

SURFACE AND UPPER AIR VOC SAMPLING AND ANALYSIS DURING THE 1997 SOUTHERN CALIFORNIA OXIDANT STUDY

Final Report
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ABSTRACT

SCOS97-NARSTO was a multi-agency, \$7 million study to collect data for regional air quality models used to design ozone attainment strategies and to resolve intra-regional air pollution transport issues. The study assembled a comprehensive network of instruments to measure both ground-level and upper-air meteorological and air quality data.

This report describes the results of measuring volatile organic compounds (VOCs) during the intensive operating periods (IOPs) of SCOS97-NARSTO. These measurements are part of the overall VOC measurement campaign performed in support of the study. The results discussed in this report will be added to the other data collected during the study to provide a comprehensive database for modeling and data analysis.

The collection effort was coordinated by Mr. Dennis Fitz, while the analyses were performed under the direction of Dr. Rei Rasmussen and Dr. Kochy Fung. Carbonyl samples were collected using sorbent cartridges coated with dinitrophenylhydrazine while SUMMA[®] polished stainless steel canisters were used to collect samples for other VOC analyses. Carbonyl concentrations were determined by analyzing the extracts from the cartridges by high-performance liquid chromatography (HPLC). VOC concentrations were measured by gas chromatography (GC). Samples were collected from two aircraft platforms (UC Davis and STI) and three ground-based sites (Azusa, Los Angeles Civic Center at the Department of Water and Power, and Los Angeles downtown at the top of the ARCO Tower).

Samples at the ground sites were collected for three-hour periods, four times a day, for each of the thirteen IOP days, resulting in the collection of 156 samples. The aircraft operated on different and varying schedules, although generally during IOP days. They collected 155 samples. Overall data capture was over 95%. In addition, blanks, collocated samples, and audit samples were collected and analyzed. Analysis data from the laboratory were combined with those from field sampling to compile the results in concentration units. The data were then validated. Examples of the data are shown by reporting formaldehyde and total non-methane hydrocarbon concentrations for each sample. The full data set has been submitted to the ARB in electronic format.

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Glossary

ARB.....	California Air Resources Board
CE-CERT	College of Engineering-Center for Environmental Research and Technology at the University of California, Riverside
CV	Coefficient of variation
DNPH	2,4-dinitrophenylhydrazine
DOAS	Differential optical absorption spectrometer
FT-IR	Fourier transform infrared
GC	Gas chromatography
HPLC.....	High-performance liquid chromatography
IOP	Intensive Operation Period
NIST	National Institute of Standards and Technology
OD	Outside diameter
QC	Quality control
SCAQMD.....	South Coast Air Quality Management District
SCOS97-NARSTO.....	1997 Southern California Oxidant Study-National Research Strategy for Tropospheric Ozone
STI.....	Sonoma Technology, Inc.
TDLAS	Tunable diode laser spectrometer
TNMHC	Total non-methane hydrocarbons
UCD	University of California, Davis

1. Introduction

1.1 Background and Statement of the Problem

Photochemical models are used to assist air pollution control agencies in adopting effective ozone control strategies. These models use meteorological data in addition to the concentrations of ozone precursors such as nitrogen oxides (NO_x) and volatile organic compounds (VOC) to simulate the production of ozone in an airshed. To improve the data base within the South Coast Air Basin (SoCAB), a comprehensive measurement study of ozone precursor concentrations and regional meteorology was conducted during the summer of 1997. Sponsored by a number of entities, this study is called the 1997 Southern California Oxidant Study-North American Research Strategy for Tropospheric Ozone (SCOS97-NARSTO). This study was planned to have fifteen intensive operational periods (IOPs), which would result in the collection of detailed information needed for photochemical simulation models. During this time meteorological parameters and ozone precursor concentrations were determined at many locations for which data are not routinely available. These locations were both ground and upper-air-based.

While speciated hydrocarbon data have long been recognized as essential to the running of these models, recent photochemical mechanism efforts have described the need for speciated carbonyl measurements as well (Carter et al., 1986; Lurmann et al., 1987). The amount and composition of both hydrocarbons and carbonyls strongly influence the rate of NO_x oxidation and ozone formation in the atmosphere (Grosjean and Fung, 1984).

In an urban environment, the main sources of these carbonyl compounds are direct emissions from automotive and stationary sources as a result of incomplete combustion, and photochemical oxidation of hydrocarbons in the atmosphere. Biogenic emissions occur from vegetation, landfills, or refuse. Industrial emissions come from manufacturing and use of these compounds. The levels of hydrocarbons and carbonyl compounds in the atmosphere have declined because of advancements in emission control technologies for automotive and stationary sources, the shrinking population of older automobiles, and recent introduction of reformulated gasoline (Fung, 1996).

Recent air quality studies such as those in California (Sacramento 1989 and 1990, San Joaquin Valley, 1990), Texas (Gulf of Mexico/COAST, 1993) and the NARSTO-NE (1995, 1996) all indicated that ozone and carbonyl compounds are formed and transported aloft. With the large uncertainties in emission inventory, measurement of hydrocarbons and carbonyl compounds, both on the ground and aloft, are important in supporting modeling efforts on better understanding and prediction of ozone formation and transport in the atmosphere.

1.2 Objectives and Scope of Work

The objective of this study was to collect samples during the IOP days of SCOS97-NARSTO and analyze them for VOC ozone precursors. Samples were collected at three ground-based sites and on two aircraft measurement platforms. The sampling schedule provided for the collection of four samples per IOP at each ground-based site and six samples per IOP for each of the two

aircraft. QC samples, which include blanks, collocated samples, duplicate analyses and audit samples were also analyzed.

Samples were collected for carbonyls using a sorbent tube coated with 2,4-dinitrophenylhydrazine (DNPH). After extraction, the eluent was assayed for carbonyls by measuring the concentration of the associated hydrazone by high performance liquid chromatography (HPLC). The measurement uncertainty, based on typical ambient concentrations, is expected to be less than 1.0 ppb. Samples for the measurement of other gaseous components were collected in SUMMA[®] passivated stainless steel canisters. These were analyzed for the following components:

- Speciated hydrocarbons (including methyl t-butyl ether) by high resolution gas chromatography with flame ionization detection (uncertainty less than ± 1.0 ppb).
- Methane and carbon monoxide and carbon dioxide by gas chromatography with FID analysis after methanation (uncertainty less than ± 10 ppb for methane and carbon monoxide; less than ± 3 ppm for carbon dioxide).

2. Approach

The approach was to collect samples during IOP days at three ground locations and from two aircraft. For the ground sites, which were operated by CE-CERT staff, samples were collected automatically four times per day (PDT):

0300-0600
0600-0900
1300-1600
1700-2000

Two aircraft were contracted by the ARB to collect samples. One, operated by UC Davis, was stationed at the El Monte Airport and collected samples above Azusa (AZSA) and El Monte (EMT). The other aircraft was operated by Sonoma Technology, Inc. (STI) and was stationed at Camarillo. It collected samples at numerous locations in the South Coast Air Basin as summarized below:

BNG Banning Airport
DP..... Dana Point
HESL Hesperia Profiler Site
L00 Rosamond Airport
M3 Overwater Location
M4 Overwater Location
M5 Overwater Location
M6 Overwater Location
M8 Overwater Location
MAL Offshore Malibu

OCL6..... Bohunk's Airport (private)
RAL..... Riverside Airport
SIM..... Simi Valley
VNY Van Nuys

Carbonyl samples were collected in Tedlar bags by the flight crew, and sampled with a DNPH cartridge by CE-CERT staff immediately after landing. On long flights, samples collected by the STI aircraft were dropped off at the Riverside Airport to minimize the amount of time between collection in the bag and sampling with the DNPH cartridge.

2.1 Ground Measurement Sites

- Azusa: 725 Loren St. (AZSA)

This is a South Coast Air Quality Management District (SCAQMD) air monitoring site and is located in a small converted house. Sampling lines were placed through a window on the north side of the building, with the inlet approximately at roof level.

- Downtown Los Angeles: 1830 North Main Street (LANM)

This is also a SCAQMD air monitoring site and is located on the second floor of Building 2 of the Los Angeles Department of Water and Power. Sampling lines were extended from the window on the south side of this building.

- Downtown Los Angeles: 515 South Flower Street (ARCO)

This sampling location was on the 52nd floor of the ARCO Tower. This level houses the air handling system and is located immediately below the roof. Quarter-inch Teflon sampling lines were placed through a louver on the northwest side of the building.

2.2 VOC Measurement

2.2.1 VOC Collection

Samples were collected using stainless steel canisters which had been internally electropolished by the SUMMA[®] process. Ground samples used a 6L canister. Aircraft canisters had a capacity of 3.2L. Each canister was individually cleaned and then certified to contain a background hydrocarbon concentration of less than 1 $\mu\text{g}/\text{m}^3$. Canisters were cleaned by evacuating to less than 10 mTorr and then filling with humidified zero grade air and heating to 155 °C for 24 hours. After cooling, the air within the canister was analyzed for total hydrocarbons using EPA method TO12 (Winberry et al., 1984). If this air, which has been exposed to this high temperature for over twenty-four hours, contained more than 20 ppbC, the process was repeated.

Samples were collected by means of an automated, constant flow sampler shown in Figure 2-1. The essential components include:

- A specially-cleaned Veriflo[™] model 423 mechanical flow regulator.

- A dump cross to maintain a constant 20 psig upstream pressure.
- A Magnalatch solenoid to minimize the outgassing of contaminants from the solenoid valve face seal by shutting off electrical power to the solenoid to eliminate heating.
- A purge tee assembly on the canister to insure proper flushing of the plumbing and to monitor initial and final canister pressure.
- A Chronotrol™ timer for automated operation.
- An ultra-clean stainless steel, Teflon™-faced diaphragm pump.
- A power supply to allow operation on 12 VDC or 110 VAC electric current.

Two samplers were installed at each ground-based site to allow sequential, unattended collection. Aircraft samplers were operated in the manual mode. Filling the aircraft samplers required a short time interval because of the need for precise location and altitude information at the time of sampling.

2.2.2 VOC Analysis

The concentrations of speciated hydrocarbons were determined by procedures similar to those of EPA method TO-14 (Winberry et al., 1984). Figure 2-2 shows a typical gas chromatographic flame ionization (GC-FID) analysis of ambient air. We have positively identified all 134 species listed by combined gas chromatography-mass spectrometry (GC-MS). A few compounds at low concentration still are not identified despite our positive identification of 738 ambient air pollutants by GC-MS. GC-MS analyses was used in this program as a quality control check for positive species identification.

The precision of the method depends on the concentration of hydrocarbons. At concentrations expected during the SCOS97-NARSTO study (50-400 ppbC total non-methane hydrocarbon) we have observed an overall precision, based on years of QC analyses, of 2 to 20 percent. The accuracy of the hydrocarbon speciation method is dependent on the 3 percent uncertainty of the NIST primary standard. Accuracy is verified on a routine basis by systems and performance audits performed through the Quality Assurance and Technical Support Division of the Environmental Protection Agency. Additional performance audits for the PAMS program and the NARSTO-NE studies also have been conducted successfully.

Each of our hydrocarbon speciation GCs has matched columns, so two analyses were obtained during a single temperature run. Six samples per day normally were analyzed. While a computer was used for peak integration, each chromatogram was visually inspected and processed manually to assure that the concentrations reported were correct.

Figure 2-1. Automated VOC Canister Sampler.

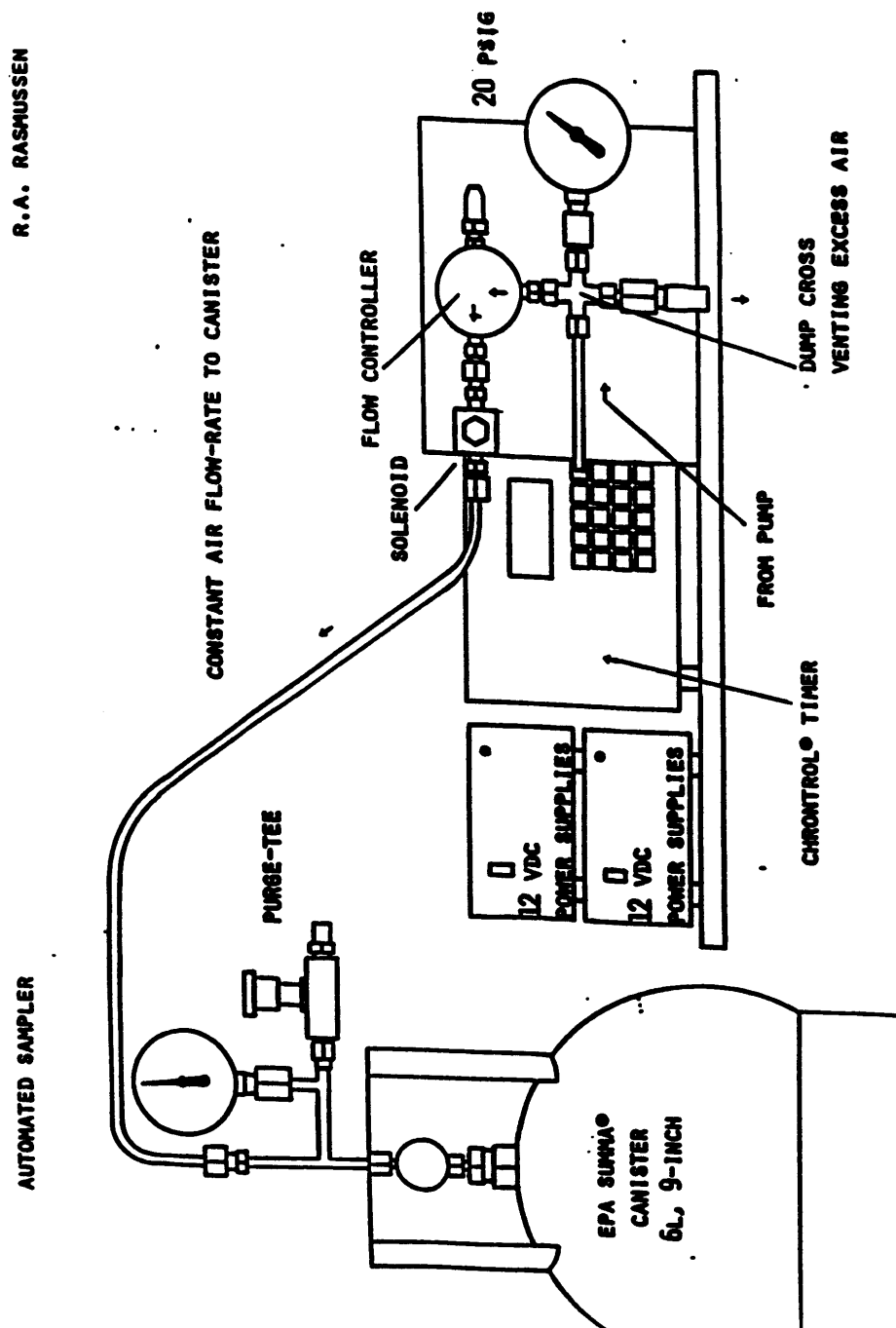
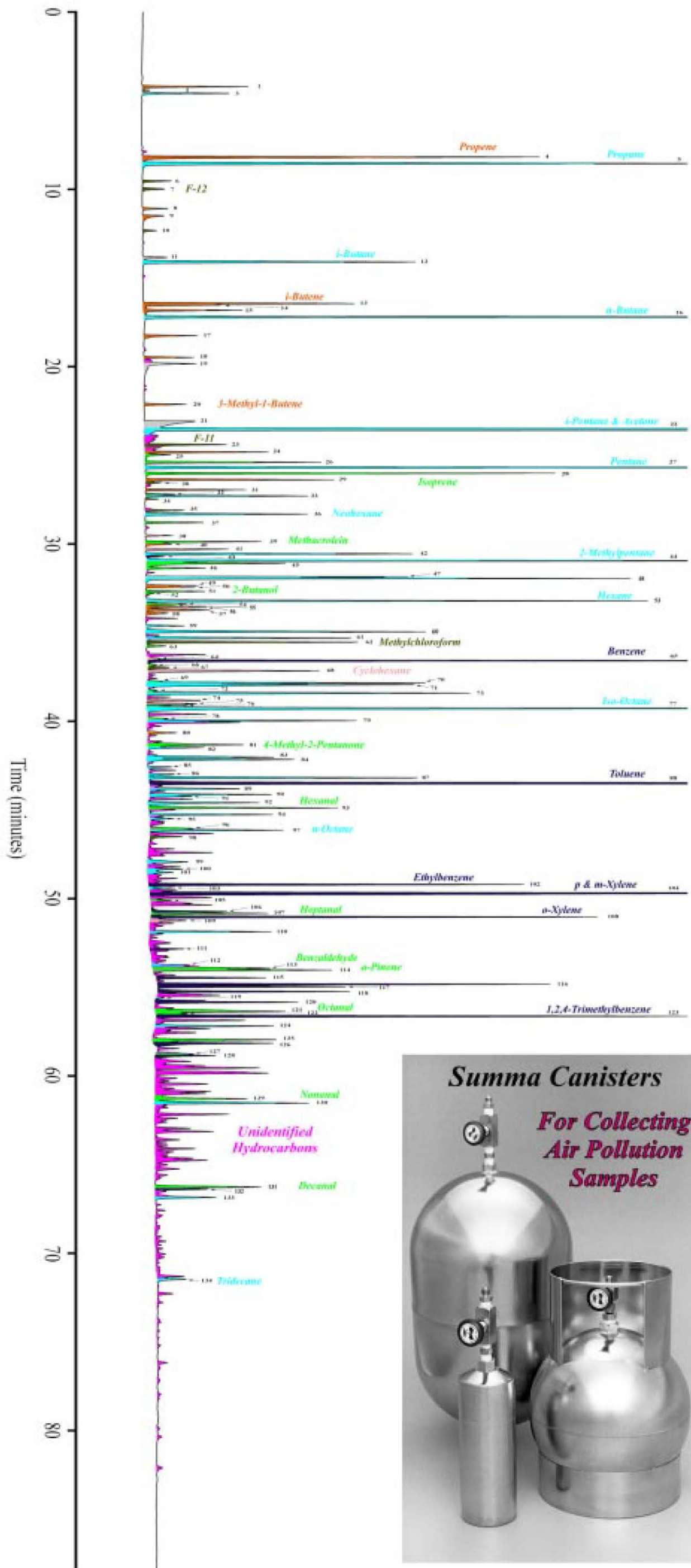


Figure 2-2. Gas Chromatographic Flame Ionization Analysis of Ambient Air.

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#	Compound
1	Butylene
2	Acetylene
3	Ethane
4	Propene
5	Propane
6	F-12
7	F-11
8	Propadiene
9	Propyne
10	CH ₄

#	Compound
11	Toluene by-product
12	i-Butane
13	i-Butane
14	i-Butane
15	i-Butane
16	i-Butane
17	n-Butane
18	n-Butane
19	Toluene by-product
20	3-Methyl-1-Butene

#	Compound
21	1-Ethanol & Acetone
22	i-Pentane & Acetone
23	F-11
24	i-Pentane
25	Pentane
26	2-Pentanol & 3-Methyl-2-Butene
27	Pentane
28	Isoprene
29	n-2-Pentene

#	Compound
30	CH ₄ CCl ₃
31	n-2-Pentene
32	CH ₄ CCl ₃
33	2-Methyl-2-Butene
34	1,3-Pentadiene
35	F-113
36	Neohexane
37	2-Methylpropanol
38	Cyclopentane
39	Methanediol

#	Compound
40	1,3-Methyl-1-Pentene
41	Cyclopentane
42	2,3-Dimethylbutane
43	MIBK
44	2-Methylpropanol
45	Butanol
46	2-Butanol
47	Toluene by-product
48	3-Methylpropanol
49	2-Methyl-1-Pentene

#	Compound
50	1-Ethanol
51	2-Butanol
52	3-Methyl-1-Pentene
53	Hexane
54	Ethyl Acetate & CHCl ₃
55	n-2-Hexene
56	n-2-Pentene
57	n-2-Methyl-1-Pentene
58	n-2-Hexene
59	2,3-Dimethylpropanol

#	Compound
60	Methylcyclopentane
61	2,4-Dimethylpropanol
62	CH ₄ CCl ₃
63	3-Methyl-1-Pentene
64	Methylcyclopentane
65	Butanol
66	1-Butanol
67	CCl ₄
68	Cyclohexane
69	2-Pentanol

#	Compound
70	3-Methyl-1-Pentene
71	2,3-Dimethylpropanol
72	Butanol
73	3-Methyl-1-Pentene
74	n-2,3-Dimethylcyclopentane
75	n-2,3-Dimethylcyclopentane
76	CCl ₄
77	2,3-Dimethylpropanol
78	Propylacetate
79	n-Heptane

#	Compound
80	2,3,4-Trimethyl-1-Pentene
81	4-Methyl-1-Pentene
82	Methylcyclohexane
83	2,3-Dimethylpropanol
84	2,4-Dimethylpropanol
85	1,2,4-Trimethylcyclopentane
86	1,2,3-Trimethylcyclopentane
87	2,3,4-Trimethylpropanol
88	Toluene
89	2,3-Dimethylpropanol

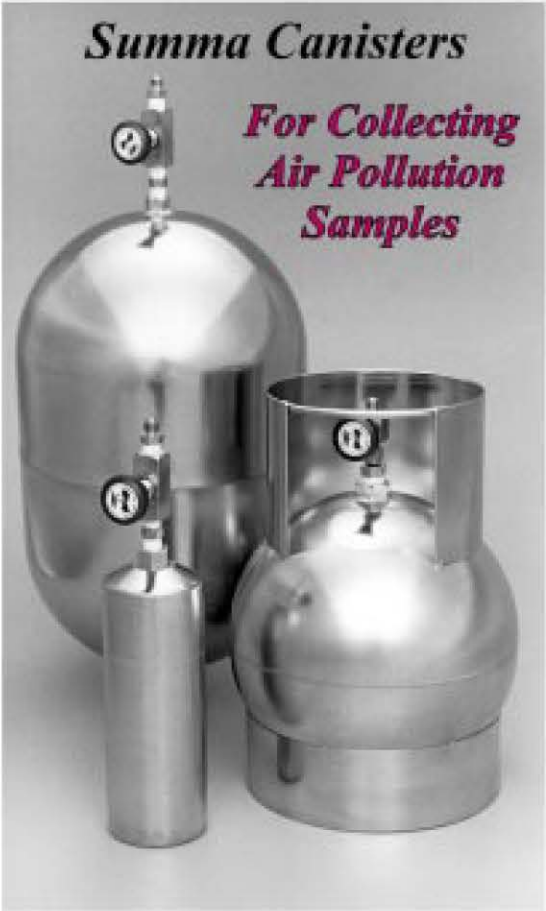
#	Compound
90	2-Methyl-1-Pentene
91	4-Methyl-1-Pentene
92	3-Ethyl-1-Pentene
93	Hexanol
94	1,4-Dimethylcyclopentane
95	2,3,4-Trimethylpropanol
96	Ethylacetate
97	n-Octane
98	PCB
99	2,4-Dimethylpropanol

#	Compound
100	Ethylcyclohexane
101	1,2,3-Trimethylcyclopentane
102	Ethylbenzene
103	1,2,4-Trimethylcyclopentane
104	p & m-Xylene
105	Heptanol
106	Heptanol
107	Heptanol
108	n-Xylene
109	n-2-Ethyl-1-Methylcyclopentane
110	Nonane

#	Compound
111	1-Propyl-1-Pentene
112	2,4-Dimethylpropanol
113	Benzoaldehyde
114	n-Pentane
115	n-Propyl-1-Pentene
116	p-Ethylbenzene
117	n-Ethylbenzene
118	1,3,5-Trimethylbenzene
119	3-Methylbenzene

#	Compound
120	n-Ethylbenzene
121	Octanol
122	n-Pentane
123	1,2,4-Trimethylbenzene
124	n-Decane
125	2-Ethyl-1-Pentene
126	1,2,3-Trimethylbenzene & p-Cresol
127	4-Decanol
128	Isobutane
129	Nonanol
130	Undecane

#	Compound
131	Decanol
132	Naphthalene
133	Decane
134	Toluene



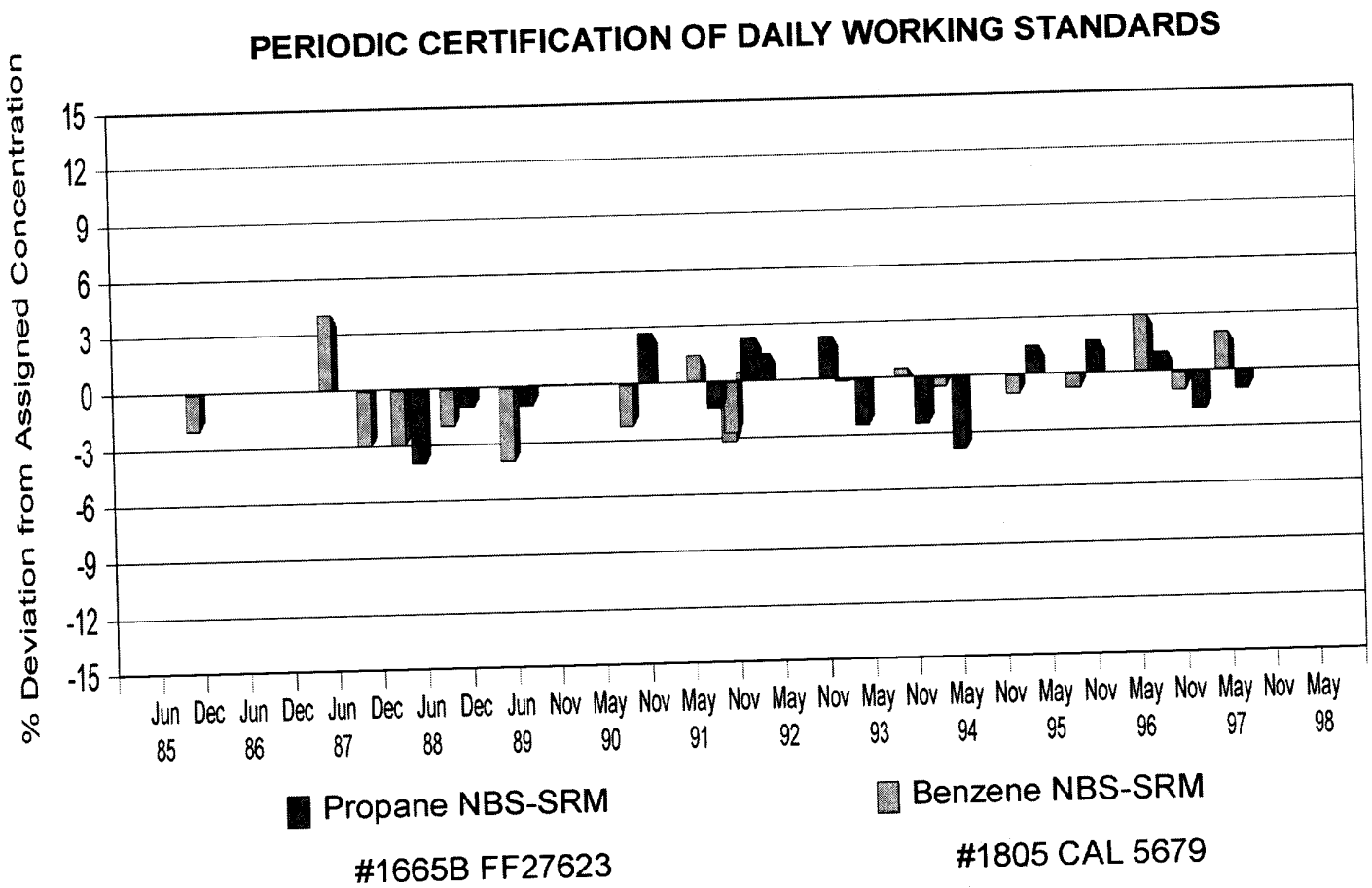
Canisters were analyzed within 5-7 days after sample collection. We have found no significant loss of most species using this holding time. Analysis of speciated hydrocarbons was made with a Hewlett-Packard model 5890A gas chromatograph equipped with a flame ionization detector and a J&W DB-1 60 m fused silica column. 500ml of sample was loaded into a trap consisting of a six-inch length of 1/8-inch OD stainless steel tubing maintained at liquid oxygen temperature. The trap was then warmed to 90 °C with hot water and contents collected at the head of the column maintained at - 60 °C for cryo-focusing. The temperature was then ramped up to 200 °C at 4C/min. Peak area data was compiled by a HP model 3396A integrator. Table 2-1 is a compilation of the species and classes of compounds we reported for each analysis. Other significant peaks were identified and reported when observed.

Table 2-1. Species and Classes of Compounds Reported from VOC Analysis.

Ethane	cis-4-Methyl-2-pentane	2-Methylheptane
Ethylene	Methylpentane	3-Ethylhexane
Acetylene	3-Methylpentane	2,2-Dimethylheptane
Propane	2-Methyl-1-pentene	2,2,4-Trimethylhexane
Propene	1-Hexene	n-Octane
i-Butane	n-Hexane	Ethylcyclohexane
i-Butene	trans-2-Hexene	Ethylbenzene
1,3-Butadiene	2-Methyl-2-pentene	M-Xylene&p-Xylene
n-Butane	cis-2-Hexene	Styrene
trans-2-Butene	Methylcyclopentane	o-Xylene
2,2-Dimethylpropane	2,4-Dimethylpentane	n-Nonane
cis-2-Butene	Benzene	i-Propylbenzene
3-Methyl-1-butene	Cyclohexane	n-Propylbenzene
i-Pentane	2-Methylhexane	p-Ethyltoluene
1-Pentene	2,3-Dimethylpentane	m-Ethyltoluene
2-Methyl-1-butene	3-Methylhexane	1,3,5-Trimethylbenzene
n-Pentane	2,2,4-Trimethylpentane	o-Ethyltoluene
Isoprene	n-Heptane	1,2,4-Trimethylbenzene &
trans-2-Pentene	2,4,4-Trimethyl-1-pentene	sec-Butylbenzene
cis-2-Pentene	Methylcyclohexane	n-Decane
2-Methyl-2-butene	2,4,4-Trimethyl-2-pentene	alpha-Pinene
2,2-Dimethylbutane	2,5-Dimethylhexane	beta-Pinene
Cyclopentene	2,4-Dimethylhexane	delta3-Carene
4-Methyl-1-pentene	2,3,4-Trimethylpentane	d-Limonene
Cyclopentane	Toluene	MTBE
2,3-Dimethylbutane	2,3-Dimethylhexane	ETBE

The primary standard was an NIST Standard Reference Material of 0.254 ppmv benzene, which is compared to a neohexane working standard weekly. The average of three analyses of a 0.220 ppmv secondary working standard was used to quantify daily GC response. Linearity of the detector response was routinely verified in the 0.1 to 10 ppbV range. Routine QC comparisons of the working and primary standards over the past ten years have shown agreement to within 3 percent with no drift. This is illustrated in Figure 2-3.

Figure 2-3. Long-Term Deviation between Working and Primary Standards.



Peaks were identified by retention time and relative retention times to propane and/or benzene. GC-MS was used quarterly or as needed to confirm peak identity with retention times.

The lower limit of detection for hydrocarbon speciation was $0.05 \mu\text{g}/\text{m}^3$, although concentrations below $0.1 \mu\text{g}/\text{m}^3$ were not reported. The sensitivity was determined daily during the morning start-up analyses for system blanks, column artifact peaks, calibration response factors, retention time checks, and stability tests of the FID. Figure 2-4 illustrates the precision based on replicate samples as a function of concentration. Four-point linearity checks are conducted on a weekly to biweekly schedule.

The C_1 compounds (methane, carbon monoxide, and carbon dioxide) were quantified by gas chromatographic separation on 1/8-inch OD packed columns (silica gel 60/80 for CO_2 , molecular sieve 5A 80/100 for CH_4 and CO), followed by methanization (Ni catalyzed at 390°C) and FID detection. The primary calibration is a NIST cylinder of carbon monoxide.

2.3 Carbonyl Measurement

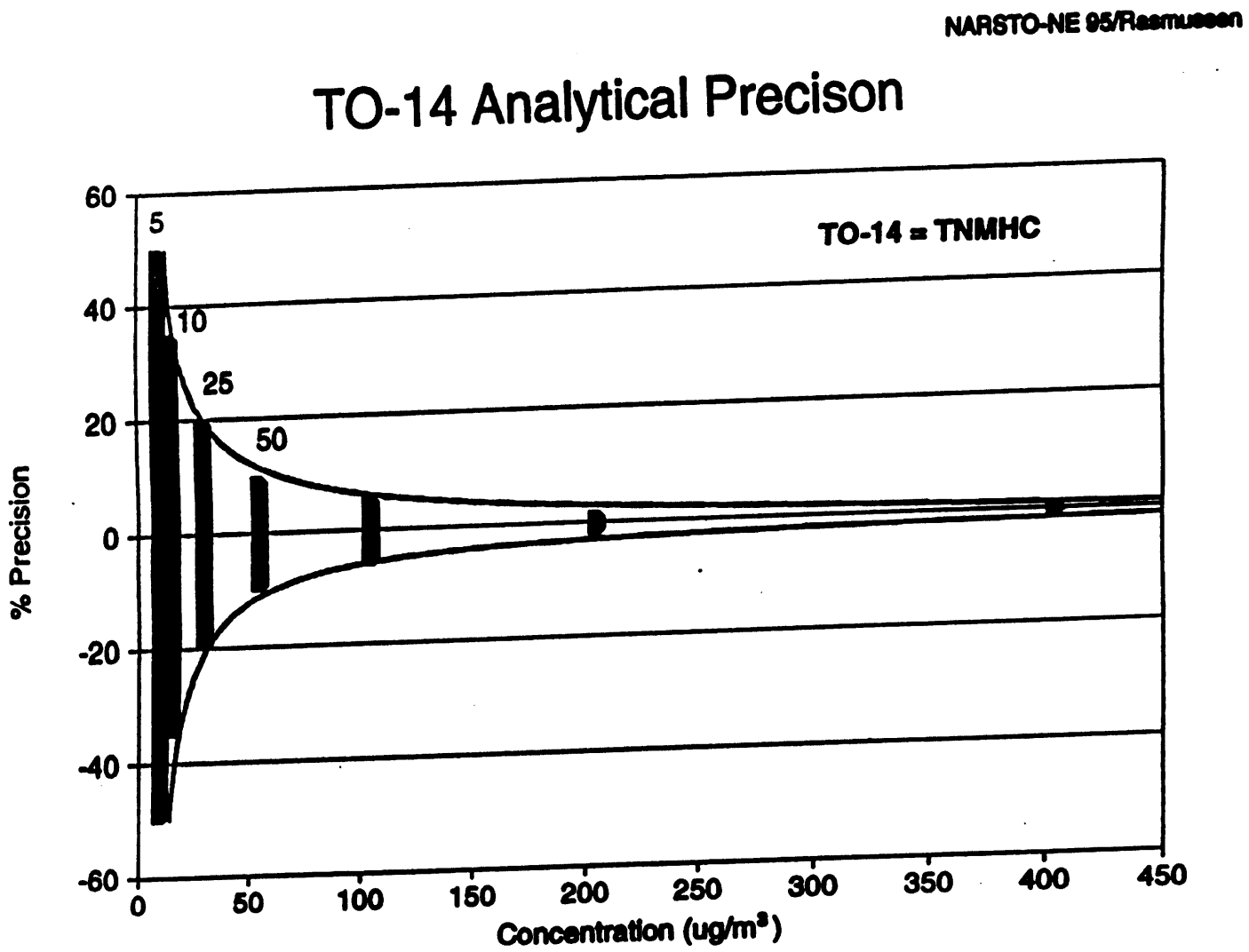
The measurement technique used in this study is a variant of EPA Method TO-11 for carbonyls in which the DNPH is impregnated on silica Sep-Pak cartridges. Our procedure used C18 Sep-Pak cartridges (Waters/Millipore Corp., Milford, MA) which have been impregnated with acidified 2,4-dinitrophenylhydrazine (DNPH) reagent for ambient sampling. The amounts of both the hydrazine and acid were optimized to achieve efficient collection of the carbonyl compounds and protection from ozone destruction of the captured carbonyl derivative. When ambient air is drawn through the cartridge, carbonyls in the air sample are captured by reacting with DNPH to form hydrazones, which are extracted and then separated and quantified using HPLC (Fung and Grosjean 1981). It has been shown that the silica cartridge when used alone has severe negative ozone artifact, and that this method measured carbonyls comparably to the silica method with an ozone removal device.

This method has been intercompared and validated against long-path spectroscopic methods, including an FT-IR, a differential optical absorption spectrometer (DOAS), and a tunable diode laser spectrometer (TDLAS) in the 1986 Carbonaceous Species Methods Comparison Study (CSMCS) in Glendora, CA (Fung and Wright, 1990; Lawson et al., 1990). During September, 1993, Fung's C18 DNPH cartridges again demonstrated good agreement on formaldehyde, with the TDLAS at ozone levels reaching as high as 250 ppb in the CARB-sponsored Los Angeles Atmospheric Free-Radical Experiment conducted at Claremont, CA (Fung, 1993).

2.3.1 Carbonyl Collection

The sampling equipment was leak-tested and calibrated prior to the delivery to the field. A standard operating procedure was provided to the site operators for reference. Samplers were recalibrated after the program to determine whether any significant change in the flow rates had occurred. The average of the pre- and post-study flow rates were used to determine the sample volume. Variability was well within the $\pm 5\%$ specification of the flow controller.

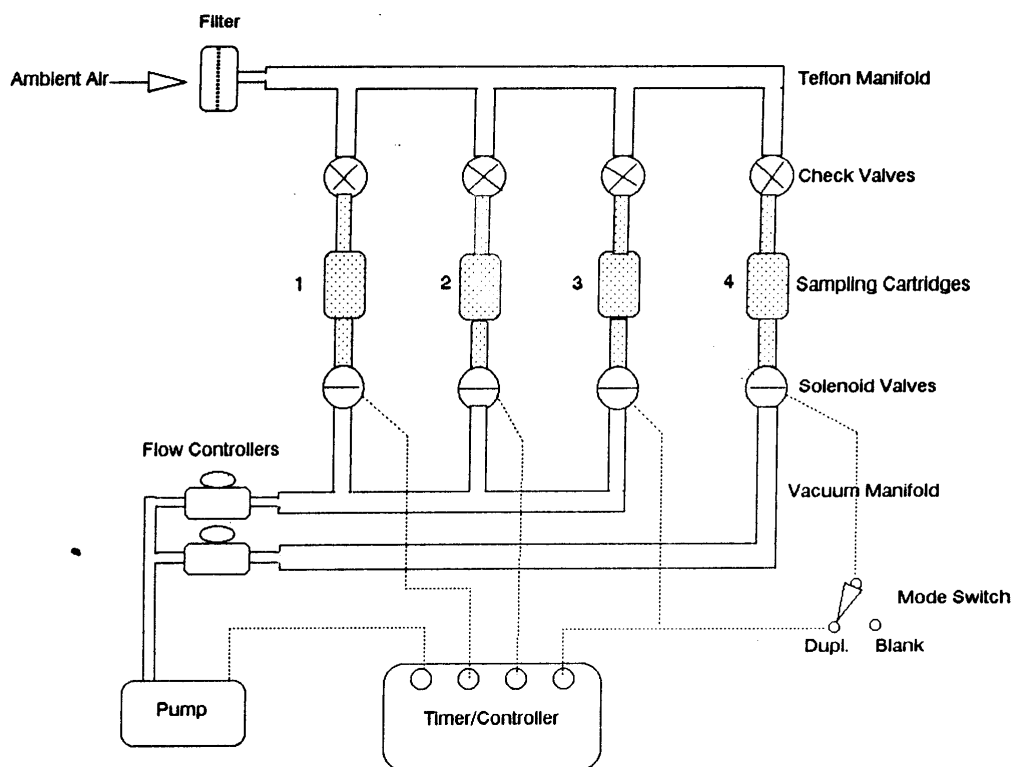
Figure 2-4. Analytical Precision Determined from Replicate Sampling



- **Ground Sampling**

Cartridge samples were taken using an automated sampler with six active channels to collect samples sequentially on an event basis. An additional channel was used for taking either a duplicate sample concurrently with one of the active channels, or a field blank. This 7-channel unit is essentially an extension of the 4-channel sampler shown in Figure 2-5.

Figure 2-5. Schematic Diagram of Automated Carbonyl Sampler



Since cartridges will naturally sorb carbonyl compounds from the surrounding air if left open, the sampler has been designed such that cartridges loaded into the sampler are isolated from the environment and from each other by check valves upstream and solenoid valves downstream. Programmable timers with memory protection were used to control the operation of the pump and the solenoid valves according to the prescribed schedule. The duplicate samples were collected on a collocated cartridge by activating a parallel channel simultaneously. A mode selection switch was used to deactivate the parallel channel for field blank collection. Sampling flow rates were controlled at ~0.8 L/min to within $\pm 5\%$ or less using a differential flow controller, which compensates for changes in flow resistance from cartridge to cartridge. Tandem cartridges for assessment of breakthrough were collected at Azusa.

Cartridges, fresh or exposed, were placed in metal containers and shipped in coolers via next-day air. They were stored in the refrigerator prior to analysis.

- **Aircraft Sampling**

Upper-air samples were collected from the STI aircraft by directly ramming air (without using any pump) through a Teflon inlet tube into a pre-cleaned 40 L Tedlar bag that had been doped with sufficient NO to react with any O₃ in the air sample. A similar procedure was used for the UC Davis aircraft except that due to the long sampling line, a pump and needle valve were used to fill the bag. The stainless steel bag valves have been specially modified to permit rapid filling, and all rubber seals replaced with inert Viton parts.

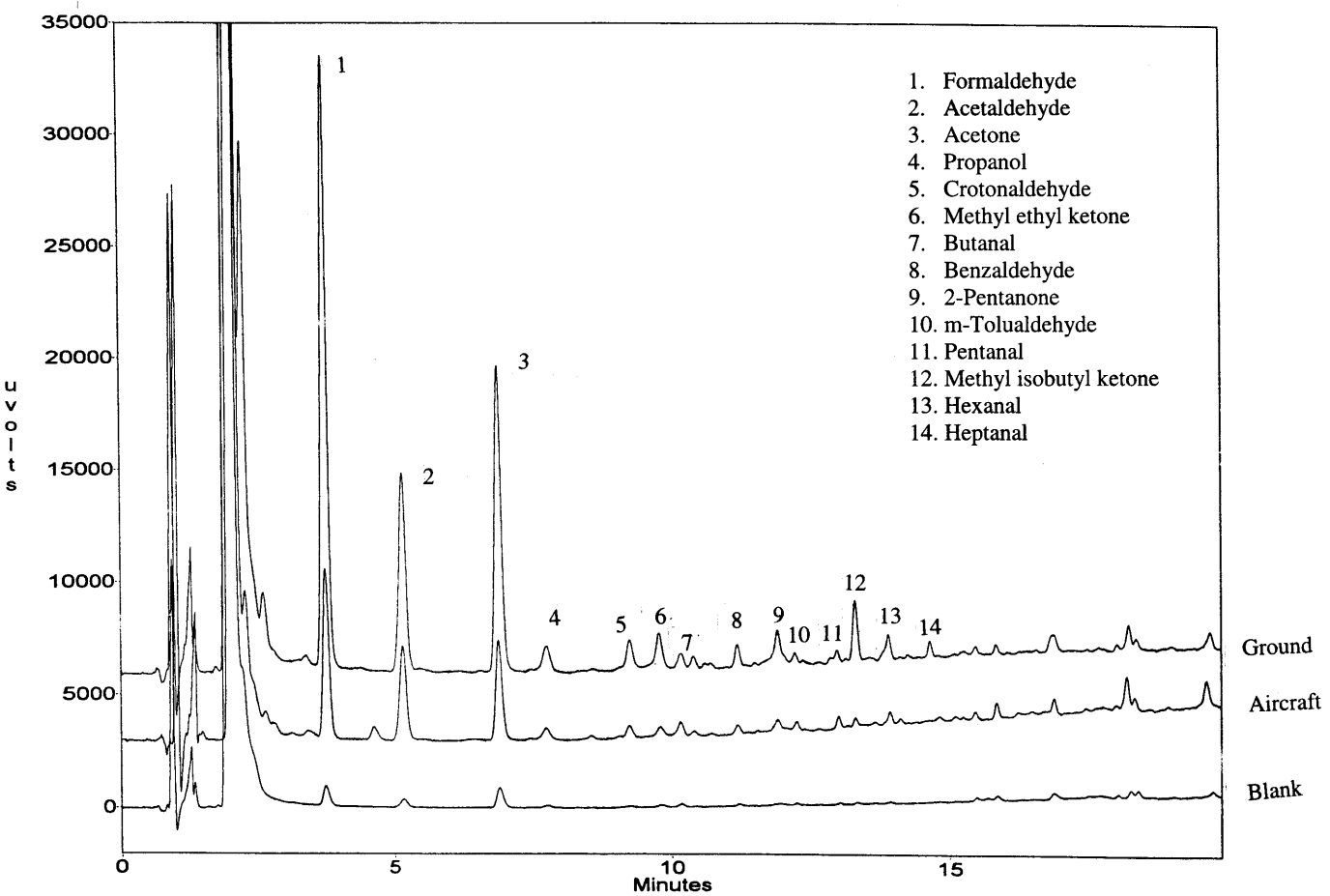
The samples were shielded from light and, upon returning to the base, transferred through C18-DNPH cartridges to capture the carbonyls. For the UCD aircraft, this was done at the end of each flight. For the longer flights performed by the STI aircraft, bag samples were retrieved at the Riverside Airport halfway through the flight. The bags collected during the remainder of the flight were sampled at the Camarillo home base.

Exposed cartridges were sealed in vials and placed in steel cans. They were kept in a refrigerator and returned in a cooler to the laboratory, where they were stored under refrigeration until analyzed.

2.3.2 Carbonyl Analysis

Samples were analyzed in batches of approximately 20 to 40. The cartridges were eluted with acetonitrile. An aliquot of the eluent was transferred into a 2-ml septum vial and injected with an autosampler into a high performance liquid chromatograph (Shimadzu LC-6) for separation and quantification of the hydrazones (Fung and Grosjean, 1981). The samples were analyzed for nine individual species: formaldehyde, acetaldehyde, acetone, propanal, crotonaldehyde, methylethyl ketone, butyraldehyde, benzaldehyde, and m-tolualdehyde, plus C₅, C₆ and >C₆ aliphatic carbonyls. C₅, C₆, and >C₆ aliphatic carbonyls are usually measurable but lower in concentrations compared with the C₁-C₄ carbonyls. Except for the straight chain aldehydes (e.g. pentanal, hexanal, etc.), resolution of the other isomers of C₅ and higher carbonyls is incomplete, and thus inaccurate. They are more appropriately reported as a group by carbon number. Figure 2-6 is an example of the analysis of carbonyls in the South Coast Air Basin.

Figure 2-6. Typical HDLC Carbonyl Analysis of Two Ambient Samples Compared with a Field Blank



The carbonyl concentrations, in ppb, were computed from the amounts measured after blank correction and the volume of air sampled using the following equation:

$$\text{ppb}_i = \frac{m_i - b_i}{f \times t} \times 1000 \times \frac{24.45}{\text{MW}_i} \quad (1)$$

where ppb_i = concentration in ppb is carbonyl species, i ,

m_i = μg of i measured in the sample,

b_i = average μg of i in the blank,

t = sampling duration, in minutes,

f = sampling flow rate, in L/min,

MW_i = molecular weight of i .

DNPH cartridges were prepared from a single batch of pre-purified DNPH (~99.9996%) reagent and analyzed to confirm that the carbonyl background were within acceptable limits. The cartridges were sealed and kept individually inside screw-capped vials to prevent contamination. Approximately 20 of these cartridges were packaged in sealed metal cans for storage in a refrigerator and shipment to the field via courier. Exposed cartridges were returned by courier in a cooler chilled with blue ice.

Field blanks, duplicate samples, and tandem cartridges were collected. Quality control measures in the laboratory include instrument calibration for each batch of samples, replicates of standards, and reanalysis of approximately 10% of the samples for estimation of analytical precision.

Field blank variability establishes the LQL (lower quantifiable limit), which for C_1 - C_7 carbonyls is typically 0.5 ppb or lower (at 3 times standard deviation of the blank variability).

Accuracy of this method is approximately within $\pm 15\%$ for formaldehyde based on comparison studies with long path spectroscopic techniques in an ambient air setting (Fung and Wright, 1990; Lawson et al., 1990). Since the basic chemistry of the DNPH method is the same for all carbonyls, the accuracy for higher carbonyls are expected to be in the same range.

2.4 Data Reduction and Validation

Data for VOCs and carbonyls were reported to CE-CERT in terms of ambient concentrations (ppbV for carbonyls, ppbC for VOCs). Data reduction for VOCs and carbonyls at CE-CERT consisted of the following:

- Key punching field data such as sample end times, sample status data, aircraft identifications, flight altitude ranges, etc. not already included in the data set.
- Calculation of sample duration from sample begin and end times.
- Calculation and assignment of absolute precisions to each data value.

- Correction of incorrectly calculated and reported carbonyl data.
- Reformatting the data to meet SCOS97-NARSTO database submission requirements including assignment of correct SCOS97-NARSTO codes for source, site, aircraft, measurement device, and parameter.
- Assignment of QC codes after data validation.

Data validation for VOCs and carbonyls included three types of activities:

- Verification of sample data entry against log sheet data.
- Verification of sampling data against QC criteria.
- Screening of sample concentrations for unusual or suspicious data.

2.4.1 VOC Data

VOC analytical results were reported referenced by sample can number. For each VOC sample can, the following data entries were checked against field log sheet entries:

- Sampling site.
- Sample date.
- Sample start time.
- Sample end time.
- Aircraft ID.
- Aircraft sampling location.
- Aircraft altitude ranges.

Based on information provided by Biospherics, absolute precisions were calculated using the larger of 0.1 ppb or 10% of sample concentration. Later review of duplicate data suggests that these precisions are very conservative for higher concentration species and could be tightened considerably should the need arise.

QC flags were applied to the data in the following situations:

- Missing data: sample location data, sample date, start time, end time, starting can pressure, or final can pressure.
- Sample duration less than 75% of designated.
- Final can pressure < 0 psig, missing, or ambiguous.

Data from replicate analyses and from duplicate sample cans were examined to assess the adequacy of stated precisions.

We examined plots of concentration versus time and plots of concentration versus species name at each ground site and for the aircraft data. Potential outliers were identified and flagged in the database.

2.4.2 Carbonyl Data

Carbonyl analytical results were reported referenced by cartridge number. For each carbonyl cartridge, the following data entries were checked against field log sheet entries:

- Sampling site.
- Sample date.
- Sample start time.
- Sample end time.
- Sample QC flag: blank, duplicate, tandem, problem.
- Aircraft ID.
- Aircraft sampling location.
- Aircraft altitude ranges.

Carbonyl concentrations for crotonaldehyde and higher carbon number species were reported incorrectly due an analytical laboratory calculation that employed incorrect molecular weights. These data were corrected using a correction factor for each species.

Based on information provided by Atmoslytics, absolute precisions were calculated using the larger of $\sqrt{2}$ *standard deviation of the blanks or 5% of sample concentration. Later review of blank data and replicate analysis data suggested that these precisions were somewhat conservative for higher concentration species and could be tightened should the need arise.

QC flags were applied to the data in the following situations:

- Mismatch between reported data set and field log sheets.
- Missing data: sample location data, sample date, start time, end time.
- Problem noted by analytical lab.
- Sample duration less than 75% of designated.

We examined scatter plots of each species versus formaldehyde by site for all ground-based and aircraft-based samples, and examined time series plots of concentration for each species at each ground site. Potential outliers were identified and flagged in the database.

We did not assess any data from laboratory intercomparisons and audits. Those analyses are being carried out by separate investigators under contract to the ARB.

3. Results

3.1 Data Summary

Tables 3-1 and 3-2 show results for VOC and carbonyl ground sampling. Tables 3-3 and 3-4 show results for VOC and carbonyl aircraft sampling. Table entries for the VOC results are TNMHC concentrations in ppbC for valid samples and for samples that may not be fully representative but still provide useful data. Missing or invalid data is shown by a table entry of "IS." Table entries for the carbonyl results are formaldehyde concentrations in ppbV for valid samples. Missing or invalid data is shown by a table entry of "IS," suspect data is shown by "SS".

Table 3-1. Ground Station TNMHC (ppbC).

Date	Start Time	ARCO	AZSA	LANM	Date	Start Time	ARCO	AZSA	LANM
970714	0300	176	299	119	970904	1300	214	446	274
970714	0600	283	IS	207	970904	1700	142	395	IS
970714	0910			197	970905	0300	299	343	371
970714	1300	161	249	IS	970905	0600	529	719	533
970804	0300	417	480	324	970905	1300	203	617	227
970804	0600	523	647	805	970905	1700	IS	253	247
970804	1300	198	404	441	970906	0300	252	400	255
970804	1700	IS	280	250	970906	0600	476	439	456
970805	0300	249	806	490	970906	1300	321	248	248
970805	0600	387	1013	1084	970906	1700	194	246	186
970805	1300	IS	539	1298	970928	0300	314	605	840
970805	1700	264	389	504	970928	0600	368	568	804
970806	0300	353	679	365	970928	1300	IS	349	465
970806	0600	434	971	792	970928	1700	175	437	260
970806	1300	IS	293	380	970929	0300	220	546	419
970806	1700	193	184	328	970929	0600	755	802	940
970822	0300	393	666	555	970929	1300	255	386	316
970822	0600	476	723	763	970929	1700	382	308	296
970822	1300	324	457	481	971003	0300	287	299	427
970822	1700	IS	453	297	971003	0600	IS	362	765
970823	0300	565	723	621	971003	1300	271	319	292
970823	0600	651	753	600	971003	1700	IS	309	223
970823	1300	380	248	355	971004	0300	480	478	614
970823	1700	174	294	193	971004	0600	624	240	672
970904	0300	339	728	867	971004	1300	177	358	194
970904	0600	549	627	1101	971004	1700	172	220	162

Table 3-2. Ground Station Formaldehyde (ppbV).

Date	Start Time	ARCO	AZSA	LANM	Date	Start Time	ARCO	AZSA	LANM
970714	0300	16.1	3.4	2.4	970904	1300	4.8	8.2	6.3
970714	0600	14.2	4.9	5.1	970904	1700	3.5	7.4	4.5
970714	1300	4.5	8.3	5.3	970905	0300	11.8	4.6	3.7
970714	1700	5.2	IS	4.3	970905	0600	10.9	8.6	7.2
970804	0300	18.6	6.7	6.0	970905	1300	5.2	8.2	6.9
970804	0600	16.1	9.7	10.5	970905	1700	3.6	7.7	4.6
970804	1300	5.4	9.7	5.8	970906	0300	11.1	4.5	3.8
970804	1700	4.6	5.7	4.8	970906	0600	13.8	5.8	6.0
970805	0300	8.0	IS	9.2	970906	1300	4.5	9.1	6.6
970805	0600	10.4		13.0	970906	1700	4.6	5.9	4.0
970805	0630		13.7		970928	0300	10.7	8.0	9.6
970805	1300	7.3	7.8	6.1	970928	0600	10.8	7.3	10.2
970805	1700	8.3	6.3	IS	970928	1300	12.2	9.2	9.9
970806	0300	9.6	7.0	IS	970928	1700	6.4	8.5	7.4
970806	0600	10.8	11.3	IS	970929	0300	11.4	7.3	7.6
970806	1300	9.2	8.8	IS	970929	0600	15.5	11.2	12.7
970806	1700	7.1	3.8	IS	970929	1300	5.5	9.4	8.1
970822	0300	13.5	5.5	IS	970929	1700	8.9	7.4	6.0
970822	0600	9.3	8.5	IS	971003	0300	6.0	3.9	5.3
970822	1300	7.5	9.6	9.1	971003	0600	10.0	4.7	9.9
970822	1700	5.7	10.2	6.3	971003	1300	6.0	7.6	6.7
970823	0300	11.2	6.2	6.3	971003	1700	5.1	8.0	4.9
970823	0600	12.6	9.2	7.7	971004	0300	17.8	5.3	5.5
970823	1300	7.1	6.3	9.2	971004	0600	17.4	4.5	7.4
970823	1700	3.8	6.7	5.0	971004	1300	5.5	11.2	5.1
970904	0300	7.4	8.1	8.4	971004	1700	10.2	5.3	4.0
970904	0600	9.2	9.4	12.9					

Table 3-3a. STIA Aircraft TNMHC (ppbC)

Date	Flight No	First Start	Last Start	Count	BNG	DP	EMT	HESL	L00	M3	M4	M5	M6	M8	MAL	OCL6	RAL	SIM	VNY
7/14/97	1	1210	1359	5		13.3				6.6	11.7		9.3	24.7					
8/4/97	2	0503	0813	5	25.3			21.1	29.8								217.2		58.6
8/4/97	3	1506	1506	1			43.3												
8/5/97	4	0500	0542	3			55.9								145.7				39.3
8/5/97	5	1406	1603	3	25.3			27								19.1			
8/6/97	6	0507	0551	2			103.9								80.8				IS
8/6/97	7	1357	1552	3	20.6			42.6								80.4			
8/7/97	8	0851	0931	3											19.3			174.3	86.3
8/22/97	10	1459	1459	1			285.2												
8/22/97	9	0515	0813	5	17.8			29.4	19.6								89.3		213
8/23/97	11	0457	0541	3			108.6								370.6				123.7
8/23/97	12	1402	1551	3	18.4			49								71.3			
9/3/97	13	1147	1426	6						11.4	15	18.3	13.7	25.6	32.9				
9/4/97	14	0525	0840	5	17.8			28.8	16.1								63.7		50.1
9/4/97	15	1507	1507	1			38.4												
9/5/97	16	0529	0850	4				33.6	IS								308.4		188.5
9/5/97	17	1500	1500					IS											
9/6/97	18	0515	0529	2											131.7				22.8
9/6/97	19	1504	1504	1				46.1											
9/28/97	20	0912	0934	2			21.4												30.4
9/28/97	21	1420	1515	3			126.1								112.9				39.2
9/29/97	22	0514	0557	3			31.9								188.6				75.7
9/29/97	23	1415	1501	3			307.9								31.8				170.9
10/3/97	24	0508	0827	5	74.4			27.2	21								161.5		209.9
10/3/97	25	1456	1456	1			276.3												
10/4/97	26	0503	0545	3			188.9								68.9				96
10/4/97	27	1448	1536	3			197.7								18.6				77.5

Table 3-3b. UCD Aircraft TNMHC (ppbC)

Date	Flight No.	First Start	Last Start	Count	AZSA	EMT
7/14/97	1	0732	0832	2	132	48
7/14/97	2	1348	1449	2	177	147
8/4/97	1	0451	0550	2	IS	75
8/4/97	2	1003	1103	2	127	22
8/4/97	3	1450	1556	2	60	71
8/5/97	1	0458	0608	2	47	56
8/5/97	2	1009	1117	2	40	30
8/5/97	3	1435	1542	2	166	138
8/6/97	1	0435	0546	2	75	107
8/6/97	2	1007	1115	2	190	139
8/6/97	3	1445	1552	2	155	44
8/22/97	1	0437	0551	2	89	73
8/22/97	2	1010	1116	2	134	51
8/22/97	3	1433	1550	2	354	292
8/23/97	1	0440	0551	2	127	198
8/23/97	2	1005	1108	2	183	227
8/23/97	3	1434	1541	2	213	286
9/3/97	1	0441	0546	2	110	121
9/3/97	2	1000	1106	2	220	171
9/3/97	3	1429	1535	2	129	84
9/4/97	1	0454	0557	2	76	101
9/4/97	2	1002	1107	2	119	48
9/4/97	3	1431	1535	2	126	90
9/5/97	1	0434	0538	2	143	79
9/5/97	2	1204	1308	2	248	320
9/6/97	1	0434	0541	2	120	145
9/6/97	2	1203	1317	2	134	193
9/27/97	2	1218	1321	2	209	202
9/28/97	1	0437	0541	2	47	41
9/28/97	2	1201	1304	2	176	125
9/29/97	1	0434	0541	2	80	50
9/29/97	2	1200	1306	2	248	196
10/3/97	1	0658	0803	2	101	161
10/3/97	2	1206	1311	2	168	181
10/4/97	1	0436	0540	2	184	190
10/4/97	2	1200	1306	2	373	442

Table 3-4a. STIA Aircraft Formaldehyde (ppbV)

Date	Flight No	First Start	Last Start	Count	BNG	DP	EMT	HESL	L00	M3	M4	M5	M6	M8	MAL	OCL6	RAL	SIM	VNY
970714	1	1210	1359	5		4.3				2.7	4.7		2.4	3.0					
970804	2	0503	0813	5	6.0			5.5	6.3								9.1		6.9
970804	3	1506	1506	1			3.7												
970805	4	0500	0542	3			9.7								6.6				6.7
970805	5	1406	1603	3	4.8			4.0								7.5			
970806	6	0507	0551	2			10.1								6.8				IS
970806	7	1510	1552	2	IS			7.9								11.0			
970807	8	0851	0931	3											1.9			8.8	6.0
970822	10	1459	1459	1			10.9												
970822	9	0515	0813	5	2.7			4.3	4.5								7.0		8.3
970823	11	0457	0541	3			11.7								8.9				5.1
970823	12	1402	1551	3	5.4			3.3								7.7			
970903	13	1147	1426	5						1.3	2.2	1.1	1.7	IS	2.1				
970904	14	0525	0840	5	2.1			3.2	2.4								4.9		4.0
970904	15	1507	1507	1			3.5												
970905	16	0529	0850	5	3.1			4.0	3.8								9.9		9.2
970905	17	1500	1500	1			3.4												
970906	18	0515	0529	2											4.6				2.0
970906	19	1504	1504	1				2.3											
970928	20	0912	0934	2			4.1												3.9
970928	21	1420	1515	3			8.0								8.2				4.3
970929	22	0514	0557	3			5.8								8.3				4.7
970929	23	1415	1501	3			10.1								1.8				10.8
971003	24	0556	0827	4	3.2			3.8	3.8								4.8		SS
971003	25	1456	1456	1			11.5												
971004	26	0503	0545	3			13.5								20.5				12.6
971004	27	1448	1536	3			12.0								2.8				6.8

Table 3-4b. UCD Aircraft Formaldehyde (ppbV)

Date	Flight No	First Start	Last Start	Count	AZSA	EMT
970714	1	0732	0832	2	SS	SS
970714	2	1348	1449	2	SS	SS
970804	1	0451	0550	2	SS	SS
970804	2	1003	1103	2	SS	SS
970804	3	1450	1556	2	SS	SS
970805	1	0608	0608	1	14.7	SS
970805	2	1117	1117	1	16.7	SS
970805	3	1435	1542	2	19.1	22.5
970806	1	0435	0546	2	11.9	15.0
970806	2	1007	1115	2	26.1	22.0
970806	3	1445	1552	2	11.9	14.9
970822	1	0437	0551	2	6.3	3.7
970822	2	1010	1116	2	9.9	12.5
970822	3	1433	1550	2	18.8	21.3
970823	1	0440	0551	2	9.3	10.6
970823	2	1005	1108	2	14.8	11.7
970823	3	1434	1541	2	15.6	18.6
970903	1	0441	0546	2	10.7	14.2
970903	2	1000	1106	2	10.7	16.4
970903	3	1429	1535	2	7.6	6.7
970904	1	0557	0557	1	4.8	SS
970904	2	1002	1107	2	11.5	11.5
970904	3	1431	1535	2	9.3	10.3
970905	1	0434	0538	2	7.0	5.7
970905	2	1204	1308	2	18.7	21.6
970906	1	0434	0541	2	7.7	9.2
970906	2	1203	1317	2	12.3	14.9
970927	2	1218	1321	2	15.0	13.9
970928	1	0437	0541	2	5.9	6.6
970928	2	1201	1304	2	15.9	12.1
970929	1	0434	0541	2	7.2	7.3
970929	2	1200	1306	2	14.9	12.8
971003	1	0658	0803	2	IS	IS
971003	2	1206	1311	2	IS	IS
971004	1	0436	0540	2	6.2	9.2
971004	2	1200	1306	2	16.3	17.7

Tables 3-1 through 3-4 show the times and locations that data were collected and the times and locations where data are missing. Table 3-5 provides a summary of data capture percentages derived from these tables. Though the only species shown in the tables are TNMHC and formaldehyde, these results are representative for all species. The species were screened individually, and individual data points were flagged, but these were few. During data entry and verification of data against field log sheets, instances of missing data and or ambiguous data were observed. These data have been recovered using data supplied by Biospherics, Atmoslytics, UC Davis, and STI. However, this process is not yet complete for UCD aircraft data. In particular, the following general problems remain:

Table 3-5. Summary of Data Capture Percentages

Site	Carbonyl Data Capture	VOC Data Capture
ARCO	100	84
AZSA	96	98
LANM	87	96
STIA	95	96
UCD	76	99

- UCD: Ambiguous use of AGL (above ground level) and MSL (mean sea level) for elevation data.
- UCD: Ambiguous use of PST (Pacific Standard Time) and PDT (Pacific Daylight Time) for aircraft flight and sample start times.

The two UCD problems affect all UCD data, and have not been flagged in the data base. When the time and altitude units are obtained from UCD, these data may need adjustment to bring them into conformance with SCOS97-NARSTO database specification.

Overall, the data capture percentages were over 90% with two exceptions. The UCD aircraft initially filled the Tedlar bag by ramming air into the sampling line. Due to the length of this line, inadequate sample was collected for accurate carbonyl analyses. The data appeared to be abnormally high and therefore were flagged as suspect. On August 5, a Teflon diaphragm pump was added to the sampling line to increase the volume of the sample collected.

From August 5 to August 22, the carbonyl sampler at LANM failed to operate for an unknown reason, resulting in background concentrations of carbonyls. These data were invalidated.

Samples were not collected at the ARCO site due to a combination of operator error and sampler malfunction. The timer on one of the samplers occasionally failed to activate for no apparent reason.

3.2 Quality Control

3.2.1 VOC

- VOC Blanks

Canister blanks were made by filling canisters that were returned without being used and then filled with an ultra zero grade air. Twelve of these were prepared and analyzed for full speciation. No identifiable peaks were observed. On some of the samples, small, unidentified peaks were seen, the average of which was estimated to be 0.1 ppbC.

- VOC Duplicate Cans

Two sets of duplicate sample cans were collected at Azusa (AZSA) on 10/3/97 and two sets on 10/4/97. These were collected manually using both VOC samplers at the site. These samplers had separate probes located a few centimeters apart. Those samples met QC criteria and thus provide four duplicate pairs for QC evaluation.

Figures 3-1 through 3-3 show scatter plots of duplicate canister concentration in ppbC versus primary canister concentration in ppbC. Figure 3-1 includes data for all species excluding methane and CO. Figure 3-2 includes these data plus category totals such as total hydrocarbons, total non-methane hydrocarbons, paraffin, olefins, aromatics, etc. Figure 3-3 includes these data, as well as methane and CO. The data show that the assumed precision of 10% provides a reasonable estimate for the non-methane hydrocarbon species, but that tolerance is much larger than need be for the CO and methane concentrations.

**Figure 3-1. Duplicate Canister Concentration for All Species.
Excludes Methane and CO (ppbC).**

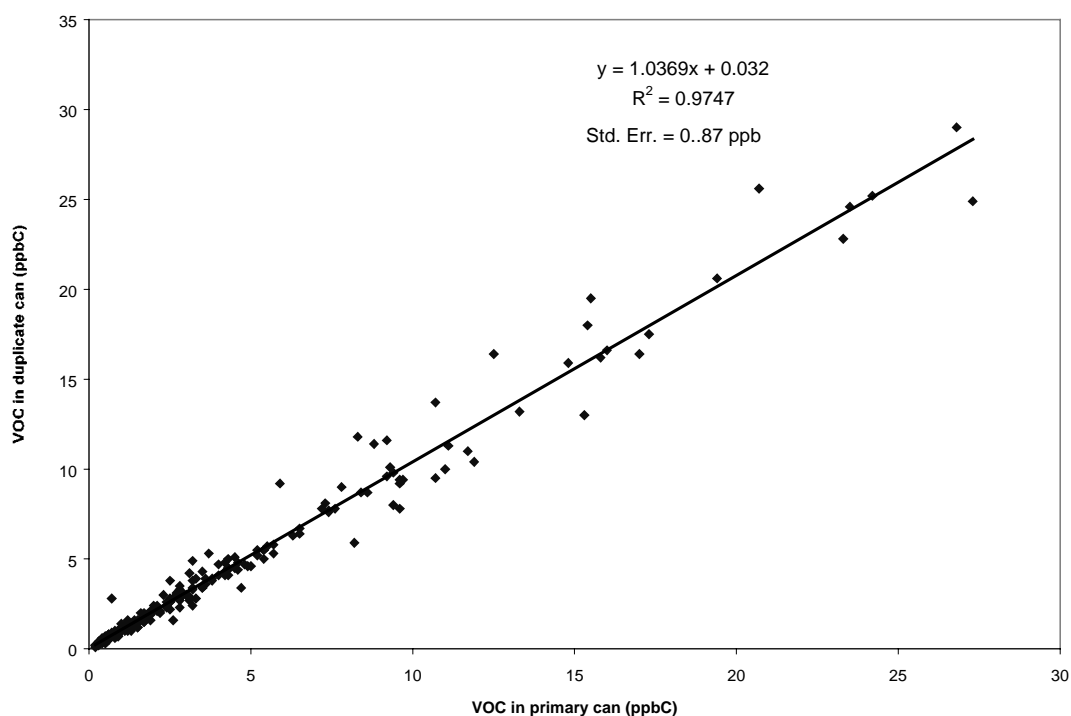


Figure 3-2. Duplicate Canister Concentrations for All Species and HC Category Totals (ppbC). Excludes Methane and CO.

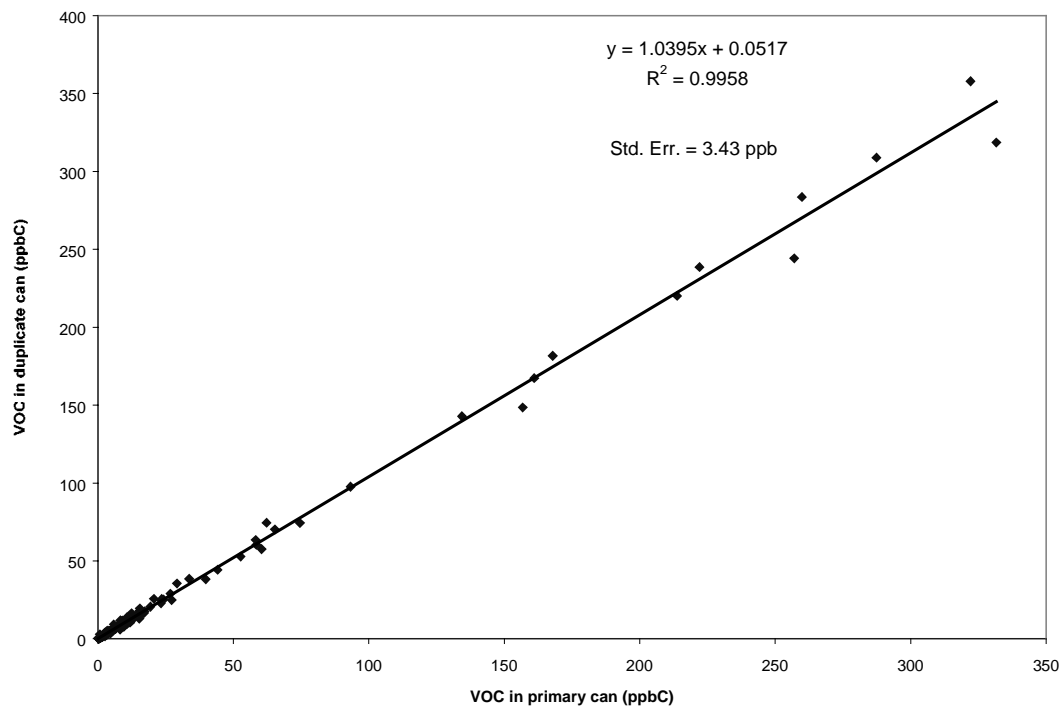
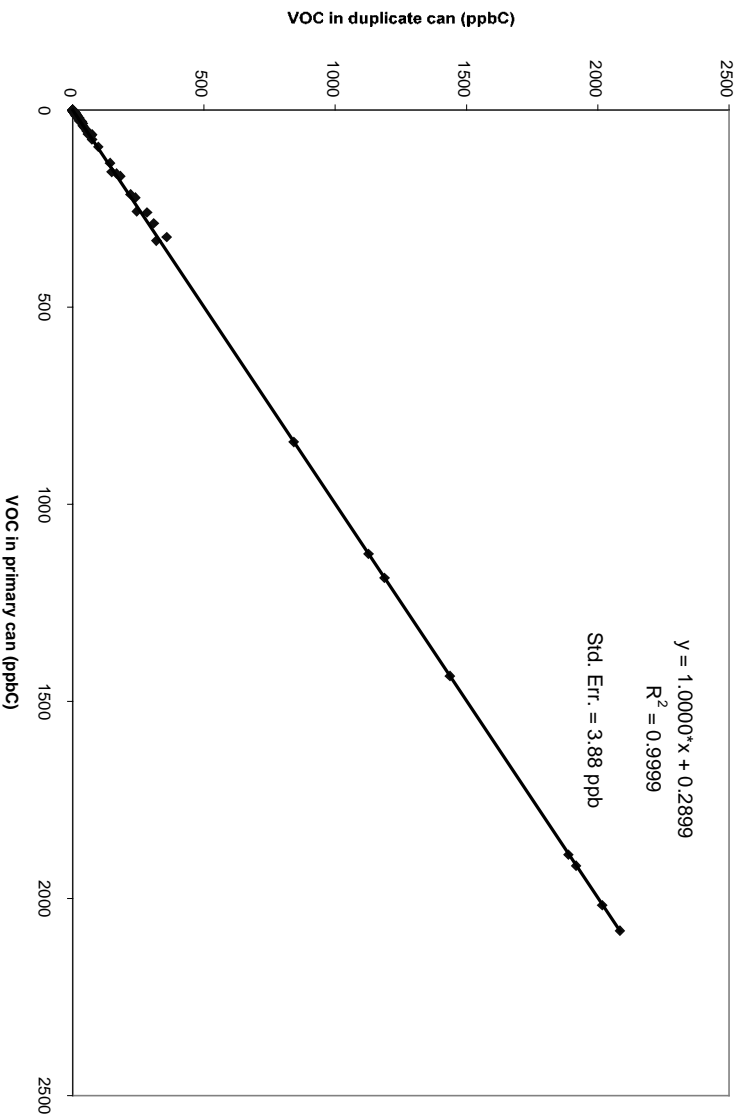


Figure 3-3. Duplicate Canister Concentrations for All Species and HC Category Totals (ppbC). Includes Methane and CO).



- VOC Replicate Analyses

Replicate analyses were performed on eight sample cans. Although this represents less than 3% of the total number of samples analyzed, we have found, after thousands of replicate analyses, and the data will show, that this is an adequate percentage of replicate samples. Figures 3-4 through 3-6 show respectively scatter plots for: all species excluding CO and methane; data in figure 3-4 plus HC Category totals; data in Figure 3-5 plus CO and methane. The replicate analyses for CO and for methane were identical. As expected, based on slopes and correlation coefficients, the replicate analyses show less variability than the duplicate cans, indicating that sample collection hardware differences contribute to overall imprecision. This is most noticeable when the plots showing all species without CO and methane since the concentrations are lower and the variability more pronounced.

**Figure 3-4. Replicate Analysis Concentrations for All Species.
Excludes Methane and CO (ppbC)**

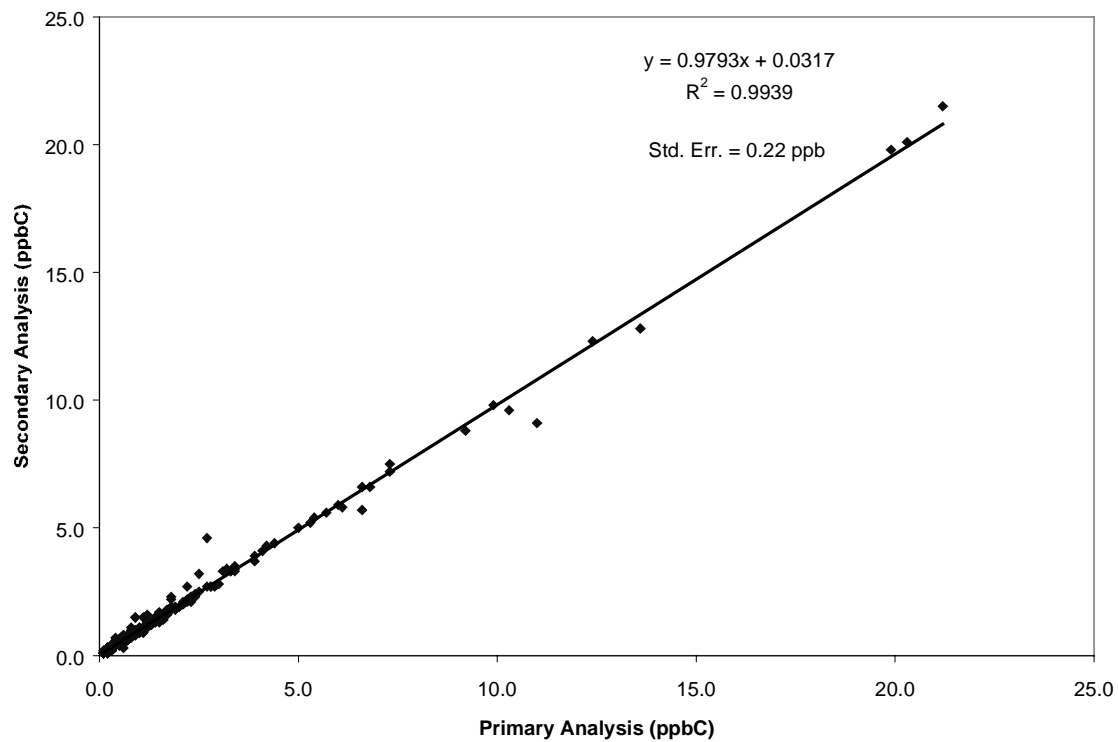


Figure 3-5. Replicate Analysis Concentrations for All Species and HC Category Totals. Excludes Methane and CO (ppbC)

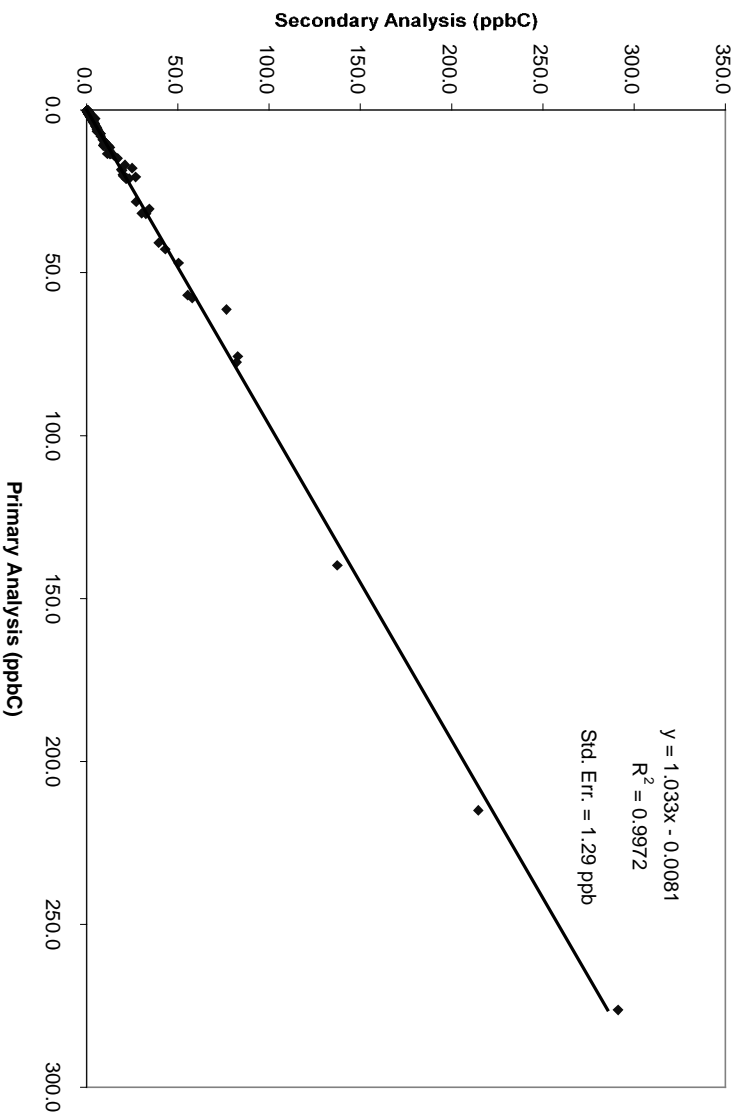
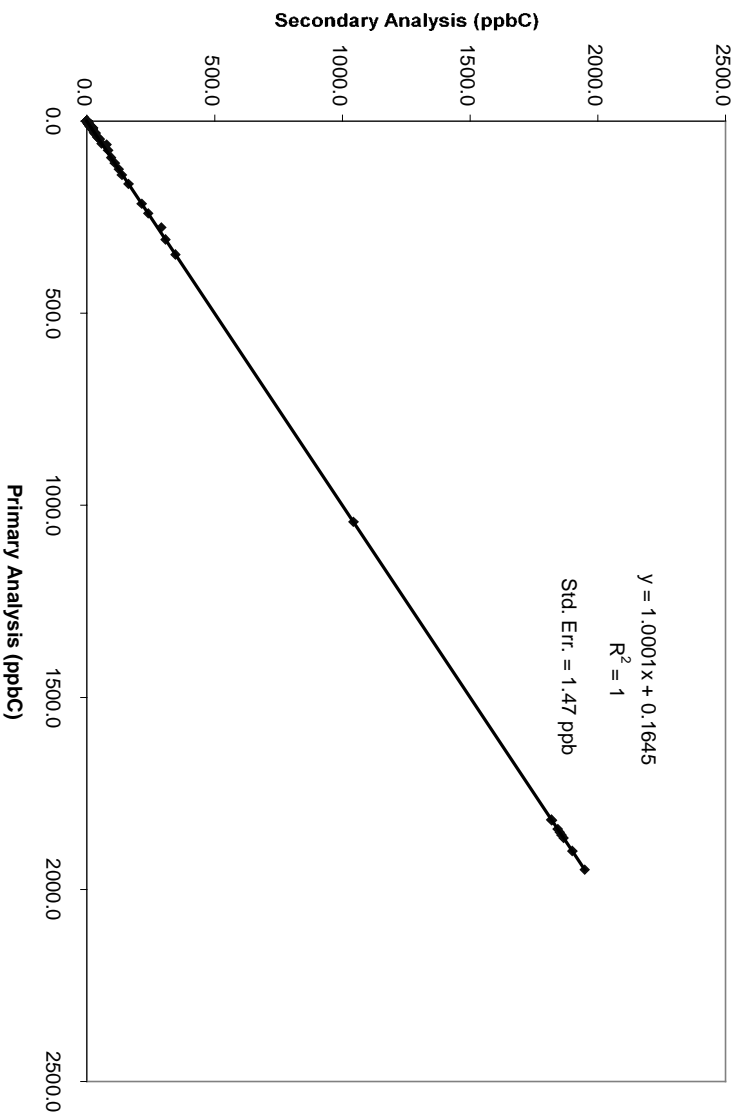


Figure 3-6. Replicate Analysis Concentrations for All Species and HC Category Totals. Includes Methane and CO (ppbC)



3.2.2 Carbonyl

- Carbonyl Data Ground Sample Blanks

Twenty-six carbonyl field blanks were collected at ground sites during the course of the study. The blank data are shown in Table 3-6. The $\mu\text{g}/\text{sample}$ data are converted to ppbV assuming a collection volume of 162 liters (0.9 L/min for 180 minutes). Lower quantifiable limits are calculated as three times the standard deviation of blank levels. The blank levels are typical for ambient measurements and were subtracted prior to reporting concentrations. Mean blank levels were subtracted from raw ambient measurements to obtain net concentrations for ambient samples. The mean blank levels shown are uncorrected, raw values.

- Carbonyl Replicates

Replicate analyses were performed on 19 ground samples and 15 aircraft samples. The root mean square (RMS) difference between replicate analyses of ground samples and for aircraft samples for each species is shown in Table 3-7. The RMS difference between replicates is less than 0.1 ppbV for each of the individually identified species in ground samples. For the compound classes, the RMS difference ranges from 0.13 to 0.37 ppbV. These differences are less than 2% of mean replicate levels for the three major compounds: formaldehyde, acetaldehyde, and acetone. Aircraft samples collect about seven times less air volume than do ground samples. Thus, sample imprecision introduced by blank variability is magnified of these samples. Even so, the RMS difference between replicate analyses of aircraft samples is less than 4% for the three major species. For other trace species the RMS percent differences are quite large. This is because the mean concentrations are very close, if not below the LQL.

Table 3-6. Carbonyl Field Blanks Collected at Ground Measurement Sites

Species	N	Avg $\mu\text{g}/\text{samp}$	std dev $\mu\text{g}/\text{samp}$	Avg PpbV	Std dev ppbV	LQL ppbV
HCHO	26	0.116	0.019	0.585	0.096	0.287
CH ₃ CHO	26	0.280	0.091	0.959	0.313	0.938
Acetone	26	0.371	0.091	0.965	0.237	0.710
Propanal	26	0.219	0.044	0.569	0.114	0.343
Crotonaldehyde	26	0.029	0.019	0.063	0.041	0.123
MEK/Methacrolein	26	0.129	0.046	0.270	0.097	0.291
Butanal	21	0.226	0.040	0.475	0.084	0.251
Benzal	26	0.070	0.020	0.100	0.029	0.086
m-Tolual	26	0.110	0.043	0.139	0.054	0.161
C5 carbonyls	26	0.180	0.082	0.315	0.144	0.431
C6 carbonyls	26	0.217	0.111	0.328	0.168	0.504
C7 carbonyls	26	0.277	0.106	0.367	0.140	0.421
>C7 carbonyls	26	0.425	0.192	0.501	0.226	0.678

Table 3-7. Carbonyl Replicate Analyses

Species	Grnd mean ppbV	Grnd RMS diff ppbV	Grnd RMS diff % of mean	Air Mean ppbV	Air RMS diff ppbV	Air RMS diff % of mean
HCHO	6.34	0.10	1.5%	10.19	0.35	3.5%
CH ₃ CHO	2.79	0.04	1.3%	5.73	0.21	3.7%
Acetone	5.02	0.06	1.2%	8.23	0.32	3.9%
Propanal	0.35	0.03	8.1%	0.84	0.13	15.9%
Crotonaldehyde	0.58	0.04	6.4%	0.56	0.15	26.5%
MEK/Methacrolein	0.95	0.05	5.2%	1.01	0.19	18.4%
Butanal	0.35	0.06	16.8%	0.42	0.35	82.9%
Benzal	0.13	0.04	28.3%	0.17	0.26	155.2%
m-Tolual	0.13	0.02	16.3%	0.11	0.35	323.1%
C5 carbonyls	0.62	0.27	43.4%	2.21	0.77	34.7%
C6 carbonyls	0.79	0.13	16.3%	1.45	0.47	32.3%
C7 carbonyls	0.40	0.16	40.0%	-0.11	0.50	-462.9%
>C7 carbonyls	0.48	0.37	77.2%	1.28	1.39	109.2%

- Carbonyl Ground Sample Duplicates

A total of 16 valid duplicate carbonyl samples were collected at ground stations. Table 3-8 shows the results for duplicate samples where both the primary and duplicate were above detection limits. The mean difference and standard deviation of the differences were less than 1 ppb for all species. A coefficient of variation (CV) was calculated for each pair by dividing the standard deviation of the two sample concentrations by the mean sample concentration. These CVs were then averaged and are shown in the table. The CVs are less than 6% for the major species. A coefficient of variation was also calculated for each species by dividing the standard deviation of the differences by the average concentration, and then further dividing by the square root of two to convert from variability of the difference to variability of the individual measurements (CV #2 on the table). The results are consistent with the average CVs. They are slightly larger because the few large differences that occur at high concentrations affect the standard deviation of the differences more than the high concentration affects the mean concentration.

- Carbonyl Tandem Samples

Eleven samples were collected with two cartridges in tandem. Front and backup cartridges were blank corrected, and the data below detection limits was not eliminated. Backup cartridge results were generally near blank values; thus, results for blank-corrected backup cartridge were sometimes negative. Breakthrough for sum of species excluding acetone ranged from -7% to +7% and averaged +3%. Breakthrough for acetone ranged from +3% to +17% and averaged 8%. Breakthrough for formaldehyde ranged from -3% to +4% and averaged +1%. Overall, breakthrough is negligible for this data set.

Table 3-8. Carbonyl Duplicate Ground Samples

Param	N	Avg Conc ppb	Mean Diff ppb	Std of Diff ppb	Avg CV %	CV #2 %
HCHO	16	7.25	-0.27	0.89	6%	9%
CH3CHO	16	5.16	-0.17	0.31	5%	4%
ACETONE	16	7.03	-0.25	0.71	5%	7%
PROPANAL	13	1.07	0.01	0.16	9%	11%
CROTONALDEHYDE	16	1.35	-0.01	0.13	5%	7%
MEK/METHACROLEIN	16	1.01	-0.02	0.12	7%	9%
BUTANAL	14	1.05	0.09	0.26	12%	18%
BENZAL	11	0.24	0.00	0.05	11%	14%
m-TOLUAL	11	0.37	-0.03	0.13	17%	25%
C5 carbonyls	13	1.15	-0.09	0.28	11%	17%
C6 carbonyls	15	1.67	-0.03	0.30	12%	13%
C7 carbonyls	8	0.98	0.10	0.21	13%	15%
>C7 carbonyls	10	1.23	0.09	0.43	23%	25%

Avg CV = mean of individual CVs (Std/Avg) calculated for each of N pairs

CV2 =(Std Dev of N Differences) /((Avg of N Average Concentrations)*sqrt(2))

4. Conclusions

A VOC and carbonyl data set has been collected for SCOS97-NARSTO study with high data capture and precision. The aircraft data capture was 98% for VOC and 95% for carbonyl measurements. For the ground samples VOC and carbonyl data capture were both 94%. Based on collocated samples, the VOC precision was well within the expected 2-20% range. Evaluation of collocated carbonyl samples showed the precision to range from 5 to 25%. In both cases the higher uncertainties were associated with species at concentrations near the detection limit.

The data set will be added to other VOC and carbonyl data collected as part of the SCOS97-NARSTO program. The VOC and carbonyl data will be placed with other information collected during the study into a database that will form one of the most comprehensive data sets collected in the southern California area. The data will be used in air quality models to design ozone attainment strategies and to resolve intra-regional air pollution transport issues. The database will be available to the public after appropriate review and will provide a wealth of information that can be analyzed to provide insight into the many issues surrounding the ozone and particulate matter problem in southern California.

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