CONTRACT NO. 95-335
FINAL REPORT
JUNE 1999

Total Non-Methane Organic Carbon Development and Validation of a New Instrument and Measurements of Total Non-Methane Organic Carbon and C_2-C_{10} Hydrocarbons in the South Coast Air Basin

CALIFORNIA ENVIRONMENTAL PROTECTION AGENCY

AIR RESOURCES BOARD
Research Division

TOTAL NON-METHANE ORGANIC CARBON: DEVELOPMENT AND VALIDATION OF A NEW INSTRUMENT AND MEASUREMENTS OF TOTAL NON-METHANE ORGANIC CARBON AND C_2-C_{10} HYDROCARBONS IN THE SOUTH COAST AIR BASIN

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JUNE 1999

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ACKNOWLEDGMENTS

The authors would like to thank the many individuals who contributed to this project. Ping Liu and Paul Northrop of UCLA contributed to instrument tests and modifications. Robin O'Brian assisted with preparation of reports. South Coast Air Quality Management District Staff Steve Barbosa, Phil O'Bell and Rudy Eden all kindly facilitated the field campaigns. ARB contract manager Randy Pasek contributed both valuable insights and logistical support. Researchers who were co-located at the Azusa site, the EPA mobile lab, managed by Charles Lewis, and Janet Arey and Roger Atkinson of UCR kindly shared hydrocarbon data for comparison.

This report was submitted in fulfillment of ARB project no. 95-335, entitled, "Total Non-Methane Organic Carbon: Development and Validation of a New Instrument, and Measurements of Total Non-Methane Organic Carbon and C_2-C_{10} Hydrocarbons in the South Coast Air Basin," by the University of California at Los Angeles under the partial sponsorship of the California Air Resources Board. Work was completed as of 8/30/98.

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Abstract

ARB project no. 95-335, entitled, "Total Non-Methane Organic Carbon: Development and Validation of a New Instrument, and Measurements of Total Non-Methane Organic Carbon and C_2-C_{10} Hydrocarbons in the South Coast Air Basin," covering the funding period from 8/96-8/98, resulted in an instrument that was successfully deployed at Pico Rivera and Azusa SCAQMD stations to measure total non-methane organic carbon (TNMOC) and the speciated VOC's. The latter field campaign was part of SCOS-NARSTO-97. At Azusa during September and early October, 1997 the TNMOC loading was an average of 30% greater than the sum of the speciated VOC's measured by standard GC/FID (TNMOC/Σ speciated VOC's ratio averaged 1.3 ± 0.3.) This ratio did not correlate with time of day or photochemical processing, but the air reaching the Azusa site was abnormally clean during this period; for example 95% of corresponding O_3 concentrations were < 60 ppb. The nature (and reactivity) of the 30% difference between the TNMOC and the Σ Speciated VOC's is still to be determined. A small fraction of the difference (c. 10%) is due to light oxygenates, ethanol, methanol and acetaldehyde. The primary cause of the variability appears to be short term fluctuations in organic concentrations in the air reaching the Azusa station. Aiming to rectify this situation, the instrument has been fitted with parallel samplers that acquire simultaneous TNMOC and speciated VOC samples. Future field measurements will be made with the dual sampler.

The campaign at Pico Rivera showed that the TNMOC instrument was in excellent agreement with the co-located South Coast Air Quality Management District (SCAQMD) instrument. Experiments carried out in conjunction with SCAQMD staff scientists revealed the source of the anomalous high levels of heavy hydrocarbons that had been observed at Pico Rivera for many years--contamination from room air that escaped through the roof and was entrained into the sample inlet. The instrument was tested and validated with the light oxygenates formaldehyde, acetaldehyde, acetone, methanol and ethanol as well as heavy aromatics and exhibited 100% trapping and conversion in all cases. The instrument does not appear to be affected by water. Preliminary results indicate that the analyzer detects >95% of carbon in smog chamber hydrocarbon oxidation experiments. Finally, a collection of FID response factors for light oxygenates has been derived.

Executive Summary

The formation of ozone and other oxidants in urban and rural areas remains a persistent problem that affects both the public health and economic vigor of many areas in California. Oxidant formation results from the photochemistry of organic compounds in the presence of nitrogen oxides. The organic component begins mainly as biogenic and anthropogenic non-methane hydrocarbons (used here to denote compounds that contain only carbon and hydrogen.) These compounds are progressively oxidized to carbon monoxide and carbon dioxide over periods of hours to weeks. The variety of primary hydrocarbons and their oxidation products is large. While separate techniques exist to measure groups of compounds (e.g., C_2-C_8 hydrocarbons with some carbonyls, or alcohols, or organic nitrates, etc.) no techniques to assess the total loading of non-methane organic carbon (TNMOC) have been widely applied in the atmosphere. The goal of this project is to determine the relationship between the total non-methane organic compounds and the sum of the speciated hydrocarbons and carbonyls measured by standard techniques. The primary scientific motivations are two: first, how much reactive organic carbon is in the air? How close to standard measurements come to reporting this total? Second, what happens to the multifunctional products of the photo-oxidation reactions of emitted hydrocarbons; do they stay in the gas phase or are they removed to the aerosol phase or surfaces? At Azusa during September and early October, 1997 the TNMOC loading was an average of 30% greater than the sum of the speciated VOC's measured by standard gas chromatograph (GC). The air reaching the Azusa site was abnormally clean during this period; for example 95% of corresponding O_3 concentrations were < 60 ppb. The nature (and reactivity) of the 30% difference between the TNMOC and the $\sum$ Speciated VOC's is still to be determined as is how its magnitude changes with location and conditions.

The technique to measure TNMOC centers on a cryogenic separation (on an inert surface) of reactive carbon from carbon monoxide, carbon dioxide and methane. After separation, the isolated organic material is oxidized to carbon dioxide, allowing quantification. The sample comes in contact only with a sampling tube and heated valve before passing through the primary trap. The target TNMOC condenses, while carbon monoxide, methane and most of the carbon dioxide pass through. Next, the primary trap is briefly purged with clean helium gas. In the second step, the trap is rapidly heated; and a helium/oxygen mix sweeps the desorbed TNMOC into an oxidation catalyst where it is converted to carbon dioxide. The carbon dioxide is focused in a second trap, desorbed, reduced to methane and quantified with a flame ionization detector.

An additional air sample is collected under identical conditions to the sample for TNMOC analysis, but in this sample the individual hydrocarbons and a few other organic components are analyzed. Taken together, these make up the "volatile organic carbon" (VOC's) that are measured by standard techniques. This sample is transferred directly to the focusing trap, and from there it is directed into a gas chromatograph. The speciated channel may also be used to determine trapping and transfer efficiencies of individual organics in the inlet. Assuring that all relevant classes of compounds are detected at 100% is crucial to a TNMOC analyzer. Under normal operating conditions all aldehydes and alcohols tested trap at 100%; including formaldehyde, acetaldehyde, methanol, and ethanol. In addition, no evidence of interference from water was found for samples containing 4-10 times the amount of water typically encountered in atmospheric samples.

Dozens of smog chamber experiments have been carried out to investigate the oxidation chemistry and ozone formation from hydrocarbons. Few of these experiments can account for 100% of the reacted carbon as products; 30-70% is typical. As the starting hydrocarbons become oxidized, their products become progressively less volatile and more polar. Some of the products may deposit on the walls of the reactor, form aerosols, or deposit in the gas chromatograph or inlet. In a sense measuring total carbon in a smog chamber experiment is the "acid test" for a TNMOC analyzer. Preliminary results show

that the TNMOC measurement works well in detecting the oxidized products from both styrene and α-pinene; decreases of less than five percent were observed in the TNMOC channel throughout the course of several oxidation experiments.

Two major design improvements have been made over the course of this project, both motivated by field measurements. It is most interesting to compare the TNMOC measurement to the sum of the speciated hydrocarbons (Σ Speciated VOC's) as they are commonly measured--in a standard GC with a flame ionization detector (FID). Initially speciated measurements were made with the same column as the TNMOC analysis, but heavy hydrocarbons (but not TNMOC, which passes through the column after conversion to CO_2) were lost in the methanation catalyst. To solve this, we added a separate channel with a second column and FID. Second, it became apparent during the measurement campaign at Azusa, CA during 9-10/1997 that a large portion in the scatter observed when comparing the TNMOC measurements with the Σ Speciated VOC's was due to the rapid fluctuations of pollutants in the air masses arriving at the station. In order to reduce the variability in the observed ratio of TNMOC/Σ speciated VOC's it was necessary to add the capability of taking both samples simultaneously rather than sequentially. Thus, the final effort of this project has been to add an additional, identical sampler in parallel.

The flame ionization detector response of organics is directly proportional to the mass of carbon present in the sample except when they contain oxygen or nitrogen atoms. These atoms reduce the flame ionization detector signals by amounts that depend on their bonding. Since the degree of difference between TNMOC and Σ Speciated VOC's may be partly due to the reduced signal of compounds such as methanol and ethanol, we measured the flame ionization detector response for several common pollutants containing oxygen.

The TNMOC analyzer was deployed in two field campaigns, one in Pico Rivera during May and June of 1997, and another during September and early October, 1997 at Azusa. The Pico site is downwind from downtown Los Angeles and is located near the 60 and 605 freeways. The air is dominated by source emissions, but it sometimes experiences high ozone levels. The Azusa site, located near the intersection of the 60 and 210 freeways at the foot of the San Gabriel mountains has both local emissions and pollution transported from the western parts of the basin. It frequently experiences very high ozone levels. The summer of 1997 was subject to a strong El Nino and had unusually clean air, so that no high ozone events were captured during this measurement campaign.

The purpose of the measurements at the Pico Rivera site was to make a head-to-head comparison of the TNMOC analyzer with a standard GC operated by the South Coast Air Quality Management District (SCAQMD), on air that could be expected to give a similar result for both analyses. The TNMOC instrument proved to be in excellent agreement with the co-located SCAQMD instrument. Further, experiments carried out in conjunction with SCAQMD staff scientists revealed the source of the anomalous high levels of heavy hydrocarbons that had been observed at Pico Rivera for many years--contamination from room air that escaped through the roof and was entrained into the sample inlet.

The goal for the measurements at Azusa was to investigate the relationship between the total loading of non-methane organic carbon (TNMOC) and the sum of the organics measured by standard methods (Σ Speciated VOC's). At Azusa during September and early October, 1997 the TNMOC loading was an average of 30% greater, equivalent to 135 ppbC, than the Σ Speciated VOC's. The variability was ±30%. Since canister samples showed excellent agreement and reproducibility for the TNMOC/Σ speciated VOC's ratio on a single air sample, the likely cause of the scatter was rapid fluctuations in organic pollutants in the air reaching the station. This ratio did not correlate with time of day. The 1997 season was unusually clean; 95% of sampled O_3 concentrations were < 60 ppb and aromatic ratios indicated minimal photochemical processing. Only a slight increase in oxygenation/nitration, of order 6%, was expected for the afternoon relative to the morning samples; a signal too small to discern given the scatter in the data. A small fraction of the difference (c. 10%) is due to light oxygenates, ethanol, methanol and acetaldehyde; the nature, reactivity and variability of the remainder is still to be determined.

1.0 Introduction

The formation of ozone and other oxidants in urban and rural areas remains a persistent problem that affects both the public health and economic vigor of many areas in California. Oxidant formation results from the photochemistry of organic compounds in the presence of nitrogen oxides. The organic component begins mainly as non-methane hydrocarbons (NMHC) from biogenic and anthropogenic sources (hydrocarbon is used here to denote compounds that contain only carbon and hydrogen). These compounds are progressively oxidized to CO and CO_2 over periods of hours to weeks. The variety of primary hydrocarbons and their oxidation products is large. While separate techniques exist to measure groups of compounds (e.g., C_2-C_8 hydrocarbons with some carbonyls, or alcohols, or formaldehyde or organic nitrates, etc.) no techniques to assess the total loading of non-methane organic carbon (TNMOC) have been widely applied in the atmosphere. The goal of this project is to determine the relationship between the total non-methane organic compounds and the sum of the speciated hydrocarbons and carbonyls measured by standard techniques. The primary scientific motivations are two: first, how much reactive organic carbon is in the air? How close to standard measurements come to reporting this total? Second, what happens to the multifunctional products of the photo-oxidation reactions of emitted hydrocarbons; do they stay in the gas phase or are they removed to the aerosol phase or surfaces?

A total reactive carbon measurement has an obvious analogy in the total reactive nitrogen (NO_y; all oxides of nitrogen except N_2O) measurement. The NO_y measurement is now widely used in both the troposphere and the stratosphere (e.g., [1-8].). Initial measurements indicated that the total NO_y signal could not be accounted for by the sum of its measurable components [9, 10], which resulted in re-evaluation of the detection and calibration methods for the component compounds (particularly nitric acid) as well as a search for additional species containing oxidized nitrogen [7, 11]. Currently NO_y itself is used as a conservative quantity for reactive nitrogen, with much to be learned about both the age and hydrocarbon/NO_x ratio history of an airmass from the relationship between NO_y and NO_x [1-7].

There are several reasons to expect the total NMOC measurement to result in a number that is much larger than the sum of the routinely measured reactive carbon species. Superimposed on the rising baseline of high resolution gas chromatograms of ambient air samples are dozens of small signals. Both the unidentified peaks and a portion of the rising baseline indicate a large number of undetected (individually) low concentration species. Further, the problem of the loss of oxygenated and semi-volatile compounds in sampling

and on columns is well known (e.g., [8], [12]), although the extent of the losses is very difficult to quantify. Finally, modeling results indicate that while the initial oxidation step of a hydrocarbon may take place within hours, if our understanding of the relevant processes is correct, complete removal of the partially oxidized fragments should take weeks (e.g., [1]). Even in controlled smog chamber photooxidations, much less than 100% of the reacted parent hydrocarbon can be accounted for as products even with advanced techniques (e.g., [9, 10]), even when the carbon in the aerosol phase is included (e.g., [13]).

1.1 Related Measurements

Several techniques and measurements similar to the proposed TNMOC measurement have been attempted, but as far as we know, only one study has been published in the open literature [14]. On the other hand, many measurements of speciated non-methane hydrocarbons (NMHC's) have been made using EPA Method TO-14 or similar techniques. This approach uses cryogenic sample concentration and separation on a capillary column. Individual NMHC's (and in some cases a few polar organics) at sub-ppb [15-20], and recently low ppt detection limits have been achieved by several groups (e.g., [21-23]).

Total NMOC in source streams--at typically 10^3-10^4 times ambient concentrations--are routinely measured by EPA Method 25 or similar [24-26]. For this measurement, a stack sample is divided into condensable and gaseous fractions. The condensable fraction is oxidized to CO_2, and analyzed with non-dispursive infrared or with a flame ionization detector (FID) after reduction to methane [25]. Part of the gaseous fraction is injected onto a column where CO_2, CH_4, and CO are separated from the NMOC. The column is then back-flushed and the organics are swept into an oxidation furnace and again measured as CO_2. The total organic concentration is the weighted sum of these two measurements. This technique measures total organics down to several ppm [26].

Methods for measuring total *NMHC's* (including other organics to varying degrees) include analyzing an air sample directly with an FID, and subtracting CH_4 (measured separately). Since CH_4 concentrations are ~1.6 ppm in the Northern Hemisphere, this method can be applied only in highly polluted areas. A variation uses a GC column to separate the NMHC's from CH_4; the CH_4 and CO_2 elute before the NMHC's, then the column is backflushed through an FID [16-18, 27, 28]. A drawback of the back-flush method, which our instrument is specifically designed to avoid, is loss of polar or heavy VOC's in the column itself. A variation backflushes the column through a series of oxidation and reduction catalysts to convert the trapped NMHC's first to CO_2 and then to

CH_4. This is intended to make the instrument response per carbon atom constant; another drawback of the FID approach is that structure and heteroatoms reduce the FID response by variable amounts [29]. The State of California Procedure for the Determination of Total Non-Methane Organic Compounds (NMOC) by Pre-concentration Direct Flame Ionization Detection (SOP NO. MLD 024) separates NMOC from methane on a cooled trap filled with silanized glass beads and directs them through an FID. Other total NMHC methods are based on sorbent traps; for example the Bendix 8202 (e.g., [30]). The sorbent may be used to separate out CH_4; quantification is usually with an FID. While these methods have advantages, they also must contend with the issues of recovery of polar compounds from sorbents, and the non-linear response of the FID to molecules that contain heteroatoms.

Dr. James Roberts at the NOAA Labs in Boulder is has developed a variation of the column back-flush approach to make a total NMOC measurement in ambient air [14]. This approach has the advantage of achieving quite low detection limits (~1 ppb) but has the disadvantage of possibly losing semi-volatile compounds to the GC column or transfer lines. Roberts et al.[14], had to compare their TNMOC measurements with speciated VOC instruments operated by other groups to calculate the TNMOC/Σ speciated VOC's ratio. Since the calibrations, sampling frequencies and averaging times were different, a fair degree of scatter is anticipated, and a systematic error is possible. Measuring in relatively clean air in Boulder, Colorado, and Nova Scotia, Canada, they found differences between the TNMOC total (which they refer to as "C_y") and the sum of hydrocarbons and carbonyls that were small in absolute terms (averaging 3.8±7.9 ppb) but were significant in percentage terms; TNMOC/Σ speciated hydrocarbons + carbonyls was 1.36±1, 1.16±0.7. and 1.33±0.4 for samples from air with < 20, $20 \leq O_3 \leq 50$, and >50 ppb O_3 respectively. These values are comparable to the ratio of TNMOC/Σ Speciated VOC's we measured in Azusa, CO during September and October of 1997 of 1.3±0.3.

The TNMOC instrument described here has several improvements compared to previous approaches. Great care has been taken to assure minimal loss of sticky or labile compounds. Samples introduced into our instrument are exposed only to an inlet tube and one valve. From there they are immediately analyzed; our measurement is not confounded by losses in plumbing, valves or GC column. At the conclusion of this project, we re-designed out inlet so that it takes simultaneous samples for analysis in TNMOC and speciated VOC modes, avoiding problems created by comparing different sample inlets, calibrations, and sampling periods.

1.2 Quantification of TNMOC

The technique to make the TNMOC measurement centers on a cryogenic separation of reactive carbon from CO, CO_2 and CH_4. This instrumental approach was chosen over a

dozen other concepts because of the minimal sample contact, the expected robustness, and absence of obvious technical pitfalls. After separation, the isolated organic material is oxidized to CO_2, allowing quantification. A schematic for the process is shown in Figure 1-1. In step 1, the first trap (I) is cooled (to -70 °C), with pulses of lN_2 vapor. The sample comes in contact only with a sampling tube and heated valve before passing through the 1° trap. The target TNMOC condenses, while CH_4, CO, and most of the CO_2 pass through. Next, Trap I is briefly purged with He. In step 2, trap I is rapidly heated; and a He/O_2 mix sweeps the desorbed TNMOC into an oxidation catalyst where it is converted to CO_2. The CO_2 is focused in the 2° trap (not shown), desorbed, reduced to CH_4 and quantified with an FID. A detailed flow schematic of the instrument is shown in Figure 1-2.

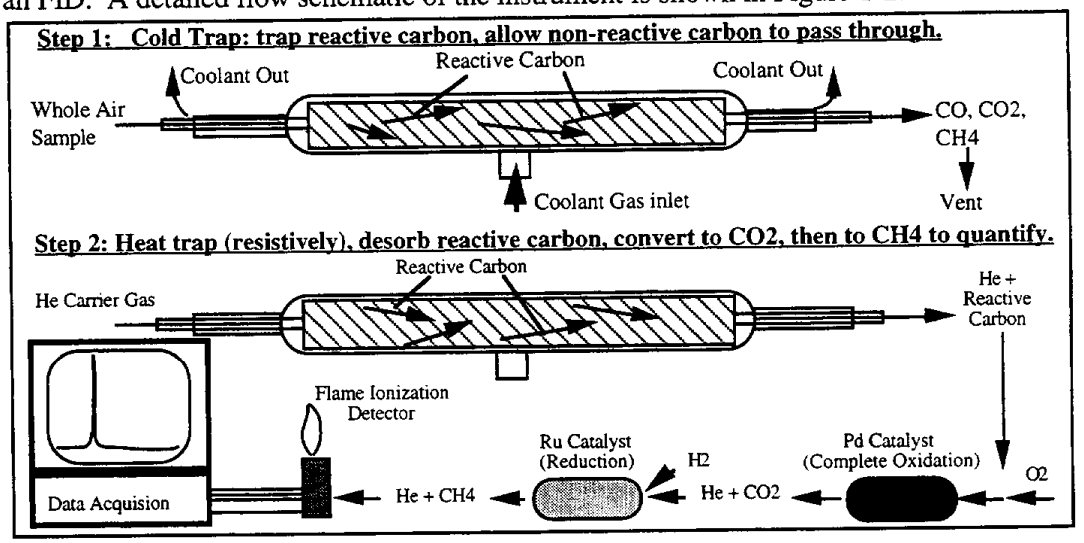

Figure 1-1. Process schematic of the approach for the total TNMOC measurement.

Ideally, 100% TNMOC in the air sample stays in trap I, and CO, CO_2, and CH_4 pass through. In practice, CO and CH_4 (boiling points of -191.5 and -164 °C, respectively) pass through. The primary trap is typically operated at -70 °C. CO_2, with an ambient concentration larger than the sum of reactive compounds by a factor of 100-40,000 and a relatively high sublimation point (-78.6 °C), traps to a minor degree. The detection limit for the measurement is determined not by the absolute amount of atmospheric CO_2 that traps but by the uncertainty and variability in the amount of CO_2 trapped. Since the ambient CO_2 concentration in cities fluctuates by up to a factor of two (P. J. Nelson, personal communication), a significant amount of variability is unavoidable, thus the less CO_2 trapped, the smaller this effect. By specifically designing the 1° trap to minimize adsorption of CO_2, we have achieved trapping of CO_2 equivalent to about 50 ± 10 ppb in a 0.5 liter sample. The amount of CO_2 trapped is traded off, however, with the trapping of

C_2-C_5 hydrocarbons (only compounds with carbon and hydrogen; oxygenates including formaldehyde trap completely). In the field, we chose conditions where we trapped 300± 20 ppbC of CO_2, thus our detection limit (~3 x the CO_2 noise level) was about 60 ppbC. In the urban air sampled, the lowest TNMOC concentration observed was 180 ppbC, well above the detection limit.

Once the sampling (cryo-trapping) stage is finished, the 1° trap is purged with an auxiliary helium stream to remove sample gas from the tubing and air space within the trap. Next, the 1° trap is heated; and an auxiliary gas stream (O_2/He) sweeps the contents of the TNMOC trap through an oxidation catalyst, converting the organics to CO_2. An advantage of this method is that decomposition or reaction of labile compounds during trapping and heating has no effect on the result, because the trapped organics are immediately oxidized to CO_2. The sample is are focused in the 2° trap, which is immersed in lN_2. This traps concentrates the (~50 cc) volume necessary to thoroughly desorb the contents of the 1° trap into a small plug for the quantification step. Finally the focusing trap is heated and the TNMOC, which has been converted to CO_2, is catalytically converted at the end of column 1 to CH_4 [31-33] and quantified with an FID.

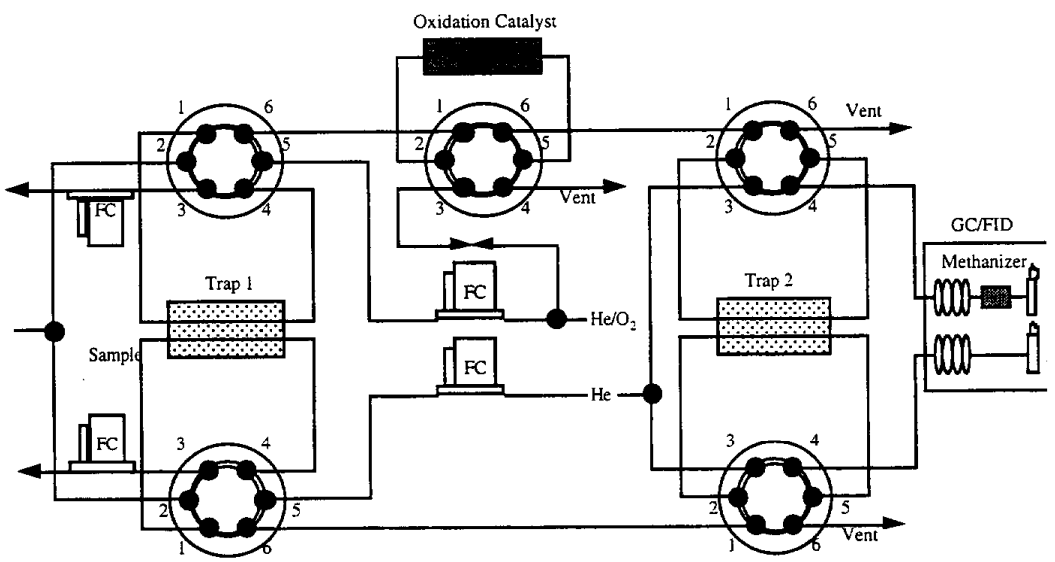

Figure 1-2. Flow schematic for the Reactive Carbon Analyzer. FC = flow controller.

1.3 Quantification of Speciated VOC's

Speciated VOC's are collected under identical conditions to TNMOC but the sample is desorbed with He and transferred directly to the 2° trap. From there it is desorbed into a separate 60 m DB-1 column (0.32 mm ID, 1μm film) for analysis with an FID. For the data collected in ARB project no. 95-335, the samples were collected sequentially in the

same trap used for TNMOC measurements. In the current instrument, samples are collected in a parallel 1° trap. This channel may also be used to determine trapping and transfer efficiencies of individual organics.

2.0 General Development During Project Period

2.1 Trapping Performance

A number of tests to determine trapping efficiency and oxidation of compounds of atmospheric interest have been carried out. In addition an investigation of the effect of high concentrations of water was made. It was found that under normal operating conditions all aldehydes and alcohols tested trap at 100%; including formaldehyde, acetaldehyde, methanol, and ethanol. An effort was made to determine how much water would plug transfer lines or the 1° trap. Evidence of plugging was not observed for samples that were 4-10 times the operational sample volume.

2.1.1 Trapping of light oxygenates.

Formaldehyde, the lightest common oxygenate, is both directly emitted and formed in numerous photooxidation reactions. Formaldehyde can contribute a non-negligible amount of the total VOC's; HCHO in ambient air varies between about 2 and 50 ppb [34, 35]. It is important to know if formaldehyde itself is trapped by our instrument, both for itself and because it is the lightest of the oxygenate family. As long as HCHO traps quantitatively we can assume that other small oxygenates such as methyl hydroperoxide also trap efficiently. It is well known that formaldehyde has a very low (almost zero) FID response (Section 3). Thus it is practically invisible in our speciated VOC analysis. Formaldehyde is, however, oxidized by the oxidation catalyst and contributes to the Total NMOC. We were also concerned that partial reduction of HCHO in speciated VOC measurements in column 1 (with the methanizer) also might effect the CO_2 background measurements which were used to correct the Total NMOC measurements. Since the temperature program used during SCOS-97 did not separate CO_2 and HCHO, we would also subtract the HCHO concentration from the Total NMOC.

A mixture of roughly 6 ± 3 ppm HCHO, prepared by heating paraformaldehyde in dry N_2 was trapped at different temperatures in the 1° trap, and analyzed in the Total NMOC mode and without oxidation on column 1 to measure the amount of CO_2 in the sample. A GC temperature program able to separate CO_2 and HCHO was used in these experiments. The results are presented in Table 2-1 and displayed in Figure 2-1. All reported CO_2 data were corrected for the CO_2 blank (the amount of CO_2 observed in the absence of any sample, primarily attributable to contamination in the He/O_2 mix), equivalent to about 450±10 ppbC. The first column in Table 2-1 gives the temperature of

the trap, the second column the total carbon from the measurements in the total NMOC mode, the third and fourth columns CO_2 and HCHO concentrations from the Σ Speciated VOC measurements on column 1, and the last column the calculated HCHO concentration, calculated as the difference of TNMOC (Col. 2) and CO_2 (Col. 3). HCHO is trapped completely; no difference is found between the amount of HCHO at -70 (our operational temperature) and -120°C in the speciation mode (3.71 vs. 3.63 ppmC) or in the calculated amount of HCHO (4.78 vs. 4.9 ppmC). The difference between the measured "speciated" and the calculated amount of HCHO results from partial reduction of HCHO to CH_4 by the methanizer. At the time of these tests, this conversion efficiency was about 0.77, but can be expected to change as the methanizer catalyst ages or is regenerated. In this case, since the HCHO concentration has been measured after conversion to CO_2 that was then reduced to CH_4 (as well as in speciation mode without oxidation), we can see that the methanizer had not reached maximum capacity when the samples trapped at less than -50 °C were introduced. When the formaldehyde is measured as CO_2, it is measured together with CO_2 trapped from the sample (squares in Figure 2-1), and CO_2 measured separately (diamonds in Figure 2-1) is subtracted to give the formaldehyde concentration (crosses in Figure 2-1). Since the CO_2 + formaldehyde curve continues to increase as the trapping temperature was lowered, the methanizer cannot be saturated. Both the difference of the CO_2 + formaldehyde and the CO_2 curve and the formaldehyde curve measured in speciated mode are flat between -70 and -120 °C, thus we can conclude that formaldehyde traps completely below -70 °C.

Table 2-1: Formaldehyde Trapping and Signals

	Total NMOC	Speciated VOC (col. 1)		
Trap Temperature [°C]	total carbon ppmC	CO_2 ppmC	HCHO(det.)[a] ppmC	HCHO(calc.)[b] ppmC
-50	2.86	0.23	1.59	2.18
-60	4.05	0.27	3.02	3.33
-70	5.55	0.32	3.71	4.78
-70	5.75			
-120	9.70	4.35	3.63	4.90

[a]This formaldehyde is detected after partial reduction to methane by the methanizer at the end of GC column 1. The reported concentrations have a ± 10% error due to significant tailing of the formaldehyde peak.

[b]This is calculated as the difference of TNMOC (Table Col. 2) and CO_2 (Table Col. 3) after correction for the CO_2 blank (450 ppbC at the time of these tests).

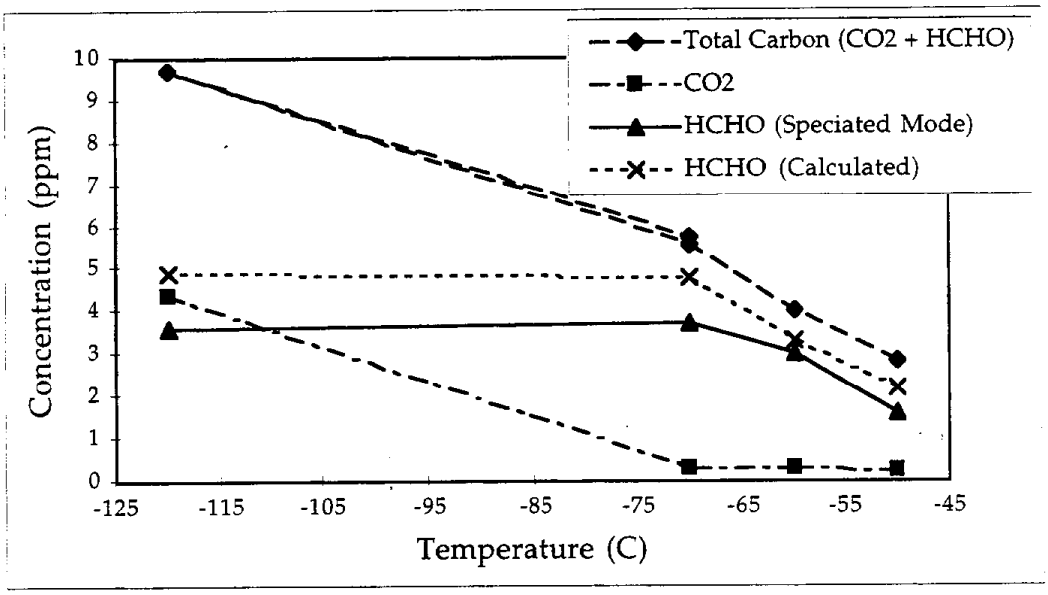

Figure 2-1: Concentration of CO_2, HCHO and Total Carbon as a function of the temperature of trap 1. The actual amount of HCHO was calculated as the difference of the Total NMOC and the amount of CO_2 trapped.

Acetaldehyde has a boiling point of 21 °C, below the boiling point of pentane (boiling point of 29 °C) which traps at about 90% at -70 °C (our operational temperature), thus we investigated the trapping of this compound. Acetaldehyde samples were prepared in a previously evacuated silica-coated, deactivated stainless steel cylinder together with a marker compound, 1,3,5-trimethylbenzene. Because acetaldehyde is lost to the cylinder walls at a relatively high rate, attempts to perform these tests at low concentrations (< 1 ppm) failed. Also, for this reason the exact concentration of acetaldehyde was not known. As is shown in Figure 2-2, the acetaldehyde signal reaches a maximum at temperatures below -50 °C. These tests were run without the oxidation catalyst in line, and acetaldehyde is partly reduced by the methanation catalyst at the end of the capillary column (Section 2.4.5); the FID response is equivalent to 0.4 carbon atoms/molecule of acetaldehyde without the methanizer and 0.75 with the methanizer. Thus in the event that the methanizer had reached maximum capacity when the samples trapped at less than -50 °C were introduced, if the amount trapped was still increasing as the trapping temperature was lowered, the observed signal would still increase somewhat. What we observe instead is a flat signal below -50 °C, and can thus conclude that acetaldehyde traps completely below this temperature.

We have tested the trapping of ethanol (boiling point = 78 °C) [36] and found that it also traps at 100% at any temperature below ambient. Methanol has a boiling point of 65 °C, thus it is expected to trap quantitatively. In conclusion, it is reasonable to assume that all oxygenates including formaldehyde trap completely in our system.

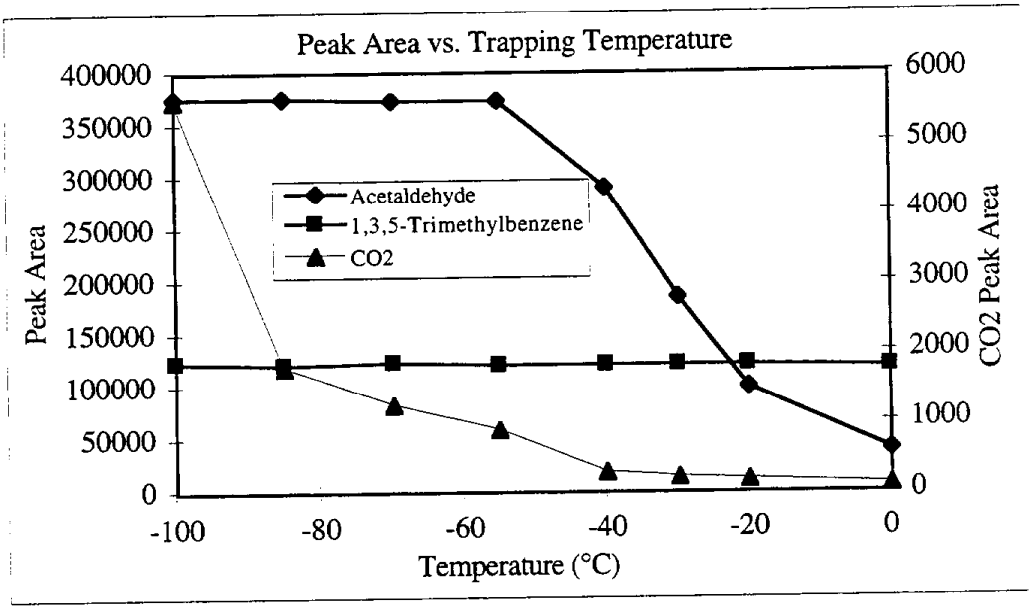

Figure 2-2. Trapping vs. temperature of acetaldehyde and 1,3,5-trimethylbenzene. This mixture was made in ultra high purity nitrogen, thus the CO_2 peak is very small. The acetaldehyde and 1,3,5-trimethylbenzene concentrations are about 12 ppm, and 0.6 ppm respectively.

2.1.2 Can H_2O Plug Traps or Lines?

In the original proposal review process concerns were raised with regard to water management and the potential for plugging traps and transfer lines with the water in the 0.5-1 liter ambient air sample volumes proposed. We have since tested this directly by flowing 2000 mL of room air (with relative humidity of 54% at 297 K) at 25 mL/min and 3000 mL at 50 mL/min with the first trap at -55 °C and found no sign of clogging--the flow rate remained steady throughout the test. The total liquid H_2O introduced in these tests is 0.22 mL and 0.34 mL respectively. Similarly in field tests no problems attributable to H_2O in the traps were observed. A possible explanation for the observation that frozen H_2O does not plug the trap or lines lies in the design: the first trap is a 1/4" OD tube, and the ends of the trap near the fittings contains a dead space of about 1 mL. The ends are also warmer than the center of the tube (where the cryogen is directed and temperature is

2.2 Addition of a Second GC Column.

Two major design improvements have been made over the course of this project. Both were motivated by measurements in the field. One of the most interesting aspects of the TNMOC measurement is its comparison to the sum of the speciated hydrocarbons as they are commonly measured--on a DB-1 column with a flame ionization detector (FID). In an effort to make this comparison with as high quality as possible we added a second column and FID. The second column was installed during the period between the Pico Rivera and Azusa measurement campaigns. It became apparent during the Azusa campaign that in order to reduce the variability in the observed ratio of TNMOC/Σ speciated VOC's, due to (large) temporal variability of air masses, it would be necessary to add the capability of taking both samples simultaneously rather than sequentially. Thus, the final effort of this project has been to add an additional, identical sampler in parallel (Section 2.5).

The second column that is identical to our current column and is amongst the most commonly used in similar applications; 60m x 0.32 mm ID x 1μm DB-1 (J&W). This required an additional 6-port valve. The performance evaluation data is discussed below. With this inlet, the instrument can make three type of measurements, summarized in Box 2-1.

Box 2-1. TNMOC Analysis Modes

1) "*Speciation, column 1*" no oxidation, column 1 (60 m DB-1, 0.32 mm ID, film 1 μm), Ru methanizer and FID.

2) "*TNMOC, column 1*" the sample is oxidized over a Pd-catalyst to CO_2, run on column 1 (60 m DB-1, 0.32 mm ID, film 1 μm), and analyzed with FID after conversion to methane over Ru.

3) "*Speciation, column 2*" no oxidation, column 2 (60 m DB-1, 0.32 mm ID, film 1 μm) analyzed with FID (no methanizer). This is the standard type of speciated hydrocarbon analysis.

Note 1: All of these modes used identical inlet conditions, thus the lightest C_2-C_5 are not trapped quantitatively. Actual total organics are probably 10-15% higher than reported here.

Note 2: (*Speciation, column 1* was necessary to establish the amount of CO_2 trapped in trap 1 to order to correct "*total carbon*" experiments for trapped ambient CO_2.

2.3 Reproducibility: Canister Sample Results

To rigorously test the comparability of the TNMOC and speciated VOC measurements, a 20 l canister sample taken on Sept.-29-97 at 10:00 - 10:15 at the Azusa site was prepared. The sample was drawn through the normal sampling line and pressurized using a diaphragm pump. This process resulted in some losses of heavy and polar compounds, but it did provide an air sample that is reasonably representative of ambient air, and which was directly comparable from run to run. The standard sampling method (used for most ambient air analyses at Azusa) was also used to analyze the canister; 500 mL sample volume, 50 mL/min sample flow rate. A tee was added before trap 1 to reduce the pressure in trap 1 to one atmosphere for all runs.

2.3.1. Speciation column 1 Results:

Results from three "Speciated Column 1" measurements are presented in Table 2-2. From these measurements a total VOC concentration of 0.478 ± 0.018 ppmC can be calculated, but this is an underestimate due to losses in the methanizer (below). The third column in this table shows the amount of CO_2 (0.362 ± 0.021 ppmC) typically trapped during the sampling procedure; this will be subtracted from the CO_2 peak measured in TNMOC mode to provide the TNMOC measurement.

Table 2-2: Speciated Column 1 Measurements.

Filename	Total VOC's [ppmC]	CO_2 [ppmC]
AZUSA2.88	0.461	0.368
AZUSA2.94	0.477	0.379
AZUSA2.95	0.497	0.338
Average	0.478	0.362
STD	0.018	0.021

Note: The amount of CO_2 trapped in these measurements is somewhat larger than in the direct air samples taken at the Azusa station. For direct air samples, trapping takes place at lower pressure when samples are drawn through the full length of inlet tubing, resulting in a background CO_2 signal of 0.30 ± 0.02 ppmC.

2.3.2. TNMOC (Total carbon column 1):

The results of five TNMOC measurements are summarized in Table 2-3. From these measurements a total carbon concentration of 1.046 ± 0.043 ppbC was determined. After correcting this value for the amount of ambient CO_2 trapped during the sampling in the 1° trap (0.362 ± 0.021 ppmC; Tab. 2-3) and the blank CO_2 signal (0.050 ± 0.010

ppmC, at the time of these tests) a total non methane organic carbon concentration of 0.634 ± 0.06 ppmC is calculated.

Table 2-3: TNMOC Measurements.

Filename	Total area of CO_2 peak [ppmC]	TNMOC [ppmC]
AZUSA2.87	0.990	0.578
AZUSA2.97	1.065	0.653
AZUSA2.98	1.103	0.691
AZUSA3.29	1.047	0.635
AZUSA3.30	1.024	0.612
Average	1.046	0.634
STD	0.043	0.049

2.3.3 Speciation column 2:

In five "speciated, column 2" measurements a total VOC concentration of 0.580 ± 0.019 ppmC was determined; the results are summarized in Table 2-4.

Table 2-4: Results from the Speciation Column 2.

Filename	Total peak area as hydrocarbons [ppmC]
AZUSA2.89	0.558
AZUSA2.90	0.599
AZUSA2.91	0.577
AZUSA2.92	0.565
AZUSA2.93	0.599
Average	0.580
STD	0.019

2.3.4 Summary

Total peak areas for each of the three analysis modes have standard deviations of less than ±8%, again confirming the very good reproducibility with this instrument. The TNMOC measurement has a higher uncertainty (~±10%) due to error propagation from corrections for non-TNMOC derived CO_2.

Comparing the results from "speciation column 2" and TNMOC we find a ratio of total carbon to speciated of 1.09 ± 0.09, indicating that even in air that is heavily influenced by sources, traditional GC/FID measurements miss a modest amount of the total. This

value is consistent with our observations during the SCOS-97 field test, where we found a ratio of about 1.1 to 1.4 over the course of a day. A lower value is expected for this morning air sample; the O_3-concentrations was between 10 and 15 ppb, thus the air had probably experienced minimal photochemical processing.

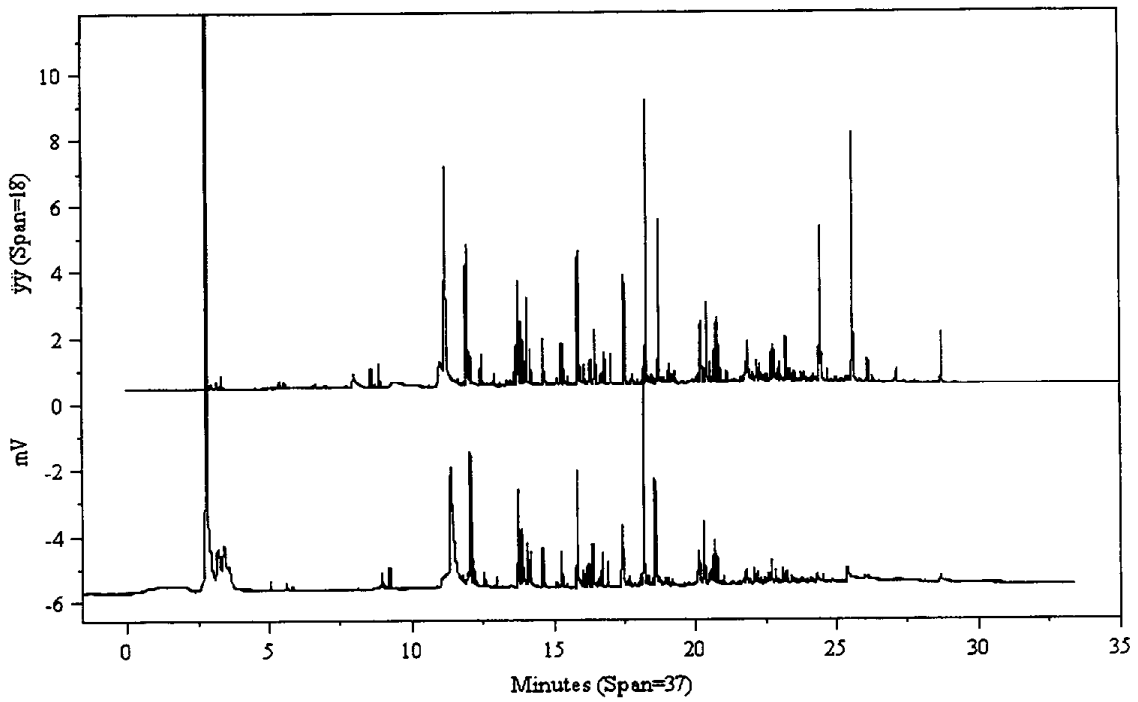

Figure 2-3: Chromatograms from the canister sample analyzed "speciated column 1" with methanizer (lower chromatogram) and "speciated column 2" (upper chromatogram). The large peak at 3.5 minutes is CO_2, and this is only visible on Column 1 which uses a methanizer. The heaviest peaks that elute after about 22 minutes appear to be lost in the methanizer (lower chromatogram). These chromatograms are not offset with respect to the abscissa.

There is a large discrepancy between the speciated measurements made on column 1 (0.362 ± 0.021 ppmC) and column 2 (0.580 ± 0.019 ppmC). The cause for this difference is readily apparent when chromatograms from the two columns are visually compared (Figure 2-3). Table 2-5 shows the peak heights and concentrations (calculated form the peak areas) for selected hydrocarbons of the two chromatograms. Clearly compounds with retention times greater than about 20 minutes are responsible for the difference. We believe that the heavier compounds are lost or severely broadened in the methanizer located at the

end of column 1 and before the FID. Inspection of the data in Table 2-5 shows that while the heights for the light compounds are lower on Col. 1, the areas on both columns are equivalent. The peaks that elute after 20 minutes, which we believe include the xylenes, terpenes and heavier compounds, however, do not make it through the methanizer immediately; these peaks are reduced in area or are lost.

Table 2-5: Summary Data for Selected Peaks for Chromatograms Shown in Fig. 2-3.

Compound	Retention time [min]	Column 1 Concentration [ppbC]	Column 2 Concentration [ppbC]	Column 1 Height (Arb. Units)	Column 2 Height (Arb. Units)
propene	9.3	1.12	0.96	115	222
n-butane	12.6	2.88	2.87	599	654
n-pentane	15.4	17.7	16.6	2659	3811
n-hexane	17.9	5.65	5.73	1288	1225
benzene	19.2	10.8	10.7	2577	3604
toluene	21.9	18.9	20.1	3251	4906
m/p-xylene	23.6	7.32	12.7	13337	2379
a-pinene	25.8	4.27	18.6	762	3637
limonene	28.4	4.51	39.8	433	9057

Note: The identification of the peaks is based on the EPA analysis report of the PAMS 1996 retention time cylinders and on reference chromatograms taken from one of these cylinders. The reference chromatograms for the hydrocarbons were taken under dry and CO_2-free conditions, so the retention times had to be corrected for the conditions in ambient air. The identification of α-pinene and limonene (not in the standard cylinder) is based on the GC/MS analysis of the EPA-instrument co-located at the same station. All peak identities should be considered tentative.

2.3 Oxidation

Routine calibration tests indicate that the oxidation catalyst converts 100±3% of the n-hexane standard. Aromatics can be considerably more difficult to oxidize, thus a test of conversion of 1,3,5-trimethyl benzene was made. Figure 2-4 shows the results of the temperature of the oxidation catalyst on conversion of 1,3,5-trimethylbenzene (TMB). For these tests 50-100 mL samples of 17 ppm TMB in zero air were used. This mixture exceeds the maximum concentration of NMOC expected in ambient air - the carbon content is equivalent to a 600 mL air sample containing 25.5 ppmC of VOC's. The data show that the earlier oxidation catalyst operation temperature of 450°C only oxidized about 80% of TMB at this concentration. Approximately 100% conversion is achieved in the temperature range 540-570°C. The oxidation catalyst is now operated at 550-560°C.

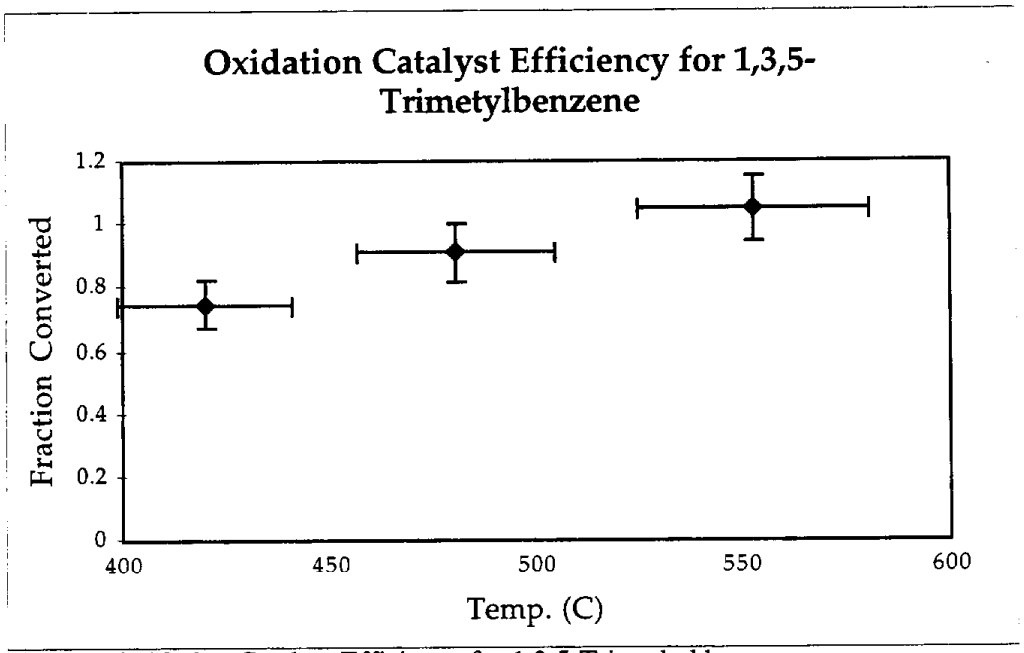

Figure 2-4. Oxidation Catalyst Efficiency for 1,3,5-Trimethyl benzene

2.4 Reduction

2.4.1 Methanizer Design

Four methanizer designs were tested before arriving at a design with satisfactory performance characteristics. The best methanizer catalyst consists of unsupported 80-100 mesh particles packed in a 4" section of 1/16" OD, 0.05" ID stainless steel tubing. A small amount of silica wool at each end holds the ruthenium in place. After packing, the methanizer was cleaned by heating to 710 °C under flowing oxygen for four hours. After cooling down to room temperature, the methanizer was then activated at 400 °C under hydrogen for four hours. The methanizer is then operated at 300 °C, and is maintained with an external temperature controller (Omega).

The pressure drop across the methanizer catalyst bed is significant. In order to preserve chromatographic quality, it is necessary to insure that the H_2 pressure does not exceed the He pressure at the end of the column. This is accomplished by setting the column head pressure to 30 psi, and the hydrogen pressure to 18 psi. A needle valve is placed before the flame ionization detector (FID) and adjusted so that about 9 mL/min H_2 flows through the catalyst, and 29 mL/min flows directly to the FID.

2.4.2 Performance Tests of the Methanizer

The performance of the methanizer catalyst is illustrated in Figure 2-5. In Figure 2-5 (a), 100 mL of hexane standard (20.2 ppm in zero air, Scott Specialty Gasses) was run without the oxidation catalyst. Figure 2-5 (b) shows the result of flowing the concentrated hexane sample over the oxidation catalyst so that the trapped hexane is converted first to CO_2 and then to methane. This amount of hexane, 60 pgC, is a useful test for both oxidation and methanization catalysts, since this is about 30 times the an upper limit of total NMOC in ambient air. For 500 mL samples, 3 ppmC TNMOC is equivalent to about 1.5 pgC.

The performance of both catalysts is quite satisfactory. Hexane (Figure 2-5 (a)) has a retention time of 6.55 min., and peak area of 935,000. There are several small peaks (including a CO_2 peak at 3.47 min.) due to impurities in the hexane cylinder. The total area of this run is 1,128,000. In Figure 2-5 (b), where the oxidation catalyst is used to convert the hexane and other organics into CO_2, the CO_2 peak (as CH_4) has an area of 1,175,000. This is larger than the total area of the sample shown in Figure 2-5 (a) by about 4%. Implicit in this discussion is the observation that hydrocarbons have a response in an FID that is directly proportional to the number of carbon atoms. This has been reported in the literature [29] and has been observed by many workers including ourselves. There are several possible reasons that the CO_2 peak is slightly larger than the sum of the peaks in Figure 2-5 (a)--the same reasons that the total carbon measurements are frequently expected to be larger than the sum of the parts. Other contamination peaks that elute later than our chromatogram time range may contribute to the larger total. Semi-volatile compounds that do not survive the column would be included in the TNMOC but not the $\sum$ Speciated VOC's.

A small peak at 6.55 min. may be seen in Figure 2-5 (b) corresponding to 1.6% of the original hexane. This indicates that a very small amount of hexane was not oxidized by the Pd oxidation catalyst. For lower concentration or smaller sample volumes, runs using the oxidation catalyst have no observable peaks, indicating that there oxidation is complete [36]. Since the total CO_2 peak (Figure 2-5 (b), measured as CH_4) is larger than the sum of the parts in Figure 2-5 (a), it appears that the methanizer is working well.

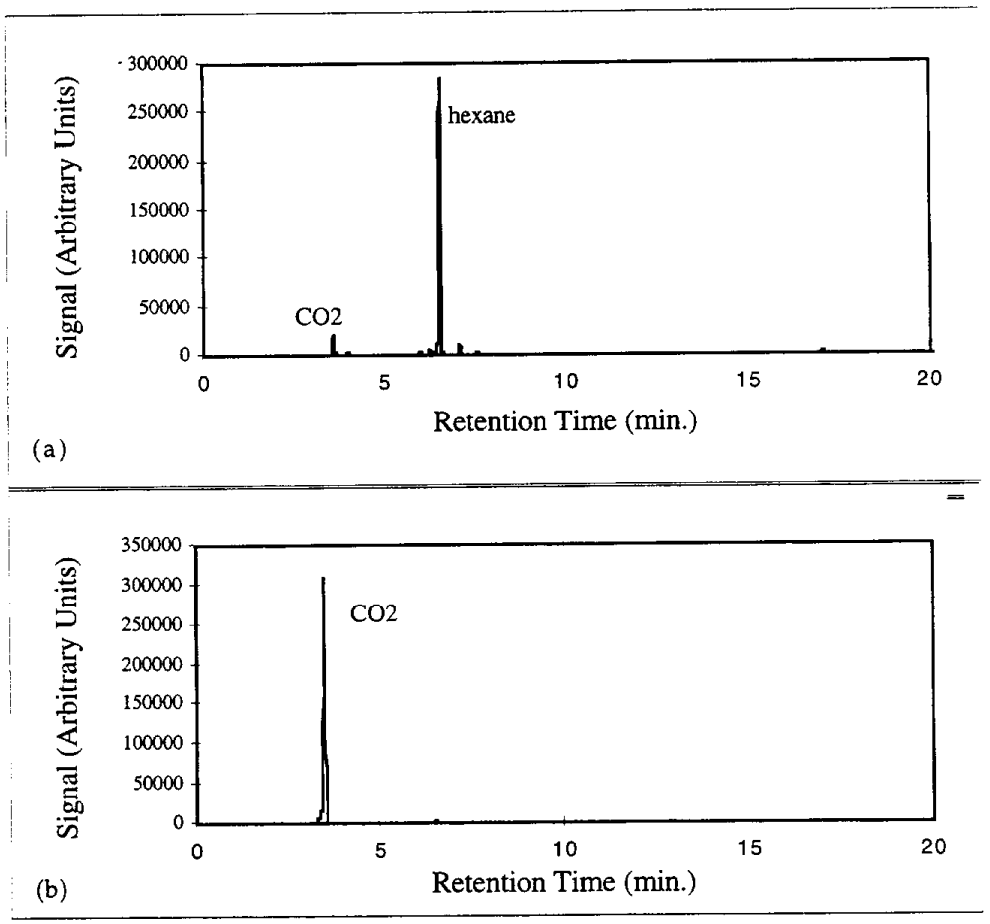

Figure 2-5. Hexane standard (20.2 ppm, 100 mL @ 50 mL/min trap I temp. = -70 °C), (a) without oxidation catalyst; (b) with oxidation catalyst.

A collection of methanizer test data are summarized in Table 2-6. Two types of samples (a mix of hydrocarbon and the hexane standard) were run over a period of several weeks. In nearly all cases the total is slightly larger than the sum of the peaks observable on the chromatogram. The standard deviation for the difference between the total and the sum of the parts (e.g., Col. 5) is ±3.5%. Much of this deviation arises from how chromatograms are integrated, and may be improved somewhat. Nevertheless, this deviation is probably acceptable in light of other sources of uncertainty in the measurement.

Table 2-6: Summary of Test Runs for Methanizer Efficiency.

1. Sample	2. Volume (mL)	3. Total Area w/o Oxidation Catalyst; Arbitrary Units ($x10^{-3}$)	4. Total Area w/ Oxidation Catalyst; Arbitrary Units ($x10^{-3}$)	5. Percent Difference **
Mixture 1*	100	53	57	7.5%
Mixture 1*	200	100	100	0.3%
Mixture 1*	400	186	186	0.6%
Mixture 1*	600	244	243	-0.4%
Mixture 1*	100	55	57	4.7%
Mixture 1*	600	264	281	6.3%
Mixture 1*	50	32.5	36	11%
Mixture 1*	200	104	107	2.7%
Hexane Std.	100	1084	1052	-3%
Hexane Std.	100	1130	1170	3.4%
Hexane Std.	100***	633	654	3.2%
Hexane Std.	50	507	520	2.6%
Hexane Std.	50	493	514	4.0%
Hexane Std.	100	1128	1175	4.1%

*Sample mixture 1 is 1.5 ppmC; approximately equal concentrations of pentane, hexane, benzene and toluene, plus about 450 ppm CO_2. Since there is some pentane breakthrough at higher volumes, and tests were carried out at different trapping temperatures, thus the areas do not scale linearly with sample volume.

**This column is calculated as 100 x (Col. 4 - Col. 3) / Col. 3.

***This run used a different trap I design, one that did not trap hexane efficiently.

A clean CO_2 standard (one without CO or methane) was obtained at 1.09 ± 0.02 ppm in N_2 (Scott Specialty Gases). Since we cannot assure complete trapping of CO_2 at the lower temperature limit of the 1° trap (-120 °C), this test is run by trapping only in the 2° trap, which is immersed in liquid nitrogen. The sample volume was measured with a flow controller placed downstream of the second trap. Table 2-7 shows the results of CO_2 compared to our 20.2 ppm hexane standard. The average response per ppm of carbon, per mL of sample for the two standards are in excellent agreement; 150 ± 3 area/(ppm·mL·carbon) for CO_2 and 154 ± 15 area/(ppm·mL·carbon) for hexane (uncertainties are 2 σ). Overall, it may be concluded that the methanizer works with 100% efficiency within the measured uncertainties.

Table 2-7. CO_2 (1.09 ppm) and Hexane (20.2 ppm) standard. Sample sizes were 100 mL.

CO_2 area/(ppm·mL·carbon)	Hexane area/(ppm·mL·carbon)
150.06	163.19
151.49	145.56
149.50	157.01
150.00	161.96
153.16	143.51
150.75	155.32
149.20	154.94
148.70	
Average: 150.4±2.8	**Average: 154±15**

2.4.4 New and Reactivated Methanizers

Two new methanizer catalysts were constructed. The first (herein after referred to as Methanizer #2) consisted of $Ru_3(CO)_{12}$ particles (which decompose to Ruthenium metal on heating under O_2) packed into a 2 and 1/2" length of 1/16" OD stainless steel tubing. The second test methanizer (Methanizer #3) was a shorter version of Methanizer #2. $Ru_3(CO)_{12}$ was chosen because this was the reported starting material for the original methanizer. Methanizer #3 was constructed in an attempt to reduce the poor chromatography created by methanizer #2, but the results from these experiments are identical to those of methanizer #2 (discussed below).

Cleaning, activation and reactivation of methanizers is accomplished as follows. First, they are cleaned by heating to 710°C for four hours under flowing oxygen. Next, the methanizers are activated at 400°C under hydrogen for four hours. The new and reactivated methanizer is then operated at different temperatures between 160 and 400°C, maintained with an external temperature controller (Omega).

Calibrations for each methanizer were performed using the n-hexane standard (the hexane was not oxidized to CO_2). Because losses of compounds with greater than 8 carbons in the methanizer have been observed (Section 5), we investigated potential loss of n-hexane at lower methanizer temperatures. Also, for high methanizer temperatures, it was necessary to increase the FID temperature, thus checks were made that this did not effect the detector response. The results of these tests are summarized in Table 2-8. From these experiments we can conclude that we have no loss of n-hexane on the methanizer surface at lower temperatures and that the FID response does not change when the FID temperature is increased from 350 to 400°C.

Table 2-8: Results from the calibration at different methanizer and FID temperatures

Methanizer temperature (°C)	FID temperature (°C)	Original Methanizer n-hexane concentration (ppm)	Methanizer #2 n-hexane concentration (ppm)
180	350		1.14
220	350	1.04	
240	350		1.07
260	350	1.07	
300	350	1.04	
320	350		1.12
350	400	1.05	
360	400	1.10	1.08
Average		1.06 ± 0.02	1.10 ± 0.03

Total NMOC measurements at different temperatures for each methanizer were performed using the same n-hexane standard (1.08 ppm). Figure 2-6 shows the temperature dependence of reduction activity for the original methanizer and reactivated methanizer, as well as methanizer #2. The original methanizer converted 100% of CO_2 (within uncertainties) above 280°C (diamonds). After regeneration 100% efficiency is accomplished at somewhat lower temperatures (triangles). For methanizer #2 the results show almost 100 % conversion above 240°C.

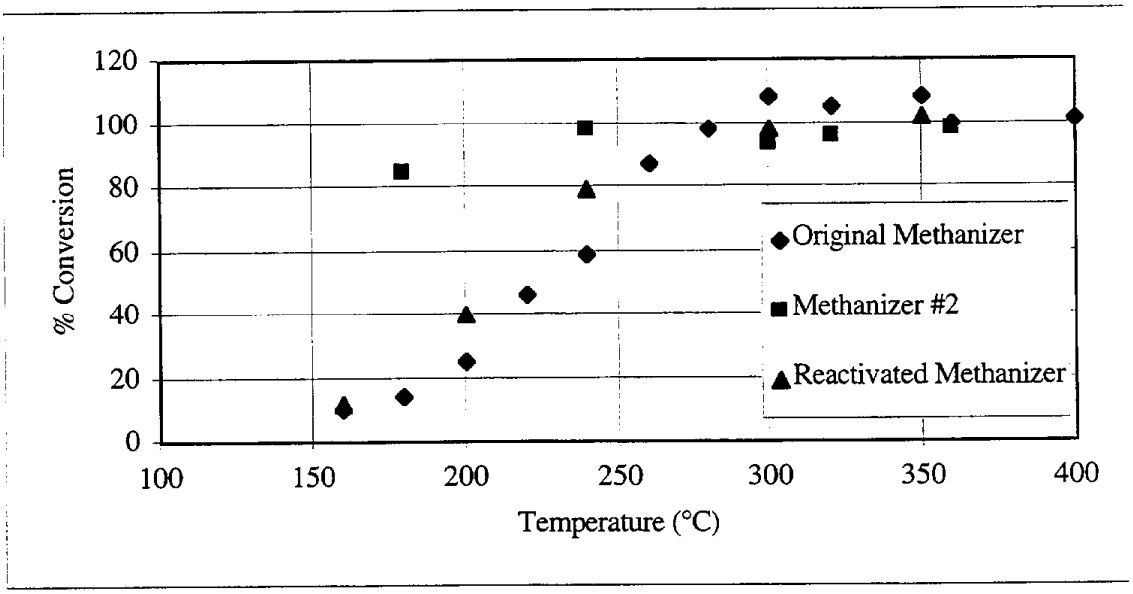

Figure 2-6. The Temperature Dependence of The Methanizer Catalyst Tested with a n-hexane Standard at 1.08 ppm

2.4.5 Reduction of Aldehydes by the Methanizer Catalyst

Another way to potentially make a TNMOC measurement would be to find a reduction catalyst that reduces oxygenates to hydrocarbons or methane, but does not reduce CO_2 and CO. In practice, literature investigations have not been successful at finding such a reduction catalyst; substrates typically are not reduced preferentially based on their redox potential. We briefly investigated the reduction of aldehydes with our Ruthenium methanizer, as described below. Clearly our ruthenium catalyst is not such a (desired) reducer; it reduces CO_2 well, but not aldehydes.

Experiments were performed to deduce the degree of reduction of aldehydes by the methanation catalyst. Because this was done before the installation of the second column and FID, these experiments were performed by using an additional GC/FID, referred to as GC-I. The TNMOC instrument is GC-II. Comparisons between GC I (standard GC/FID with 2 mL sample loop, no cryo-concentration) and the TNMOC instrument *without* the oxidation catalyst (GC II--the TNMOC instrument with the oxidation catalyst removed; GC/FID with 100 mL sample concentration and methanizer catalyst at the end of the column) were carried out to test the effect of the methanizer catalyst on aldehydes. Experiments were performed with acrolein (CH_2=CHCHO) and acetaldehyde (CH_3CHO). We prepared a series of mixtures by adding known quantities of the liquids to Teflon chambers filled with zero air. This method of preparing a mixture with known concentration is, in our experience, accurate to within about ±10% for pure compounds that are liquids at room temperature. The results (summarized in Table 2-9) show that the methanizer does partially reduce aldehydes; the response is larger on GC II than GC I for both acrolein and acetaldehyde. Because acetaldehyde is not a liquid at room temperature (it is a liquid as long as it is refrigerated, but it evaporates rapidly from the syringe needle as it is added to a chamber), and it is easily oxidized, the true concentration of the acetaldehyde mixture is uncertain. From the acetaldehyde data we can only conclude that the acetaldehyde is partly reduced by the methanizer. The concentration of acrolein on the other hand, is accurate to within ±10%. From these data we can conclude that the methanizer does not fully reduce acrolein to a 3-carbon hydrocarbon.

Table 2-9. The effective carbon number of acetaldehyde and acrolein with and without a methanizer reduction catalyst

Compound	Number of Carbons	Effective Carbon Number on GC I (GC/FID)	Effective Carbon Number on GC II (GC/FID with methanizer catalyst; same as TNMOC instrument but without oxidation catalyst)
Acrolein	3	1.75	2.4
Acetaldehyde*	2	0.4	0.75

*The actual concentration of the acetaldehyde in this mixture is not very certain since the purity of the liquid was not verified, and acetaldehyde is not a liquid at room temperate.

2.5 Addition of a Parallel Sampler Inlet

Note: This section describes work that was carried out at the end of the project period. These innovations were not on the instrument that was deployed in Pico Rivera or Azusa.

An important conclusion from the Azusa campaign (Section 5.2) was that it was difficult to compare the results from the Total NMOC measurements with the $\sum$ Speciated VOC measurements because of the short time scale variability of NMOC concentrations. During the Azusa Campaign, we took 10 minute TNMOC and $\sum$ Speciated VOC samples each hour, with the two samples acquired 15-20 minutes apart. Comparing these measurements, we found a ratio for TNMOC/$\sum$ Speciated VOC's of 1.3±0.3. Since comparisons of this ratio to other parameters such as O_3 concentration, time of day or apparent level of photochemical processing (which was limited for this data set) did not reveal any clear trends, and because the TNMOC and speciated VOC measurements vary widely from hour to hour, we believe that a large fraction of the observed variability in the ratio is due to rapidly changing, fairly local NMOC sources. In order to remove the scatter in our data due to variability in the sampled air, we have redesigned our sampling unit. The original instrument consisted of one 1° trap in a cooled (temperature controlled) housing that allowed the trapping of one sample at a time. The new sampler has two traps in one temperature controlled housing to collect two samples simultaneously. One sample is then oxidized over the Palladium catalyst and analyzed on column 1 with the methanizer (TNMOC), while the other sample is analyzed directly after separation on a 60 m DB-1 column (Speciated VOC's). The new valve diagram is shown in Figure 1-2.

Preliminary Results

The new inlet was installed at the close of this project, thus only preliminary validation tests are presented. The most critical aspect of the new inlet is that both traps have the same trapping efficiency. To check this, a mixture containing 10 different alkenes and alkanes was prepared. Samples from this mixture were simultaneously trapped at

temperatures ranging from -50 °C to -130 °C. Another purpose of these experiments was to establish the optimal temperature at which the samples should be taken, since the recorded temperature depends strongly on the location where the thermocouples are placed in the trap.

Figures 2-7 and 2-8 show the trapping efficiencies for alkenes and alkanes for the two traps; the TNMOC side of the inlet was run in speciated mode to allow comparison of the hydrocarbon trapping in the parallel 1° traps. For the most part trapping efficiencies for the same species in the two different traps agree very well; 100% trapping for a certain species is accomplished at the same temperature. There are slight differences in the fall-off region (100 % > trapping efficiency > 10 %). In this region, somewhat smaller amounts trap in the Speciated VOC trap than in the Total NMOC trap. We have not yet attempted to minimize these differences, and may be able to improve this difference. In the current state, these small differences are not a serious problem for ambient measurements. Samples are normally taken at temperatures where C_5 carbons (and higher) are trapped completely, and trapping for C_3 and C_2 compounds is only a few percent, thus only for the partially trapped C_4 hydrocarbons can we expect some difficulties. C_4 hydrocarbons contribute less than 10% to the TNMOC in typical urban air [37].

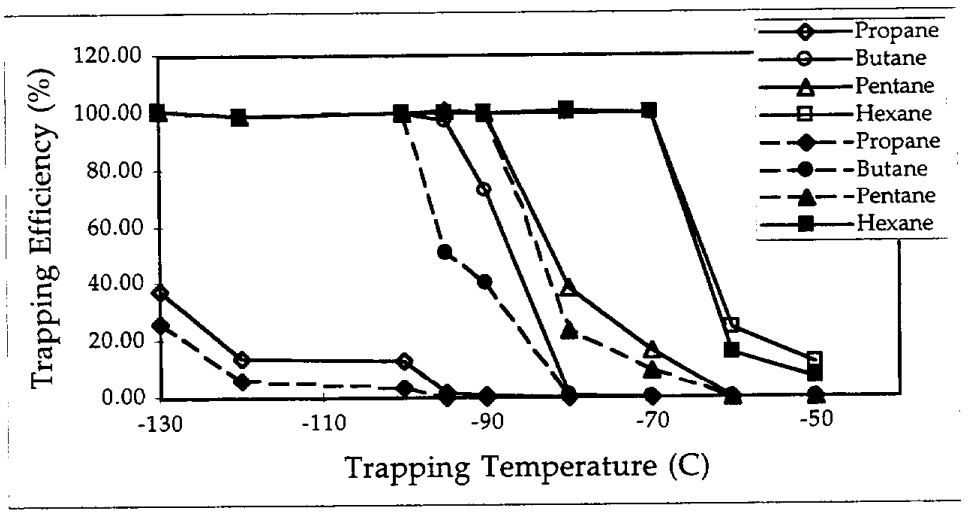

Figure 2-7. Trapping of several alkanes as a function of temperature in the parallel inlet. Column 1 (open symbols, solid lines) is normally the TNMOC channel; for these tests the sample was not oxidized. Column 2 (solid symbols, dashed lines) is the Speciated VOC's channel.

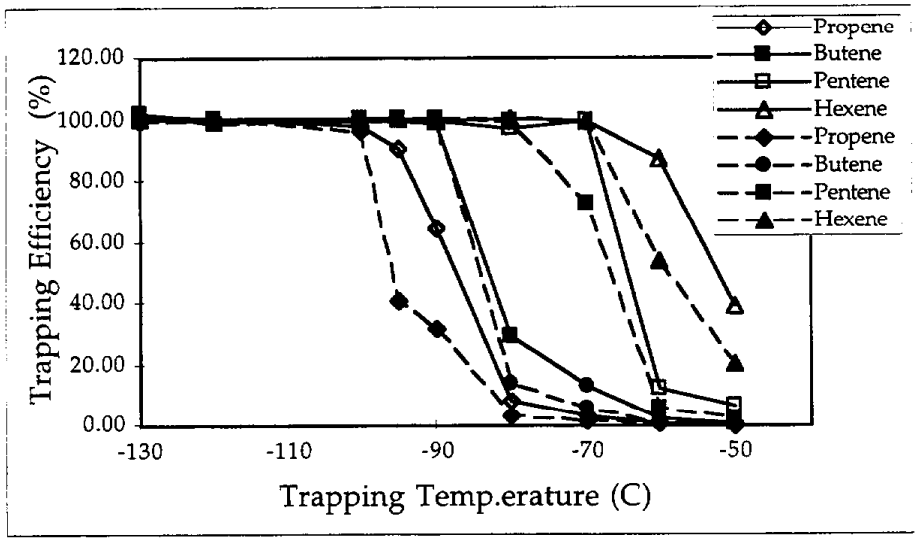

Figure 2-8. Trapping of several alkenes as a function of temperature in the parallel inlet. Column 1 (open symbols, solid lines) is normally the TNMOC channel; for these tests the sample was not oxidized. Column 2 (solid symbols, dashed lines) is the Speciated VOC's channel.

2.6 Summary of Operating Conditions

The key operating parameters that were used for most of these studies are summarized in here. Oxidation catalyst and methanizer temperatures are ranges; generally fresh catalysts deliver 100% efficiency at the lower end of the temperature range, and these need to be increased as the catalyst ages. The operational temperature of Trap I is subject to change as the design evolves.

Component	Operating Temperature Range (°C)
Trap 1	-70
Trap II	liquid nitrogen
Methanizer	300-400
Oxidation Catalyst	550-600

3.0 Flame Ionization Detector Response Factors for Oxygenated Compounds

3.1 Introduction

The flame ionization detector (FID) response of hydrocarbons is generally directly proportional to the mass of carbon present in the sample. Partially oxidized VOC's exhibit a degree of signal reduction that varies markedly with heteroatom and bond types (e.g., [29]. The response factors for common oxygenates in an FID is of interest in the analysis of TNMOC and Speciated VOC data. From the combination of these data with the measured concentrations of common oxygenates in the Speciated VOC chromatograms, the fraction of the difference between TNMOC and $\sum$ Speciated VOC's due to light oxygenates can be calculated.

3.2 Results

Mixtures of about 10 ppmC in zero air were prepared for acetaldehyde, formaldehyde, acetone, acrolein, methyl vinyl ketone, methyl alcohol, and ethyl alcohol. Acetaldehyde and the other liquids were injected rapidly from the syringe needle filled from a refrigerated bottle. Formaldehyde was prepared by flowing zero air into a Teflon bag through a heated (up to about 120 °C) 4" section of 1/4" OD glass tubing containing para-formaldehyde powder. The n-hexane standard (1.08 ppm) was used to calibrate each FID. Total NMOC and Speciated VOC's measurements were performed for each compound. Speciated VOC measurements on column 1 were also made to determine the amount of CO_2 trapped during the sampling procedure. The amounts of CO_2 in the sample, and CO_2 impurities in the transfer gas ("CO_2 blank") are subtracted from the CO_2 peak measured in Total NMOC mode. The FID responses from these measurements are used to calculate the effective carbon number (ECN), i.e., the equivalent number of carbon atoms in a hydrocarbon that would produce the same response. The results are shown in Table 3-1. Also shown in this table are results for di-n-butyl ether and 1,2-epoxy-3-butene from earlier studies performed in this group. We find the average difference of the ECN and the number of carbon atoms for carbonyls and primary alcohols of 0.93 and 0.3, respectively. Values reported by Jorgensen et al. (1990) were 0.8 for carbonyls and 0.4 for primary alcohols, but these ECN's were obtained for larger molecules (C_5-C_9). ECN's for acetone, ethanol, and methanol have been reported previously. The ECN's reported for acetone were 2.06, 2.0 and 1.8 ([38-40], respectively). Reported values for methanol, 0.5 [39], and ethanol, 1.7 and 1.5 ([38, 39], respectively) are in good agreement with our values.

Table 3-1. The Effective Carbon Numbers for oxygenated Compounds of Atmospheric Interest

Compounds	Number of Carbons	Effective Carbon Number(ECN)	Difference of Number of Carbons and ECN
Formaldehyde	1	0.07	0.93
Acetaldehyde	2	1.02±0.2	0.98
Methyl vinyl ketone	4	3.03±0.12	0.97
Methyl alcohol	1	0.77±0.15	0.23
Ethyl alcohol	2	1.65±0.15	0.35
1,2-epoxy-3-butene	4	2.7±0.3	1.3
Di-n-butyl ether	8	7.6±0.2	0.4
Acrolein	3	2.11±0.20	0.89
Acetone	3	2.12±0.2	0.88

* Results are from earlier studies performed in this group, associated with another study [41].

** Uncertainties represent the range of scatter for the measurements.

This value is based on only one measurement.

4.0 Chamber Experiments to Compare TNMOC with Speciated Organics

Dozens of smog chamber experiments have been carried out to investigate the oxidation chemistry and ozone formation from hydrocarbons. Very few of these experiments can account for 100% of the reacted carbon as products (e.g., [42-46]). As the starting hydrocarbons become oxidized, their products become progressively less volatile and more polar. Some of the products may deposit on the walls of the reactor, undergo homogeneous aerosol formation, or may deposit in the GC column or inlet. The large number of small GC signals may be difficult to identify and consequently quantify, and the total area of the chromatograms decrease as the carbon backbones become oxygenated and reduce the FID response per ppmC.

4.1 Styrene

One of our indoor chambers was used to investigate the relationship between TNMOC and compounds measured on a standard GC (GC I) during an ozone oxidation of styrene in the dark. The chamber was sampled simultaneously with the TNMOC instrument and on a different GC, referred to as GC-I. GC-I was used for speciated measurements because these experiments were performed before the second column was added to the TNMOC instrument. GC-I is usually used for laboratory investigations of the O_3 and OH reactions of hydrocarbons, and therefore uses a heated 2 mL sample loop without pre-concentration. Because of this, the initial concentration of styrene was fairly high; about 8 ppmC.

The experiments exhibited the following pattern: The TNMOC measurement was lower than the initial styrene concentration measured with GC-I. As the styrene reacted away and products begin to form, the total area decreases on GC-I overall by about 27%. By comparison, the TNMOC measurement stays nearly constant throughout the experiment--decreasing overall by about 4%. After some investigation the source of the problem with the initial concentrations was determined to be the incomplete oxidation of aromatics by the oxidation catalyst, a problem that has been rectified (Section 2.3). The observation that the TNMOC measurement decreases only slightly through the experiment indicates that it performs well and is able to detect the many unidentified products of styrene oxidation.

4.2 α-Pinene/Methylnitrite Photooxidation

In an effort to investigate the difference between TNMOC measurements of hydrocarbons and sum of their oxidation products in a controlled environment, we have conducted several smog chamber experiments of α-pinene oxidation. Monoterpenes and isoprene are emitted into the atmosphere from natural vegetation [47]. The monoterpenes are highly reactive toward gas-phase reaction with OH and NO_3 radicals and O_3 [48, 49]. Of the terpenes, the oxidation chemistry of α-pinene is probably best characterized. Quantitative studies have been performed for the OH radical reactions, using *in situ* Fourier transformation infrared (FTIR) spectroscopy [50], gas chromatography with flame ionization detection (GC-FID) and atmospheric pressure ionization tandem mass spectrometry (API-MS)[49] [51]. As α-pinene is oxidized, a variety of oxygenated and nitrated compounds are formed, making it an interesting compound for measurement of TNMOC vs. Σ Speciated VOCs.

4.2.1 Experimental Description

Experiments were carried out in a 250 liter Teflon chamber at room temperature (296 ± 2 K) and atmospheric pressure (760 ± 10 Torr). The chamber was surrounded by variable intensity UV lights, which were regulated with a potentiometer (Silvania Blacklights, 40 W, F40/350BL). Hydroxyl radicals were generated in the presence of NO by the photolysis of methyl nitrite (CH_3ONO) in air. Nitric oxide was added to the reactant mixtures to convert peroxy radicals to OH and to suppress the formation of O_3 [52].

$$CH_3ONO + h\nu \rightarrow CH_3O + NO \quad (1)$$
$$CH_3O + O_2 \rightarrow CH_2O + HO_2 \quad (2)$$
$$HO_2 + NO \rightarrow OH + NO_2 \quad (3)$$
$$NO_2 + h\nu \rightarrow NO + O(^3P) \quad (4)$$
$$O(^3P) + O_2 + M \rightarrow O_3 + M \quad (5)$$
$$NO + O_3 \rightarrow NO_2 + O_2 \quad (6)$$

Measurements of "Total Non Methane Organic Carbon" (TNMOC) from column 1 (60m × 1μm film × 0.32 mm ID DB -1 column) , "Speciated VOCs, column 2" (60m × 1μm film × 0.32 mm ID DB -1 column) and "Speciated VOCs, column 1" were made. Because making all three of these measurements takes about 70 minutes, the lights were turned off during measurements to minimize chemistry that would change the composition of the sample. The GC was calibrated with 1.08 ppm n-hexane standard (Scott Specially Gases).

The chemicals used were α- pinene (99+%), Aldrich Chemical Company; NO (≥99.0%) and Zero Grade Air, Puritan - Bennett Gas Products. Methyl nitrite was synthesized as described by Taylor et al. [53] and was stored in mixture of acetone and dry ice. Three experiments were performed with different initial concentrations and photolysis times.

4.2.2 Results

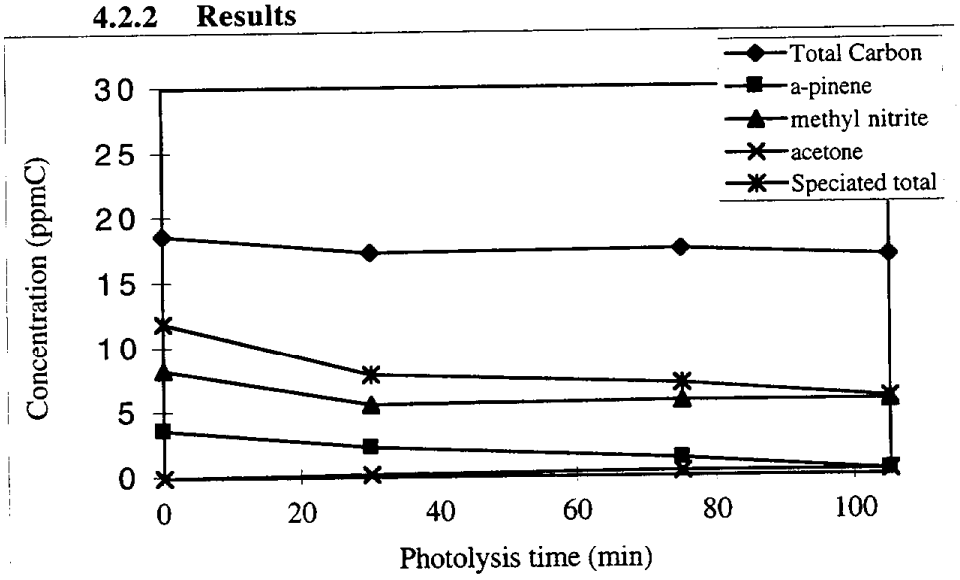

Figure 4-1. Concentrations of TNMOC, α-pinene, methylnitrite and acetone as a function of photolysis time (the sum of the time the UV lights had been on), for experiment 1.

Experiments 1 and 2: The ratio of initial reactant concentrations for these experiments were about 10:10:1 for CH_3ONO : NO : α-pinene. After chamber contents were mixed well, samples were analyzed in three different modes ("TNMOC", "Speciated VOCs, column 1" and "Speciated VOCs, column 2") before irradiation and after different photolysis intervals. Figures 4-1 and 4-2 show concentrations (in ppmC) for each compound in the mixture vs. photolysis time for experiments 1 and 2. TNMOC was corrected for trapped CO_2 obtained from "Speciated VOCs, column 1" mode and blank measurements. α-Pinene, methyl nitrite, and acetone were measured from "Speciated VOCs, column 2" mode. The concentrations of methyl nitrite and a minor product of α-pinene oxidation, acetone, were calculated using their FID response factors (Section 3). Speciated total carbon was calculated from the sum of corrected area counts of α-pinene, methyl nitrite and acetone. Ideally, TNMOC and Σ Speciated VOCs are equal before photolysis, and TNMOC will remain constant throughout the run. A significant difference between Total Carbon and Σ Speciated VOCs was observed for both experiments; Σ

Speciated VOCs was only about 65% of TNMOC for experiment 1 and 86% for experiment 2. The source of this discrepancy was decomposition of methyl nitrite and is discussed in section 4.2.3. TNMOC is approximately constant throughout both of the photooxidation runs.

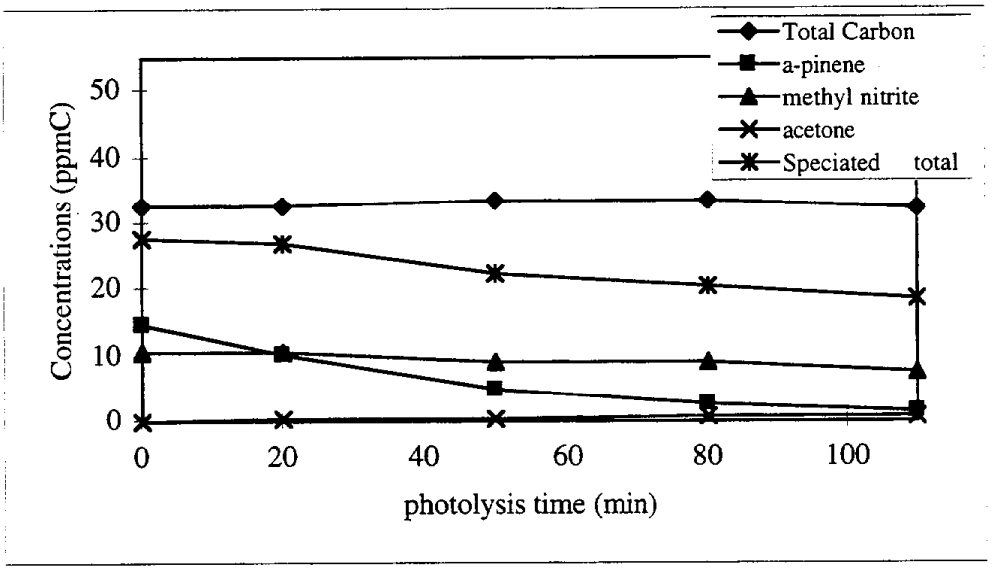

Figure 4-2. Concentrations of TNMOC, α-pinene, methylnitrite and acetone as a function of photolysis time (the sum of the time the UV lights had been on), for experiment 2.

Experiment 3: The initial concentrations of methyl nitrite, NO and α-pinene in the air were changed to investigate the difference between the initial Total NMOC and Σ Speciated VOC's. The concentration of methyl nitrite was decreased to half that of the first experiment and that of α-pinene was increased to twice that of the first experiment. The results are shown in Figure 4-3. The difference between TNMOC and Σ Speciated VOCs before irradiation decreased relative to experiments 1 and 2; Σ Speciated VOCs was about 92% of TNMOC. However, area counts of Total Carbon decreased somewhat (by about 10%) over the course of the experiment, possibly due to increased formation of aerosol [13].

4.2.3 Decomposition of Methyl Nitrite

The source of the variable discrepancy between TNMOC and Σ Speciated VOCs was determined to be methyl nitrite decomposition. Figure 4-4 shows chromatograms of methyl nitrite with and without a heated sample line (lower and upper chromatograms, respectively). It appears that a significant fraction of the methyl nitrite decomposed, in the heated sampling line, probably forming and formaldehyde and methanol. Formaldehyde is not detected in the "Speciated VOCs" mode but is included in TNMOC. The variable

decomposition of methyl nitrite may also explain the apparent lack of a decrease in methyl nitrite concentration for most photolysis intervals in the three experiments above.

4.3 Conclusions

Preliminary results verify that the TNMOC measurement works well in detecting the oxidized products from both styrene and α-pinene. In future a different oxidation system (e.g., O_3) will be used to avoid the problems with methyl nitrite in our laboratory sampling line.

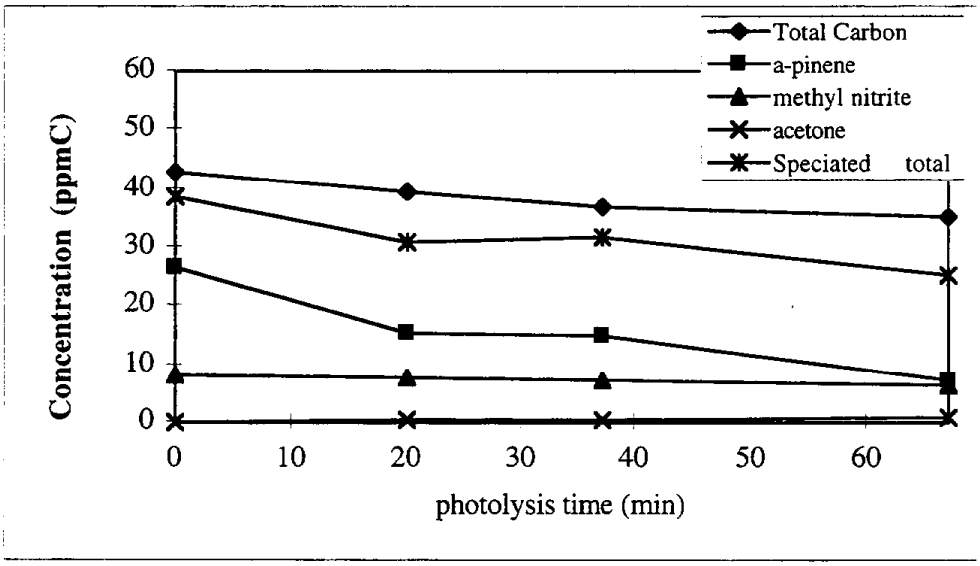

Figure 4-3. Concentrations of TNMOC, α-pinene, methylnitrite and acetone as a function of photolysis time (the sum of the time the UV lights had been on), for experiment 2.

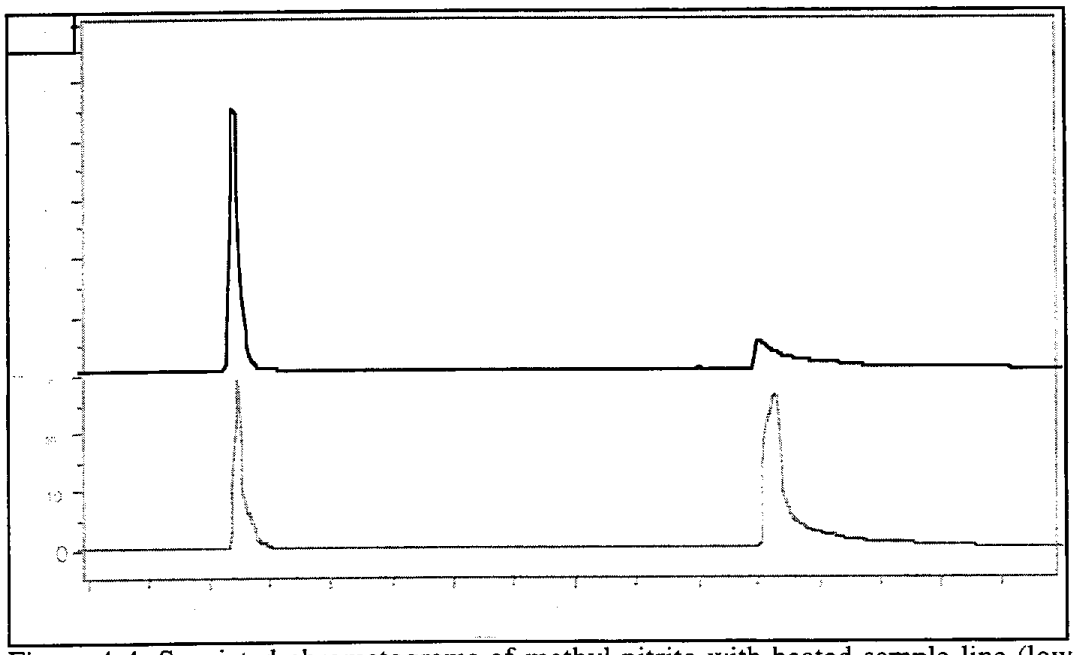

Figure 4-4. Speciated chromatograms of methyl nitrite with heated sample line (lower chromatogram) and without heated sample line (upper chromatogram).

5.0 Field Measurements

5.1 Pico Rivera

Initial field tests were carried out at the South Coast AQMD's Pico Rivera Station during May and June of 1997. The Pico site has been in operation for many years, and became a Photochemical Assessment Monitoring Station (PAMS) in 1997. Pico Rivera is a type 2 PAMS site, located down wind but near source areas. The station is in a light industrial park near the intersection of the 60 and 605 freeways. We are indebted to the generous and able assistance of Steve Barbosa and Phil O'Bell for the success of this field project.

5.1.1 Sample Introduction

The inlet of the TNMOC instrument was connected via a 3m length of 1/4" Teflon tubing to the main manifold that the hydrocarbon instrument inlet at the Pico Rivera Station. The main manifold is connected to a 2 m x 5 cm OD. glass tube, with the open end about 3 feet above the roof. The open end is sheltered by a metal cover. A fan on the outlet of the manifold inside the station assures a fast flow through the glass tube.

Initially the Teflon line was heated to minimize wall losses in the Teflon tube, with the sample drawn at 10 mL/min. Runs using N_2 from a liquid nitrogen tank as a clean gas sample to check possible hydrocarbons coming from the Teflon line, and air samples were compared to the AQMD speciated hydrocarbon instrument. Differences between both types of samples showed a significant background signal from the heated Teflon. Figure 5-1 shows the chromatograms of N_2 using heated and unheated Teflon (upper and lower traces, hydrocarbons total at least 1.3 ppmC for the heated Teflon and about 130 ppbC for the unheated line). We believe that the hydrocarbons in the two lower chromatograms with retention times between 20 - 26 minutes are caused from the grease or oil used in the valves of the lN_2 tank. The peak at 12.2 minutes is tentatively identified as benzene. When the tubing is heated, many more peaks can be found, indicating that the heating of the Teflon tubing is responsible for the additional hydrocarbons found. In addition there was some indication that the unheated Teflon adsorbed some of the heavier compounds in ambient air samples, since these peaks were highest in runs where the Teflon was heated and that immediately followed a run with an unheated sample line.

In order to minimize the hydrocarbons coming from the Teflon inlet tube, a pump with a total flow of 2.8 L/m was attached to the downstream end of the sample inlet, with the sample flow (10 cc/m) drawn from this line. The middle trace in Figure 5-1 shows the results; a liquid nitrogen vapor sample appears somewhat cleaner than that with unheated

Teflon tubing. The total hydrocarbons in this trace are about 100 ppbC. Later chromatograms taken at Pico showed a slow improvement in this result.

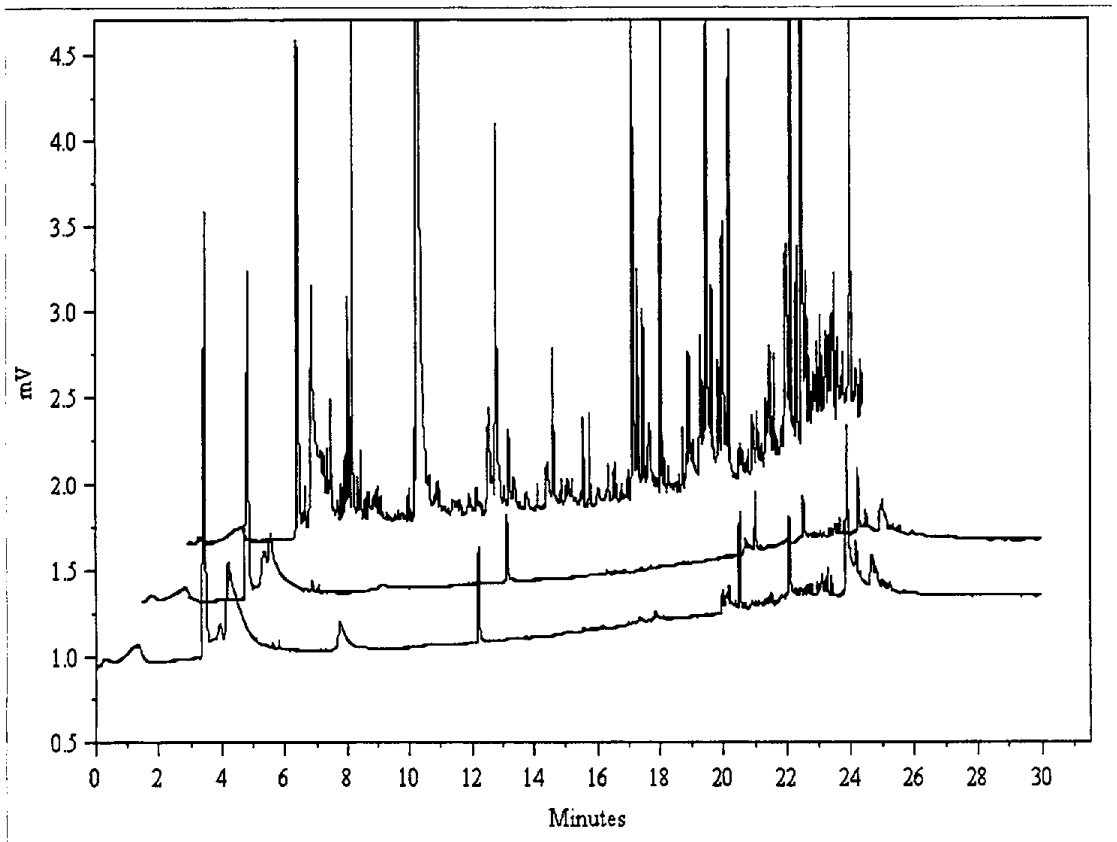

Figure 5-1. Chromatograms showing the effect of sample line choice. All runs used a 100 mL sample of vapor from a liquid nitrogen tank. Upper chromatogram: heated Teflon line, no by-pass flow, middle chromatogram: heated Teflon line, with bypass flow, and lower chromatogram, unheated Teflon line, no by-pass flow. Each chromatogram is offset so that the beginning of each trace is at 0.0 minutes.

5.1.2 Results from the PAMS Retention Time Standard

A Photochemical Assessment Monitoring Station (PAMS) Retention Time Standard cylinder belonging to the South Coast Air Quality Management District and originating from the EPA containing 58 hydrocarbons each in the mid ppbC range (Table 5-2) was used to: a) determine retention times at different GC temperature programs for these hydrocarbons and b) determine the efficiency of trapping the hydrocarbons at different flow

rates. The studies are important for later analysis for speciated hydrocarbons and to correct for losses of lighter hydrocarbons (C_2 - C_4) because of incomplete trapping in the 1° trap.

Peak identification was made by comparing the order of elution from out column to the AQMD instrument operated by Phil O' Bell, and the EPA report for the cylinder (similar columns). The identifications should be considered tentative. Retention times at different temperature programs for the hydrocarbons in the EPA Retention Time Standard cylinder were determined using the following temperature programs:

Program	Initial temp.	Initial time	Rate	End temp.	total time
	[°C]	[min]	[°C/min]	[°C]	[min.]
1	35	1	10	210	20
2	-20	1	10	210	30
3	-70	1	10	210	30

For the integration of these peaks it is sufficient to start at -20°C. Starting at -70°C effects only the separation of the lighter hydrocarbons (C_2 - C_4). Table 5-1 contains the retention times for the three temperature programs, allowing to identification of these hydrocarbons in chromatograms of air samples taken with these temperature programs.

Table 5-1. Retention times for the EPA/PAMS standard for different GC temperature programs.

	Program 1	Program 2	Program 3
Hydrocarbon			
C_2's	3.35	3.57	5.68
propene	not resolved	4.17	7.60
propane	not resolved	4.29	7.77
isobutane	not resolved	5.30	9.99
1-butene	3.56	5.81	10.86
n-butane	not resolved	5.99	11.13
t-2-butene	3.95	6.23	11.48
c-2-butene	4.16	6.54	11.92
i-pentane	4.60	7.74	13.38
1-pentane	4.75	8.11	13.81
n-pentane	4.88	8.40	14.12
isoprene	not resolved	8.51	14.24
t-2-pentene	4.96	8.60	14.34
c-2-pentene	not resolved	8.79	14.55
2,2 dimethylbutane	5.06	9.30	15.09
cyclopentane	5.35	10.01	15.83
2,3 dimethylbutane	not resolved	10.06	15.88
2-methylpentane	not resolved	10.17	15.99

3-methylpentane	5.53	10.53	16.35
2-methyl-1-pentane	not resolved	10.65	16.47
n-hexane	5.80	10.96	16.78
unknown	6.10	11.13	16.95
methylcyclopentane	6.42	11.66	17.48
2,4 dimethylpentane	6.53	11.73	17.53
benzene	6.98	12.28	18.06
cyclohexane	7.48	12.52	18.30
2-methylhexane	7.66	12.67	18.43
2,3dimethylpentane	7.79	12.74	18.50
3-methylhexane	7.90	12.89	18.64
2,2,4 trimethylpentane	8.21	13.25	18.98
n-heptane	8.38	13.48	19.18
methylcyclohexane	8.97	14.10	19.77
2,3,4 trimethylpentane	9.55	14.77	20.39
toluene	9.71	14.92	20.52
2-methylheptane	9.81	15.09	20.66
3-methylheptane	9.99	15.28	20.84
n-octane	10.53	15.87	21.38
unknown			21.55
ethylbenzene	11.79	17.15	22.55
m/p-xylene	11.98	17.35	22.73
styrene	12.37	17.75	23.09
o-xylene	12.49	17.87	23.21
n-nonane	12.67	18.10	23.40
i-propylbenzene	13.14	18.56	23.83
n-propylbenzene	13.77	19.20	24.42
m-ethyltoluene	13.90	19.21	24.54
p-ethyltoluene	13.95	19.38	24.59
1,3,5 trimethylbenzene	14.06	19.48	24.69
o-ethyltoluene	14.31	19.74	24.93
1,2,4 trimethylbenzene	14.71	20.05	25.22
n-decane	15.21	20.18	25.33
1,2,3-trimethylbenzene	15.65	20.66	25.80
m-diethylbenzene	15.79	21.11	26.26
p-diethylbenzene	16.62	21.25	26.40
n-undecane	18.55	22.10	27.23

The TNMOC instrument does not efficiently trap C_2-C_5 hydrocarbons when operated under the conditions chosen for the Pico Rivera and Azusa measurements. In order to establish a trapping percentage for EPA retention time for these hydrocarbons, we performed the following experiments. Samples of the standard were taken at different flow rates through the 1° trap ranging from 10 to 50 mL/min and analyzed using the temperature

program starting at - 70° C. Table 5-2 shows the trapping efficiencies for each of the compounds versus the sample flow rate.

Table 5-2. Trapping Efficiencies for the 58 Compounds in the EPA Retention Time Standard. (Note that the sample flow rate is decreasing from left to right).

	Flow rate [mL/min]	50	40	30	20	10
Peak no.	Hydrocarbon	Effic. [%]	Effic. [%]	Effic. [%]	Effic. [%]	Effic. [%]
1	CO_2 + C2	26.65	35.74	39.02	35.74	45.67
2	propene	9.98	13.77	14.97	14.59	16.59
3	propane	4.68	4.34	5.31	5.23	7.35
4	isobutane	3.50	4.02	4.71	5.22	7.37
5	1-butene	51.26	58.13	63.22	67.83	78.60
6	n-butane	30.23	33.95	37.46	43.49	54.06
7	t-2-butene	67.05	73.34	77.55	83.87	90.41
8	c-2-butene	69.42	74.82	79.76	85.55	93.99
9	i-pentane	31.61	35.63	39.89	43.89	56.75
10	n-pentane	118.39	102.11	103.41	108.92	102.25
11	1-pentene	77.75	80.51	87.09	94.47	98.81
12	isoprene	97.74	97.83	97.72	100.96	94.21
13	t-2-pentene	105.22	102.29	104.46	108.83	104.18
14	c-2-pentene	107.01	104.80	107.68	111.74	106.82
15	2,2 dimethylbutane	37.59	41.15	45.16	45.02	55.23
16	cyclopentane	56.17	59.81	76.53	74.55	87.27
17	2,3 dimethylbutane	69.36	75.80	77.01	83.33	93.31
18	2-methylpentane	91.77	96.22	100.68	104.83	103.27
19	3-methylpentane	94.98	97.22	100.59	104.51	102.39
20	2-methyl-1-pentene	14.75	13.27	14.40	14.18	13.45
21	n-hexane	101.16	100.90	101.15	105.39	101.13
22	unknown	503.37	488.25	498.71	481.83	459.57
23	methylcyclopentane	94.72	96.71	99.09	104.40	98.79
24	2,4 dimethylpentane	104.40	105.65	104.99	108.79	106.03
25	benzene	101.64	100.85	100.54	104.01	100.14
26	cyclohexane	94.97	97.26	99.92	103.66	101.01
27	2-methylhexane	102.62	101.40	102.65	106.38	101.70
28	2,3dimethylpentane	101.99	102.93	102.85	107.43	103.89
29	3-methylhexane	100.79	100.75	102.10	106.04	102.62
30	2,2,4 trimethylpentane	110.19	110.57	109.16	112.31	109.52
31	n-heptane	100.99	100.75	100.09	104.12	100.81
32	methylcyclohexane	102.16	102.38	102.00	106.06	101.80
33	2,3,4 trimethylpentane	100.49	100.70	99.19	102.89	101.12
34	toluene	97.35	98.47	96.30	97.79	99.15
35	2-methylheptane	107.42	109.79	107.68	113.38	110.49
36	3-methylheptane	103.91	105.30	103.01	107.06	106.36
37	n-octane	99.23	102.12	100.11	102.96	103.02
38	unknown					
39	ethylbenzene	82.02	102.61	109.97	107.82	106.83

40	m/p-xylene	84.61	101.52	112.01	108.86	108.92
41	styrene	19.86	85.12	90.18	91.35	39.78
42	o-xylene	81.55	95.65	111.38	107.52	104.07
43	n-nonane	93.91	104.17	120.25	115.96	114.90
44	i-propylbenzene	102.54	120.25	138.85	142.17	107.41
45	n-propylbenzene	101.83	134.94	142.77	157.05	100.27
46	m-ethyltoluene	85.78	110.82	113.29	126.93	84.55
47	p-ethyltoluene	92.36	133.51	134.51	148.00	87.72
48	1,3,5 trimethylbenzene	105.89	128.41	143.38	160.60	101.26
49	o-ethyltoluene	97.70	119.76	133.96	146.33	92.06
50	1,2,4 trimethylbenzene	79.70	112.29	110.56	121.94	74.83
51	n-decane	109.08	188.33	185.06	213.57	110.53
52	1,2,3-trimethylbenzene	69.50	133.94	115.49	131.34	68.18
53	m-diethylbenzene	16.42	54.67	25.94	33.75	10.60
54	p-diethylbenzene	14.29	50.73	29.33	33.99	13.54
55	n-undecane	9.44	38.69	16.19	20.02	5.98

The data shown in Table 5-2 shows that the trapping for light hydrocarbons (C_2 - C_5) is more efficient at lower flow rates. Trapping of the C_2 and C_3 compounds (boiling points lower than -42 °C), as well as isobutane (b.p. = -12 °C) is small (e.g., less than 20%) even at low flow rates. The remainder of the C_4 compounds (b.p. = -6 - 4 °C) trap at 40-85% at flow rates of 20 mL/min or less. For the C_5 compounds an analogous pattern was observed: isopentane (b.p. = 30 °C) traps at 40% at 20 mL/min, while the other C_5 compounds (b.p. = 29-36 °C) trap at 100±15%. This result for isopentane is difficult to rationalize since its boiling point indicates isopentane should behave more like the other C_5 compounds and trap quantitatively under these conditions. After returning from Azusa, additional experiments were run to investigate the behavior of isopentane, and the data are shown in Figure 5-2. These experiments, which were performed with a later generation trap, but one that was constructed the same way and exhibits very similar behavior to the one that was field-deployed, shows that isopentane traps completely at -70 °C even with a sample flow rate of 50 mL/min, exhibiting a "transition" temperature just slightly below that of pentane, as expected. Therefore in our calculations in section 5.5, we have assumed trapping of isopentane was 100%. We believe that the earlier isopentane results were subject to a calculation error of some type and that the trapping was 100% throughout, although this cannot be proven. For most hydrocarbons in the range from C_5 to C_8 a complete (100%) trapping is observed. As indicated in the cover letter for the EPA standard (attached to the 3rd quarterly progress report), there is a problem with 2-methyl-1-pentene and styrene in the cylinder, so these results are not quantitative. For hydrocarbons with retention times later than styrene (primarily C_9 - C_{11} compounds) the results are quite variable. The reason for the variability probably a combination of the methanation catalyst (see also section 2.3), and a problem with the line from the cylinder that was also observed

by Phil O' Bell of SCAQMD. During the time when these samples were run, there was a problem with the line from the standard cylinder. Phil O'Bell, observed that most of the higher hydrocarbons at one point "disappeared" and the slowly one after another came back. The problem was solved after we had left the Pico site by cleaning the line by rinsing with some solvent follow by heating and flushing the line. After this procedure he observed all the peaks in the correct concentration. The packed bed methanizer catalyst broadens all peaks, and retains compounds with more than about eight carbons. This is clearly illustrated in Figure 2-3, which shows a direct comparison of an ambient air sample run on DB-1 columns with and without a methanizer.

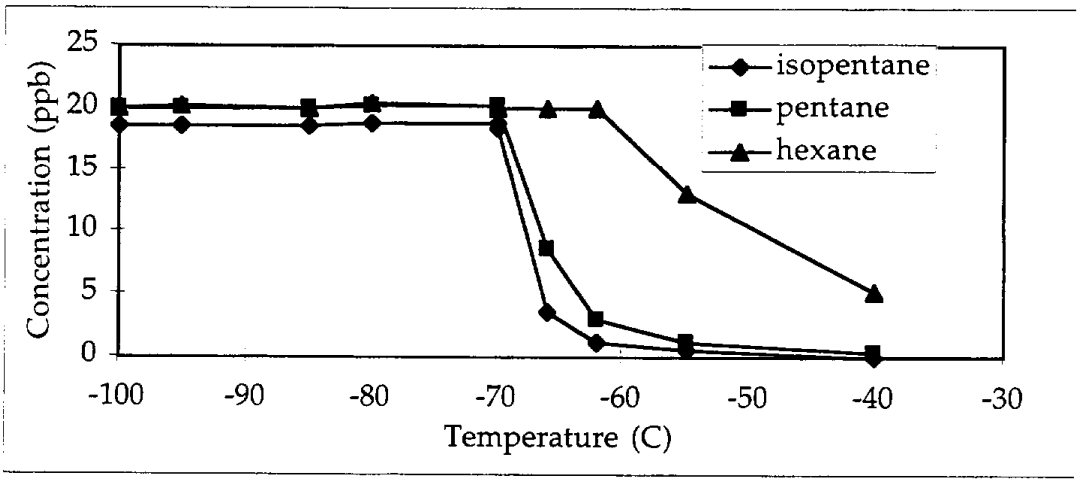

Figure 5-2. Trapping efficiency as a function of trap temperature for isopentane, pentane and hexane. Sample flow rate was 50 mL/min.

5.1.3 Ambient Air Measurements

Several direct comparisons between the TNMOC instrument and the SCAQMD PAMS GC located at the Pico Rivera station were made. Since the PAMS instrument was not running continuously, Phil O'Bell kindly performed several additional measurements and analysis for this comparison.. The standard sampling procedure for the Pico Rivera instrument had three hour sampling intervals. The TNMOC instrument is designed for shorter sampling intervals, thus we made two measurements each of one hour with 30 minutes time in between to take the chromatogram. Three comparisons with the Pico Rivera Instrument were made, all under conditions with minimal photochemistry; O_3 did not exceed 60 ppb. The first was made from 10:00 to 13:00 local time. The TNMOC sampling intervals were from 10:00 to 11:00 and from 11:30 to 12:30. After these measurements one more sample was acquired, which was analyzed in the speciated

hydrocarbon mode to check the CO_2 background. For the first sample, an average TNMOC concentration of 4.3±0.3 ppmC (Table 5-3) was measured. This value was much higher than the SCAQMD instrument than these from the other instrument (1.2 ppmC) due to the problems with the heated Teflon tubing (Section 5.1.1).

Table 5-3. Results from first comparison

File name	sample time	total area	CO_2 area*	concentration
TEST.52	10:00 - 11:00	2516	(220)	4.7 ppmC
TEST.53	11:30 - 12:30	2289	(220)	4.2 ppmC
TEST.54**	14:00 - 15:00	2145	214	4.0 ppmC

* numbers in parentheses are assumed CO_2 backgrounds that were used to calculate the total carbon concentration in the sample.
** indicates this run was in speciated hydrocarbon mode.

Table 5-4. Results from second comparison

File name	sample time	total area	CO_2 area*	concentration
TEST.74	10:00 - 11:00	910	(220)	1.4 ppmC
TEST.75	11:30 - 12:30	1064	(220)	1.7 ppmC
TEST.76**	14:00 - 15:00	924	188	1.5 ppmC

* numbers in parentheses are assumed CO_2 backgrounds that were used to calculate the total carbon concentration in the sample.
** indicates this run was in speciated hydrocarbon mode.

The second comparison was made between 9:00 and 12:00, with a resulting TNMOC concentration of 1.55±0.2 ppmC (Table 5-4). The estimated uncertainty includes uncertainties in the measurement, in the amount of CO_2 trapped, in the blank and in the calibration. For comparison to the SCAQMD GC, this value should be increased by roughly 5 % due to the untrapped light hydrocarbons that are included in the total from the AQMD instrument. Normally this increase might be 10-15% (section 5.2.8), but the Pico samples were particularly high in heavy hydrocarbons (see below). This resulting TNMOC value of ~1.65±0.2 is in good agreement with the AQMD instrument measurement, which found 1.53 ppmC total hydrocarbons (the total area of the speciated chromatogram).

The results from the third intercomparison are as follows:

Table 5-5. Results from third comparison

File name	sample time	total area	CO_2 area*	concentration
TEST1.71**	11:30 - 12:30	459	214	0.5 ppmC
TEST1.72	13:00 - 14:00	672	(220)	0.9 ppmC
TEST1.73**	14:30 - 15:30	1103	248	1.8 ppmC
TEST1.74	16:00 - 17:00	2734	(220)	5.2 ppmC

* numbers in parentheses are assumed CO_2 backgrounds that were used to calculate the total carbon concentration in the sample.

** indicates this run was in speciated hydrocarbon mode.

The third comparison was made from 11:00-14:00 and 14:00-17:00. The TNMOC instrument was run in alternating speciated hydrocarbons (with methanizer) and TNMOC modes. Mean concentrations of 0.7 and 3.5 ppmC can be calculated for the time from 11:30 to 14:00 and 14:30 to 17:00, respectively. Concentrations of 0.63 and 3.22 ppmC were found by the Pico Rivera instrument, again in excellent agreement with our results.

Intercomparison with our own instrument, comparing the speciated (with methanizer) and total carbon modes using ambient air samples, were also made. Results were variable and difficult to interpret, because of the contamination in the air samples from the room air conditioner (next section). The air conditioner has an unknown duty cycle, but is clearly highly variable from hour to hour (e.g. Table 5-5), thus we have not attempted to analyze these results.

5.1.4 Heavy hydrocarbons at the Pico Rivera Station

Discussions with Phil O'Bell raised the question of the origin of the large number of peaks in the C_8 to C_{10} range, a phenomenon that is only observed at the Pico Rivera Station. A likely explanation was a (very) nearby source. To investigate this, a canister was evacuated and an air sample taken simultaneously at the station (our instrument) and on the other side (east) of the 605 freeway about 0.5 miles from the station (canister). In Figure 5-3 these two chromatograms are displayed. The lower trace is the canister sample, the middle one is a typical "ambient air" chromatogram taken at the station, both run in speciated hydrocarbon mode. Also shown in this figure is a chromatogram from an air sample taken inside the room at the Pico Rivera station. Examination of the chromatograms shows that the "ambient air" sample appears to be qualitatively a combination of the room air sample and the canister sample; the canister had more light and less heavy hydrocarbons, and is qualitatively similar to the Azusa air samples (Figure 2-3), and the room air is dominated by very high heavy hydrocarbons with fairly low light hydrocarbons. The "ambient air" sample from the sample manifold is in between from the point of view of both heavy and light hydrocarbons. From these findings and follow-up tests we concluded that air from inside the station air got into the sampling line. Indeed it was found that the (large) hole in the roof, through which the sample line runs, was poorly sealed.

A typical day at the Pico Rivera site had a lower concentration of hydrocarbons in the morning (< 2 ppmC) which increased over the day and reached a maximum in the late evening. This can be explained with the hole in the roof. In the night it is cooler and the air

conditioning is not working. Over the day the temperature increases and the activity of the air conditioner reaches a maximum in the late afternoon. This can be seen in the data in Table 5-5. In late July the roof was sealed and the sampling line inlet was extended to six feet above the roof. We were told that the chromatograms taken after this no longer shows a large lump of higher hydrocarbons.

5.1.5 Conclusions

In conclusion, our instrument performed well when compared to the SCAQMD GC, on both the EPA/PAMS retention time standard and on ambient air samples. In both cases our instrument was within about 10% of the AQMD instrument. Unfortunately we were not able to sample any air that had experienced significant photochemical processing, so we cannot say anything about the comparison between these total and the sum of the speciated hydrocarbons for polluted air. The field test highlighted problems with the Teflon sampling line and with the speciated chromatography created by the methanizer.

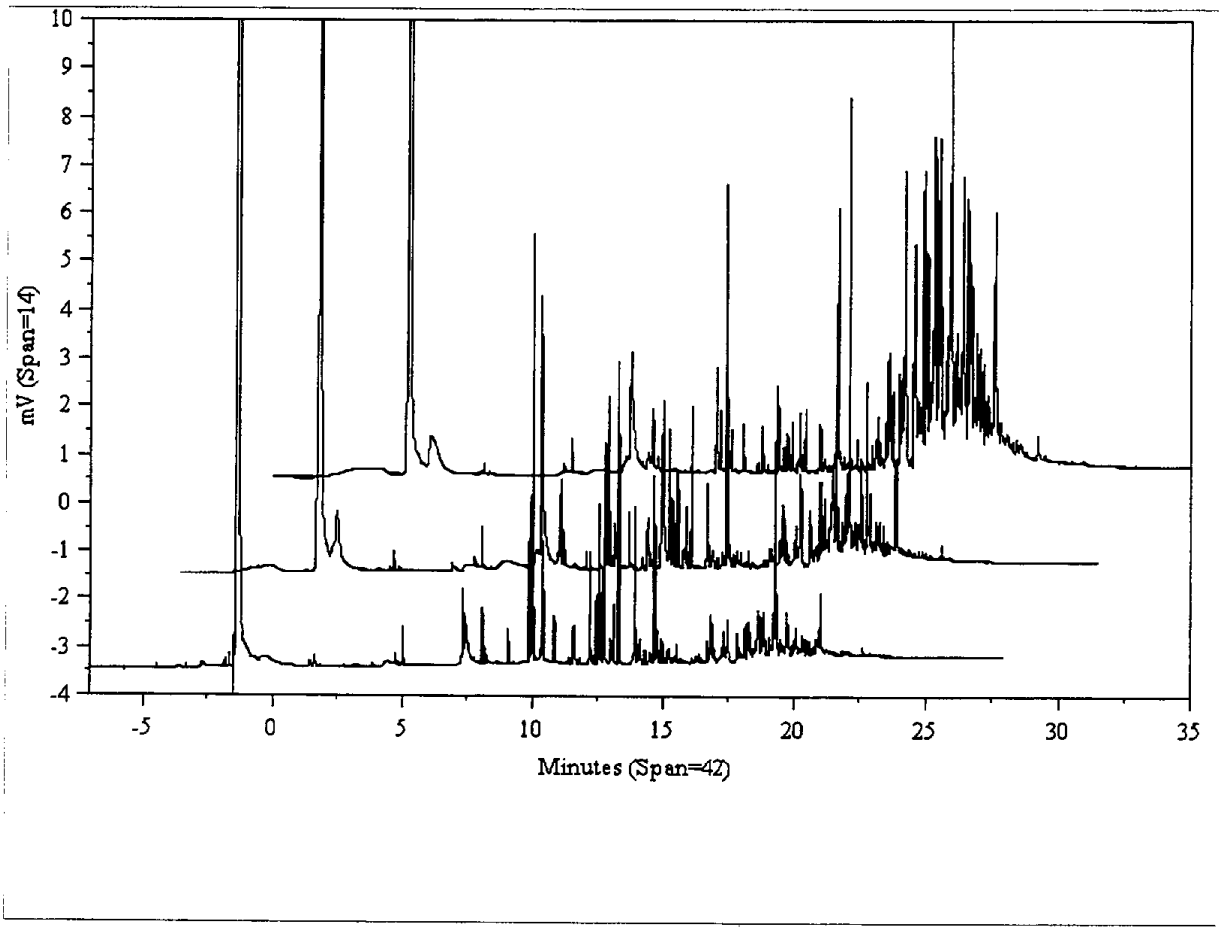

Figure 5-3. Lower chromatogram: canister sample from 0.5 mile from Pico Rivera Station; middle chromatogram: typical "ambient" air sample at Pico; top chromatogram: room air in the Pico Station. The first large peak is CO_2. Each chromatogram is offset with respect to the abscissa so that the beginning of each trace is at 0.0 minutes.

5.2 Measurements During SCOS-97 at Azusa

5.2.1 Set-up of the Total NMOC instrument

The total non-methane organic carbon instrument was set-up at the Azusa SCAQMD station as described above with a few significant changes. The instrument deployed in Azusa had a second column which provides for analysis of samples without going through the methanizer. The other major change was the new sampling line. For the campaign in Azusa we used our own separate sampling line, constructed from 9.7 m of 1/8" Silcosteel tubing. The first 3 meters (from the GC) inside the station (which was heavily air-conditioned) were wrapped with heating tape and maintained at about 50° C to prevent condensation of water in the sampling line. Flow through the sampling line was maintained at 1 L/m with a diaphragm pump, from which the sample was drawn at 20-50 cc/min. The residence time in the sampling line was about 4 s. The line was put out a window and up to the roof where it was mounted so that the inlet was about 2.5 m above the roof. Our sampling line was located at the back side of the station, whereas the sampling line of EPA mobile lab was located in front of the building about 12 meters away.

5.2.2 Sampling Protocols

Samples were analyzed in three different modes:

1) "*Total NMOC*": the sample is oxidized over a Pd-catalyst to CO_2, run on column 1 (60 m DB-1, ID 0.32 mm, film 1 μm), and analyzed with FID after conversion to methane over Ruthenium granules.
2) "*Speciated VOC's, column 1*": no oxidation, column 1 (60 m DB-1, ID 0.32 mm, film 1 μm), Ru methanizer and FID. The primary purpose of this mode is to quantify trapped CO_2 to correct TNMOC measurements for CO_2. The speciated VOC measurement in this mode is only accurate for compounds with less than about 8 carbon atoms.
3) "*Speciated VOC's*": no oxidation, column 2 (60 m DB-1, 0.32 mm, film 1 μm) analyzed with FID (no methanizer). This is the standard type of speciated hydrocarbon analysis.

5.2.3 Intensive Operation Period (IOP) and Other Sampling Periods

First IOP (September 4 - September 6)

September 4

During each three hour interval, three samples were taken. The sampling time was 40 minutes at a sample flow rate of 20 mL/min (total 800 mL) starting on the hour. Analysis according to the three protocols in the table above:

Speciated VOC's, column 1:	3:00 - 3:40, 6:00 - 6:40, 13:00 - 13:40, 17:00 - 17:40
Total NMOC:	4:00 - 4:40, 7:00 - 7:40, 14:00 - 14:40, 18:00 - 18:40
Speciated VOC's:	5:00 - 5:40, 8:00 - 8:40, 15:00 - 15:40, 19:00 - 19:40

The trapped CO_2 observed in the measurements on Sept. 3 and 4 was quite constant (380 ± 50 ppbC ($1\ \sigma$)), so we decided to omit "speciated VOC's, column 1" measurements and measure CO_2 trapping two times per day. Thus on Sept. 5 and 6 we focused more on the data that is of greater interest, Total NMOC and Speciated VOC's.

Sept. 5:	Total NMOC:	3:00 - 3:40, 5:00 - 5:40, 7:00 - 7:40, 13:00-13:40, 15:00 - 15:40, 18:00 - 18:40
	Speciated VOC's:	4:00 - 4:40, 6:00 - 6:40, 8:00 - 8:40, 14:00 - 14:40, 17:00-17:40, 19:00 - 19:40
Sept. 6:	Total NMOC:	3:00 - 3:40, 5:00 - 5:40, 7:00 - 7:40, 15:00 - 15:40, 17:00 - 17:40
	Speciated VOC's:	4:00 - 4:40, 6:00 - 6:40, 8:00 - 8:40, 14:00 - 14:40, 19:00 - 19:40

Second IOP (September 28 and September 29)

For the measurements from mid-September on, the sampling frequency was increased; for the later IOP's one measurement each of Total NMOC and Speciated VOC's were made each hour, the first at the full hour and the second at 20 minutes after the hour. The sampling time was 10 minutes at a flow rate of 50 mL/min (total volume 500 mL).

Total NMOC:	3:00 - 3:10, 4:00 - 4:10, 5:00 - 5:10, 6:00 - 6:10, 7:00 - 7:10, 8:00 - 8:10, 13:00 - 13:10, 14:00 - 14:10, 15:00 - 15:10, 17:00 - 17:10, 18:00 - 18:10, 19:00 - 19:10
Speciated VOC's:	3:20 - 3:30, 4:20 - 4:30, 5:20 - 5:30, 6:20 - 6:30, 7:20 - 7:30, 8:20 - 8:30, 13:20 - 13:30, 14:20 - 14:30, 15:20 - 15:30, 17:20 - 17:30 , 18:20 - 18:30, 19:20 - 19:30

Data from noon September 28 - noon September 29 were contaminated by room air due to operator error. These points are not included in the figures and are discussed separately.

Third IOP (October 3 and October 4)

On Oct. 3 data could only be collected for the first hour (3:00 - 4:00) due to defective lN_2 cylinders. For Oct. 4 data from 3:00 - 9:00, 13:00 - 16:00 were collected using the protocol described for the second IOP. No data were collected for the period 17:00 - 20:00, due to operator error.

Oct. 3:	Total NMOC:	3:00 - 3:10
	Speciated VOC's:	3:20 - 3:30
Oct. 4:	Total NMOC:	3:00 - 3:10, 4:00 - 4:10, 5:00 - 5:10, 6:00 - 6:10, 7:00 - 7:10, 8:00 - 8:10, 13:00 - 13:10, 14:00 - 14:10, 15:00 - 15:10
	Speciated VOC's:	3:20 - 3:30, 4:20 - 4:30, 5:20 - 5:30, 6:20 - 6:30, 7:20 - 7:30, 8:20 - 8:30, 13:20 - 13:30, 14:20 - 14:30, 15:20 - 15:30

Additional measuring times:

Additional measurements were made on non-IOP days. These are summarized as follows:

Sept. 10	Spec.:	9:20 - 10:00, 11:15 - 11:55, 13:05 - 13:45, 15:05 - 15:45
	Total	10:20 - 11:00, 12:05 - 12:45, 14:15 - 14:55, 16:20 - 17:00
Sept. 11	Spec.	16:50 - 17:30
	Total	15:30 - 16:10, 17:50 - 18:30
Sept. 17	Total	15:50 16:00
	Spec.	16:10 16:20
Sept. 18	Total	9:20 - 9:30, 10:30 - 10:40, 11:40 - 11:50, 13:50- 14:00, 15:00 -15:10
	Spec.	9:40 - 9:50, 10:50 - 11:00, 12:00 - 12:10, 14:10 - 14:20, 15:25 -15:35, 16:35 - 16:45, 17:45 - -17:55
Sept.: 19	Total	9:10 -9:20, 10:20 - 10:30, 11:40 - 11:50, 12:50 - 13:00, 13:50 - 14:00, 15:00 - 15:10, 16:10 - 16:20, 17:20 - 17:30
	Spec.	9:30 - 9:40, 10:40 - 10:50, 12:00 - 12:10, 13:10 - 13:20, 14:10 - 14:20, 15:20 - 15:30, 16:30 - 16:40, 17:40 - 17:50
Sept. 20	Total	9:30 - 9:40, 10:25 - 10:35, 12:35 - 12:45, 13:40 - 13:50
	Spec.	9:45 - 9:55, 10:55 - 11:05, 12:50 - 13:00, 14:15 - 14:25, 16:35 - 16:45
Sept. 21	Total	9:20 - 9:30, 10:20 - 10:30, 11:20 - 11:30, 13:50 - 14:00, 15:15 -15:25, 16:15 - 16:25
	Spec.	9:35 - 9:45, 10:40 - 10:50, 11:40 - 11:50, 14:25 - 14:35, 15:30 -15:40, 16:30 - 16:40
Sept. 22	Total	9:40 - 9:50, 12:45 - 12:55, 14:05 - 14:15, 15:10 - 15:20, 16:10 - 16:20

	Spec.	10:05 - 10:15, 13:00 - 13:10, 14:20 - 14:30, 15:35 - 15:45, 16:35 -16:45
Sept. 23	Total	9:30 - 9:40, 10:30 - 10:40, 11:55 - 12:05, 13:00 - 13:10, 14:10 -14:20, 15:20 - 15:30, 17:00 - 17:10, 18:10 - 18:20
	Spec.	9:45- 9:55, 10:45 - 10:55, 12:10 - 12:20, 13:15 - 13:25, 14:30 -14:40, 15:40 - 15:50, 17:20 - 17:30, 18:30 - 18:40
Sept. 24	Total	9:20 - 9:30, 10: 40 - 10:50, 13:00 - 13:10
	Spec.	11:00 - 11:10, 12:15 - 12:25, 13:20 - 13:30
Sept. 25	Total	9:30 - 9:40, 10:35 - 10:45, 11:40 - 11:50
	Spec.	9:45 - 9:55, 10:55 - 11:05, 11:55 - 12:05
Oct. 9	Total	10:00 - 10:10, 11:00 - 11:10, 12:00 - 12:10, 13:00 - 13:10
	Spec.	10:15 - 10:25, 11:15 - 11:25, 12:15 - 12:25, 13:15 - 13:25
Oct. 10	Total	15:00 - 15:10, 16:00 - 16:10, 17:00 - 17:10
	Spec.	15:20 - 15:30, 16:20 - 16:30, 17:20 - 17:30

5.2.4 Identification of peaks in "Speciated VOC's" measurements

In a series of plots (Figure 5-4, in the Appendix) we show a speciated VOC's chromatogram of an ambient air sample taken on 9/4/1997 at the Azusa site from 11:00 to 11:40. Table 5-6 (also in the Appendix) lists the peaks, their tentative identification and their abundance in ppmC. The identification of the peaks is based on the analysis report and on reference chromatograms taken from a PAMS 1996 retention time cylinders (Section 5.1.2). The reference chromatograms for the hydrocarbons were taken under dry and CO_2-free conditions, so the present retention times were adjusted for the conditions in ambient air by using the most dominant and easily identifiable peaks as markers. The identification of methanol, acetaldehyde, ethanol, α-pinene, limonene, and several other species is based on the EPA GC/MS-instrument (which uses the same type of column phase) which was co-located at the Azusa station in September 1997. All identities, but particularly the oxygenates and biogenics, should be considered tentative.

Each speciated chromatogram was analyzed for concentrations of a number of individual compounds. n-Heptane, benzene, toluene, ethylbenzene, *o*- and *m&p*-xylene (*m*- and *p*-xylene elute at the same time), were quantified to provide an estimate of the age of air masses arriving at the Azusa station. C_3-C_5 hydrocarbons were estimated for the correction of TNMOC concentrations due to incomplete trapping. The oxygenates acetone, acetaldehyde, methanol and ethanol were quantified to estimate the fraction of the difference between TNMOC and $\sum$ speciated VOC's attributable to these species.

5.2.4 Comparison of Total NMOC Measurements with Speciated VOC's

One of the primary goals of our TNMOC instrument is to determine the amount of organic carbon in ambient air that is not detected in conventional GC analysis. Our instrument, which uses the same inlet for the Total NMOC and Speciated VOC's, has the advantage that it avoids many calibration issues that would inevitably arise were the measurements being made on two different instruments. Analysis of canister samples reported in Section 2.3 show impressive agreement and reproducibility between the Total NMOC and Speciated VOC measurements. For the measurements in Azusa we had yet to build a dual sampler inlet, thus samples were taken sequentially for TNMOC and speciated VOC's. We used two different approaches, the first for the first two weeks of the campaign (prior to Sept. 17), and the second for the remaining 4 weeks:

1: One sample/hour, alternating Total NMOC and Speciated VOC measurements, 40 minute samples (800 mL at 20 mL/min)

2: Two samples/hour, Total NMOC on the hour and then Speciated VOC measurements 20 minutes later, 10 minute samples (500 mL at 50 mL/min).

Note also the sample frequency is limited by the time needed for chromatography of the Speciated VOC's, which typically lasted 35-40 minutes. The Total NMOC measurement (10 minute chromatogram) was always made first, because this allowed the two samples to be collected as close together as possible.

The variability in the Total NMOC/$\sum$ Speciated VOC's ratio (T/S) is essentially the same for both sampling protocols, indicating that the short term variability in local sources (below) are probably of similar magnitude to the averaged variations of the airmasses that arrive at the station over periods of a few hours.

5.2.5 A Local Source of Limonene?

Even for samples taken 20 minutes apart, direct comparison of Total NMOC and Speciated VOC's was difficult. In the industrial neighborhood of the Azusa station, local sources appeared to be strong and variable. One particular compound, identified as limonene by the EPA and Riverside groups [54], was occasionally observed at very high concentrations and may be responsible for a large fraction of the variability we observed, particularly in the early morning hours. The large limonene peak was accompanied by an additional large peak that was unidentified but probably contained 10 or more carbons. Limonene has a very short lifetime; ~ 70 minutes at [OH] = 5×10^6 molecules cm^{-3}. This coupled with the observation that the highest limonene peaks were in the early morning when biogenic emissions should near their minimum, suggests an anthropogenic source for

this compound [54]. Typical limonene concentrations were at or below 5 ppbC, corresponding to about 0.5 % of the total organic carbon in the air. In some samples however, observed concentrations of limonene increased up to 150 ppbC, which corresponds to almost 30% of the total organic carbon detected in those samples (Table 5-7). Depending on when the samples were taken, presumably either the Total NMOC or the Speciated VOC measurement (or both) covers the peak concentration of limonene and its companion peak. For all of the cases where the Total NMOC/Σ speciated VOC ratios (T/S) was less than 1, a prominent limonene peak was identified in the Speciated VOC chromatogram. Similarly, this limonene peak may have been captured by the Total NMOC measurements in those cases where T/S is greater than about 1.8 (Figure 5-6). It should also be noted that there are several measurement pairs where the speciated measurement showed a very high limonene peak, yet the T/S ratio is in the normal range. A possible explanation for this is that both the Total NMOC and the Speciated VOC measurement taken 20 minutes later sampled high limonene concentrations.

Table 5.7: Limonene and sum of Speciated VOC's on the morning of Sept. 28

Filename	Time	Ret. time [min]	Conc.(Limonene) [ppbC]	Conc.(sum of all peaks) [ppbC]	Limonene as percent of total
AZUSA2.28R	3:20 - 3:30	24.16	2.3	668	0.35
AZUSA2.30R	4:20 - 4:30	24.2	2.4	526	0.46
AZUSA2.32R	5:20 - 5:30	24.29	2.0	416	0.47
AZUSA2.34R	6:20 - 6:30	24.26	66.9	520	12.9
AZUSA2.36R	7:20 - 7:30	24.26	149.0	520	28.7
AZUSA2.38R	8:20 - 8:30	24.41	2.7	536	0.50

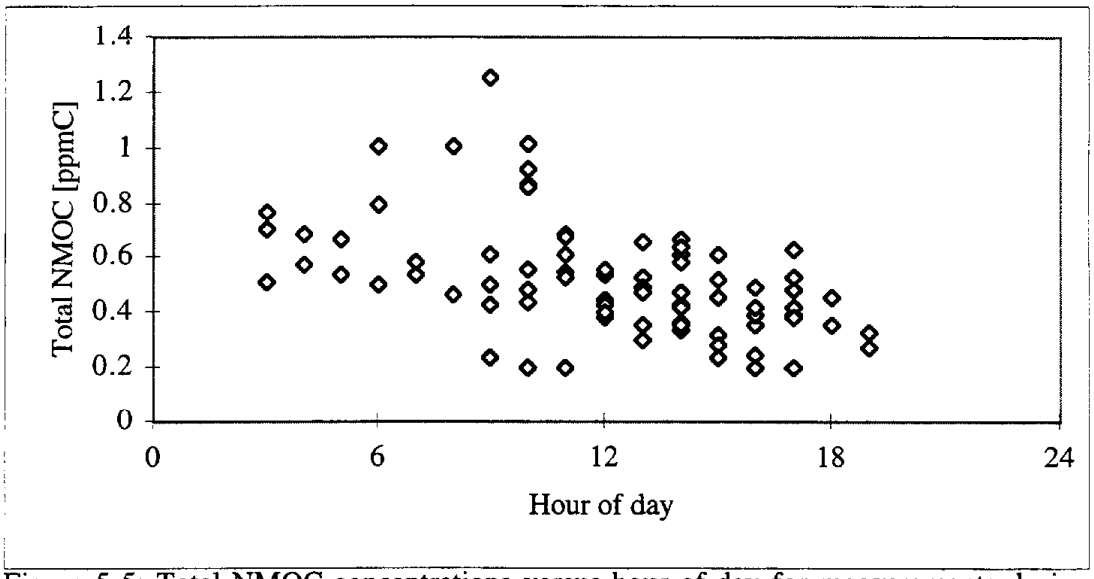

Figure 5-5: Total NMOC concentrations versus hour of day for measurements during SCOS97.

5.2.6 TNMOC vs. Time of Day

Figure 5-5 shows a plot of TNMOC versus the hour of day for the measurements during SCOS-97. In this plot one can see that the maximum concentration of hydrocarbons was observed in the early morning hours and that the concentration generally decreases over the day. Note that the four measurements with 1 ppmC or more are probably influenced by limonene (above), thus the detailed shape of the diurnal pattern less limonene (which may be from a very local source, Section 5.2.5) is obscured.

The ratio of Total NMOC/Speciated VOC's (T/S) for 83 pairs of measurements made between Sept. 4 and Oct. 10 are plotted versus time of day in Figure 5-6. The average T/S ratio is 1.3 ± 0.3 ($1\ \sigma$). A ratio greater than 1 indicates that in conventional VOC measurements using GC analysis underestimates the amount of Total NMOC. Again, the values below 1.0, as well as the extreme high values are probably due to large short term fluctuations in a few compounds such as limonene. This TNMOC/Σ speciated VOC's (T/S) ratio may be effected by corrections due to incomplete trapping of light hydrocarbons and by co-elution of formaldehyde with the CO_2 peak, which are discussed below.

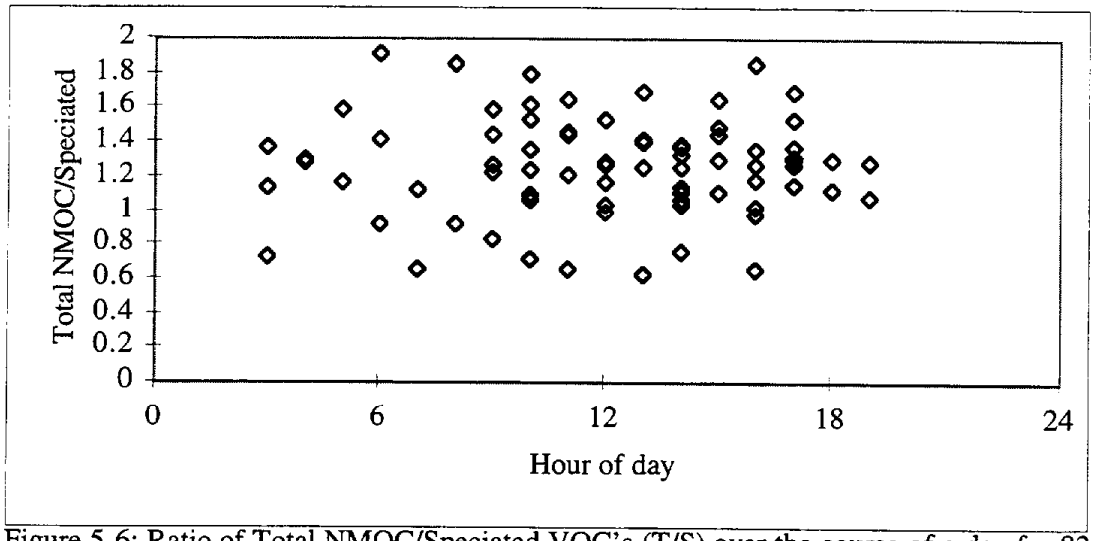

Figure 5-6: Ratio of Total NMOC/Speciated VOC's (T/S) over the course of a day for 83 pairs of measurements taken between September 4 and October 10.

5.2.7 Formaldehyde

Formaldehyde, the lightest common oxygenate, is both directly emitted and formed in numerous photooxidation reactions. Formaldehyde can contribute a non-negligible amount of the total VOC'; HCHO in ambient air vary between about 2 and 50 ppb [34, 35]; at the Azusa station in September of 1993 during a high ozone event, the average formaldehyde concentration was about 6.5 ppb [55] with no strong correlation with time of day. Formaldehyde is oxidized by the oxidation catalyst and contributes to the Total NMOC. However, because the temperature program used during SCOS-97 in Azusa did not separate CO_2 and HCHO, and HCHO is partially reduced by the methanizer (~75%) in the speciated VOC measurements in column 1, it was partly included in the CO_2 background measurements which were used to correct the Total NMOC measurements. Thus the HCHO concentration was included with the TNMOC measurement and then subtracted from the Total NMOC. The Total NMOC carbon concentration was between 300 and 800 ppbC during SCOS-97, thus HCHO probably contributes less than about 2-5% to the Total NMOC. Like the other corrections (incomplete trapping of lighter hydrocarbons and lower FID response of oxygenated species, below) HCHO probably contributes only a minor amount (~< 4 %) to the ratio of Total NMOC to Σ Speciated VOC's; changing the ratio T/S ratio from 1.3±0.3 to ~1.33 This correction is in the direction of increasing the value for TNMOC, and thus offsets the small effect of the incomplete trapping of light hydrocarbons discussed next. In future we plan to run the measurements of trapped CO_2 at a temperature program that permits separation of HCHO.

5.2.8 Corrections for Losses of Lighter Hydrocarbons Due to Incomplete Trapping

In Section 5.1.2, trapping efficiencies for the 58 compounds in the PAMS retention time standard are reported, together with some additional tests. Hydrocarbons with 3 to 5 carbon atoms trap efficiencies between 5 and 85%. At the time of those tests only one column, equipped with the methanizer, was installed. CO_2 is not well separated from C_2 compounds by a DB-1 column, thus in a system where CO_2 is measured (with a methanizer) the C_2 compounds cannot be quantified. Since we did not have an accurate trapping efficiency for the C_2 compounds (which trap at less than 5%) we have assumed the average values measured by the SCAQMD during a similar period at the Azusa station. The SCAQMD measurements were also made during September and October of 1997, but the measurement times did not completely overlap with our measurement times. Table 5-8 shows a list of the molecules for which corrections were made, in addition to isopentane. Values for propane, n-butane, and isopentane are all in good agreement with the SCAQMD values. It is possible that the large difference for 1-butene resulted from an error in its identity or co-elution of another compound; the source of the propene discrepancy is not known. The other C_4 and C_5 hydrocarbons for the PAMS retention time standard which are not listed here were either in very low concentration or had trapping efficiencies of 65-85 % or more, and thus would have had a minimal effect on the calculated Total NMOC and Σ Speciated VOC's concentrations.

The correction for untrapped light hydrocarbons (which effects both TNMOC and Σ Speciated VOC's almost equally) also has a minor effect on the ratio of TNMOC/Σ Speciated VOC's. Correcting the amount of carbon for both measurements by 15% of the Carbon in the Speciated VOCs analysis, the ratio changes from 1.30 to 1.25. Considered together with the correction for formaldehyde, the ratio of TNMOC/Σ Speciated VOC's remains essentially unchanged.

Table 5-8: List of several light hydrocarbons, their trapping efficiencies, average concentrations and their fraction of the total carbon (see text).

Molecule	Trapping efficiency, 9/4-9/16 (%)[a]	Trapping efficiency, 9/16-10/30 (%)[a]	Concen-tration[b] (ppbC)	SCAQMD Concen-tration[c] (ppbC)	% of total NMOC	% of total NMOC not measured due to incomplete trapping of this compound
Ethene*	--	--	--	11.3	2.2	2.2
Acetylene*	--	--	--	9.3	1.8	1.8
Ethane*	--	--	--	14	2.7	2.7
Propene	15	10	11 ± 10	4.4	2.1	1.9
Propane	5	5	21 ± 10	22.5	4.1	3.9
i-Butane	5	3.5	7 ± 3	5.4	1.3	1.2
1-Butene	68	51	5 ± 3	1.0[c, d]	1.0	0.4
n-Butane	43	30	10 ± 4	9.5	2.0	1.3
i-Pentane[e]	100	100	34 ± 11	27.9	6.6	0.0
	Sum				23.8	15.4

*The trapping efficiencies were measured when the GC temperature program was not sufficient to separate the C2 compounds from the CO_2, thus these were not measured directly. We have assumed the SCAQMD concentrations to calculate the percent of total NMOC.

[a] The sample flow rate was changed on 9/16 from 20 to 50 mL/min, resulting in a lower trapping efficiency for a few compounds in the later period.

[b] The scatter reflects the sample variability in ambient concentrations.

[c] Personal communication, Eileen McCauley, California Air Resources Board. Perfect agreement is not expected since not all sampling was simultaneous.

[d] This value was measured by CE-CERT and is an average value for all IOP's.

[e] Isopentane is included only for comparison. No corrections were made for this compound since it traps completely.

5.2.9 Are Light Oxygenates Responsible for the Excess TNMOC over the Σ Speciated VOC's?

The source of the excess TNMOC compared to the Σ Speciated VOC's observed in Azusa is an interesting question. The influence of local sources and variability in the air masses may be partly responsible, but another likely candidate is the oxygenated VOC's that are have reduced FID responses (Section 3) and thus contribute less to the Σ Speciated VOC's than to TNMOC. We did not identify multifunctional oxygenates or oxygenates with more than two carbons, but we could estimate the concentrations of methanol, ethanol and acetaldehyde, and here calculate their contribution to the difference between the TNMOC and Σ Speciated VOC's concentrations.

Methanol typically has a concentration of about 6 ppb or about 1.3% of the total carbon. Scatter in its concentration increases with time of day, but there is no correlation

with time of day. It appears to have a weak correlation to the total carbon loading (R^2 = 0.19; 10% chance that the data are un-correlated). Acetaldehyde and ethanol each typically contribute about 2% to the Total NMOC. The acetaldehyde concentration ranges from undetected to about 25 ppbC (=12.5 ppb), and is at most weakly correlated with the time of the day (R^2 = 0.12, 35% chance that the data are un-correlated) but is positively correlated with the total carbon loading (R^2 = 0.47). The average acetaldehyde concentration was 8.4 ppbC (= 4.2 ppb), or about 1.8% of TNMOC, in good agreement with the average concentration reported by Grosjean et al. for Azusa in 1993 [55]--about 6 ppb. Ethanol concentrations begin in the early morning hours between 10 and 25 ppbC, and afternoon concentrations were mostly at or below 10 ppbC, but the correlation with time of day is weak; (R^2 = 0.2; 10% chance that the data are un-correlated). TNMOC follows a similar pattern, thus ethanol is positively correlated with TNMOC (R^2 = 0.59). The average ethanol concentration was 11 ppbC, or 2.3% of TNMOC. Figure 5-7 shows the concentrations of methanol, ethanol, and acetone vs. time of day for all speciated samples.

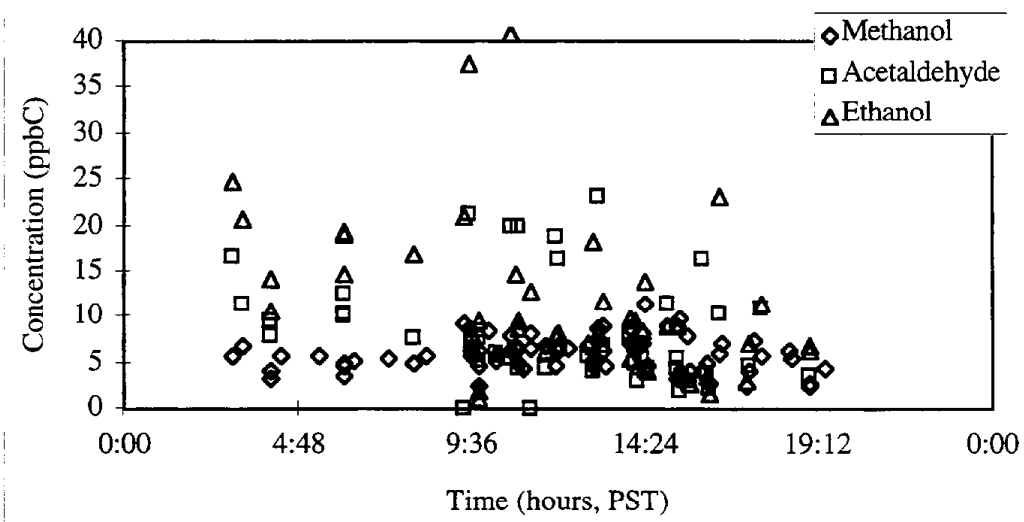

Figure 5-7: Concentration in ppbC of methanol, acetaldehyde and ethanol as a function of the time when the samples were taken.

Roughly half of the carbon in the methanol, ethanol and acetaldehyde is already accounted for in the Σ Speciated VOC measurement (effective carbon numbers are 0.77, 1.65 and 1.02, respectively). These three compounds sum to about 5% of the total VOC loading, 2-3% of which is already included in the Σ Speciated VOC's. Thus these three common oxygenates can account for 10% or less of the difference between TNMOC and the Σ Speciated VOC's.

5.2.10 Hydrocarbon Age/Photochemical Processing

To estimate the extent of photochemical processing of hydrocarbons in the air arriving at the Azusa station, and compare this to the TNMOC/Σ Speciated VOC's ratio, ratios for several pairs of aromatic hydrocarbons from the speciated VOC chromatograms were calculated [30, 56]. Upon emission into the atmosphere each species is removed by one or more chemical or physical processes on a characteristic time scale. The ratio of the concentration of two simultaneously measured species (hydrocarbons) can provide an estimate of photochemical aging, (1) if the two species are simultaneously introduced into an air parcel, (2) if they are removed by photochemical reactions that follow pseudo-first-order kinetics, (3) if they have negligible concentrations in the air that dilutes the emission and (4) if their rates of removal are significantly different [56]. In this analysis, criteria (3) is not met since air that arrives at the Azusa station is a mix of partially processed air and fresh local emissions that contain some of these tracer hydrocarbons. Thus the calculation provides an average of the degree of photochemical processing of the hydrocarbons.

If dilution effects are neglected, the concentration of A can be expressed as

$$[A] = [A]_0 e^{-k_A [OH] t} \qquad \text{(E 1)}$$

where [A] and $[A]_0$ are the concentration of species A at the time of the measurement and the time of release, respectively, k_A is the rate constant for reaction of A with OH radicals and <[OH]> is the average OH concentration during the time period t.

The ratio of two hydrocarbons will be unaffected by dilution, if the diluting air has a negligible concentration for each compound, and can then be described by the following equation:

$$\ell n \frac{[A]}{[B]} = \ell n \frac{[A]_0}{[B]_0} - (k_A - k_B)[OH]t \qquad \text{(E 2)}$$

Measurements of more than two species presents the opportunity to check if the two independent measurements of the photochemical age give the same result. Here we focus on the m&p-xylene/ethylbenzene ratio, since these compounds are highly correlated and the peaks could be reliably quantified. These compounds are presumably emitted in fairly constant proportion since they are not easily separated by distillation; their boiling points span a range of less than 3 C. Ethylbenzene, and m&p-xylene concentrations were calculated from the 83 speciated chromatograms. Rate constants for reaction with OH are 7.1 $\times 10^{-12}$, 22.0 $\times 10^{-12}$ and 14.3$\times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}, respectively [48, 57].

At night the m&p-xylene/ethylbenzene ratio has a value of 3.8 - 3.9 (ln 3.85 = 1.35) in good agreement with the value reported for gasoline in Los Angeles in 1975 [58,

59]. This m&p-xylene/ethylbenzene ratio appears to have changed little up to at least the late 1980's; the average ratio for the 7:00 AM 1987 SCAQS measurement was also about 3.8-4.0 [30]. In our data set, the ratio begins to decrease after 8:00 AM, reaching a minimum in the afternoon, and increases again after 16:00 to reach the original value after 20:00.

The magnitude of the decrease during the day is (presumably) dependent on the level of photochemical activity. Figure 5-9 shows the relationship between m&p-xylene/ethylbenzene ratio and the ozone concentration; a reasonable correlation coefficient is observed.

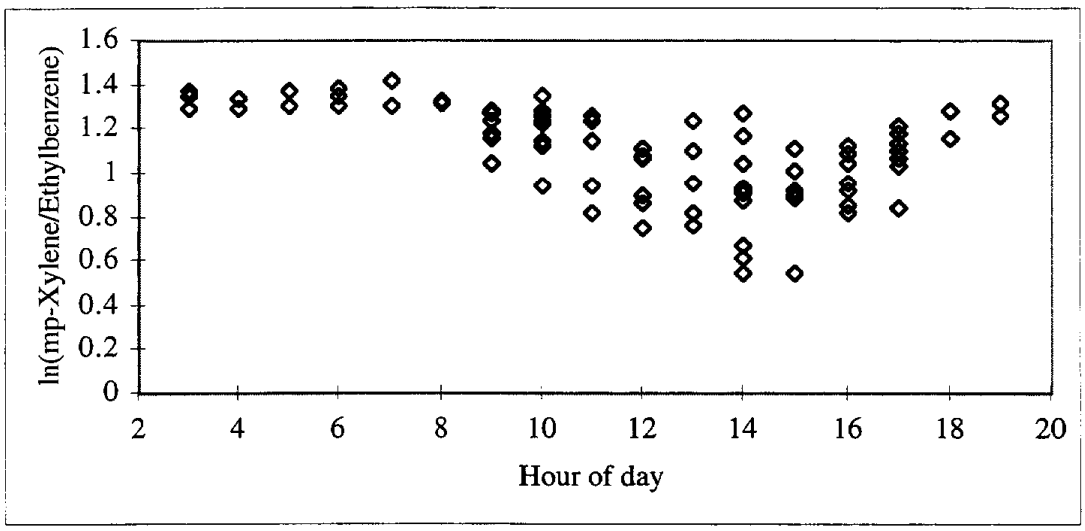

Figure 5-8: ln(m&p-xylene / ethylbenzene) versus hour of day.

From the decrease of the ratio ln (m&p-xylene/ethylbenzene) from 1.35 (at night) to values between 0.8 and 1.0 (in the afternoon, Figure 5-9), an average level of hydrocarbon processing can be calculated from (E1) and (E2). This decrease in the m&p-xylene/ethylbenzene ratio corresponds to 1.8 hours of exposure to an (assumed) OH radical concentration of 5×10^6 molecules cm^{-3}.

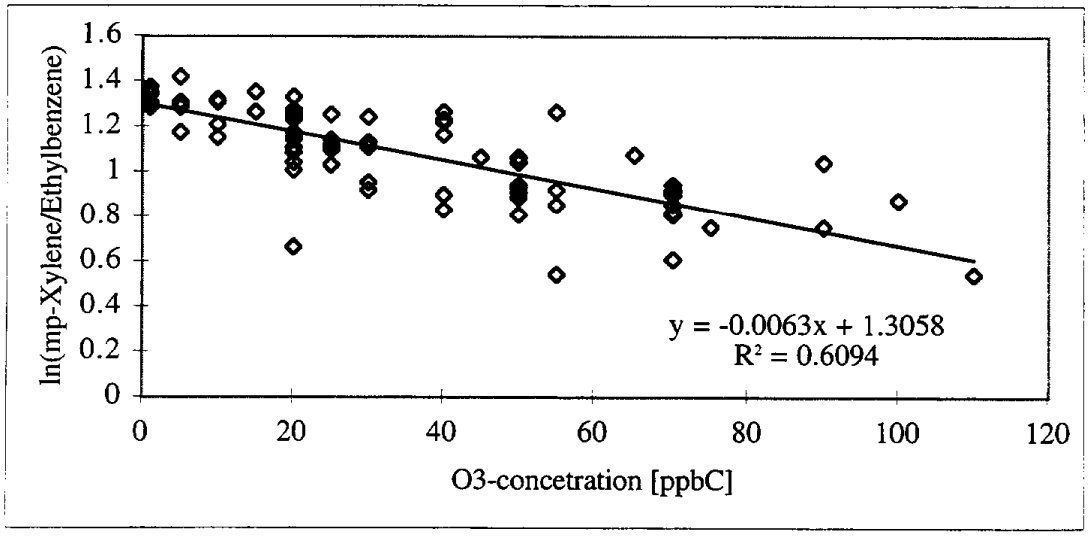

Figure 5-9: ln(m&p-xylene / ethylbenzene) versus the O_3 concentration.

With this estimate of hydrocarbon processing, a calculation of the expected degree of increased oxygenation/nitration can be made. This calculation assumed 1) the average speciated mix of hydrocarbons (100 compounds) from the EPA for 29 cities at 6-9 AM (Jeffries, 1995), 2) rate constants for reactions of each hydrocarbon with OH, and (for alkenes) with ozone and 3) exposure to OH = 5×10^6 molecule cm^3, and an O_3 concentration of 50 ppb for 1.8 hours, and 4) equation (E1) for alkanes, and the following equation for alkenes:

$$[A] = [A]_0 e^{-(k_A[OH] + k_{O3}[O_3])t} \qquad \text{(E 3)}$$

Under these conditions, an average of 27% of the hydrocarbons react once with either OH or ozone. Since the compounds have an average of 7 carbons, and can be expected to add ~1.5 functional groups (primarily alcohol, carbonyl, or nitrates) per OH or ozone reaction, the total mix might be expected to an increased level of oxygenation/nitration of about 6%. The expected effect of this modest increase on the TNMOC/Σ Speciated VOC's (T/S) ratio cannot be calculated precisely, however, since the effect of oxygenation/nitration can be to either reduce the FID response somewhat (section 3) or to cause the compound to be lost or broadened in the column so as not to be quantifiable. The latter effect has a larger effect on the sum of speciated VOC's measurement than the former. It is clear, however, that given the low level of photochemical processing in this data set, the T/S ratio could be expected to have relatively little dependence on the time of day, ozone level, or the ratio of m&p-xylene/ethylbenzene. Figures 5-10 and 5-11 show the relationship between T/S and m&p-

xylene/ethylbenzene and ozone, respectively. Neither show any trend; the correlation coefficients are <0.05 in both cases.

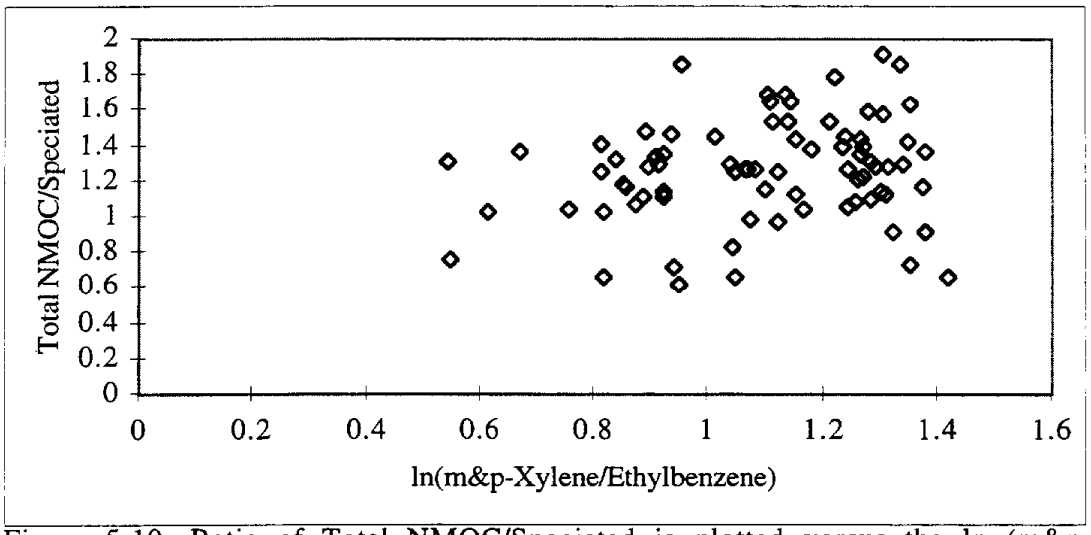

Figure 5-10: Ratio of Total NMOC/Speciated is plotted versus the ln (m&p-xylene/ethylbenzene).

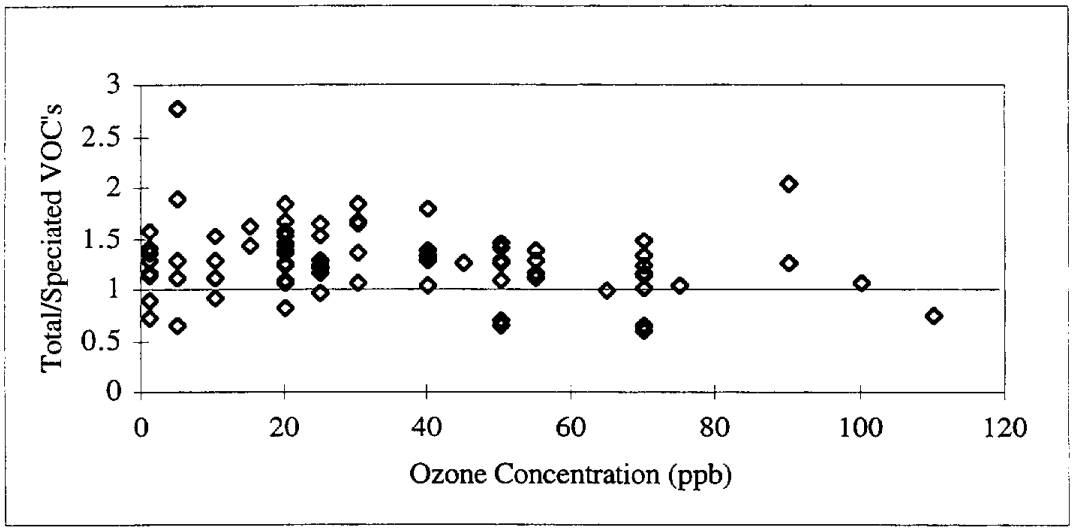

Figure 5-11. Total/sum of speciated VOC's vs. ozone.

5.3 Conclusions

The average Total NMOC/Sum of Speciated VOC's ratio (T/S) is 1.3±0.3. The variability is probably largely due to local and/or longer term average variability in the air masses sampled for the two measurements. From the measurements analyzed here we

cannot derive a correlation between the ratio of Total NMOC/Speciated VOC's vs. the m&p-xylene/ethylbenzene ratio. There are several reasons for this: (1) due to the unusually clean air in the 1997 season, the sampled air was heavily source influenced. Only a slight increase in oxygenation/nitration, of order 6%, was expected for the afternoon relative to the morning samples. (2) Given the relatively large scatter in the Total NMOC/Speciated VOC ratio, a change of this magnitude would be difficult to discern. Since canister samples showed excellent agreement and reproducibility for the T/S ratio on a single air sample, it is likely that the scatter in the T/S ratio is due largely to air mass variability. This has been rectified by adding a dual sampler inlet to acquire TNMOC and Σ speciated VOC's simultaneously.

6.0 References

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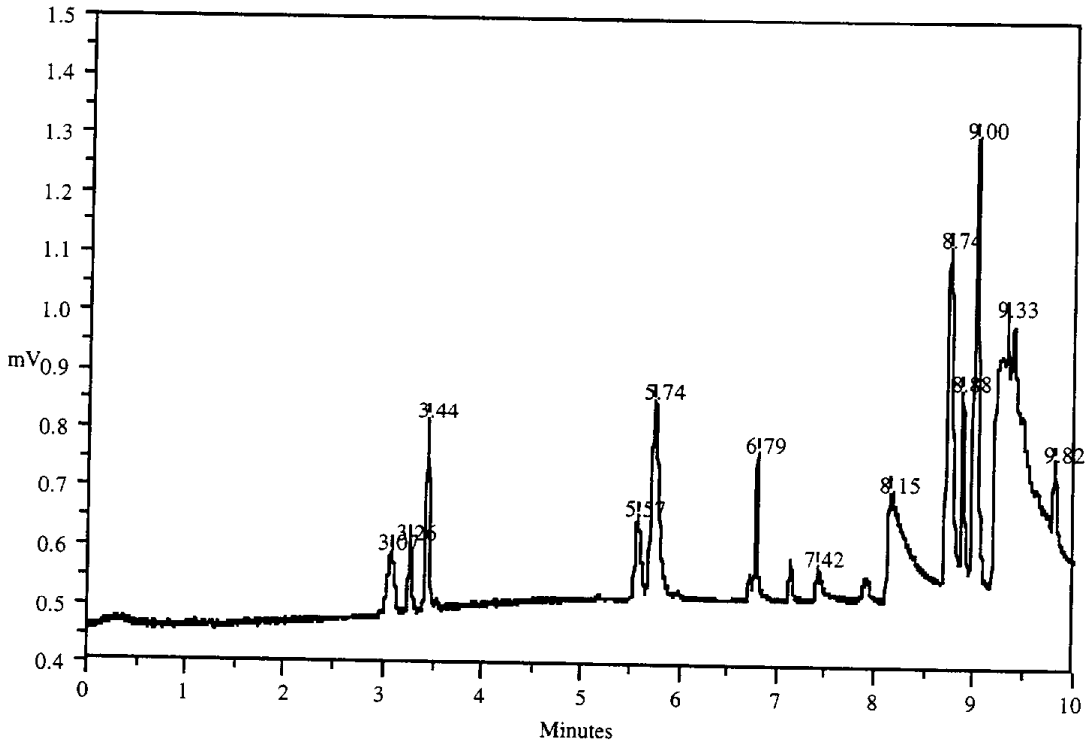
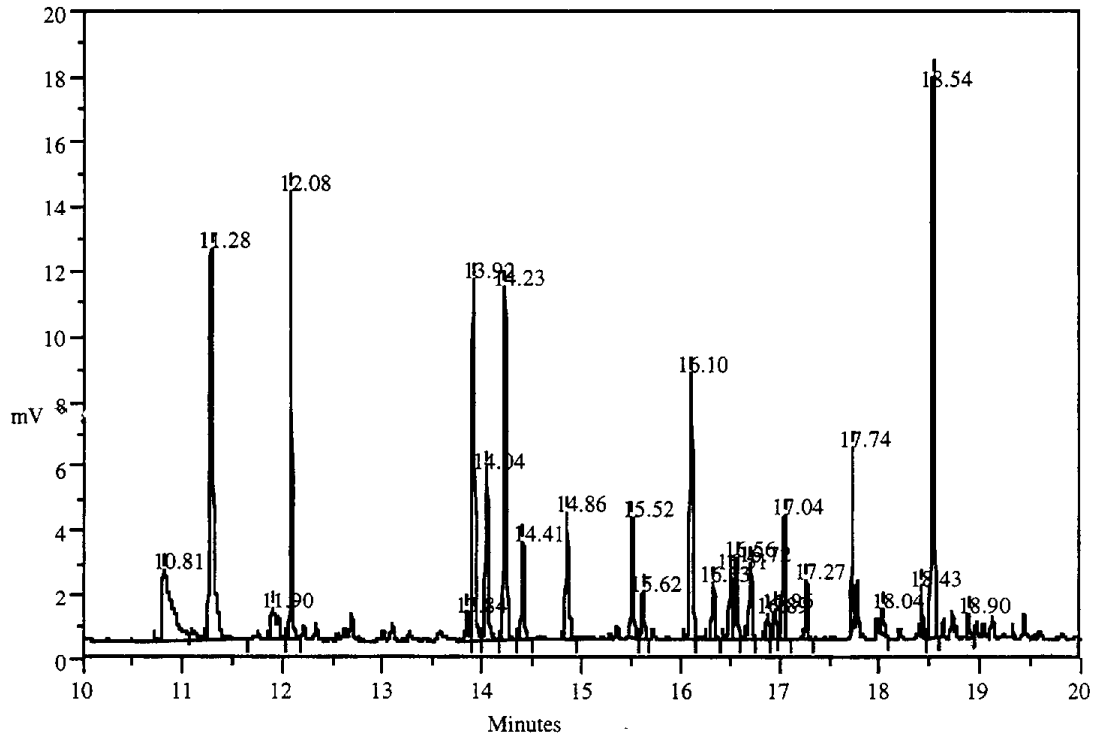
7.0 Glossary of Terms, Abbreviations, and Symbols

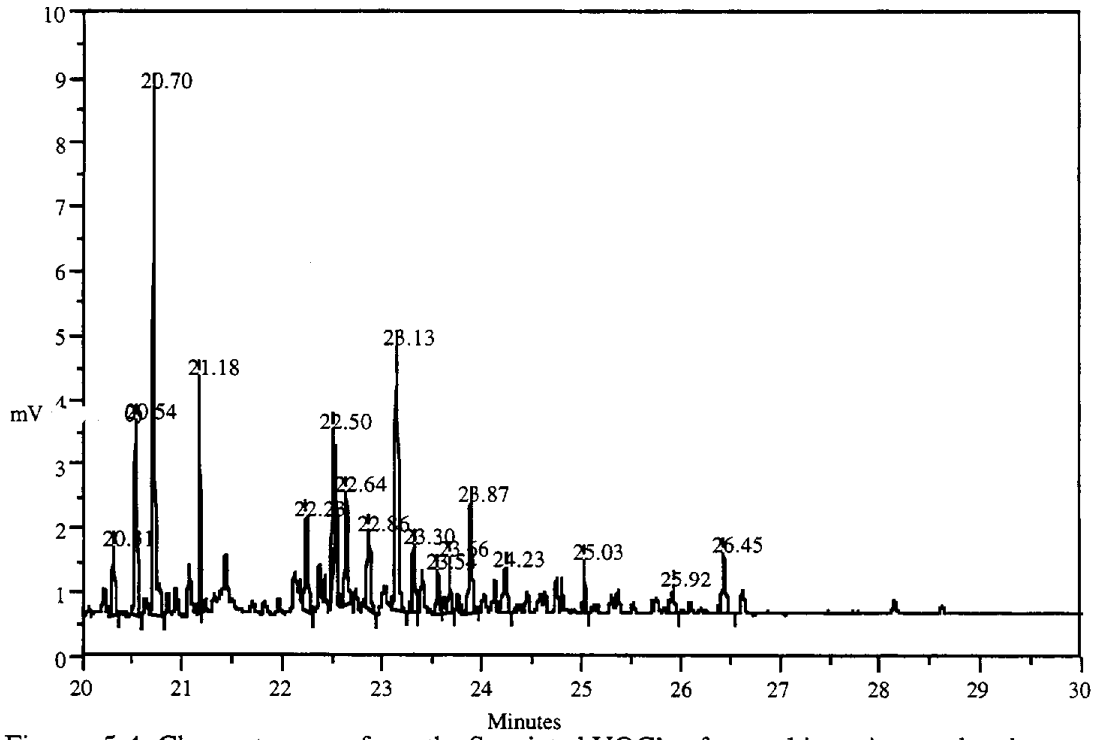
GC:	Gas Chromatograph
FID:	Flame Ionization Detector
IOP:	Intensive Operation Period
NMHC's:	Speciated Non-methane Hydrocarbons
PAMS:	Photochemical Assessment Monitoring Station
SCAQMD:	South Coast Air Quality Management District
$\sum$ speciated VOC's:	Sum of the Speciated Hydrocarbons and Carbonyls
TNMOC:	Total Non-methane Organic Carbon
T/S	Total NMOC/Sum of Speciated VOC's ratio

Appendix: Sample Chromatogram, Peak Identities and Concentrations

A.1 Figure 5-4.







Figures 5-4: Chromatograms from the Speciated VOC's of an ambient air sample taken on 9/9/1997 at the Azusa site from 11:00 to 11:40

A.2 Table 5-6.

Concentrations and identities of peaks for the chromatogram shown in Figure 5-4. The concentrations for the lighter hydrocarbons (C_2-C_5) are not corrected for losses due to incomplete trapping. C_6 and higher hydrocarbons should be trapped completely.

Retention time [min]	Molecule	Concentration [ppbC]
3.072	ethylene	0.675
3.264	acetylene	0.373
3.443	ethane	1.007
5.574	propene	0.747
5.744	propane	2.336
6.723		0.137
6.785		1.015
7.134		0.210
7.417		0.537
7.901	i-butane	0.304
8.151	methanol	3.580
8.735	1-butene	3.113
8.881		1.330
9.002	n-butane	3.127
9.263	acetaldehyde	13.168
9.328	t-2-butene	0.207
9.393		0.265
9.817	c-2-butene	0.343
10.246		0.159
10.811	ethanol	21.456
11.094		0.608
11.283	i-pentane/acetone	37.870
11.750	1-pentene	1.255
11.903	isopropanol	3.144
11.956		2.233
12.082	n-pentane	35.048
12.205	isoprene	1.234
12.340	t-2-pentene	1.254
12.551	c-2-pentene	0.607
12.616		0.980
12.681		1.889
13.001		0.949
13.086	2,2 dimethylbutane	1.426

13.264		0.845
13.563		0.991
13.705		0.278
13.842	cyclopentane	2.085
13.918	2,3 dimethylbutane/MTBE	28.145
14.041	2-methylpentane	13.778
14.228		23.439
14.409	3-methylpentane	7.487
14.563	2-methyl-1-pentene	0.675
14.696		0.151
14.857	n-hexane	10.401
14.977		0.387
15.036		0.388
15.112		0.250
15.210		0.356
15.297		0.531
15.362		0.989
15.463		0.471
15.521	methylcyclopentane	8.781
15.616	2,4 dimethylpentane	3.734
15.722		1.030
15.865		0.242
15.985		0.150
16.102	benzene	21.494
16.227		0.704
16.331	cyclohexane	4.409
16.512	2-methylhexane	5.449
16.565	2,3-dimethylpentane	6.089
16.717	3-methylhexane	6.145
16.893		2.040
16.958	trichloroethylene	2.453
17.042	2,2,4 trimethylpentane	11.157
17.168		0.133
17.265	n-heptane	4.350
17.739		14.016
17.793	methylcyclohexane	4.913
17.993		1.477
18.042		3.244
18.217		0.930
18.379		0.588

18.428	2,3,4 trimethylpentane	4.358
18.539	toluene	38.298
18.634		1.699
18.734	2-methylheptane	3.047
18.840		0.354
18.902	3-methylheptane	2.323
18.975		1.416
19.038		1.882
19.141		1.852
19.245		0.681
19.293		0.424
19.338		1.384
19.441	n-octane	2.502
19.543		0.531
19.610		0.916
19.749		0.184
19.829		0.822
19.952		0.446
20.026		0.203
20.071		0.448
20.125		0.460
20.209		1.594
20.315		2.644
20.376		0.535
20.478		0.234
20.538	ethylbenzene	6.722
20.627		0.850
20.704	m/p-xylene	25.713
20.850		0.846
20.918		1.021
20.960		0.553
21.068	styrene	2.222
21.179	o-xylene	8.006
21.236		0.493
21.316		0.535
21.368		0.717
21.440	n-nonane	2.193
21.703		0.749
21.808	i-propylbenzene	0.734
21.962		0.725

22.028		0.220
22.128		2.391
22.171		1.262
22.233	α-pinene	3.942
22.310		0.452
22.372	n-propylbenzene	2.023
22.420		1.435
22.497	m-ethyltoluene	6.730
22.539	p-ethyltoluene	6.819
22.637	1,3,5 trimethylbenzene	5.328
22.715		1.604
22.808		0.650
22.858	o-ethyltoluene	3.840
23.023	β-pinene	2.654
23.127	1,2,4 trimethylbenzene	10.854
23.303	n-decane	2.626
23.378		2.407
23.543		1.627
23.595		0.796
23.660	1,2,3-trimethylbenzene	2.852
23.748		0.815
23.867	limonene	6.368
24.019		1.277
24.134	m-diethylbenzene	2.133
24.233	p-diethylbenzene	2.514
24.329		0.532
24.386		0.421
24.447		0.980
24.594		1.628
24.633		0.793
24.735		1.448
24.798		1.725
24.915		0.401
25.031	n-undecane	1.988
25.120		0.156
25.309		0.906
25.369		0.954
25.530		0.480
25.637		0.145
25.703		0.590

25.758		0.871
25.841		0.401
25.925		1.974
26.016		0.231
26.091		0.455
26.215		0.133
26.447		2.972
26.642		1.495
26.781		0.222
26.892		0.320
26.987		0.322
27.400		0.176
27.486		0.214
27.631		0.152
27.732		0.230
27.801		0.247
28.011		0.306
28.145		0.740
28.619		0.362