2*0.02*Tspan2/Tspan1

8375   Ar = Ar+Incr | Rent[5] = I*Tspan2+Imax*Tspan1

8380 NEXT I

8385 Ar2[5] = Ar | N = 5 ! | Rent[4] = I*tspan2+ Imax*Tspan1

8390 GOTO 5000

8400 Xmin = 0 | Xmax = 12 | Xint = 1 | Ymin = -150 | Ymax = 2500 | Yint = 200

8405 CALL Tg

8410 SOUND "g" | MOVE 0,0

8415 FOR I = 4000 TO Imax-4 STEP 5 ! 2=<I<=(Imax-4)

8430   LINE I*Tspan1,S1[I];

8435   PRINT AT 1,30:"i=",I,"s1[i]=",S1[I],"   " ! | INPUT A$

8440 NEXT I

8445 FOR I = 1 TO I0 ! I0-4 ! Imax-4 ! 2=<I<=(Imax-4)

8475 NEXT I | IF R=1 THEN 8480 ELSE 8485

8480 RETURN

8485 INPUT PROMPT "Save this experimental data?(y/n)":C9$

8490 IF C9$="Y" THEN GOTO 2000

8495 END

8500 ! !!!

8505 PRI "F1: prepare screen with function s(t)" | PRI "F2: rubber band with key board-driven cursor and start and end points" | END

8515 Imax = 200

8520 DIM T[Imax],S[Imax]

8525 FOR I = 1 TO Imax | T[I] = I | S[I] = I^2 | NEXT I

9001 Xmin = 0 | Xmax = Imax | Xint = Imax/10 | Ymin = 0 | Ymax = 4.E+04 | Yint = 1.E+04 | X1b$ = " " | Y1b$ = " "

```
9011 CALL Tg
9021 MOVE T[1],S[1] | LINE T,S;
9031 PRI AT 1,1:"cursor movement: right and left arrow keys;
s=start pt, e=end pt; ENTER to exit"
9051 Ipt = 1 | Is = 0 | Ct = 0 | MOV Y[1],S[1] | DRA PIC Cursor
(1,Xran,Yran)
9061 INPUT KEY WAIT K$ | K = ASC(K$) | Ct = Ct+1
9071 IF K=1 AND Ipt <Imax THE | SET LIN COL 0 | DRA PIC
Cursor(1pt,Xran,Yran) | Ipt = Ipt+1 | SET LIN COL 15 | DRA PIC
Cursor(Ipt,Xran,Yran) | END IF ! right arrow
9081 IF K=2 AND Ipt>1 THE | SET LIN COL 0 | DRA PIC
Cursor(Ipt,Xran,Yran) | Ipt = Ipt-1 | SET LIN COL 15 | DRA PIC
Cursor(Ipt ,Xran,Yran) | END IF ! left arrow
9091 IF Ct>10 THE | LIN T,S; | IF Is>0 THE POI T[Is],S[Is] | Ct = 0
| END IF
9101 IF K=115 THE | Is = Ipt | SET POI STY 6 | POI T[Is],S[Is] |
END IF ! starting point
9111 IF K=101 THE | Ie = Ipt | SET LIN COL 0 | DRA PIC
Cursor(Ie,Xran,Yran) | SET LIN COL 15 | POI T[Ie],S[Ie] | LIN
T[Is],S[Is];T[Ie],S[Ie] | LIN T,S; | GOT 9151 | END IF ! ending point
9121 IF K=13 THEN GOTO 9201
9131 GOTO 9061
9141 IF Is>Ie THEN | Itemp = Is | Is = Ie | Ie = Itemp | END IF
9151 Iran = Ie-Is+2 | DIM Ta[Iran],Sa[Iran]
9161 FOR I = Is TO Ie | Ta[I-Is+1] = T[I] | sa[I-Is+1] = S[I] | NEXT
I
9171 Ta[Iran] = T[Is] | Sa[Iran] = S[Is]
9181 A = AREA(Ta,Sa) | PRINT "Start, end:",T[Is],T[Ie],"area=",A
9191 Is = 0 | GOTO 9061
9201 END
9211 PICTURE Cursor(Ii,Xr,Yr)
9221     Ygap = Yr/100 | Xgap = Xr/100
9231     ! !!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!
!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!
!!!!!!!!!!!
9241 CLE | DEC INTE Imax,I | Imax = 32000.0 | DEC INTE
S[Imax],Hb,Lb,Dt
9251 CALL Timenow | T0 = Tn
9281 FOR I = 1 TO 20000 ! Imax
9291     Dbas = 768
9301     CALL S_OUT(Dbas+2,5) ! CH 5=gc
```

```
9311    CALL S_OUT(Dbas+1,0)
9321    CALL S_IN(Dbas+2) RETURN Stat
9331    IF Stat>=128 THEN 9321
9341    CALL S_IN (Dbas) RETURN Hb | CALL S_IN(Dbas+1)
RETURN Lb
9361    Dt = Hb/16+Lb*16 | S[I] = Dt-2600
9371 NEXT I
9381 CALL Timenow | Tmax = Tn-T0 | Tspan = Tmax/Tmax |
PRINT "Tspan= ",Tspan
9391 PRINT "            THE    END    OF    RUN"
9401 SOUND "g" | INPUT PROMPT "Plot this experimental
data?(y/n)":C11$
9411 IF C11$="Y" THEN GOTO 8395
9421 END
9431 PRINT MEMORY | END
```