# Molecular Speciation of Secondary Organic Aerosol from Various Anthropogenic Hydrocarbons

by

**Hali J. L. Forstner**

Research report submitted in partial fulfillment of the requirements for admission to candidacy for the degree of Doctor of Philosophy and in partial fulfillment of the requirements for admission to the degree of Master of Science

March 31, 1993

Division of Chemistry and Chemical Engineering
California Institute of Technology
Pasadena, California 91125

## Abstract

Gas-to-particle conversion is a ubiquitous process in the atmosphere, understanding its detailed chemistry and physics will allow one to predict the effects of primary gaseous and particulate emissions on airborne particulate matter composition and size. This research proposes to determine the mechanisms of secondary organic aerosol formation in the atmosphere for a number of important anthropogenic hydrocarbons. A 6 $m^3$ outdoor smog chamber will be used to generate organic aerosols for molecular speciation analysis by gas chromatography/mass spectrometry. Gas-phase photooxidation mechanisms of the parent hydrocarbon will be formulated based on the results from this analysis.

# Table of Contents

# List of Figures



# List of Tables

## 1. Introduction

Gas-to-particle conversion is a ubiquitous process in the atmosphere. An understanding of its detailed chemistry will allow for the prediction of the effects of primary gaseous and particulate emission changes on airborne particulate matter in the polluted urban atmosphere and in the regional setting.

Hydrocarbons found in the gas phase result from anthropogenic and biogenic sources, as well as from transformation processes in the atmosphere. Typically, gas phase constituents include alkanes, alkenes, ketones, aldehydes, alkanoic acids, and nitrated organics. With reference to organic aerosols, the general components of gas-to-particle conversion are outlined in Figure 1 (Seinfeld, 1986; Wang *et al.*, 1992). In steps 1 and 2, gas phase hydrocarbons react with ozone, hydroxyl radicals or nitrate radicals, to yield oxygenated and nitrated products which are either volatile or potentially condensable. The actual gas-to-particle conversion, step 3, may occur by nucleation to form ultra-fine particles, or by condensation of the gas-phase products onto existing particles. Primary particles in the atmosphere may remain chemically stable (step 4), or undergo transformation (step 5). The gas-phase chemistry of organic compounds is complex and a number of condensable products may be formed from a single precursor. The potential for a product to condense is determined by its saturation vapor pressure.

The goal of this research is to elucidate steps 1 and 2b. In particular, the purpose is to place the aerosol-forming capability of various hydrocarbons on a firm basis of reaction mechanism and product properties through careful molecular product identification.

## 2. Literature Review of Secondary Organic Aerosol Studies

Table 1 presents a compilation of organic aerosol formation studies. Only a few studies have attempted to determine the molecular composition of secondary organic aerosol (SOA) and the gas-phase reaction mechanisms leading to SOA. It is clear from the data in the table that although many of the organics studied are aerosol precursors, few have

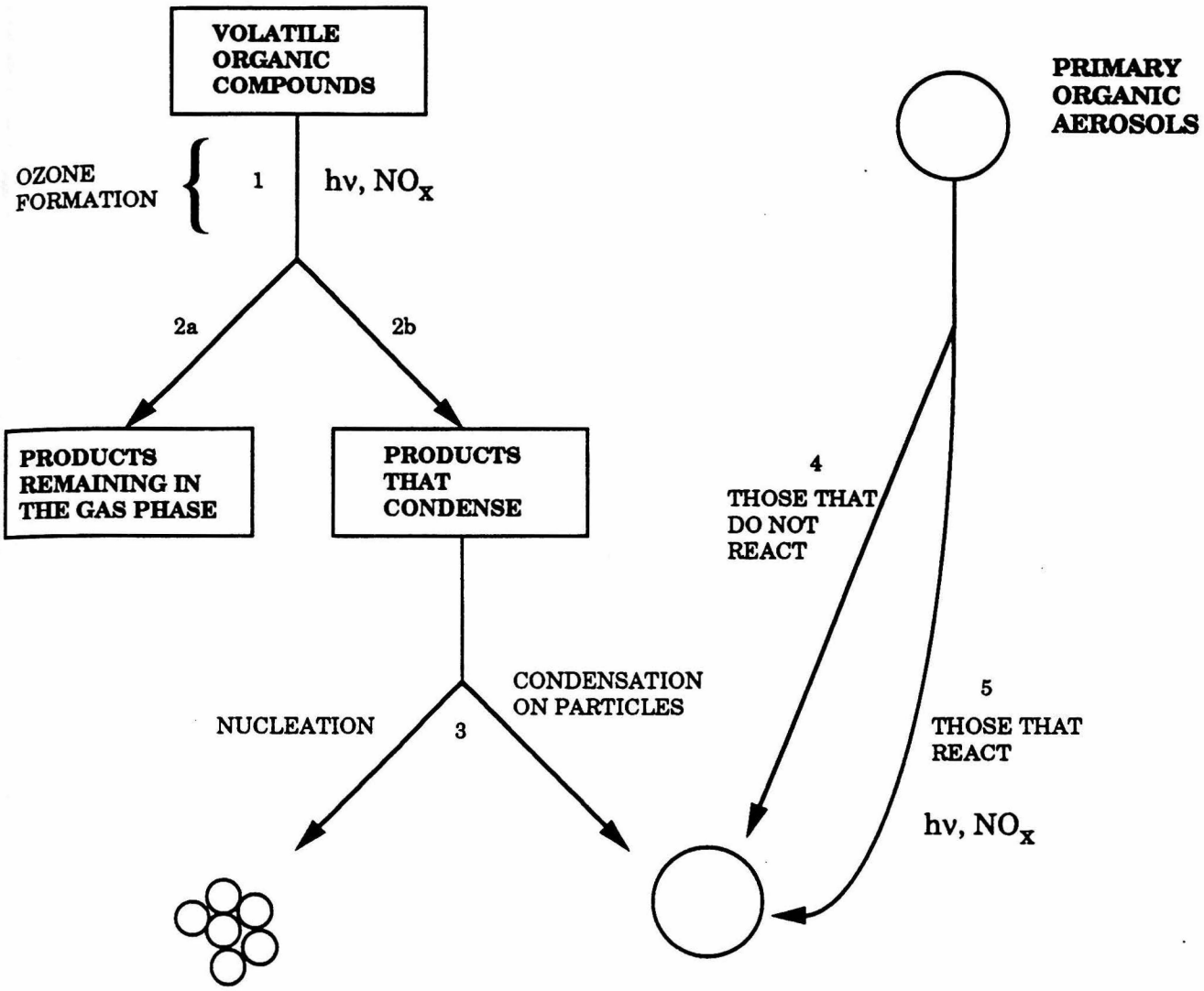



Figure 1 Outline of Gas-to-Particle Conversion

**Table 1 Studies on Secondary Organic Aerosol Formation**

| COMPOUNDS | FAC:$NO_x$[a] | FAC:$O_3$[a] | AEROSOL SPECIES IDENTIFIED | METHOD OF IDENTIFICATION | RESEARCHER | YEAR |
|---|---|---|---|---|---|---|
| **Alkanes** | | | | | | |
| n-heptane | <0.06 | | | | McMurry and Grosjean | 1985 |
| n-octane | <0.001 | | | | Wang et al. | 1992 |
| 2,6-dimethylheptane | 0.65 | | | | O'Brien et al. | 1975 |
| cyclohexane | <0.017 | | | | McMurry and Grosjean | 1985 |
| methylcyclohexane | 9.2 | | | | Wang et al. | 1992 |
| **Aromatics** | | | | | | |
| benzene | <1 | | | | Multiple (incl. Izumi) | 1990 |
| toluene | 1.7 | | | | Schwartz | 1974 |
| | 1.0-3.0 | | | | Grosjean | 1977 |
| | 0.6-1.4 | | | | Leone et al. | 1985 |
| | 2 | | | | Stern et al. | 1987 |
| | 0.5-1.7 | | | | Gery et al. | 1985 |
| | 3 | | | | Izumi and Fukuyama | 1990 |
| | 18.6 | | | | Wang et al. | 1992 |
| m-, o-, p-ethyltoluene | 3.7,3.3,1.5 | | | | Izumi and Fukuyama | 1990 |
| o-xylene | 6.3 | | | | O'Brien et al. | 1975 |
| m-xylene | 2.5 | | | | Stern et al. | 1987 |
| m-, o-, p-xylene | 2.4,2.7,0.95 | | | | Izumi and Fukuyama | 1990 |
| ethylbenzene | 0.6 | | | | Stern et al. | 1987 |
| | 0.78 | | | | O'Brien et al. | 1975 |
| | 3.1 | | | | Izumi and Fukuyama | 1990 |
| n-propylbenzene | 0.98 | | | | Izumi and Fukuyama | 1990 |
| isopropylbenzene | 2.3 | | | | Izumi and Fukuyama | 1990 |
| 1,2,3-trimethylbenzene | 2.2 | | | | Izumi and Fukuyama | 1990 |
| 1,2,4-trimethylbenzene | 1.1 | | | | Izumi and Fukuyama | 1990 |
| 1,3,5-trimethylbenzene | 1.8 | | | | Izumi and Fukuyama | 1990 |
| | 2.4 | | | | Stern et al. | 1987 |
| | 1.94 | | | | O'Brien et al. | 1975 |
| **Phenols** | | | | | | |
| o-cresol | 21 | 0 | 2-hydroxy-3-nitrotoluene | mass spectrometry | McMurry and Grosjean | 1985 |

| | | | | | | |
|---|---|---|---|---|---|---|
| | | | 2-hydroxy-5-nitrotoluene<br>2-hydroxy-3,5-dinitrotoluene | | | |
| 4-hydroxy-2-nitrotoluene | 57 | | 3,5-dinitro-4-hydroxytoluene | mass spectrometry | McMurry and Grosjean | 1985 |
| **Esters** | | | | | | |
| methoxybenzene | 2.7 | | | | Izumi and Fukuyama | 1990 |
| **Olefins** | | | | | | |
| 1-hexene | 0.34 | 0.24 | | | McMurry & Grosjean | 1985 |
| 1-heptene | 0.85 | | | | O'Brien et al. | 1975 |
| | | 18 | hexanoic acid | Teflon filter/gas chromatography | Grosjean | 1984a |
| 1-octene | 4.2 | | 5-propyl furanone<br>heptanoic acid | Gas Chromatography /Mass Spectrometry | Wang et al. | 1992 |
| cyclopentene | | 1.0-5.0 | succinic acid<br>glutaraldehyde<br>5-oxo-pentanoic acid<br>glutaric acid | GC/MS | Hatakeyama et al. | 1987 |
| cyclohexene | 18.3 | 18.3 | | | Izumi et al. | 1988 |
| | | 13 | adipaldehyde<br>6-oxo-hexanoic acid<br>adipic acid<br>gluataraldehyde<br>5-oxo-pentanoic acid<br>glutaric acid | GC/MS | Hatakeyama et al. | 1987 |
| cycloheptene | | 4.0-10.0 | glutaric acid<br>adipaldehyde<br>6-oxo-hexanoic acid<br>adipic acid<br>pimelaldehyde<br>7-oxo-heptanoic acid<br>pimelic acid | GC | Hatakeyama et al. | 1987 |

| | | | | | | |
|---|---|---|---|---|---|---|
| isoprene | 0 | | | | Paulson et al. | 1991 |
| indene | + | | | | O'Brien et al. | 1975 |
| 1,5-hexadiene | 20.3 | | | | O'Brien et al. | 1975 |
| 1,6-heptadiene | 69 | | | | O'Brien et al. | 1975 |
| 2-methyl-1,5-hexadiene | 47.6 | | | | O'Brien et al. | 1975 |
| 1,7-octadiene | 68 | | | | O'Brien et al. | 1975 |
| | 10.3 | | | | Grosjean and Friedlander | 1975 |
| 2,6-octadiene | 0.9 | | | | O'Brien et al. | 1975 |
| **Terpenes** | | | | | | |
| α-pinene | 55 | | | | O'Brien et al. | 1975 |
| | 38-55 | | | | Hooker et al. | 1985 |
| | | 18.3 | pinonaldehyde<br>nor-pinonaldehyde<br>pinonic acid<br>nor-pinonic acid | GC/MS | Hatakeyama et al. | 1989 |
| β-pinene | | 13.8 | nopinone | GC/MS | Hatakeyama et al. | 1989 |
| | 8 | | nopinone<br>pinocamphone | GC/MS and infrared spectroscopy | Pandis et al. | 1990 |
| limonene | >50 | | | | Schuetzle and Rasmussen | 1978 |
| **Other** | | | | | | |
| styrene | 0.3 | | | | Izumi and Fukuyama | 1990 |
| α-, β-methylstyrene | 0.7-4.9,0.57 | | | | Izumi and Fukuyama | 1990 |



---

[a] $FAC = \frac{\text{aerosol from reactive organic gases } \mu g\ m^{-3}}{\text{initial reactive organic gases } \mu g\ m^{-3}}$

had their reaction products conclusively identified as components of secondary organic aerosol. This lack of data, and consequent lack of a comprehensive understanding of mechanistic factors leading to aerosol formation, is a serious weakness in our understanding. This information is crucial to accurately predict aerosol dynamics and saturation vapor pressures.

The 1987 Southern California Air Quality Study (SCAQS) VOC (volatile organic compounds) monitoring program resulted in a comprehensive database of C1-C12 hydrocarbon and C1-C7 carbonyl concentrations at nine stations, sampled three or six times per day in two different seasons (Lurmann and Main, 1992). Both surface and air samples were collected. The VOCs identified in the study are listed in Table 2. The non-methane organic compounds are 45% paraffins, 9% olefins, 18% aromatic compounds, and 13% carbonyl compounds. Previous work has generally established that if a linear alkane has fewer than seven carbon atoms or if a cycloalkane has fewer than six carbon atoms, products of their photooxidation will have vapor pressures too high to condense to form aerosol (Grosjean and Seinfeld, 1989). On this basis alone, of the paraffins identified in Table 2, 60% have the potential to be aerosol precursors.

## 3. General Description of the Proposed Experiments

Various hydrocarbons which have been identified as typical components of urban air will be studied. The goals of the experiments are to determine which hydrocarbons are aerosol precursors, to identify the components of the aerosol, and to determine to the extent possible the gas-phase oxidation mechanisms leading to SOA formation.

The initial hydrocarbons proposed for study are listed in Table 3. Most compounds are chosen for their predominance in the ambient (refer to Table 2). In addition, the alkanes are chosen to examine any effect of branching on the photooxidation of linear alkanes and cycloalkanes. Some compounds previously studied are included for consistency checks on former work. The hydrocarbons to be studied initially are methylcyclohexane, methylcyclopentane, 2,2,4-trimethylpentane (isooctane), and 2,2,5-trimethylhexane.

Table 2 SCAQS Morning Composition of Nonmethane Organic Compounds[a]

| COMPOUND | % NMOC | COMPOUND | % NMOC |
|---|---|---|---|
| propane | 7.888 | 2,3,4-trimethylpentane | 0.381 |
| toluene | 7.876 | 3-methylheptane | 0.377 |
| isopentane | 7.841 | n-decane | 0.353 |
| n-butane | 6.166 | 1-pentene | 0.347 |
| ethane | 4.538 | trans-2-pentene | 0.324 |
| ethene | 4.202 | butanal | 0.296 |
| n-pentane | 3.709 | 1,3-butadiene | 0.282 |
| acetylene | 3.007 | isoprene | 0.279 |
| isobutane | 2.820 | n-propylbenzene | 0.278 |
| benzene | 2.776 | nonane | 0.271 |
| 2-methylpentane | 2.545 | C7 carbonyl | 0.270 |
| p-xylene | 2.442 | cis-2-pentene | 0.263 |
| m-xylene | 2.442 | 4-methyloctane | 0.209 |
| acetone | 2.359 | 3-methyloctane | 0.209 |
| o-xylene | 1.805 | trans-2-butene | 0.185 |
| 3-methylpentane | 1.789 | C5 carbonyl | 0.184 |
| n-hexane | 1.750 | cis-2-butene | 0.181 |
| methylcyclopentane | 1.721 | 2,2,5-trimethylhexane | 0.170 |
| propylene | 1.680 | cycloheptane | 0.110 |
| 1,2,4-trimethylbenzene | 1.656 | 3-methyl-1-butene | 0.098 |
| 2,2,4-trimethylpentane | 1.414 | 2-methyl-2-pentene | 0.093 |
| ethylbenzene | 1.292 | 3,3-dimethylpentane | 0.083 |
| acetaldehyde | 1.226 | 2,5-dimethylheptane | 0.067 |
| 3-methylhexane | 1.167 | 2,2-dimethylbutane | 0.037 |
| methylcyclohexane | 1.100 | 1-nonene | 0.029 |
| pentanal | 1.088 | 3-methyl-trans-2-pentene | 0.017 |
| formaldehyde | 1.042 | 1-octene | b |
| methylethylketone | 1.035 | 2,2,3-trimethyl-1-butene | b |
| C6 carbonyl | 1.034 | 2,3-dimethylheptane | b |
| m-ethyltoluene | 1.008 | 2,3-dimethylhexane | b |
| 2-methylhexane | 0.981 | 2,4-dimethylheptane | b |
| n-heptane | 0.958 | 2,4-dimethylhexane | b |
| 1-butene | 0.743 | 2,5-dimethylhexane | b |
| 2,3-dimethylbutane | 0.686 | 2-methylpropene | b |
| 2,3-dimethylpentane | 0.662 | 4-methyl-1-pentene | b |
| p-ethyltoluene | 0.522 | α-pinene | b |
| propanal | 0.505 | cis-2-octene | b |
| cyclohexane | 0.493 | cis-3-methyl-2-pentene | b |
| 2,4-dimethylpentane | 0.451 | cis-4-methyl-2-pentene | b |
| o-ethyltoluene | 0.448 | cyclohexene | b |
| cyclopentane | 0.433 | ethylcyclohexane | b |
| 2-methyl-1-butene | 0.423 | 3-methylcyclohexene | b |
| 2-methylheptane | 0.409 | trans-4-methyl-2-pentene | b |
| n-octane | 0.389 | trichloroethene | b |

[a]Adapted from Lurmann and Main (1992)
[b]Detected, but below the limit to assign a percentage.

**Table 3 Hydrocarbons to be Studied as Aerosol Precursors**

| Hydrocarbons | Comments |
|---|---|
| ***Alkanes*** | |
| 2,2,4-trimethylpentane<br>2,2,5-trimethylhexane<br>nonane<br>decane | Alkanes comprised about 45% of the hydrocarbons identified in SCAQS. Little is known about the aerosol forming potential of large straight chain and branched alkanes. |
| ***Cycloalkanes*** | |
| methylcyclopentane<br>methylcyclohexane<br>cycloheptane<br>dimethylcyclohexane | Methylcyclohexane has been identified as an aerosol former (Wang et al., 1992) but other cycloalkanes have largely not been studied. |
| ***Alkenes*** | |
| 1-octene<br>1-decene<br>1-dodecene<br>3-methylcyclohexene | Alkenes react with $^{\bullet}OH$ and $O_3$, both routes are expected to lead to aerosol for sufficiently high carbon number. 3-methylcyclohexene will be studied to compare to previous work of Izumi et al. Other alkenes for products and aerosol forming thresholds. |
| ***Aromatics*** | |
| toluene<br>*m,p*-xylene<br>ethylbenzene<br>*m,p*-ethyltoluene<br>1,2,4-trimethylbenzene | Aerosol-forming potential has been studied (Table 1) but significant uncertainties exist in gas-phase mechanisms (Atkinson et al., 1989). Aromatics are important compounds in view of ozone and aerosol formation. |

To determine the molecular speciation of the aerosol, experiments will involve irradiation of the individual hydrocarbons with $NO_x$ in an outdoor smog chamber of approximate size 6 $m^3$. The hydrocarbon will be injected to a concentration of about 5 ppm. Although this concentration exceeds ambient concentrations by several orders of magnitude, it is necessary in order to generate sufficient aerosol for subsequent analysis. At least 100 μg of organics are required for GC/MS analysis (Mazurek *et al.*, 1989). If the extraction process has an overall efficiency of 40%, then 250 μg of organics must be collected on the quartz fiber filter. As described in a later section, aerosol will be collected at 10 L $min^{-1}$ until the bag is deflated. The approximate time for deflation is five to six hours. Thus the necessary aerosol mass concentration in the chamber is:

$$\text{aerosol concentration} = \frac{\text{mass of aerosol on filter}}{\text{flowrate}} \frac{1}{\text{time for collection}} = 83\ \mu g\ m^{-3}$$

The yield of aerosol from a hydrocarbon precursor, the fractional aerosol coefficient (FAC), depends on the size and the functional group of the organic. As an example, methylcyclohexane has an estimated FAC of 1.0% (Grosjean and Seinfeld, 1989). Based on the definition of FAC in the article, the initial concentration of methylcyclohexane required to yield at least 100 μg of organics for analysis is:

$$\left(\begin{matrix}\text{aerosol} \\ \text{concentration } \mu g\ m^{-3}\end{matrix}\right) \frac{\left(\begin{matrix}\text{initial concentration} \\ \text{of hydrocarbon } \mu g\ m^{-3}\end{matrix}\right)}{\left(\begin{matrix}\text{aerosol from} \\ \text{hydrocarbon } \mu g\ m^{-3}\end{matrix}\right)} \frac{RT}{PM} = 2.1 \text{ppm}$$

In order to convert units from μg $m^{-3}$ to ppm, the conditions are taken as 1.0 atm of pressure and 298K. Although the above calculation itself is rather conservative, the concentration of organic used in the experiments will be around 5 ppm to ensure enough aerosol is generated.

Once the species in the aerosol have been identified, their vapor pressures in the atmosphere can be obtained from theory or Tandem Differential Mobility Analyzer experiments (Zhang *et al.*, 1993). If the

hydrocarbon precursor's ambient concentration is known, the possibility of aerosol formation in the atmosphere can consequently be determined. Thus the utilization of such a large initial hydrocarbon concentration will not result in misleading data.

The ratio of initial hydrocarbon to $NO_x$ in the chamber will be at least 25 ppmC/ppm, a level that has been found previously to be optimal for SOA formation (Zhang *et al.*, 1992). The ratio of NO:$NO_2$ must also not be greater than two in order for the reaction to move quickly. Propene at a concentration of about 1 ppm will be added to enhance reactivity (Wang *et al.*, 1992). If necessary, seed particles may also be added to the chamber at a concentration of about 1000 particles $cm^{-3}$ to encourage condensation. Table 4 lists the initial conditions for the proposed experiments.

## 4. Detailed Description of the Experimental Facility and Experimental Protocol

### 4.1. Outdoor Smog Chamber System: Gas Phase and Aerosol Phase Measurements

The experiments will be performed in a flexible outdoor smog chamber, similar to that described by Pandis *et al.*, 1991 and Wang *et al.*, 1992. The chamber is constructed by heat sealing four panels of 2 mil (50 μm) thick Teflon (DuPont 200-A Fluorocarbon film). Each panel measures 1.38 m x 5 m, resulting in an approximate volume of 6 $m^3$ when the chamber is fully inflated. Previous experience has shown that the type of seal used in constructing the bag is crucial to prevent leaks. An overlapping seal is best. All seams are reinforced with 3M Mylar tape. The tape reduces the stress on the seams by spreading the stress over the area of the tape.

The chamber is supported 0.6 m above the rooftop to allow for circulation of air beneath the Teflon bag. A black tarpaulin is spread on the roof below the chamber to reduce reflection of radiation. A dark tarpaulin is also used to cover the bag during the injection of purified air and reactants prior to the start of an experiment. The chamber contents are readily mixed by the action of the wind on the chamber walls.

**Table 4 Initial Conditions for Smog Chamber Experiments**

| HYDROCARBONS | C atoms per molecule | [Hydrocarbon] (ppm) | [Hydrocarbon] (ppmC) | [NO] (ppm) | [NO2] (ppm) |
|---|---|---|---|---|---|
| ***Alkanes*** | | | | | |
| 2,2,4-trimethylpentane | 8 | 5 | 40 | 1.067 | 0.533 |
| 2,2,5-trimethylhexane | 9 | 5 | 45 | 1.200 | 0.600 |
| nonane | 9 | 5 | 45 | 1.200 | 0.600 |
| decane | 10 | 5 | 50 | 1.333 | 0.667 |
| ***Cycloalkanes*** | | | | | |
| methylcyclopentane | 6 | 5 | 30 | 0.800 | 0.400 |
| methylcyclohexane | 7 | 5 | 35 | 0.933 | 0.467 |
| cycloheptane | 7 | 5 | 35 | 0.933 | 0.467 |
| dimethylcyclohexane | 8 | 5 | 40 | 1.067 | 0.533 |
| ***Alkenes*** | | | | | |
| 1-octene | 8 | 5 | 40 | 1.067 | 0.533 |
| 1-decene | 10 | 5 | 50 | 1.333 | 0.667 |
| 1-dodecene | 12 | 5 | 60 | 1.600 | 0.800 |
| 3-methylcyclohexene | 7 | 5 | 35 | 0.933 | 0.467 |
| ***Aromatics*** | | | | | |
| toluene | 7 | 5 | 35 | 0.933 | 0.467 |
| m,p-xylene | 8 | 5 | 40 | 1.067 | 0.533 |
| ethylbenzene | 8 | 5 | 40 | 1.067 | 0.533 |
| m,p-ethyltoluene | 9 | 5 | 45 | 1.200 | 0.600 |
| 1,2,4-trimethylbenzene | 9 | 5 | 45 | 1.200 | 0.600 |

On the morning of an experiment, the chamber, covered with its dark tarpaulin, is inflated with purified air. Laboratory compressed air is passed through three packed beds. The first bed contains activated charcoal to remove hydrocarbons. Activated charcoal removes gasoline, ether, benzol, alcohols, light oils, and solvents from natural gas, still gases and air. The second bed contains Purafil for the removal of $NO_x$. The third bed contains equal amounts of silica gel and 13X molecular sieves. The silica gel removes water, while the molecular sieves remove water and carbon dioxide. The air then passes through a total particle filter to remove any aerosol particles, and the purified, particle free air is then injected to the chamber. Approximately two hours are required for inflation, and an additional hour for injection of the reactants. The hydrocarbon is injected with a micro-syringe into a glass bulb which is gently heated to evaporate the hydrocarbon into an air stream flowing to the chamber. NO and $NO_2$ are injected using certified cylinders, containing several hundred ppm of the gas in ultra-pure nitrogen. The reactants are allowed sufficient time to mix and the initial gas phase and aerosol phase measurements to stabilize. The experiment then begins when the chamber is uncovered and exposed to sunlight. Refer to Appendix A for more detailed instructions.

A schematic of the experimental facility is presented in Figure 2. The on-line gas-phase measurements include ozone, NO, and $NO_x$ concentrations. The relative humidity of the chamber can also be measured instantaneously using the dew point hygrometer. The concentrations of the parent hydrocarbon are measured with the on-line gas chromatograph equipped with a flame ionization detector (FID). Calibration curves for each hydrocarbon are generated after each experiment using certified cylinders of the hydrocarbon in ultra-pure nitrogen. Table 5 lists all the measurements and the instruments used in the experiments.

The occurrence of nucleation during a smog chamber experiment is monitored by a Condensation Nucleus Counter (TSI Model 3760) and a frequency counter. If seed particles are used, then a Differential Mobility Analyzer (DMA, TSI Model 3071) and CNC will measure shifts in the aerosol size distribution. Copper tubing is used to minimize particles losses as the aerosol is pumped from the chamber to the aerosol instruments. Once significant particle concentrations or increases in the size

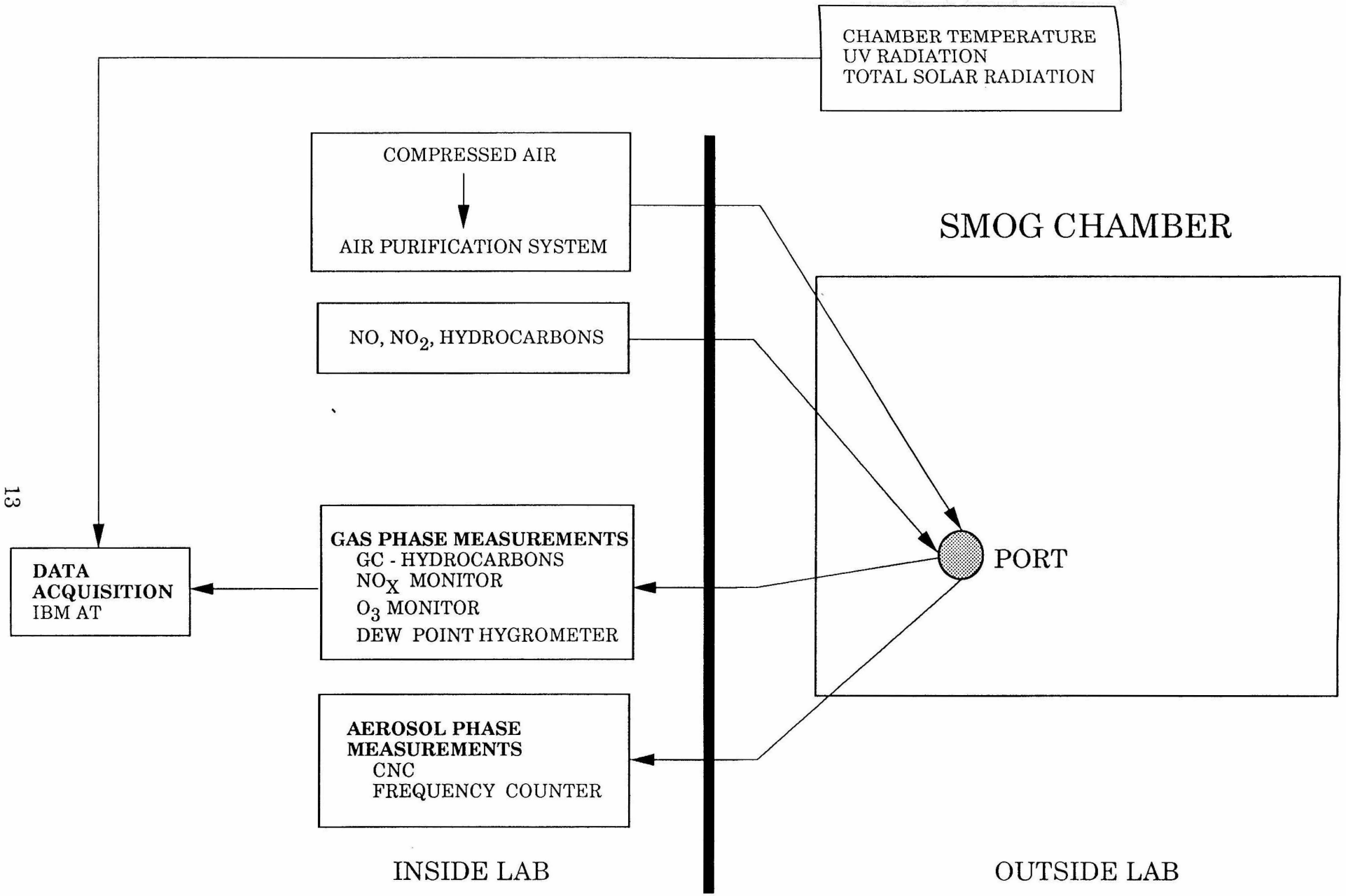



Fig. 2 Schematic of the Outdoor Smog Chamber Facility

**Table 5 Instrumentation for Gas Phase and Aerosol Phase Measurements**

| PARAMETER | METHOD | INSTRUMENT | COMMENTS |
|---|---|---|---|
| **Gas Phase Measurements** | | | |
| NO, NO2, NOx | Chemiluminescence | Thermo Environmental Model 42 | Calibration performed with certified cylinders of NO, NO2 and ultra-pure N2. Range of instrument is 0.5ppb to 20 ppm. |
| Ozone | UV absorption | Dasibi Model 1008-PC | Calibrated yearly by the South Coast Air Quality Management District. Full scale range of 0-1ppm. |
| Hydrocarbons | Gas chromatography with flame-ionization detection | Hewlett Packard 5890 GC | Calibrated after each experiment with certified gas cylinders. |
| Humidity | Dew point hygrometer | EG&G Dew Point Hygrometer, Model 880 | |
| Temperature | Sensor | Yellow Springs Instrument Co., Model 43 Single Channel Tele-Thermometer | |
| Total Solar Radiation | Differential electro-plated thermopile | Eppley Black & White Pyranometer, Model 8-48 | |
| UV Radiation | | | |
| **Aerosol Phase Measurements** | | | |
| Presence of Particles | Single-particle counting laser-diode optical detector | TSI Condensation Nucleus Counter, Model 3760 | |

distribution are observed, sampling will begin. The aerosol will be collected via two parallel filter samplers, at 10 L $min^{-1}$ through each sampler for several hours. Each filter sampler consists of two stainless steel filter holders in series. One series will have two 47 mm quartz fiber filters to collect aerosol for analysis. The other series will have a 47 mm Teflon filter preceding a 47 mm quartz fiber filter, to measure the adsorbed organic vapor background on the quartz fiber filters (Turpin and Huntzicker, 1991). The filters are stored below 0°C immediately after collection. In preparation for sampling, the quartz fiber filters are baked at 750°C for at least two hours (Hildemann, 1990; Hildemann *et al.*, 1991). The sampling tubes and filter holders are cleaned prior to use by sonication in distilled water, methanol, and then in hexane, each for 20 minutes. Refer to Appendix B for more details on the cleaning and preparation protocol for quality control.

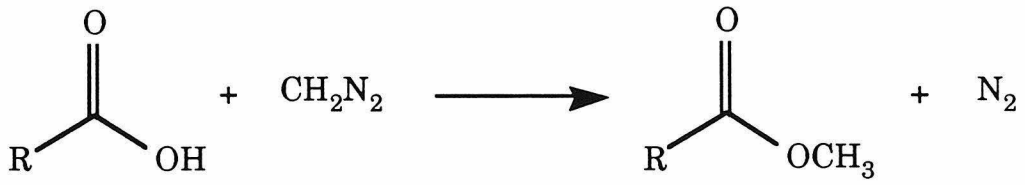
The aerosol is collected until the bag is almost deflated. After each experiment, the smog chamber is filled with purified air and "baked" in the sunlight the next day to remove any residual products or reactants from the walls of the chamber (Pandis *et al.*, 1991). Clean air continually flows through the Teflon chamber during this time. Previous investigators (Stern *et al.*, 1987) confirmed the reproducibility of experimental results within a few percent for ozone formation when using this cleaning process.

## 4.2 Extraction of the Collected Aerosol

### 4.2.1 Description of the Extraction Processes

The aerosol will be extracted from the quartz fiber filters by either one or both of the following methods: solvent extraction and supercritical fluid extraction. Immediately prior to extraction, each filter will be spiked with an aliquot of a standard containing species differing from the expected aerosol components (Mazurek *et al.*, 1987). This addition is necessary to estimate the recovery efficiency of the extraction. Solvent extraction (Rogge *et al.*, 1991) involves sonicating a filter sequentially in two 30 mL aliquots of

hexane, and then in three 30 mL aliquots of a 2:1 benzene-isopropanol mixture. After each solvent addition and sonication interval of 20 min., the extract is collected into a flask via an aspirator pump. The resulting solution of extract and solvents is then reduced in volume from about 60 mL to approximately 5 mL using a rotary evaporator. The volume is further reduced to less than 1 mL by nitrogen blow-down. After measuring the volume with a syringe, the sample is then split into two vials. One vial will be derivatized to convert organic acids to their methyl ester analogs by the addition of a solution of diazomethane in benzene.




This last step is necessary to allow for the elution of the acids through the gas chromatograph column. Refer to Appendix C for complete instructions on this solvent extraction method.

Supercritical fluid extraction (SFE) often uses carbon dioxide, ammonia, nitrogen oxide, fluoroform, methane, pentane, and other gases as the extraction fluid (Richards and Campbell, 1991; and Katauskas and Goldner, 1991). For the samples tested on a SFE unit, carbon dioxide has been utilized. The filter is placed in a stainless steel cell (rated to 10 000 psi) of typical volumes of 0.5 to 50 mL. Glass wool or beads can also be added to the cell to ensure equal distribution of carbon dioxide ($CO_2$) throughout the cell. The cell is pressurized and heated above the critical point of $CO_2$: 72.9 atm and 31.3°C. The supercritical $CO_2$ either steeps in the cell or washes continuously over the matrix. Typical runs last 30 to 40 min. The solutes are then trapped into a small volume (1-2 mL) of solvent either by direct bubbling into the solvent, or by first trapping the extract on glass beads and then rinsing the beads with solvent. At this point, the extract can divided between two vials, as discussed above, to convert the acids in part of the sample to their methyl esters.

### 4.2.2 Recovery Efficiencies of the Extraction Methods

The recovery efficiencies of both the solvent technique discussed above and the Dionex SFE unit were tested with spiked filters. The filter which was extracted by the solvent technique was spiked with 60 ± 0.3 μL of a standard. The components of the standard are listed in Table 6 below.

**Table 6 Components of the Standard Solution and Quantities Spiked onto Filter**

| COMPOUND | CONCENTRATION ($\mu g\ mL^{-1}$) | MASS ON FILTER ($\mu g$)[a] |
|---|---|---|
| Decane | 490 ± 5 | 29.4 ±0.15 |
| Heptanal | 370 ± 5 | 22.2 ± 0.11 |
| Octanal | 890 ± 5 | 53.4 ±0.27 |
| Octane | 360 ± 5 | 21.6 ± 0.11 |
| Pentadecane | 270 ± 5 | 16.2 ± 0.08 |
| Tridecane | 370 ± 5 | 22.2 ± 0.11 |

[a]mass on filter = concentration (60 ± 0.3 μL)

The filter which was extracted using the Dionex SFE unit was spiked with 40.9 μg heptanal, 41.05 μg octanal, and 70.3 μg octane.

The quantification was performed using the gas/chromatograph and mass/spectrometer (GC/MS) in the Environmental Analysis Center, as well as a gas chromatograph equipped with a flame-ionization detector in the Hartley Laboratories. For details on the temperature programs used for the analysis and copies of the chromatograms, refer to Appendix D. For details on calculating the recovery efficiencies, refer to the following section 5.4 "Quantification of the Recovery Efficiency." The efficiencies for each compound, using the solvent extraction technique, are listed in Table 7, along with the relative response factors for each hydrocarbon. Over the usage of the sample, it was observed that the sample degraded. In particular, the recovery of tridecane and pentadecane decreased. The

loss of the sample, which occurred only when pulling small aliquots into the syringe (the sample was stored otherwise in a freezer between uses), resulted in the significant decrease in calculated recoveries.

**Table 7 Recovery Efficiencies for the Solvent Extraction Technique**

| HYDROCARBON | RELATIVE[a] RESPONSE FACTOR | RECOVERY[a] | RELATIVE[b] RESPONSE FACTOR | RECOVERY[b] |
|---|---|---|---|---|
| Decane | 6.02 | 0% | 0.97 | 0% |
| Heptanal | 0.48 | 0% | 0.68 | 1.5% |
| Octanal | 2.78 | 0% | 0.45 | 0.55% |
| Octane | 1.75 | 0% | 1.07 | 0% |
| Pentadecane | 9.15 | 46% | 1.36 | 0.67% |
| Tridecane | 7.48 | 8.9% | 1.15 | 0.19% |

[a]The data used to calculate these response factors and recoveries were obtained from the initial runs on the GC/MS.
[b]The data used to calculate these response factors and recoveries were obtained from final runs on the GC with FID.

The sample obtained from the Dionex SFE extraction resulted in the recovery of none of the initial components on the spiked filter. Appendix E includes the method for extraction of the sample, in addition to the gas chromatogram obtained using a GC/MS. Possible reasons for the lack of recovery are numerous. Unfortunately, some technical difficulties occurred with the SFE unit during the extraction. At the start of the extraction, it appeared that the plumbing connecting the cell to the $CO_2$ source was not secure and consequently, carbon dioxide, and possibly the sample, was lost. Further, the computer was indicating no flow through the cell while extraction was taking place. Because the components on the filter were fairly volatile hydrocarbons, they could also have bubbled straight through the collection solvent and vented.

### 4.2.3 Future Work on Method Development of the Aerosol Extraction Procedure

It is clear from the recoveries discussed in the previous section that significant method development of the aerosol extraction procedure is required. This step in the overall experiments is crucial, not only to identify all components in the aerosol but also to quantify yields of various products. It is necessary to first establish a method that will result in adequate overall recoveries for a variety of compounds. It is proposed that the following issues be addressed:

1. Maximizing the recoveries obtained (for the compounds of interest) with supercritical fluid extraction, by varying such parameters as temperatures during extraction and collection, pressures, the choice of modifier, and collection techniques:
    a. Constant temperature or ramped temperature during extraction
    b. Constant pressure or ramped pressure during extraction
    c. Static, dynamic, or a combination of modes for the carbon dioxide during extraction
    d. Type of modifier and the appropriate percentage
    e. Collection with glass beads, or Tenax, or straight bubbling into solvent
    f. Temperature during collection of the extract
2. In addition to developing a method with supercritical fluid extraction, also considering solvent techniques that are less rigorous in terms of solvent evaporation than the technique discussed in Appendix C. An example would be Soxhlet extraction with methylene chloride.
3. A series of recovery curves should be generated for the following classes of compounds in a tentative range of C5 to C15: alkanals, alkanoic acids and aromatics.

Once an extraction protocol is decided, it is also important to identify sources of contamination. Since the collection of aerosol involves such minute quantities of sample, it is crucial to be able to distinguish between contaminants and the actual components of the aerosol. The following list tentatively outlines sources to test.

1. parent hydrocarbons used in the smog chamber experiments
2. all solvents used in the extraction procedure
3. blank, baked filters
4. the recovery standard
5. baked filters with background aerosol collected from a recently "baked" smog chamber
6. all solvents used to clean the syringes for hydrocarbon injection into the smog chamber and for GC/MS work.

A further problem experienced during the testing of the various extraction methods, was the degradation of the sample after extraction. Despite the fact that the vial was stored in a freezer between uses, large amounts of the extract were lost while analyzing the data. Various methods, such as keeping the vials in an ice bath or in a dry ice/acetone slush while injecting samples into the GC, need to be tried.

## 5. Analysis of the Aerosol Sample

### 5.1 Recovery Standards to Estimate Extraction Recoveries

Prior to the extraction of the filter, it is necessary to spike the filter with a known solution of hydrocarbons in order to determine the recovery achieved with the extraction process (Mazurek *et al.*, 1987). The spike should be similar to the organics that are expected to be components of the aerosol, by not only containing species with the same functional groups, but also species with similar carbon numbers. The compounds in the spike should also be deuterated, or significantly different structurally from the aerosol constituents, to ensure distinction of the spike from the aerosol. By tailoring the spike for each parent hydrocarbon, greater confidence in the recovery efficiencies is obtained.

The first branched alkane on the proposed list of hydrocarbons is 2,2,4-trimethylpentane. Potential products include 4,4-dimethyl-2-pentanone; 2,4,4-trimethylpentanal; acetone; 2,2-dimethylpropanal; 2,4-dimethylpentanal; 2-methylpropanal; 2,4-dimethyl-3-pentanone; and

various alkyl nitrates and nitrites. The products consist largely of branched, 2- or 3-ketones and branched aldehydes of carbon number ranging from 3 to 7 and 4 to 8, respectively. A possible spike could consist of such straight chain alkanals and ketones as butanal, heptanal, nonanal, 2-butanone, 3-hexanone, and 2-octanone. These compounds could be deuterated, but because they are straight chain molecules, they are sufficiently different from the branched products and could be used in the non-deuterated form.

### 5.2 Measurement of the Organic Carbon Loading of the Filter

It is desired to spike the filter so that the peaks on the gas chromatogram of the spiked species are similar in size to those peaks of the constituents of the aerosol sample. To achieve this balance, it is necessary to know the carbon content on the filter. Rather than utilizing an entire filter for organic carbon analysis, it is possible to punch out a small circle from the filter and measure the carbon content on the small circle. The carbon loading on the filter can then be estimated from the loading per unit area of the small circle and the area of the remainder of the filter. The diameter of the punched circle can be accurately measured to within 1.0 μm by a micrometer. The organic carbon can be weighed by using the DuPont 951 Thermogravimetric Analyzer in the Hartley Laboratories. This thermogravimetric analyzer can constantly measure the amount and the rate of weight change of material of the sample as a function of temperature or time. The range of the instrument is 0.02 to 500 mg.

### 5.3 Identification of Components of the Aerosol

After the extraction process, the aerosol sample will be qualitatively analyzed by gas chromatography/mass spectrometry analysis, using the GC/MS in the Bank of America Center for Environment Analysis. The gas chromatograph will separate the aerosol sample into its individual compounds, while the mass spectrometer measures and records the abundances of the compounds' fragments. By comparing each compounds' mass spectra with spectra in the NIST library (loaded into the workstation

controlling the GC/MS), species can be tentatively identified. The ChemSystem software rates the match of the sample's and library's spectra. If a match has a "quality" greater than 70, then authentic samples of the tentatively identified compounds will be purchased. Verification of identification will be performed by comparing the residence times and the mass spectra obtained in the GC/MS of the authentic sample to the aerosol sample. If a species cannot be adequately matched to a species in the library (a match quality less than 70), the mass spectra will be studied for characteristic fragmentation patterns of functional groups on organics. All aldehydes, for example, fragment in the mass spectrometer such that the observable peaks include the molecular ion peak, the molecular ion peak minus one atomic mass unit, a peak at 29 m/e corresponding to the $HCO^+$ fragment, and a peak at 44 m/e corresponding to $CH_2CHOH^+$ which may result when the alkanal undergoes a McLafferty rearrangement (Pavia *et al.*, 1979). Alkanes, alkenes, ketones, carboxylic acids and so forth, all fragment differently, allowing for identification of the compound. Again, once a species has been tentatively identified, authentic samples will be used to verify identification.

### 5.4 Quantification of the Recovery Efficiency

When injecting the aerosol sample into the gas chromatograph, a co-injection standard is included. A small volume of the sample, such as 0.5 μL, is pulled into the syringe, followed with a 0.5 μL air plug, and then a 0.1-0.5 μL plug of the co-injection standard (Mazurek *et al.*, 1987). This co-injection standard is necessary to calculate recoveries. It is a solution of a hydrocarbon in solvent at a concentration similar to what would be found in the aerosol sample. This balance is to achieve similar peak areas of the sample and the co-injection standard on the gas chromatogram. The solvent would be the same solvent used in the extraction process. The co-injection standard used in calculating the recoveries in section 4.2.2 was mesitylene at 400 $\mu g\ mL^{-1}$ in methanol.

To calculate recoveries of the spiked compounds, two different chromatograms are needed. The first chromatogram is of the spike and co-injection standard, and is required to calculate the response factors of the

hydrocarbons in the spike. The second chromatogram is of the sample and co-injection standard and is used to estimate the recovery efficiency of the extraction process. Using the chromatogram of the spike, the relative response factor is defined as:

$$RRF = \frac{\begin{pmatrix}\text{peak area}\\ \text{of organic}\end{pmatrix}}{\begin{pmatrix}\text{mass of organic}\\ \text{injected}\end{pmatrix}} \frac{\begin{pmatrix}\text{mass of coinjection}\\ \text{standard injected}\end{pmatrix}}{\begin{pmatrix}\text{peak area of}\\ \text{coinjection standard}\end{pmatrix}}$$

Recoveries are estimated using the chromatogram of the sample, and by the following equation:

$$\text{RECOVERY} = \begin{pmatrix}\text{peak area}\\ \text{of organic}\end{pmatrix} \frac{\begin{pmatrix}\text{mass of coinjection}\\ \text{standard injected}\end{pmatrix}}{\begin{pmatrix}\text{peak area of}\\ \text{coinjection standard}\end{pmatrix}} \frac{1}{RRF} \frac{\begin{pmatrix}\text{total volume}\\ \text{of sample}\end{pmatrix}}{\begin{pmatrix}\text{volume of}\\ \text{sample injected}\end{pmatrix}} \frac{1}{\begin{pmatrix}\text{quantity of organic}\\ \text{spiked onto filter}\end{pmatrix}}$$

These equations were used to calculate the recoveries listed in Table 7.

## 5.5 Gas Phase Mechanisms of the Parent Hydrocarbon Leading to Aerosol

Once species in the aerosol are identified, gas-phase mechanisms leading to these products can be proposed. In urban air, the oxidizing species include the following three electrophiles: ozone, hydroxyl radicals, and nitrate radicals. Reaction with ozone is a predominant removal pathway of hydrocarbons during the night and day; while reaction with hydroxyl radicals is significant only during the day and reaction with nitrate radicals only during the night (Seinfeld, 1986). The potential oxidizing species in the smog chamber are ozone and hydroxyl radicals. It is known that aromatic hydrocarbons, saturated aliphatics, and oxygenated aliphatics react only with hydroxyl radicals, while unsaturated aliphatics react with all three oxidants (Seinfeld, 1986). Based on these guidelines and knowledge of the parent hydrocarbon and the aerosol products, detailed steps in a reaction mechanism can be identified.

## 6. Summary

The ultimate goal of this research is to propose feasible mechanisms of the gas phase oxidation of various hydrocarbons, leading to condensable products. These mechanisms will be based on the identification of the species in the aerosol resulting from a single hydrocarbon precursor. The aerosol used in the analysis will be generated by irradiating the hydrocarbon with $NO_x$ in smog chamber experiments. Successful completion of the research will not only contribute significantly to our understanding of secondary aerosol formation, but will also aid in endeavors to predict the effects of primary gaseous and particulate emissions in the atmosphere.

## REFERENCES


Grosjean D. (1984a) Photooxidation of 1-heptene. *Sci. Total. Envir.* **37**, 195-211.

Grosjean D. (1984b) Atmospheric reactions of ortho cresol: gas phase and aerosol product. *Atmospheric Environment* **18**, 1641-1652.

Grosjean D. (1985) Reactions of o-cresol and nitrocresol with $NO_x$ in sunlight and with $O_3$-$NO_2$ mixtures in the dark. *Environ. Sci. Technol.* **19**, 968-974.

Grosjean D. and Seinfeld J.H. (1989) Parameterization of the formation potential of secondary organic aerosols. *Atmospheric Environment* **23**, 1733-1747.

Hatakeyama S., Tanonaka T., Weng J., Bandow H., Tagaki H. and Akimoto H. (1985) Ozone-cyclohexene reaction in air: quantitative analysis of particulate products and the reaction mechanism. *Environ. Sci. Technol.* **19**, 935-942.

Hatakeyama S., Ohno M., Weng J., Takagi H. and Akimoto H. (1987) Mechanism for the formation of gaseous and particulate products from ozone-cycloalkene reactions in air. *Environ. Sci. Technol.* **21**, 52-57.

Hatakeyama S., Izumi K., Fukuyama T. and Akimoto H. (1989) Reactions of ozone with α-pinene and β-pinene in air: yields of gaseous and particulate products. *J. Geophys. Res.* **94:D10**, 13013-13024.

Hildemann L.M. (1990) A study of the origin of atmospheric organic aerosols. Ph.D. Thesis, California Institute of Technology, CA.

Hildemann L.M., Markowski G.R. and Cass G.R. (1991) Chemical composition of emissions from urban sources of fine organic aerosol. *Environ. Sci. Technol.* **25**, 744-759.

Hooker C.L., Westberg H.H. and Sheppard J.C. (1985) Determination of carbon balances for smog chamber terpene oxidation experiments using a 14C tracer technique. *J. Atmos. Chem.* **2**, 307-320.

Izumi K. and Fukuyama T. (1988a) Photochemical aerosol formation from aromatic hydrocarbons in the presence of $NO_x$. *Atmospheric Environment* **24A**, 1433-1441.

Izumi K., Murano K., Mizuochi M. and Fukuyama T. (1988b) Aerosol formation by the photooxidation of cyclohexene in the presence of nitrogen oxides. *Environ. Sci. Technol.* **22**, 1207-1215.

Katauskas T. and Goldner H. (1991) SFE: Will it solve your lab's solvent waste problems? *R&D Magazine* **33**, 40-44.

Leone J.A., Flagan R.C., Grosjean D. and Seinfeld J.H. (1985) An outdoor smog chamber modeling study of toluene-$NO_x$ photooxidation. *Int. J. Chem. Kinetics* **17**, 177-21.

Lurmann F.W. and Main H.H. (1992) Analysis of the ambient VOC data collected in the Southern California Air Quality Study. Final report, ARB Contract No. A832-130, California Air Resources Board, Sacramento, CA, 28 February.

Mazurek M.A., Cass G.R. and Simoneit B.R.T. (1989) Interpretation of high-resolution gas chromatography and high-resolution gas chromatography/mass spectrometry data acquired from atmospheric organic aerosol samples. *Aerosol Science and Technology* **10**, 408-420.

Mazurek M.A., Simoneit B.R.T., Cass G.R. and Gray H.A. (1987) Quantitative high-resolution gas chromatography and high-resolution gas chromatography/mass spectrometry analyses of carbonaceous fine aerosol particles. *Intern. J. Environ. Anal. Chem.* **29**, 119-139.

McMurry P.H. and Grosjean D. (1985a) Photochemical formation of organic aerosols: growth laws and mechanisms. *Atmospheric Environment* **19**, 1445-1451.

McMurry P.H. and Grosjean D. (1985b) Gas and aerosol wall losses in Teflon film smog chambers. *Environ. Sci. Technol.* **19**, 1176-1182.

O'Brien R.J., Holmes J.R. and Bockian A.H. (1975) Formation of photochemical aerosol from hydrocarbons: chemical reactivity and products. *Environ. Sci. Technol.* **9**, 568-576.

Pandis S.N., Paulson S.E., Seinfeld J.H. and Flagan R.C. (1991) Aerosol formation in the photooxidation of isoprene and β-pinene. *Atmospheric Environment*, **25A**, 997-1008.

Paulson S.E. (1991) Contributions of biogenic and anthropogenic hydrocarbons to photochemical smog formation. Ph.D. Thesis, California Institute of Technology, CA.

Pavia D.L., Lampman G. M. and Kriz Jr. G.S. (1979) *Introduction to spectroscopy: a guide for students of organic chemistry,* Saunders College, Phildaelphia.

Richards M. and Campbell R.M. (1991) Comparison of supercritical fluid extraction, Soxhlet, and sonication methods for the determination of priority

pollutants in soil. *LC-GC* **9**, 358-361.

Rogge W.F., Hildemann L.M., Mazurek M.A., Cass G.R. and Simoneit B.R.T. (1991) Sources of fine organic aerosol. 1. charbroilers and meat cooking operations. *Environ. Sci. Technol.* **25**, 1112-1125.

Schueltze D. and Rasmussen R.A. (1978) The molecular composition of secondary aerosol particles formed from terpenes. *J. Air Pollut. Control Assoc.* **28**, 236-240.

Seinfeld J.H. (1986) *Atmospheric chemistry and physics of air pollution*, John Wiley & Sons, New York.

Seinfeld J.H., Flagan R.C., Petti T.B., Stern J.E. and Grosjean D. (1987) Aerosol formation in aromatic hydrocarbon-$NO_x$ systems. Final report, CRC Project AP-6, Coordinating Research Council, Atlanta, GA, 26 January.

Stern J.E., Flagan R.C., Grosjean D. and Seinfeld J.H. (1987) Aerosol formation and growth in atmospheric aromatic hydrocarbon photooxidation. *Environ. Sci. Technol.* **21**, 1224-1231.

Turpin B.J. and Huntzicker J.J. (1991) Secondary formation of organic aerosol in the Los Angeles basin: a descriptive analysis of organic and elemental carbon concentrations. *Atmospheric Environment* **25A**, 207-215.

Wang S.C., Paulson S.E., Grosjean D., Flagan R.C. and Seinfeld J.H. (1992) Aerosol formation and growth in atmospheric organic/$NO_x$ systems-I. Outdoor smog chamber studies of C7- and C8-hydrocarbons. *Atmospheric Environment* **26A**, 403-420.

Zhang Z.-H., Seinfeld J.H. and Flagan R.C. (1993) Determination of particle vapor pressures using the tandem differential mobility anlyzer. *Aerosol Science and Technology* (in press).

Zhang Z.-H., Shaw M., Seinfeld J.H. and Flagan R.C. (1992) Photochemical aerosol formation from α-pinene and β-pinene. *J. Geophys. Res.* **97:D18**, 20717-20729.

# Appendix A

## Detailed Description of the Outdoor Smog Chamber Facility

**Instructions for Performing an Outdoor Smog Chamber Experiment**

Figure A.1 **Flow Diagram of Gas Phase Injection to Smog Chamber**
Figure A.2 **Flow Diagram of Sampling from Smog Chamber**
Figure A.3 **Flow Diagram of $NO_x$ Monitor Calibration**
Figure A.4 **Flow Diagram of Gas Chromatograph Calibration**

**Instructions for Performing an Outdoor Smog Chamber Experiment**

1. On the morning of the experiment, around 6:30 a.m. to 7:00 a.m., begin inflating the Teflon bag. With the tarpaulin off the bag (the net is always over the chamber), insert the Teflon tube extending outside the lab labeled "Clean Air" into one of the holes of the Teflon port. Ensure the remaining holes of the port are taped over with 3M Mylar (green) tape. Open the On/Off valve labelled "BAG INFLATION." It is found behind the flowmeter and instrument panel. Tighten the pressure regulator to the house air, found to the right of the ozone monitor and $NO_X$ monitor by the window, to a pressure near 30 psi. Inflate the chamber partially, about 30 minutes. Insert Teflon tube labeled "NO/$NO_2$/Organic Injection" into another hole in port. Carefully drag tarpaulin onto bag, ensuring there are no light leaks under the tarp, and continue to inflate with air.

2. While the chamber is inflating:
    a. Clean filter holders. Refer to Appendix B.
    b. Condition column to remove any products from previous experiments. Typically, a ramp from 50°C to 250°C at 20°C $min^{-1}$ with a 10 minute hold at 250°C should be adequate.
    c. Set up the CNC, pump, and frequency counter inside the laboratory.
        i. Ensure the 1/4" tube is securely attached to the front end of the CNC.
        ii. Ensure the tubing behind the CNC is securely connected to the pump, and the tubing from the pump's exhaust to an outlet on the metal exhaust pipe inside the roof lab.
        iii. Attach a BNC cable from the CNC to the frequency counter.
    d. Rinse a 10μL Hamilton Gas Tight Syringe with methanol at least 20 times. It is not recommended to expel contents of the syringe back into the fresh methanol. The Hamilton Syringe cleaner may also be used after the solvent rinse.
    e. Change the following filters:
        i. The 47 mm filter at the inlet to the ozone monitor, located at

the back of the instrument. New filters can be found in the top drawer of the lab bench across from the monitor.

ii. The ~22 mm filter at the inlet to the Vici valve on the gas chromatograph. The new filter, located in the top drawer to the left of the GC, has to be trimmed with scissors to fit in the filter holder.

f. Calculate the times for injection of NO, $NO_2$ and $C_3H_6$ necessary to achieve the desired concentration in the smog chamber. Calculate the volume of organic to inject to achieve the desired concentration in the bag.

g. Turn on the ozone monitor, as it requires 30 min. to warm up. Ensure stopcocks leading to the $O_3$ and $NO_x$ monitors and temperature probe are open.

3. Once the bag is three-quarters full, turn down the pressure regulator to approximately 20 psi.

*In the next few steps, open the window in the laboratory, and attempt to measure the gas flow rates as quickly as possible. Refer to figures 1 through 4 in this appendix for the following instructions.*

4. Injection of NO

a. Close the On/Off Valve for injection of clean house air for inflation.

b. Ensure valves VD, VF, and VC are in the upward position and valve VG is in the downward position during the next few steps.

c. Turn valve VI down, valve VB up, and valve VE down.

d. Turn valve V6 upward to measure the flow rate with flow meter F8.

e. Open valve on cylinder labeled NO at 423 ppm.

f. Measure the flow rate of NO from the tank with the bubble flowmeter located to the right of the $NO_x$ and $O_3$ monitors. To achieve a concentration of 370 ppb in the chamber, NO must flow for 11 min. at a flow rate of 0.42 L $min^{-1}$.

g. Turn valve V6 down to inject NO into chamber. Inject for 2 minutes, then chase with air by turning valve VD down and valve VE

up. Verify flow into chamber by noting flow, or the lack thereof, in rotameter F10. (Do not forget to open F10.)

h. Repeat step g until the total flow time is achieved. Chase with air after injection is complete. Turn valve VI upwards, and close valve on top of gas cylinder.

5. Injection of $NO_2$

a. Ensure valves VB, VC, VD, VF, and VI are in the up position, and valves VE and VG are in the down position.

b. With valve V6 in the up position, open the on/off valve on top of the $NO_2$ (610 ppm) cylinder. Measure the flow rate of $NO_2$ from the cylinder with flow meter F8 and the bubble flowmeter: ~0.2 mL $min^{-1}$ is adequate.

c. Turn valve V6 to the down position, and time the flow of $NO_2$ into chamber for approximately 3-4 minutes, to achieve a concentration of 190 ppb in the chamber.

d. Chase with air by turning valve VD down and valve VE up.

e. After injection is completed, turn valve V6 upward and close gas cylinder.

6. Injection of Propene ($C_3H_6$)

a. Ensure valves VC, VD, and VF are in the up position and valves VE and VG are in the down position.

b. With valve V6 in the up position and valve VB in the down position, open the on/off valve on top of the $C_3H_6$ gas cylinder (concentration of 503 ppm).

c. Measure the flow rate of propene: approximately 0.5 L $min^{-1}$ is sufficient. To achieve a concentration of 1 ppm of propene in the chamber, the flow of propene should be around 24 minutes.

d. Turn valve V6 down, and inject propene for 2-3 minutes. Chase with air by turning valve VD down and valve VE up.

e. Continue repeating step d until the total flow time is reached.

f. Turn valve V6 up again, and close gas cylinder.

7. Injection of Organic

a. Ensure valves VC, VD, and VG are in the upwards position, and flow meter F10 is open.
b. Close flow meter F9 and stopcock on glass manifold labeled "Pure Air."
c. Inject organic into bulb with the syringe.
d. Open stopcocks at both ends of the glass bulb.
e. Heat bulb gently with hot air dryer.
f. Let air flow through bulb for at least 30 minutes to ensure all of the organic reaches the smog chamber.

8. Open on/off valve again to add more clean air to chamber to ensure it is fully inflated. Adjust pressure to 25 or 30 psi.

9. Once chamber is fully inflated, close on/off valve and turn valve VC into up position. Remove injection tubes from port and cover holes with tape. Insert Teflon tube labeled "Sampling Line" into a hole in port and insert copper tube into another hole.

10. Turn the stopcock for the dew point hygrometer to the open position. Turn the hygrometer and its pump on (located in cupboard below hygrometer). Measure relative humidity of contents of chamber. (Refer to "Roof Lab Notes" for details on operating the dew point hygrometer.) Turn pump and hygrometer off, and CLOSE STOPCOCK!! Record the temperature outside as well.

11. Ensure the amplifier is on and start data acquisition on the computer.

12. Turn the three-way valve to the GC to the "SAMPLE" position. (Located below the flow meters and valves.) Plug in the pump to the left of the GC. Program temperature ramp and begin sampling by typing SEQ START on integrator. Refer to the "Roof Lab Notes" and the integrator manual for more complete details.

13. Plug in the pump to the CNC.

14. Once the initial concentrations have stabilized, approximately 15 minutes, take the tarpaulin off carefully. Note the starting time of the experiment.

15. During the course of the experiment, monitor the occurrence of nucleation by noting any drastic increases in the particle concentration on the frequency counter. A typical experiment lasts approximately four hours.

16. While waiting for aerosol to be generated in the smog chamber, load the pre-baked filters into the clean filter holders. Cover open ends with foil. Connect the needle valve which has been calibrated to pull the appropriate flow rate of 10 L $min^{-1}$ through each filter sampler, onto a pump, and tubing from the filter holders to the pump.

17. When significant particle concentrations are seen, on the order of several hundred particles per cubic centimeter, collection of the aerosol onto the filters begins and continues until the bag is almost deflated. Insert the stainless steel tubes into holes in the port so that the tubes extend 15 cm into bag. Use a support under the filter holders to ensure the sampling tubes do not slip out. Be careful of the pump sucking the Teflon bag into the sampling tubes.

18. Once aerosol collection has begun, stop the gas-phase data acquisition on the computer and on the GC. Cover the smog chamber with its tarpaulin.

19. While calibrating the gas chromatograph, (refer to the "Roof Lab Notes"), begin clean-up:

a. Clean syringe

i. Wipe outside of needle with a Kimwipe dipped in acetone to remove any gummy residue from the electrical tape on the glass injection bulb.

ii. Clean inside of needle with cleaning wire.

iii. Flush syringe at least 20 times with acetone then at least 20

times with methanol.

iv. Flush syringe in heated syringe cleaner. Wrap syringe in clean foil and store in the styrofoam case until the next use.

b. When the Teflon bag is almost empty, unplug the pump connected to the filter holders. Carefully remove samplers from port and immediately wrap open ends in foil. Disconnect the plumbing from the filter samplers and wrap open ends in foil. Take the filter holders to the hood in Room 210. Remove the filters from the holders, using tweezers to handle the filters. DO NOT USE YOUR FINGERS! Place the filters into annealed jars and store in the freezer immediately. Refer to Appendix B for the cleaning protocol of storage glassware.

c. Cover all holes in the Teflon port except for one.

20. At the end of the experiment, turn off the FID on the GC and close all FID gas cylinders. Turn off the ozone monitor. DO NOT TURN OFF THE $NO_x$ MONITOR. If this should happen, the monitor must be recalibrated before the next run. However, the monitor should be calibrated once a week for NO and $NO_2$. Refer to the "Roof Lab Notes" for more details.

21. After an experiment, the bag should be flushed continually with clean air and allowed to bake for a day before the next experiment.

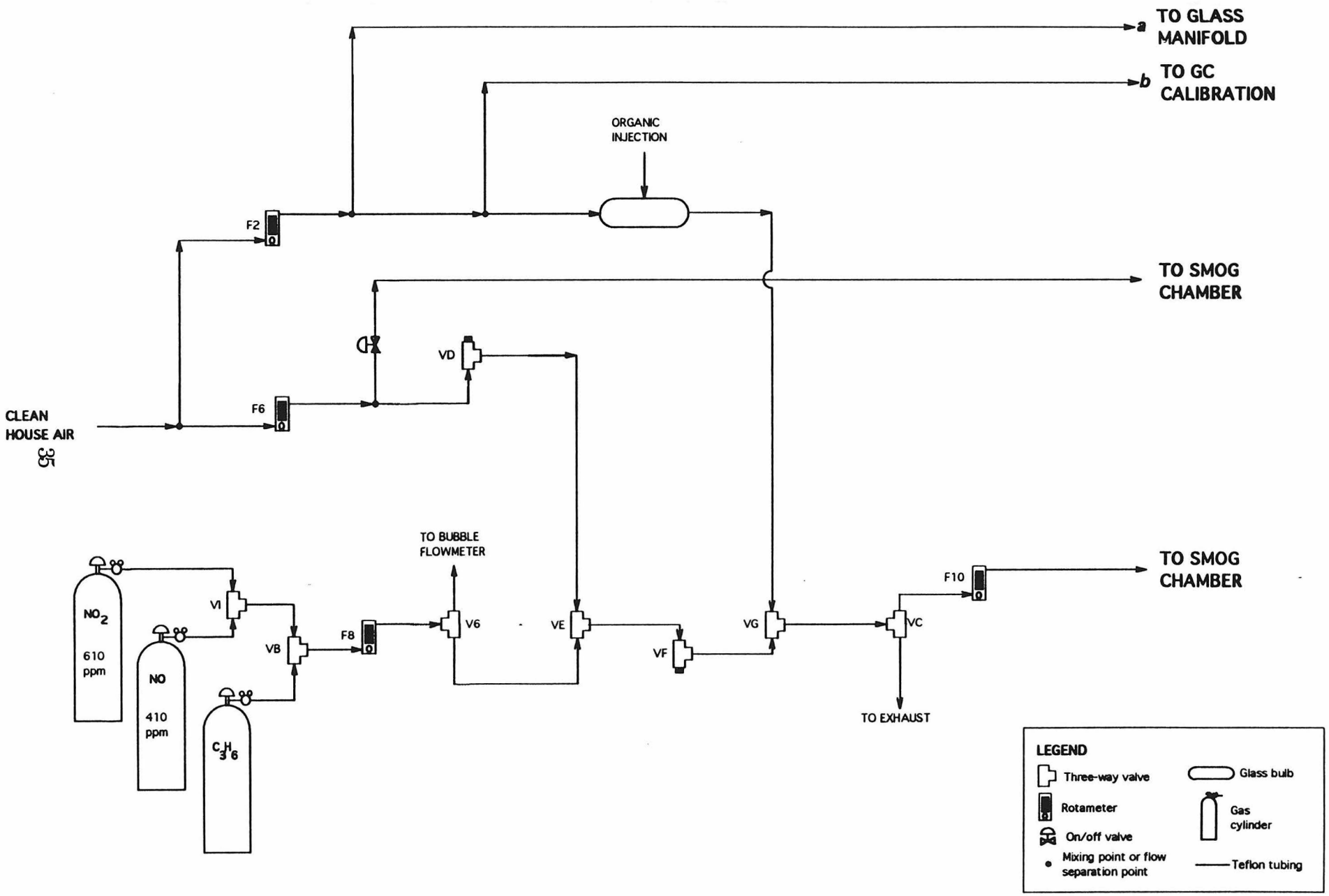



Fig. A.1 Flow Diagram of Gas Phase Injection to Smog Chamber

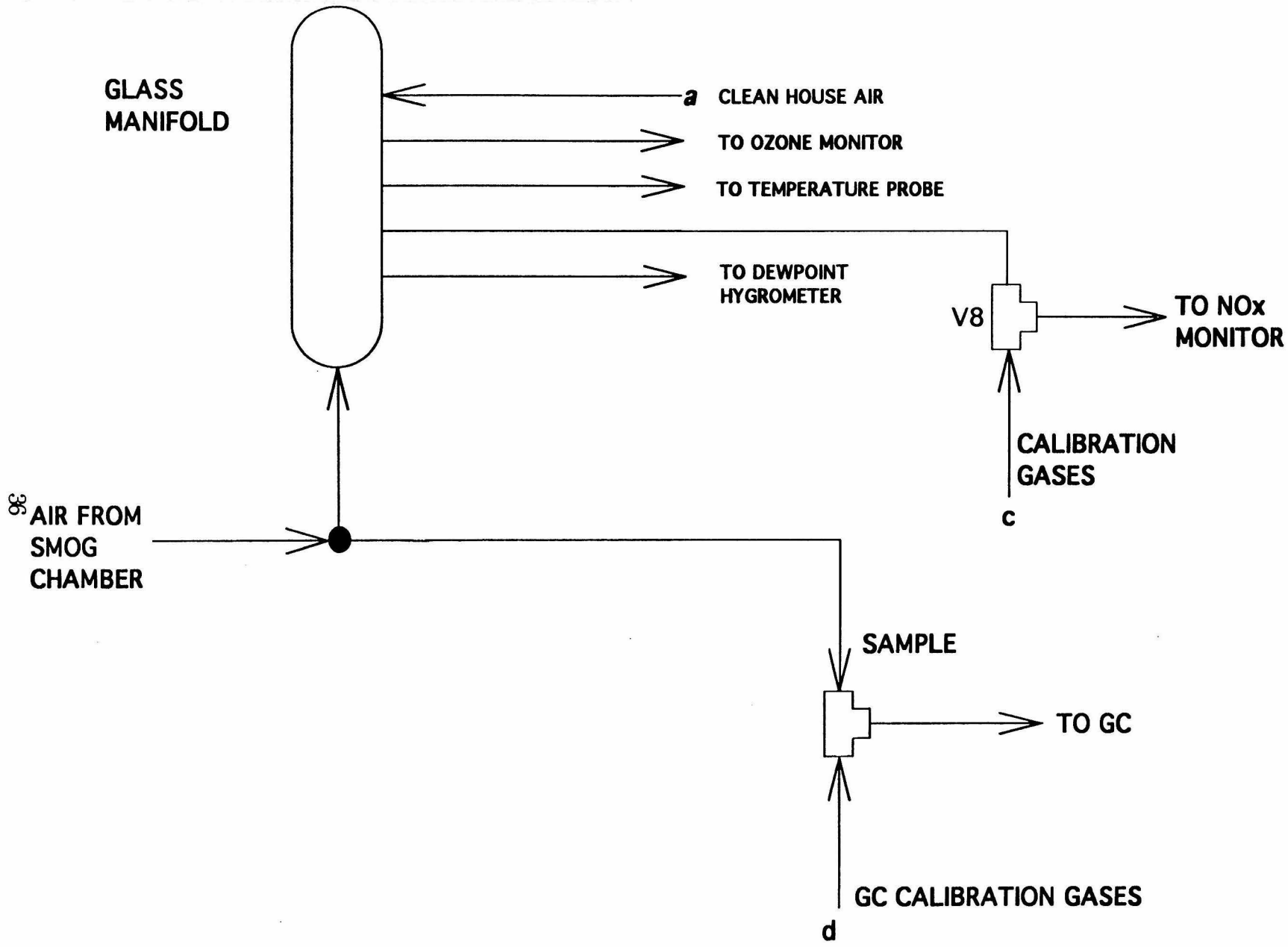



Fig. A.2 Flow Diagram of Sampling from Smog Chamber

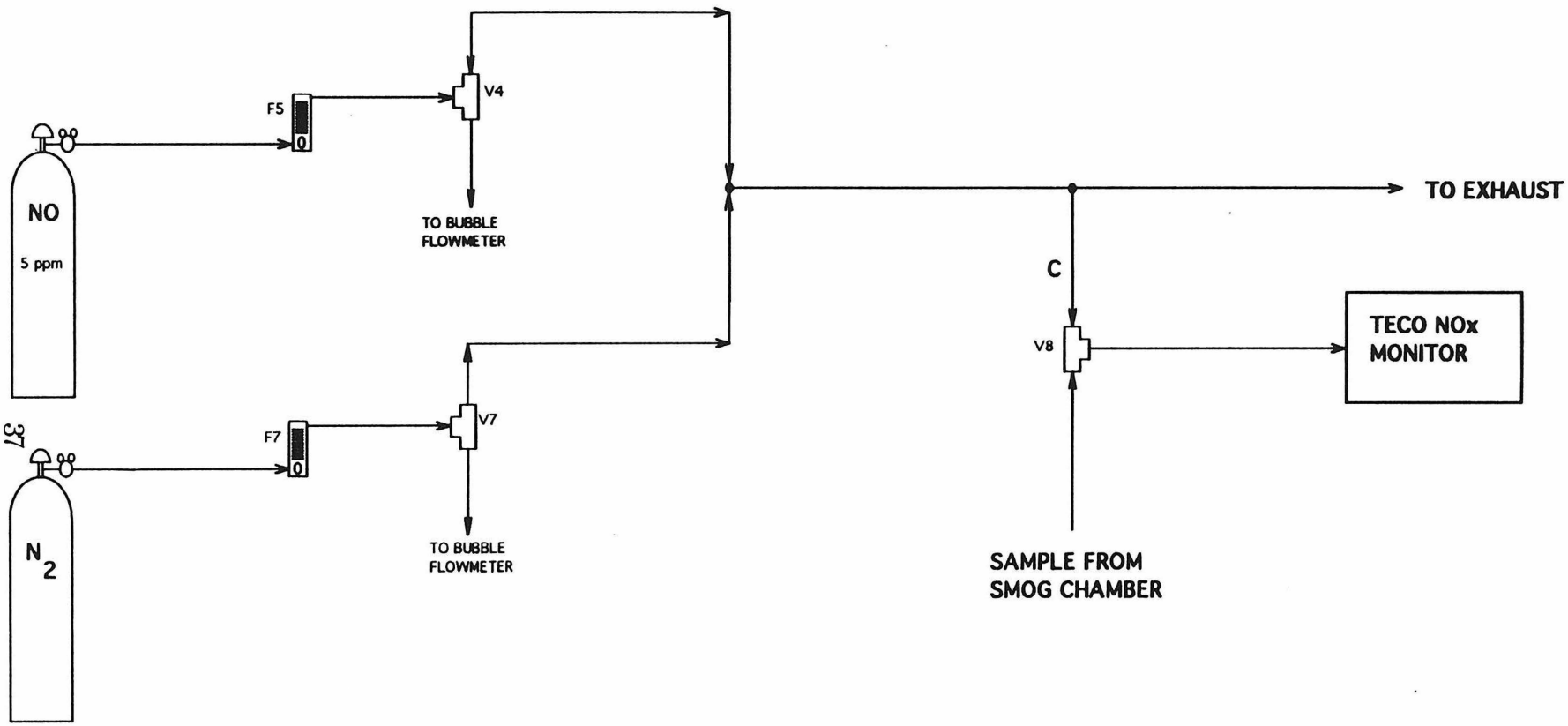



Fig. A.3 Flow Diagram of $NO_x$ Monitor Calibration

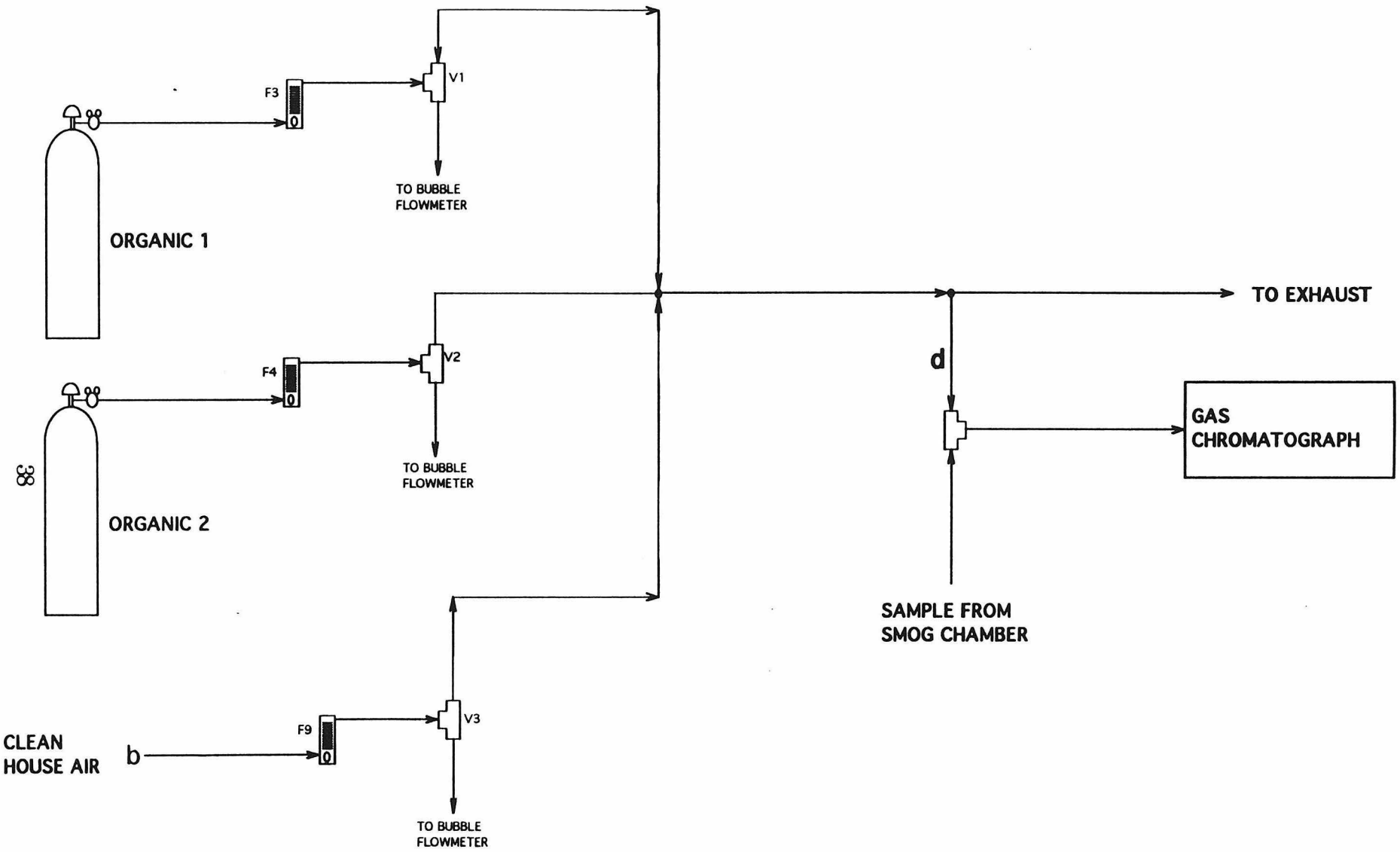



Fig. A.4 Flow Diagram of GC Calibration

# Appendix B

## Quality Control for Aerosol Samples

## Quality Control of Aerosol Samples for GC/MS Analysis

### A. Filter Preparation

The quartz fiber filters used for the collection of aerosol are the Pallflex 2500 QAO 47 mm filters or the 2500 QAT 47 mm filters. Prior to usage, the filters are baked at 750°C for at least two hours. Temperatures above 1100°C are not to be employed as thermal decomposition of the filters may occur. The best method for baking the filters is sandwiching the filters between two sheets of quartz fiber filters, also manufactured by Pallflex. This measure prevents particles from the oven's walls from depositing on the filters. Immediately after baking, the filters should be stored in annealed glass jars with Teflon-lined lids. Alternatively, the filters may also be stored in petri dishes lined with foil, which have been baked for at least two hours at 500°C, and the edges are sealed with Teflon tape.

### B. Storage Container Preparation

Baked filters and filters with aerosol samples are stored in annealed glass containers with Teflon-lined lids. For one or two filters, the 33 mm wide-mouth bottle is adequate, while the 58 mm wide-mouth bottle is recommended for storing numerous filters.

If wide-mouthed bottles are not purchased pre-cleaned according to EPA standards, then the jars should be cleaned according to steps one through four in part **C**, "Glassware Cleaning Protocol."

1. The bottles are covered with aluminum foil and are baked for at least four hours at 550°C. Since flint glass bottles are not rated for temperatures this high, the following precautions are taken to avoid breakage. The bottles are placed in a cool oven and then the oven is turned on. The oven takes approximately an hour to reach its final temperature. After four hours of annealing, the oven is turned off and allowed to cool slowly. During cooling, the door may be opened slightly. The jars are removed after the oven has cooled to below 100°C.

2. The Teflon-lined lids are cleaned according to the following protocol for the filter holders in part **D**.

### C. Glassware Cleaning Protocol

If glassware is cleaned immediately after use, steps one and two may be skipped.

1. Wash bottles and lids in a non-organic soap solution, such as Alconox and water. Distilled water is used for the final rinsing.

2. Rub an aluminum oxide ($Al_2O_3$) and distilled water slurry on glassware

to remove stains. Rinse in triply-distilled water. If any smears are not removable, discard glassware.

3. Rinse glassware in methanol twice and then once in methylene chloride. The methanol and methylene chloride are of HPLC quality (distilled in glass).

4. Cover open ends of glassware in aluminum foil and bake at 550°C for at least four hours.

## D. Filter Holder and Teflon-lined Lid Preparation

The 47 mm filters holders are either aluminum or stainless steel, and consist of the following parts:

bottom portion of holder
top portion of holder
screw cap for top portion of holder
stainless steel mesh support
stainless steel fine mesh support
stainless steel gasket
Teflon o-ring
stainless steel sampling tubes
stainless steel Swagelok connections

*In the following steps, clean tweezers are used to handle all filter holder parts.*

1. The filter holders are first washed with a dilute, household dish soap, if they are dirty. Detergents are not used to avoid damaging the anodized surface of the aluminum filter holders. The final rinsing is done with distilled water.

2. The disassembled filter holders and the Teflon-lined lids are sonicated for 20 minutes in distilled water. The containers holding the parts are washed, and then rinsed with distilled water and methanol prior to use.

3. The parts are then sonicated again for 20 minutes in methanol, and then for another 20 minutes in hexane. The methanol and hexane are HPLC-quality (distilled-in-glass).

4. The filter holders are allowed to dry on clean foil. All parts of the filter holders that directly contact the filters are arranged so as to not touch the foil. The parts are covered with a large Kimwipe to avoid dust deposits while air-drying.

5. Once all parts are dry, the baked filters are loaded into the filter holders, and the filter holders assembled. All open ends are covered with foil.

# Appendix C

## Solvent Extraction Technique

## EXTRACTION PROCEDURES 11 June 1989

### (A) PREPARATION

(1) Thaw the samples completely. Record in labbook when samples were removed from freezer. Calculate how much spike to add. Thaw the spike. Choose the appropriate size(s) of dedicated spike syringe(s).

(2) Prepare FEP (clear) Teflon liners for each sample jar by cutting out square pieces of Teflon sheeting, washing them in MeCl, and storing them in KimWipes.

(3) Add a Teflon liner to each jar top to ensure that solvents do not come into contact with the plastic lid during sonication. (Note: Jars are already lined with a TFE Teflon liner, but this extra measure is needed to ensure there is NO contact between lid and solvents.)

(4) Rinse out crimptops with methanol.

(5) Record in labbook the date and time of the spike addition, the type and aliquot of spike used, amount of spike added, and size of syringe used. Note error in accuracy, which equals one half the volume of the smallest gradation on the syringe. Be sure to note which samples were spiked using which syringe.

### (B) SPIKING

(1) Examine meniscus line on spike to make sure it has not evaporated since its last use. Then shake the vial a few times to mix the thawed contents.

(2) Rinse an annealed 50 ml beaker three times (3X) with benzene, then fill with benzene. (Use fresh beaker for each syringe used.) Loosen cap on sample(s) to be spiked, but leave sitting on top of the jar.

(3) Rinse the dedicated spike syringe to be used with the benzene, 21x for smaller sizes, 15x for the 500 ul size.

(4) Open the crimptop on the spike vial, and put the septum in the new crimptop, Teflon side (the lighter side) so it will touch the vial. Set the new crimptop with the septum on top of the spike vial.

(5) Rinse the syringe with spike, pulling a small plug the entire length of the syringe, squirting it out into the waste container, and then repeating TWICE more.

(6) Pull in amount of spike desired, plus a little. Invert the syringe to move any bubbles toward the tip, and then squirt them out. For the very narrow bore syringes, the bubbles will probably not budge, so you must pull in the spike SLOWLY to avoid bubbles. Holding the syringe horizontal, squirt spike into the waste container until you have the EXACT amount you want. Then squirt onto the filter surface, spreading it out as much as possible. Touch end of the syringe needle to the filter to deliver the last drop on the end.

(7) Screw the sample lid on tightly. Then immediately replace crimptop on spike vial. Wipe needle off with a Kimwipe between samples to remove any particulate material.

(8) When spiking is completed, crimp the top onto the spike vial using crimping device. If the seal is good, you should NOT be able to twist around the crimptop. Wrap Teflon tape around the neck of the spike vial, and mark the new meniscus, with the current date, on the vial.

(9) Make some mark on the sample bottle to indicate you have spiked it.

(10) Rinse the syringe 21x (or 15x, for large syringes) with benzene when spiking is completed.

## (C) SONICATION AND EXTRACTION

- ITEMS NEEDED: For each sample, need an annealed boiling flask; a 24/40 stopper; a 24/40 "sidearm"; a 125-ml Erlenmeyer flask; a 100-ml beaker (to cover the Erlenmeyer); a pipette [packed with glass wool that has been annealed and has on it a Viton o-ring, then a threaded Teflon bushing, then Teflon tubing that slides snugly over the pipette, then a Teflon 1/4in to 1/16in reducing union, and finally a piece of 1/16in O.D. Teflon tubing]; and a 150ml beaker (to cover the pipette setup). Also need a graduated solvent delivery flask (aka Pharmaceutical Flask), a 200-ml beaker (to put over it), a wash (boiling) flask, a 250-ml Erlenmeyer flask, a 150ml beaker (to cover the Erlenmeyer), tweezers and a thin probe.

(1) Make sure water in sonicator is at or below room temperature. WASH HANDS.

(2) Rinse Pharmaceutical flask 3x with hexane. Fill with a set amount of hexane to add to filters. Amount must be enough to completely cover filters. (Use at least 30 ml as an aliquot; for 15–30 47ml filters, use 60 ml. Must use less than 80ml per step to make the total volume a manageable size for the concentration step. If 80ml doesn't cover the filters, can use up to 120ml, but then must concentrate the sample down an extra time after the first benzene/isopropanol wash.) Screw lid tightly on sample jar, and put in sonicator for 10-min (timed).

(3) Meanwhile, put labels on necks of boiling flasks, using scotch tape. Leave aluminum covering the top. Record amount of Hexane and bottle number used in labbook, along with the temperature of the sonicator water (=ambient temp).

(4) Also meanwhile, set up WASH flask with sidearm adaptor, clamping it to a ringstand for stability. Attach sidearm to the vacuum manifold with the swagelok.

(5) Also meanwhile, rinse all the Erlenmeyer flasks 3x with benzene. Fill the 250ml Erlenmeyer with about 200ml of benzene, and cover with the 150ml beaker. Fill each 125-ml Erlenmeyer with about 75-ml benzene, and cover with the 100-ml beaker. Designate each 125-ml Erlenmeyer for a particular sample by setting it close to a boiling flask.

(6) Wash hands AGAIN. Turn on vacuum. Wash about 100-ml of benzene in the 250ml Erlenmeyer through the pipette setup into the wash flask. Then remove the wash flask from the sidearm and put on the sample boiling flask to be used. Pour contents of wash flask into waste.

(7) Cover the sidearm setup with a large KimWipe with a 150-ml beaker over the top to preserve cleanness. Adjust the clamp to hold the larger flask.

(8) Repeat the procedure if there is a second sidearm setup to be used.

(9) When sonication of the jar(s) is completed, remove the beaker and KimWipe from the pipette setup, open valve to the vacuum manifold, take off cap of sample bottle, and vacuum solvent from the jar into the flask. Try to avoid taking up filter fiber as much as possible. Hold end of vacuum tip on top filter to pull as much of solvent as possible. Then replace the cap loosely on the sample jar. Vacuum through a "chaser" of a few ml of benzene from the appropriate 125-ml Erlenmeyer a total of three times (3x). Close the vacuum manifold valve. Recover top of pipette with KimWipe and beaker, and recover Erlenmeyer with its beaker.

(10) Repeat for any other samples.

(11) Mark on sample jar(s) that "H1" (the first hexane wash) has been done. Turn off the vacuum (and its water) at the source.

(12) Rinse the Pharmaceutical flask 3x with hexane (again!), then measure out another aliquot of hexane for each sample. Wrap up the pharmaceutical flask in a KimWipe when it is not being used. Swirl the filters in the jar in the hexane, then sonicate for another 10 min. (timed).

(13) Meanwhile, prepare fresh benzene/isopropanol mixture (good for $\leq$ 2 days only!), using a dedicated brown-glass bottle. Rinse the bottle 3x with benzene. Then add 2 parts benzene (600 ml). (Replace cap loosely on top of dedicated bottle between solvents.) Then add 1 part isopropanol (300 ml). Swirl contents to mix WITHOUT getting solvent on the cap. Then cover bottle with aluminum foil to protect it from the UV light.

(14) Wash hands AGAIN. Turn back on vacuum and water. Then repeat step (9) to vacuum out second hexane wash, and mark the bottles with "H2"s when completed.

(15) Rinse the Pharmeceutical flask 3x with the benzene/isopropanol mixture, and then add an aliquot to each sample container. Swirl, screw lid on each jar tightly, and sonicate for another 10 min. Meanwhile, record details of benzene/isopropanol preparation in labbook.

(16) Repeat step (9) for each jar, and then mark each one with a B/I 1.

(17) Repeat step (15) for B/I 2. Repeat step (9) for B/I 2.

(18) Repeat step (15) for B/I 3. Repeat step (9) for B/I 3.

NOTE: With B/I washes, filter fibers may accumulate upstream of the glass wool, clogging it. If this happens, turn off the vacuum valve to the manifold, take the thin probe and stir up the filter fibers, and then open back up the vacuum valve.

(19) After 3rd rinse with the benzene/isopropanol mixture, screw the jar lid on tight. Then pull out side arm setup and close flask with the 24/40 glass stopper. Remove pipette setup from sidearm and wrap back up in the tissue and foil, placing a label on the outside of the foil packet. Remove the flask and the packet from the hood. Mark top of jar with "Extracted: [date]"

(20) Rinse sidearms inside and out with methanol before extracting next set of samples.

## (D) CONCENTRATION OF EXTRACT

(1) Start up coolant system. It will take 20–30 min to be fully operational. Also turn on Buchi bath, aiming for a temperature of 30 C. (Dial is NOT accurate – use a thermometer to verify temperature.)

(2) Turn on Aspirator pump, turning valves so that valve to the Buchi is open. Leave suction on low to begin with.

(3) Put flask onto end of Buchi, SECURING WITH CLIP. Immerse the flask about halfway into the bath. Make sure that liquid inside the flask is NOT touching the ground-glass portion of the flask. Turn on rotator so that flask is rotating 3–4 times/second. WATCH.

(4) After about 1 minute, gradually add more vacuum. WATCH. If small bubbles appear in the solution inside the flask, immediately reduce the vacuum! (This gradual approach is intended to minimize the risks of the solution suddenly boiling (aka "bumping") and throwing most of its contents outside of the flask.) Should see the solvent front move up into the condensor coil.

(5) Once the vacuum is fully on, it takes about 30 minutes to concentrate the solution down. Near the end of this reduction, the drips coming off the condensor coil will slow way down, and the solution in the flask will appear viscous.

(6) When the solution is about the size of a half-dollar, turn off the rotator, slowly break the vacuum by dialing toward "OPEN", raise the flask out of the water bath, remove the flask from the setup, and replace the 24/40 cap.

(7) Before starting the next sample, remove the splash bulb, and rinse it with methanol outside and inside. Dump out the contents of the catch flask and put it back on.

## (E) TRANSFER OF CONCENTRATED SAMPLE

- ITEMS NEEDED: An Erlenmeyer flask, a "pointy" graduated test tube, a clamp, a 14/20 side arm joint, and the designated pipette saved from the last transfer.

(1) Set up test tube in hood, securing with a clamp. Move Teflon joint on the pipette further down, and put onto the top of the tube. The tip of the pipette should be about even with the 15 ml mark. Move the label from the foil packet containing the pipette onto the top of the tube.

(2) Open the vacuum to the manifold and aspirate (siphon out) the contents of the flask into the test tube.

(3) Fill the empty flask with about 1 ml of benzene. Swish around the benzene in the flask, and then aspirate the contents into the test tube. Repeat a second time. Contents of the test tube should not exceed 15 ml, or there will be bumping problems.

(4) Turn off vacuum. Remove side arm, and immediately put 14/20 stopper on test tube. Put scotch tape over label and store test tube in a tall jar.

(5) Then disassemble pipette setup, setting pipette with the jar of leftover filters from the extraction. The Teflon pieces should be washed for reuse.

(6) Rinse sidearm setup with methanol and leave in the hood wrapped in Kimwipes to dry.

(7) Set waterbath at 35–40 C. Put splash bulb with 14/20 end onto the Buchi. Turn on the vacuum, and attach on the pointy test tube with a clip. Set rotations at 2–3 times/second. WATCH.

(8) After 1 minute, gradually increase the vacuum. Will not see much condensation onto the catch bulb; most of the solvent vapor will go out the vacuum line. GO SLOW on this step! Will not see any warning signs before bumping occurs. Make sure the liquid in the test tube is not touching the ground glass.

(9) Process will take 20–30 min. Aim for a reduced volume of 2 to 3 ml.

(10) When desired volume is reached, turn down the vacuum, remove the test tube, cap it, and put in large jar. Then rinse the splash bulb with methanol before starting with the next sample.

(11) For the final step in the concentration process, move the samples in the test tubes to the nitrogen blowdown apparatus. Install fresh needle parts on the apparatus. Turn on the apparatus. Turn on the small valve on the nitrogen tank, and then gradually turn on the flow through the needle until a slight deformation can be seen in the meniscus. Blowdown to about 500 ul, watching it towards the end to make sure it doesn't evaporate to dryness. (Typically, it takes 60 min to blowdown a sample.) Using a Teflon squirt bottle that has been freshly filled with benzene, add enough benzene to increase the volume back up to about 3 ml, and then blow down again to about 500ul. (The second blowdown after addition of benzene is intended to reduce the amount of isopropanol left in the sample, for better behavior of the neutral fraction on the GC column.) The second blowdown will take about 30–45 min.

(12) After the second volume reduction is completed, put the 14/20 stopper back on the test tube, and gently tilt and rotate to wet the sides of the test tube with solution in order to redissolve any salt-adsorbed organics present on the test tube walls.

## (F) VOLUME DETERMINATION AND SAMPLE SPLITTING

After neutral sample is injected onto the column, a precise volumetric measurement of the extract must be made. Materials needed are the 500ul syringe dedicated for volume determination, 2 vials with Teflon-lined lids that have FAME and Neutral labels on top, and a small beaker (rinsed 3x with benzene and filled).

(1) Rinse syringe 15x with benzene. Then withdraw sample from pointy test tube into the syringe, and RECORD total volume to the nearest 2ul. Decide on split between the neutral and FAME fractions. (Customarily, the split is about 50/50, but for very concentrated samples, may want to use a smaller fraction of the total extract for the FAME in order to reduce the amount of diazomethane that must be generated.)

(2) Add sample back into the vial with the Neutral label on its lid) until the amount left in the syringe is the amount desired for the FAME fraction. Put lid on Neutral vial. Then RECORD the amount of sample left in the syringe. Finally, discharge that amount into the FAME vial, and put the FAME vial's cap back on.

(3) Immediately disassemble the syringe and rinse the pieces with methanol (to remove the more polar organics and the inorganic salts before they stick to the walls), first rinsing the plunger 3x, and then filling the barrel 3x with methanol and using the plunger to push it through. Then reassemble and rinse the assembly 15x with benzene.

(4) Scotch-tape labels onto sides of vials after adding on volume information and the date. Then mark and date the location of the meniscus. (This mark becomes useful if the samples are stored in the freezer for an extended period of time before being injected.) Wrap Teflon tape around the top. Put vials in freezer.

NOTE: If sample has lots of particulate matter left in it, an alternate approach should be taken. After the sample has been concentrated, allow it to set for an hour or so to allow the particles to settle. Then draw off the supernatant carefully with a volumetric syringe, and put into a vial. Then add benzene (about 150 ul), let set another hour, and then draw off the supernatant a second time and add to the vial. Swirl vial to mix contents together. Then use same syringe to make volumetric determination and split, using the vial to ultimately hold the neutral sample.

## (G) GENERATION OF DIAZOMETHANE FOR DERIVATIZATION

(1) Thaw the samples. Calculate the amount of MNNG to add, assuming a 50% yield on the conversion to diazomethane and shooting for about 50-fold excess based on the amount of OC (organic carbon) calculated to be present.

(2) Gather together the supplies. Two batches of diazomethane can be generated at a time. For two batches, the following equipment is needed:

2 50-ml beakers (1 for water, 1 for benzene), 2 diazomethane generators, 2 Perfectum ground-glass 1-ml syringes (one for water, one for benzene), baked foil (for weighing; can also use pieces of the foil packet that contains the generator), 1 22-guage luer-lok 5ml glass/metal syringe, a spatula and "poker" for weighing out the MNNG, 2 vials, 2 lids for the vials, 2 Teflon-lined septa, 2 clamps for the lids, and 2 heavy-walled glass 1 liter beakers.

(3) Wash the weighing tools and the septa in methanol.

(4) Assemble outer tube of generator onto ringstand clamp in the hood, leaving the foil on top. Place a 1-liter beaker underneath each one.

(5) Rinse the small beaker 3x in benzene, then half fill. Rinse a 1-ml syringe 3x in benzene, then add approx. 3 ml of benzene to outer tube. Then put in coldfinger (inner tube) into assembly, with hole in the REAR. Wrap Teflon tape around joint 3x, then clamp. Arrange assembly so that clamp is sitting directly on top of the ringstand holder.

(6) Weigh out MNNG using the aluminum as weighing paper. WEAR RUBBER GLOVES! (MNNG is a carcinogen.) Aim for a net weight of 160 mg. DO NOT weigh out more than 180 mg per sample. Record weights. Fold each sample into its aluminum, using distinctive folding patterns so you can tell which sample is which.

(7) Take Al piece off top of generator, and add MNNG to inner tube, using a powder funnel or being REALLY careful. (You should still be wearing gloves.) Is doable using the seam in the aluminum foil and the poker to guide the MNNG into the cold finger. Put aluminum piece back on top.

(8) Rinse other small beaker 3x with bottled HPLC-quality water, and then rinse the other 1-ml syringe 3x with the water. Then add 0.5 to 0.55 ml of water into the inner tube, running it down the front inner-wall of the cold finger to avoid the hole. Put septa in cap, Teflon side (the lighter of the two sides) towards the sample, and screw tightly onto apparatus.

(9) Fill up each 1-liter beaker with ice, then add tap water to ice in beaker (fill up). Make sure the coldfinger is pushed far into the icewater, with the ringstand holder touching the rim of the beaker.

(10) With gloves on, withdraw 0.6 ml of 5 N KOH into luerlok syringe. Then working quickly, insert the needle through the septa at an angle so that needle points toward the front. Inject the sample quickly so that it runs down on the front side of the inner tube (along the path the water took, away from the hole), and then quickly withdraw the needle. Immediately rinse the luerlok syringe 5x in the HPLC water, then separate the pieces. (Note: this syringe cannot be annealed!)

(11) Keep an eye on the generation equipment. If you have added too much reagent, the seal that is wrapped in Teflon tape will pop. You should see development of intense yellow color within the first couple of minutes of the reaction. Total time to reach completion will be about 30 min. When reaction is complete, you will no longer see minute bubbles coming from the cold finger.

NOTE: Diazomethane must be added to sample as soon as it is generated. It CANNOT be made a day ahead of time.

## (H) DERIVATIZATION OF SAMPLES

(1) While the diazomethane is generating, double check calculations on amounts of diazomethane to add to each vial. Should be adding at least a 20-fold excess to each sample.

(2) Put on gloves.

(3) Pour diazomethane sample into a 20-ml vial, put on lid, and keep cool in shallow beaker with ice water.

(4) Take off gloves. Rinse tip of micro-plunger with methanol. Stick into end of solvent-washed 200ul pipette.

(5) Loosen cap of sample. Take off cap from diazomethane. Measure necessary ul of diazomethane into the FAME vial. Recap both vials. Examine sample color to see that it remains a bright yellow. If color fades, more diazomethane must be added.

(6) When adequate diazomethane has been added to all samples, mark tops of containers with yellow pen to indicate that the sample has been derivatized.

(7) Make sure the caps are tightly on, and let samples sit for at least 1 hour. Then reexamine them to confirm that they still have the vivid yellow color of the diazomethane. (If color has faded, more diazomethane should be added.)

(8) Blow down the FAME vials as described in (E)(11). Process will take 5—15 min. Constantly check the samples as they blow down! DO NOT allow them to evaporate to dryness. After shooting FAME sample on, must make volume determination of FAME fraction using the dedicated volumetric syringe, and record it in labbook.

File Contained in: [EPA.HRGC]EXTRACTION.TEX

# Appendix D

## Data to Estimate the Recovery Efficiency of the Solvent Extraction Technique

**Temperature Program and Data Acquisition Method for the Gas Chromatograph/Mass Spectrometer**

Figure D.1 **GC/MS Chromatogram of the Standard to Determine Response Factors**
Figure D.2 **GC/MS Chromatogram of the Sample Extracted by the Solvent Technique**

**Temperature Program for the Gas Chromatograph with a Flame Ionization Detector**

Figure D.3 **GC/FID Chromatogram of the Standard to Determine Response Factors**
Figure D.4 **GC/FID Chromatogram of the Sample Extracted by the Solvent Technique**

**Temperature Program and Data Acquisition Method for the Gas Chromatograph/Mass Spectrometer**

GC: Hewlett Packard 5890 Series II
MS: Hewlett Packard 5989A MS Engine
Column: 12 m HP-1, 100% dimethylpolysioxane (gum), 0.33 μm film thickness, 0.2 mm i.d.

Method/File Name: rec_std_15.m
Tune File: target.u
Acquisition Mode: SCAN mode
MS Voltage: 2314
Run time: 27.00 minutes

*GC Temperature Information*

Injection B Temperature: 250°C
Detector B Temperature: 280°C
Oven Temperatures: 35°C initially for 6 minutes
Rate 1 is 5°C $min^{-1}$ until 100°C
Rate 2 is 25°C $min^{-1}$ until 250°C
250°C for 2 minutes

*Injector Information*

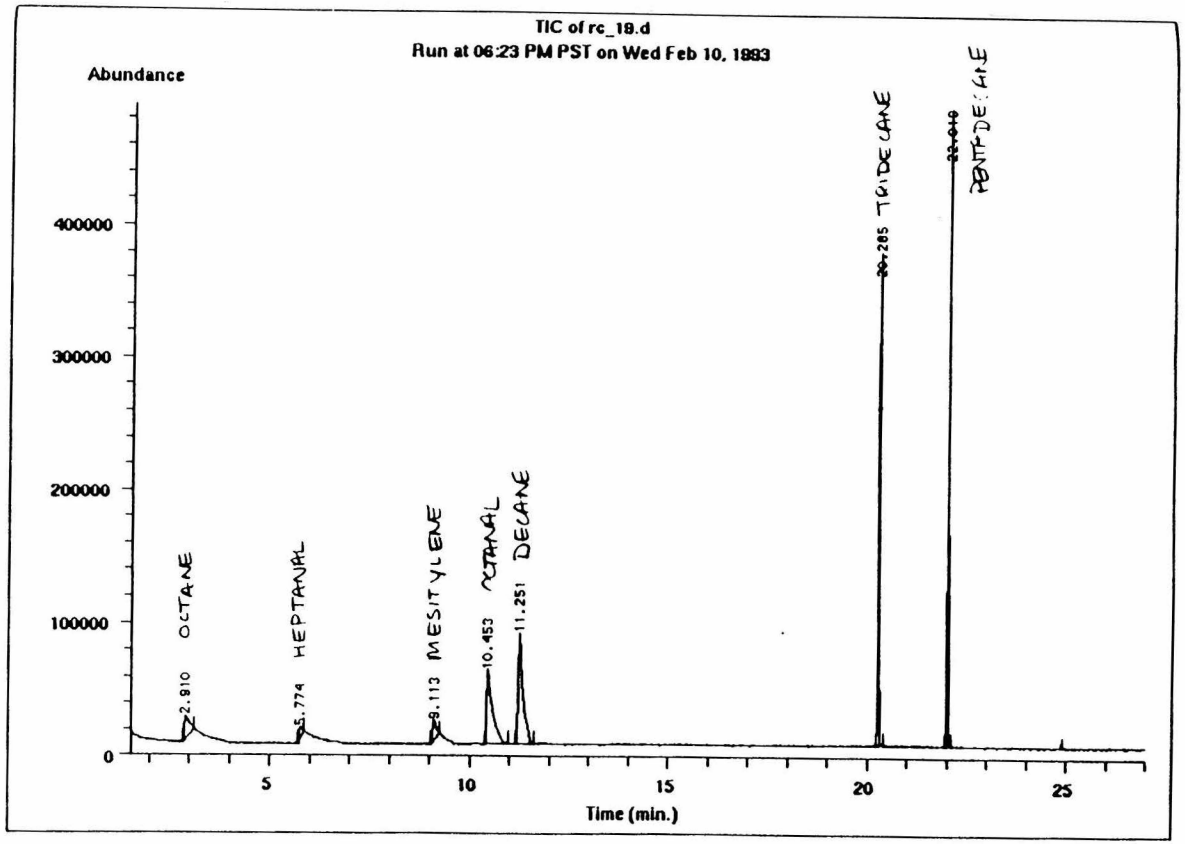
Manual injection
Purge B ON

*Acquisition Parameters*

Low Mass: 20.00
High Mass: 215.00
Threshold: 0
Samples: 2

*Mass Spectrometer Temperatures*

Source: 250°C
Quadrupole: 100°C

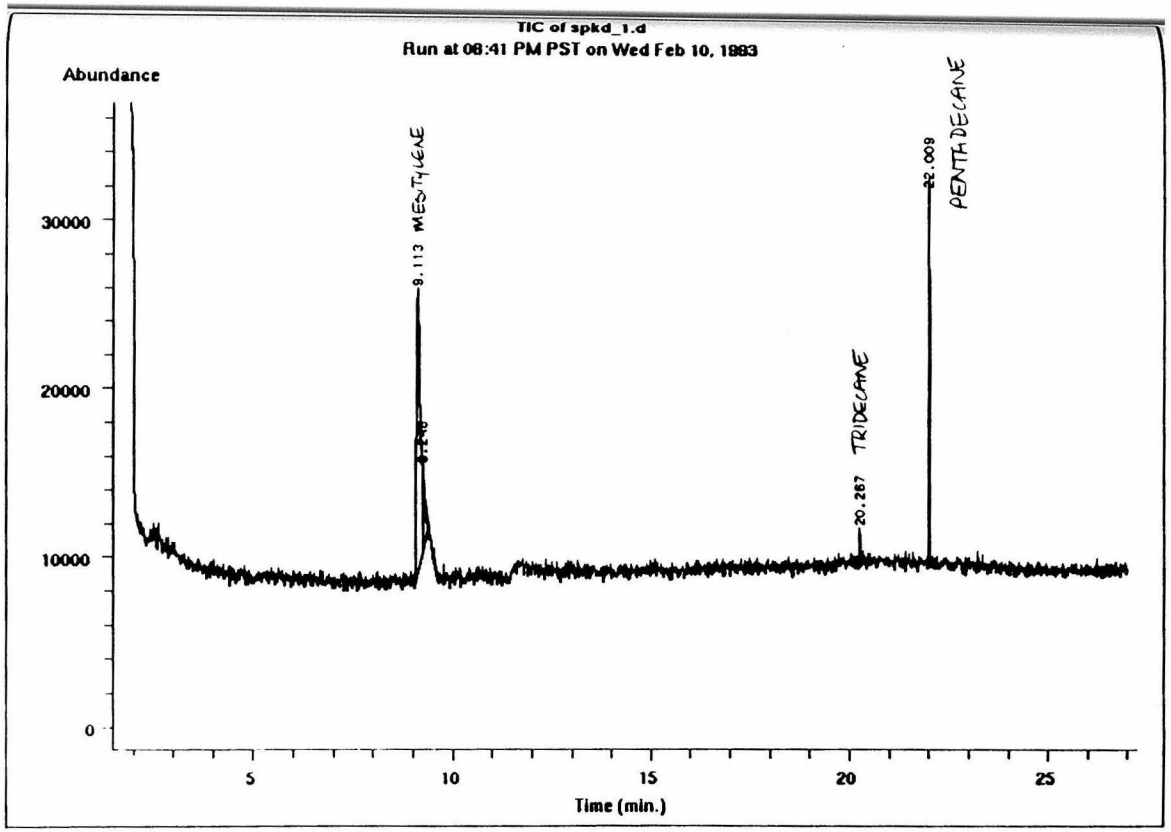



Area Percent Report
Sorted by Retention Time

Information from Current Data File Header:
File: /chem/hpl/seinfeld/hali/data/rec_std/rc_19.d
Operator: hali
Date Acquired: Wed Feb 10 93 06:23:24 PM
Sample Name:
Misc Info:
Bottle Number: 0 Repetition Number: 1

| Ret Time | Signal Descr | Type | Area | Height | %Pk | %Sg | %Lpk | %Lsg |
|---|---|---|---|---|---|---|---|---|
| 2.910 | Total Ion | BB | 1477649 | 18392 | 100.00 | 5.28 | 100.00 | 21.32 |
| 5.774 | Total Ion | BB | 416003 | 9506 | 100.00 | 1.49 | 100.00 | 6.00 |
| 9.113 | Total Ion | PV | 1033876 | 15854 | 100.00 | 3.69 | 100.00 | 14.92 |
| 10.453 | Total Ion | BB | 5812926 | 56413 | 100.00 | 20.77 | 100.00 | 83.88 |
| 11.251 | Total Ion | BB | 6930009 | 83396 | 100.00 | 24.77 | 100.00 | 100.00 |
| 20.285 | Total Ion | BB | 6506967 | 354638 | 100.00 | 23.25 | 100.00 | 93.90 |
| 22.019 | Total Ion | BB | 5804252 | 453222 | 100.00 | 20.74 | 100.00 | 83.76 |

**Figure D.1 GC/MS Chromatogram of the Standard to Determine Response Factors**




Area Percent Report
Sorted by Retention Time

Information from Current Data File Header:
File: /chem/hp1/seinfeld/hali/data/rec_std/spkd_1.d
Operator: hali
Date Acquired: Wed Feb 10 93 08:41:15 PM
Sample Name:
Misc Info:
Bottle Number: 0 Repetition Number: 1

| Ret Time | Signal Descr | Type | Area | Height | %Pk | %Sg | %Lpk | %Lsg |
|---|---|---|---|---|---|---|---|---|
| 9.113 | Total Ion | PV | 1086118 | 16982 | 100.00 | 70.06 | 100.00 | 100.00 |
| 9.246 | Total Ion | VV | 196853 | 5143 | 100.00 | 12.70 | 100.00 | 18.12 |
| 20.267 | Total Ion | PV | 47411 | 2455 | 100.00 | 3.06 | 100.00 | 4.37 |
| 22.009 | Total Ion | PV | 219970 | 22380 | 100.00 | 14.19 | 100.00 | 20.25 |

Figure D.2 GC/MS Chromatogram of Sample Extracted by Solvent Technique

**Temperature Program for the Gas Chromatograph with a Flame Ionization Detector**

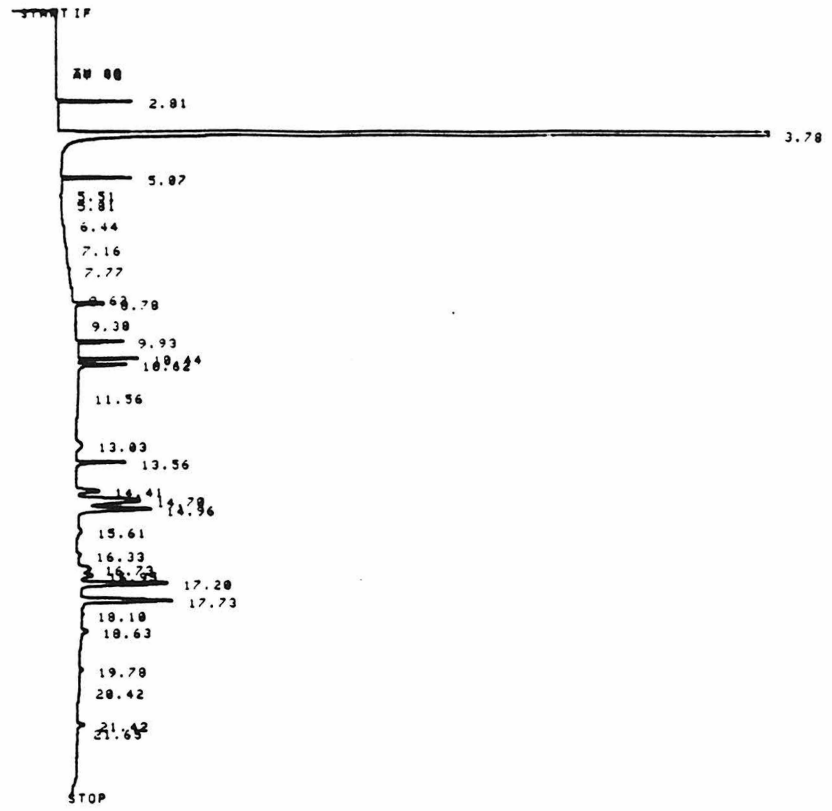
GC: Hewlett Packard 5890 Series II
Column: 25 m HP-FFAP, polyethylene glycol (TPA modified), 0.52 μm film thickness, 0.32 mm i.d.

*GC Temperature Information*

Injection B Temperature: 250°C
Detector B Temperature: 280°C
Oven Temperatures: 50°C initially for 3 minutes
Rate 1 is 10°C $min^{-1}$ until 200°C
250°C for 5 minutes

*Injector Information*

Manual injection
Purge B ON



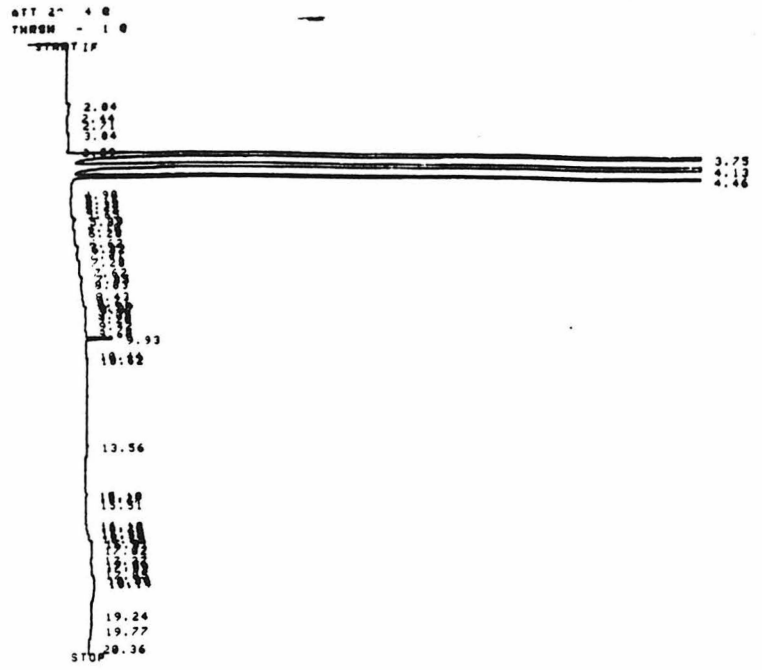

RUN # 303 FEB/14/93 19:28:12

AREA%

| RT | AREA | TYPE | AR/HT | AREA% |
|---|---|---|---|---|
| 2.81 | 24178 | PB | 0.030 | 0.077 |
| 3.78 | 3.0778E+07 | ^SHB | 0.060 | 97.645 |
| 5.07 | 30039 | TPP | 0.039 | 0.095 |
| 5.51 | 211 | TPP | 0.113 | 6.6941E-04 |
| 5.81 | 264 | TPP | 0.126 | 8.3756E-04 |
| 6.44 | 208 | TPP | 0.102 | 6.5989E-04 |
| 7.16 | 2086 | TPV | 0.247 | 0.007 |
| 7.77 | 5343 | TVV | 0.405 | 0.017 |
| 8.63 | 13969 | TVV | 0.685 | 0.044 |
| 8.78 | 22215 | TVV | 0.063 | 0.071 |
| 9.38 | 6777 | TVV | 0.391 | 0.022 |
| 9.93 | 27649 | TVV | 0.854 | 0.088 |
| 10.44 | 26490 | PB | 0.040 | 0.084 |
| 10.62 | 26715 | BB | 0.058 | 0.085 |
| 11.56 | 3891 | BV | 0.178 | 0.012 |
| 13.03 | 17829 | BP | 0.220 | 0.057 |
| 13.56 | 23823 | PB | 0.044 | 0.076 |
| 14.41 | 27682 | PV | 0.107 | 0.088 |
| 14.78 | 122220 | VV | 0.174 | 0.388 |
| 14.96 | 95526 | VB | 0.118 | 0.303 |
| 15.61 | 10135 | PP | 0.100 | 0.032 |
| 16.33 | 3973 | PP | 0.091 | 0.013 |
| 16.73 | 12025 | PV | 0.095 | 0.038 |
| 16.95 | 16884 | VV | 0.105 | 0.054 |
| 17.20 | 89334 | VP | 0.093 | 0.283 |
| 17.73 | 103940 | PB | 0.105 | 0.330 |
| 18.10 | 1719 | BP | 0.069 | 0.006 |
| 18.63 | 10085 | BP | 0.122 | 0.032 |
| 19.78 | 3944 | PB | 0.084 | 0.013 |
| 20.42 | 2185 | BP | 0.102 | 0.007 |
| 21.42 | 8447 | BV | 0.097 | 0.027 |
| 21.65 | 2511 | VV | 0.122 | 0.008 |

TOTAL AREA= 3.1520E+07
MUL FACTOR= 1.0000E+00

Figure D.3 GC/FID Chromatogram of the Standard to Determine Response Factors




RUN # 393 FEB/15/93 01:10:09

AREA%

| RT | AREA | TYPE | AR/HT | AREA% |
|---|---|---|---|---|
| 2.04 | 1196 | PV | 0.038 | 0.003 |
| 2.44 | 162 | BV | 0.039 | 3.9039E-04 |
| 2.71 | 317 | PV | 0.035 | 7.6392E-04 |
| 3.04 | 873 | PV | 0.036 | 0.002 |
| 3.59 | 166 | PH | 0.040 | 4.0003E-04 |
| 3.75 | 1.2976E+07 | SHH | 0.045 | 31.271 |
| 4.13 | 2.7660E+07 | VSHB | 0.054 | 66.675 |
| 4.46 | 714270 | TBB | 0.043 | 1.721 |
| 4.98 | 113 | PP | 0.038 | 2.7231E-04 |
| 5.16 | 92 | PP | 0.090 | 2.2170E-04 |
| 5.33 | 126 | PP | 0.096 | 3.0364E-04 |
| 5.47 | 214 | VV | 0.081 | 5.1570E-04 |
| 5.65 | 230 | PV | 0.058 | 5.5426E-04 |
| 5.89 | 1696 | VV | 0.048 | 0.004 |
| 6.10 | 12 | PP | 0.010 | 2.8918E-05 |
| 6.20 | 305 | PV | 0.039 | 7.3508E-04 |
| 6.62 | 43 | PP | 0.045 | 1.0362E-04 |
| 6.82 | 1263 | PV | 0.053 | 0.003 |
| 7.01 | 564 | VV | 0.088 | 0.001 |
| 7.28 | 2489 | VV | 0.194 | 0.006 |
| 7.62 | 3991 | VV | 0.238 | 0.010 |
| 7.85 | 6136 | VV | 0.158 | 0.015 |
| 8.03 | 2795 | VV | 0.124 | 0.007 |
| 8.43 | 8188 | VV | 0.319 | 0.020 |
| 8.61 | 2834 | VV | 0.109 | 0.007 |
| 8.77 | 3289 | VV | 0.099 | 0.008 |
| 8.87 | 5439 | VV | 0.094 | 0.013 |
| 9.05 | 3103 | VV | 0.124 | 0.008 |
| 9.20 | 3717 | VV | 0.137 | 0.009 |
| 9.42 | 2538 | VV | 0.098 | 0.006 |
| 9.60 | 3864 | VV | 0.239 | 0.009 |
| 9.93 | 16958 | VV | 0.049 | 0.041 |
| 10.44 | 328 | PV | 0.048 | 7.9842E-04 |
| 10.62 | 1289 | VV | 0.057 | 0.003 |
| 13.56 | 1624 | VB | 0.049 | 0.004 |
| 15.18 | 236 | PP | 0.104 | 5.6872E-04 |
| 15.27 | 86 | PB | 0.051 | 2.0725E-04 |
| 15.51 | 378 | VV | 0.077 | 9.1092E-04 |
| 16.18 | 186 | PV | 0.047 | 2.5544E-04 |
| 16.26 | 297 | VV | 0.051 | 7.1572E-04 |
| 16.45 | 1901 | VV | 0.124 | 0.005 |
| 16.58 | 882 | VV | 0.044 | 0.002 |
| 16.63 | 3200 | VV | 0.113 | 0.008 |
| 16.91 | 9372 | VV | 0.144 | 0.023 |
| 17.02 | 6432 | VV | 0.165 | 0.016 |
| 17.37 | 1265 | VV | 0.038 | 0.003 |
| 17.51 | 4921 | VV | 0.131 | 0.012 |
| 17.59 | 3588 | VV | 0.088 | 0.009 |
| 17.85 | 3845 | VV | 0.106 | 0.009 |
| 18.04 | 8721 | VV | 0.142 | 0.021 |
| 18.14 | 13681 | VV | 0.211 | 0.033 |
| 19.24 | 1163 | VV | 0.077 | 0.003 |
| 19.77 | 2178 | VV | 0.104 | 0.005 |
| 20.36 | 218 | PP | 0.053 | 5.2534E-04 |

Figure D.4 GC/FID Chromatogram of Sample Extracted by Solvent Technique

# Appendix E

## Data to Estimate the Recovery Efficiency of the Dionex Supercritical Fluid Extraction Unit

**Protocol Utilised with the Dionex Supercritical Fluid Extractor**

**Protocol Utilised with the Dionex Supercritical Fluid Extractor**

Cell Volume: 10 mL
Oven: 450 atm, 70°C
Restrictor Size: 250 mL $min^{-1}$
Restrictor Temperature: 150°C
Modifier: Methanol at 5% of the total molar flow rate of carbon dioxide
Collection Vial: approximately 10 mL of methanol

*Note: The flow of carbon dioxide ($CO_2$) through the cell was continual--steeping was not an option.*

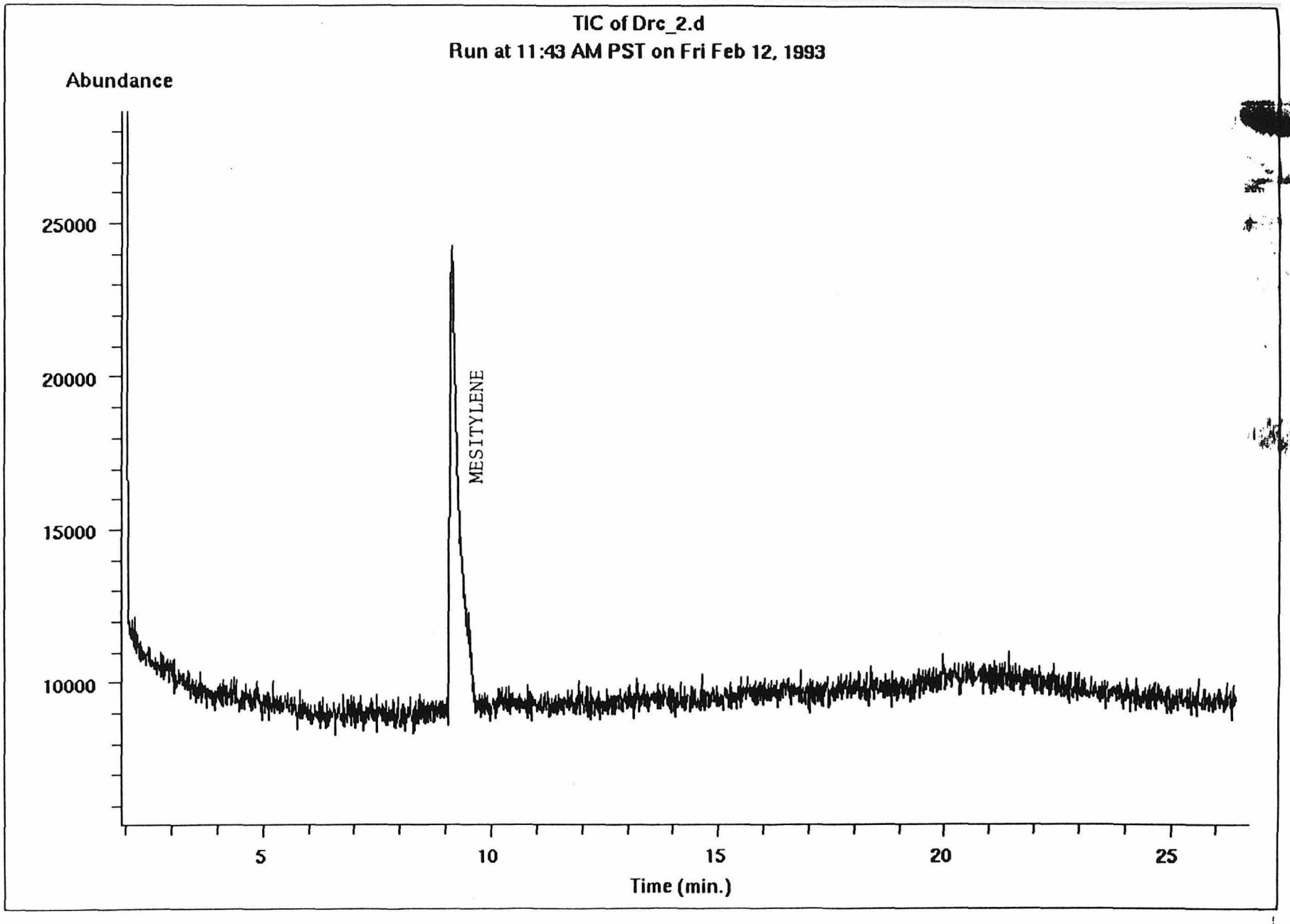



Figure E.1 GC/MS Chromatogram of the Sample Filter Extracted by SFE

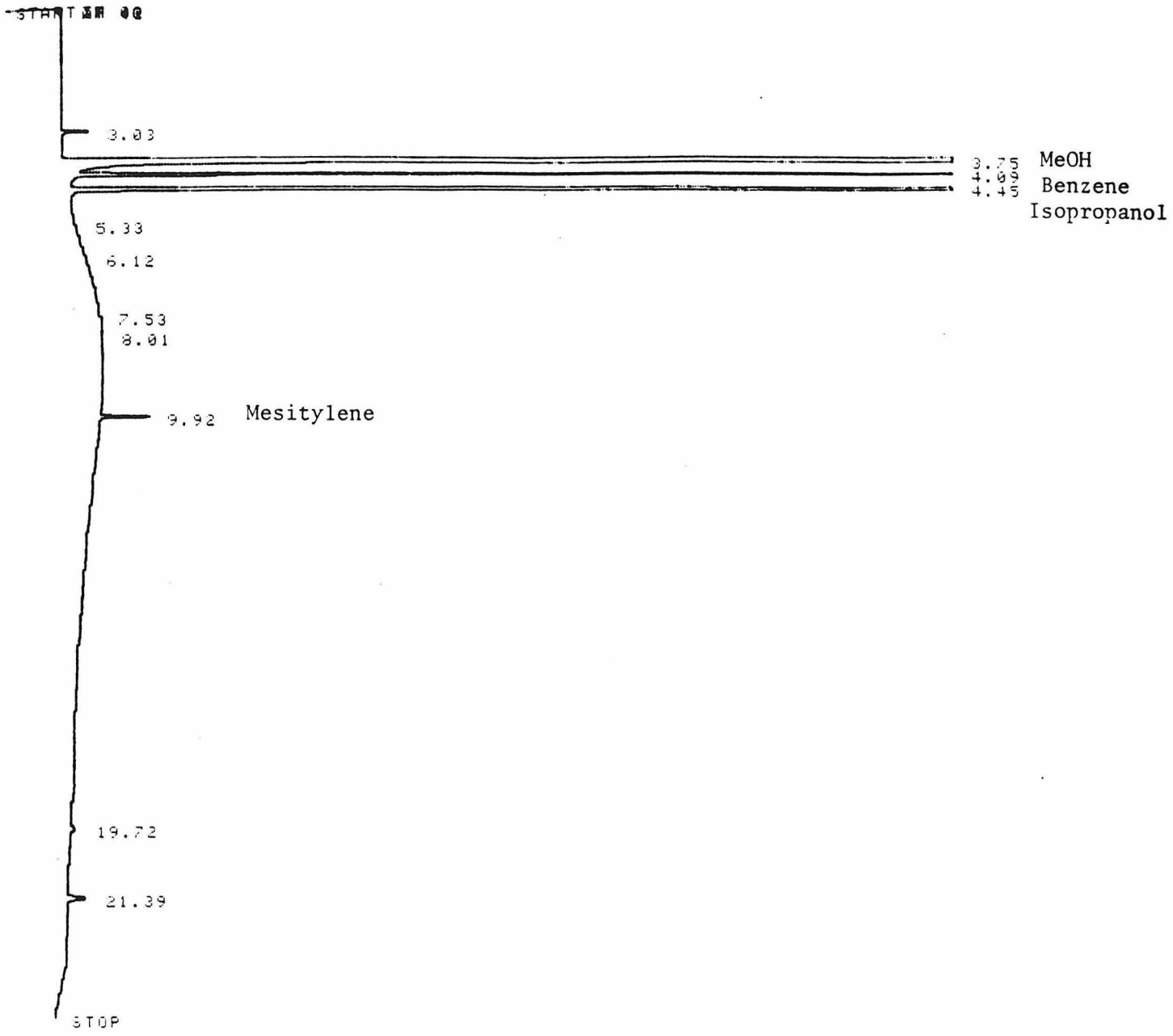



Figure E.2 GC/FID Chromatogram of the Sample Extracted by SFE