

5. VOLATILE ORGANIC COMPOUND MEASUREMENT

This section describes the performance audits and laboratory comparisons that were conducted as part of the SCOS97-NARSTO quality assurance program for speciated hydrocarbons, carbonyl compounds, halogenated compounds, and biogenic compounds. Protocols for the audits and measurement comparisons are provided in Appendices A through E. The audits and measurement comparisons are designed to document potential measurement biases among measurement groups and methods that may affect the interpretation and validity of subsequent modeling and data analysis.

5.1 SCOS97-NARSTO VOC Measurements

Several organizations participated during SCOS97-NARSTO in collecting data for a wide range of volatile organic compounds using a variety of sample collection and analysis methods. Table 5.1-1 provides a summary of the VOC data that were collected at each of the SCOS97 measurement sites. The Photochemical Assessment Monitoring Stations (PAMS) in the study region provided the foundation for the SCOS97-NARSTO VOC measurements. PAMS ozone precursor monitoring is conducted annually in California during the peak ozone season (July 1 to September 30). There were 13 PAMS sites in operation during SCOS97-NARSTO (three in Ventura County, five in the South Coast Air Basin, one in the Southeast Desert Air Basin, and four in the San Diego Air Basin).

EPA methods TO-14 and TO-11 are specified by the EPA for sampling and analysis of speciated hydrocarbons (EPA, 1991) and carbonyl compounds, respectively. Table 5.1-2 lists the 55 PAMS target hydrocarbons. The EPA rule requires eight 3-hour hydrocarbon samples (midnight-3 am, 3-6 am, 6-9 am, 9-noon, noon-3 pm, 3-6 pm, 6-9 pm, and 9-midnight PDT) every day at Type 2 sites and every third day at all other PAMS sites. Sampling for carbonyl compounds is required at Type 2 sites only. Appropriate PAMS sampling requirements, different than other hydrocarbon requirements, are included as Appendix A2. In addition, one 24-hour sample is required every sixth day year-round at Type 2 sites and during the summer monitoring period at all other sites. Under the California Alternative Plan, four 3-hour samples (3-6 am, 6-9 am, 1-4 pm, and 5-8 pm, PDT) are collected every third day during the monitoring period at all PAMS sites for speciated hydrocarbons and at Type 2 sites only for carbonyl compounds. In addition to the regularly scheduled measurements, samples are collected on a forecast basis during up to five high-ozone episodes of at least two consecutive days. Episodic measurements consist of four samples per day (6-9 am, 9-noon, 1-4 pm and 5-8 pm, PDT) for speciated hydrocarbons at all PAMS sites and for carbonyl compounds at Type 2 sites. The Ventura County Air Pollution Control District (VCAPCD) and San Diego Air Pollution Control District (SDAPCD) operate their PAMS sites according to the alternative plan, while South Coast Air Quality Management District (SCAQMD) operates theirs according to the EPA Rule. SCAQMD's 3-hour sampling schedule (on PST year round) begins one hour later than sampling times used by VCAPCD and SDAPCD (on PDT for PAMS).

Total nonmethane hydrocarbon (NMHC) concentrations were monitored at some PAMS sites by automated Pre-concentration Direct Injection Flame Ionization Detection

(PDFID) (e.g., Xontech 850). Total NMHC is measured by passing the air sample through a chromatographic column to separate methane from other hydrocarbons and analyzing the bulk hydrocarbon sample by FID. In the FID, sample is burned in a hydrogen flame creating a quantity of ions from the hydrocarbon molecules in the sample. The ions generate a small electrical current that is measured by an electrometer, which in turn produces an electronic signal proportional to the number of ions collected. Total hydrocarbon data are reported as parts per billion carbon (ppbC).

VCAPCD and SDAPCD supplemented their existing sampling schedule by including all SCOS97 IOP days. Field operators from the University of California, Riverside College of Engineering – Center for Environmental Research and Technology (CE-CERT) collected VOC samples in the SoCAB during SCOS97 IOPs at Azusa, Anaheim, Burbank, Los Angeles – N. Main, and Los Angeles – ARCO Plaza. Airborne VOC samples were also collected onboard the four instrumented aircraft that were deployed during the study. Additional VOC sampling were collected at background locations at San Nicolas Island, Catalina Island, Point Conception, Rosarito Beach and SE Mexicali. The VOC samples that were collected specifically for SCOS IOPs were analyzed at Desert Research Institute (DRI), Biospheric Research Corporation (BRC), Atmospheric Assessment Associates, Inc. (AtmAA), and Atmospheric Analysis and Consulting, Inc. (AAC) as indicated in Table 5.1-1.

The United States Environmental Protection Agency (EPA) and their contractor ManTech Environmental Technology, Inc. (ManTech) monitored hydrocarbons at Azusa on a continuous (hourly) basis during the month of September. The species measured also included carbonyl compounds, biogenic hydrocarbons, and chlorinated hydrocarbons. Daniel Grosjean and Associates (DGA) and Desert Research Institute measured the halogenated hydrocarbons. DGA Measurements of perchloroethylene were successful and those of methyl chloroform were not. These measurements at Simi Valley, Azusa, and Lancaster may be used as "tracers of opportunity" that can be used to distinguish emissions from the South Coast Air Basin into from local emissions at the Mohave Desert air basin. Azusa location admittedly did not enhance this feature of these measurements. DRI measured several other halogenated compounds at the Lancaster site.

During SCOS97-NARSTO, researchers from the University of California, Riverside measured biogenic hydrocarbon (BHC) in the South Coast Air Basin and the Ojai area. Isoprene, monoterpenes, and methylvinylketone (MVK) were measured during afternoon upslope flows at a high elevation site in the San Gabriel Mountains. In addition, UC Riverside measured methylnitronaphthalenes to infer 12-hour-average nitrate radical concentrations, the dominant night-time sink of BHC. Several other groups made surface and aircraft measurements of isoprene and monoterpene for later comparison with UC Riverside.

5.2 Performance Audits for Speciated Hydrocarbons

This section describes the performance audits that were conducted as part of the SCOS97-NARSTO quality assurance program for speciation of ambient hydrocarbons. Participants included the Air Resources Board (ARB), Atmospheric Processes Research Division of National Exposure Research Laboratory of the Environmental Protection Agency

(EPA), ManTech, Bay Area Air Quality Management District (BAAQMD), the three contract laboratories (AAC, BRC, and DRI), and the PAMS laboratories in the study area (SDAPCD, SCAQMD, and VCAPCD). DRI and the Research Division of the ARB coordinated the audits with assistance from the Monitoring and Laboratory Division of the ARB.

5.2.1 Audit Objectives, Approach, and Protocol

The objectives of the performance audits were to determine the consistency among laboratories in reported concentrations for individual species and total NMHC, hydrocarbon species identification, and fraction of identified NMHC. The objectives of the performance audit did not extend to diagnosis of the differences among the laboratories. A summary of the audit results was sent to each laboratory with recommendations for further examination by the individual laboratories of significant differences that were revealed as a result of the performance audits.

The hydrocarbon measurement comparisons consisted of three sets of ambient samples. Appendix A provides details of the protocol. Participating laboratories include ARB, AAC, EPA, BRC, DRI, ManTech, SDAPCD, SCAQMD, VCAPCD, and BAAQMD. Each participating laboratory supplied to up to three cleaned, evacuated 6-liter canisters to ARB's Monitoring and Laboratory Division. EPA, ARB and DRI supplied additional canisters for collection of duplicate samples. A DRI manifold sampling system (described in Appendix B) was used by ARB staff to collect up to twelve collocated samples at three sites. One set of canisters was collected in the morning in an area heavily influenced by on-road motor vehicles (at downtown Los Angeles). The second set was collected in the afternoon in a downwind ozone receptor area (Azusa). The third set represents upwind background, and was collected at Santa Monica Beach in the late afternoon after the marine layer had moved inland. Duplicate samples were collected for EPA, ARB and DRI. Each laboratory analyzed the samples within five working days after receiving the canisters.

All data were submitted to the Research Division of the ARB, who forwarded the data to DRI for compilation and analysis after all data were submitted. Each laboratory was requested to submit copies of chromatograms and data report (species identification, retention times, and individual species concentrations in ppbC, total identified and total unidentified species). The total concentrations of identified and unidentified hydrocarbons that were reported by different laboratories for the same sample depends on the particular requirements of the sponsor which determined how the chromatographic data were obtained and processed.

5.2.2 Analytical Methods

Hydrocarbon speciation measurements consisted of canister sampling followed by gas chromatographic analysis with flame ionization detection (Method TO-14). Laboratories employed commercial gas chromatographic systems equipped with flame ionization detectors (GC-FID), a cryogenic concentration step, and computerized data acquisition systems. Procedures used for instrument calibration varied among the groups. For calibration of the FID, propane is commonly used for C₂ to C₄ hydrocarbons and benzene or hexane is used for greater than C₄ hydrocarbons. The systematic differences resulting from variations in FID

response among different calibration gases are typically less than 5 percent. With the exception of BRC, all groups calibrated their chromatographs in volume concentration units (area response/ppbC). The calibration by BRC is in terms of mass (area response/ng) of an internal standard which is added to each sample. Conversion from $\mu\text{g}/\text{m}^3$ units to ppbC vary among hydrocarbons because the molecular weight/number of carbon atoms ratios are not constant for all hydrocarbons. At one atmosphere pressure and 25 °C, the ($\mu\text{g}/\text{m}^3$) to ppbC conversion factor for methane is 1.5 and 1.88 for benzene. The conversion factor for propane (1.67) was used by BRC. If conversion factors specific to each hydrocarbon are employed instead, the corresponding concentrations will be up to 5 percent higher for alkane, 5 to 10 percent higher for alkenes and cycloalkane, and 10 to 15 percent higher for aromatic hydrocarbons. Besides selection of the endpoint of the gas chromatographic run, the primary factors that can affect total measured concentrations include selection of threshold levels for peak integration and losses during cryogenic concentration and desorption and surface adsorption within the inlet system.

Automated, semi-continuous hydrocarbon speciation was obtained by SCAQMD at the Pico Rivera PAMS site using an Entech 2000 preconcentrator and HP5890 gas chromatograph. In this arrangement, the samples are collected into an evacuated 6L summa canister over a 170 minute interval. Five minutes are required for sample loading and five minutes for heating and evacuating the canister between samples. The Entech 2000 preconcentrator is a multibed sorbent trap containing Carbopack B and Carbosieve S III. The sorbent trap is dry purged with a 250 mL volume of He gas. The sample is thermally desorbed and injected onto the chromatographic column. Speciation is accomplished with a dual column/FID method. Initially, the DB-1 capillary and the Astec GasPro GSC PLOT columns are in series. After the C_2 through C_4 hydrocarbons have eluted off the DB-1 column and onto the PLOT column, a rotary valve disconnects the columns and puts them into a parallel configuration. Hence the C_2 - C_4 hydrocarbons are resolved on the PLOT column and C_5 - C_{12} hydrocarbons are separated on the DB-1 column. Machine also daily runs a standard containing all PAMS targets and certified for propane and benzene and zero-air blank. This machine uses propane standard to quantify C_2 - C_4 analytes and benzene standard to quantify C_5 - C_{12} analytes. The average detection limit for PAMS target is 0.2 ppbC.

Hourly volatile organic compound speciation was obtained by Mantech at Azusa using a Xontech/Saturn AutoGC ion trap mass spectrometer system. The VOCs are desorbed from a Stirling cryotrap onto a DB-1 chromatographic column. Target compounds include the PAMS list, selected terpenes, oxygenates (n-aldehydes, methyl tert-butyl ether [MTBE], methyl vinyl ketone [MVK], and others.

5.2.3 Results

The results of the comparison are shown in Appendix A.1, and are grouped by the 55 PAMS target compounds, other identified hydrocarbons, and oxygenated compounds. In addition to subtotals for these three groups, totals are provided for unidentified compound, total non-methane hydrocarbons (sum of the above four subtotals) and sum of paraffins, olefins, and aromatics by carbon number. The results are summarized and examined in this

section for consistency in calibration, peak identification, and reported values for sum of species.

Measurement Sensitivity and Calibration

Measurement calibration is normally verified by challenging the measurement/analysis system with a known standard that is traceable to a primary standard. For this present performance audit, the values reported by each of the audited laboratories for the three ambient samples are compared against corresponding values reported by the Desert Research Institute's Organic Analytical Laboratory. Table 5.2-1 presents a summary of the correlations between the audited laboratories versus DRI. Scatterplots of the data are shown in Figures 5.2-1, 5.2-2, and 5.2-3 for the 55 PAMS target compounds reported by each laboratory versus those reported by DRI for the Los Angeles, Azusa and Santa Monica samples, respectively. Summary data include regression values (slope, intercept, and correlation coefficient), averages of Laboratory/DRI ratios for compounds exceeding a mean concentration of 1 ppbC and ratios less than 0.7 or greater than 1.3. The data used in the regressions were also screened in order to minimize the effect of inconsistent identification on the correlations. Table 5.2-1 also includes numbers of observations that met the screening criteria ($0.7 < \text{Laboratory/DRI} < 1.3$); outliers were species with average concentrations greater than 1 ppbC with Laboratory/DRI ratios less than 0.7 or greater than 1.3. It also includes numbers and identities of species reported as below detection, and numbers and identities of outliers. It is important to note that AAC and BAAQMD both had problems at low concentrations. In the ManTech Los Angeles figure, there is some missing data as well.

In general, the values reported by the audited laboratories are well correlated with values obtained by DRI. All laboratories had average Laboratory/DRI ratios within 10 percent of 1.00 for the urban ambient samples from Azusa and Los Angeles. Of the laboratories that also analyzed the background ambient sample from Santa Monica, BRC, SDAPCD, and VCAPCD had average ratios to DRI of 1.02, 1.06, and 1.11, respectively. EPA had consistently higher values with an average ratio to DRI of 1.18.

These correlations indicate the degree of consistency among the laboratories. While the correlations for several of the laboratories show considerable scatter at lower concentrations (especially for values below 5 ppbC), the values reported by each of the laboratories for the most abundant species are generally in good agreement. Acetylene is a notable exception with reported values varying by as much as a factor of three among the laboratories. Analysis by DRI of an acetylene standard showed that its response on the FID is about 20 percent lower than propane (i.e., measured mixing ratios are 20 percent higher for acetylene than other hydrocarbons). Most laboratories typically do not take the lower FID response of acetylene into account in their data processing. Because values for ethylene and ethane are in good agreement among the laboratories, misidentification of acetylene or incomplete transfer from the preconcentrator to the column are unlikely causes for the variability. A more plausible explanation may be loss of acetylene in the canister or within the analytical system. Acetylene undergoes chemical reaction on surfaces more readily than alkanes and alkenes. Acetylene may be lost on internal surfaces of canisters, dryers used for water management, or adsorbents used for sample preconcentration. These factors are not addressed in this comparison study.

More work is needed to investigate these and other potential explanations for the large variations that exists among laboratories in reported values for acetylene.

The species detected by DRI that are not detected by the other laboratories indicate the relative sensitivity of the measurements. For the Azusa and Los Angeles ambient samples, the average percentages of detectable species (i.e., reported by DRI) that were reported as below detection are less than 10 percent for SCAQMD-Auto GC and EPA, between 10 and 15 percent for BRC, Mantech, BAAQMD, and AAC, and between 15 and 20 percent for ARB, SCAQMD-Lab, SDAPCD, and VCAPCD. For the background sample from Santa Monica, these percentages are 7.3, 6.3, 58.8, and 60.8 for BRC, EPA, SDAPCD, and VCAPCD, respectively.

Peak Identification

In gas chromatography analysis, compounds are identified by the time required for individual compounds to pass through the column to the detector. Peak identification algorithms adjust for small shifts in retention times caused by run-to-run variations in operating condition and compare the adjusted times to a retention time library which assigns individual species to reference retention time windows. This section examines the consistency in peak identification among the audited laboratories.

Because calibration differences are generally within 10 percent, the outliers identified in Table 5.2-1 are likely due to differences in peak identification among the audited laboratories. Ratio of outliers to number of compounds in the sample with concentrations greater than 1 ppbC may indicate a degree of inconsistency in peak identification relative to DRI. The average (Azusa and Los Angeles ambient samples) percentages of outliers are less than 10 percent for BRC and SCAQMD-Lab, between 10 and 15 percent for ARB, EPA, and SDAPCD, and between 15 and 20 percent for SCAQMD-Auto GC and VCAPCD. The percentage of outliers are 25.5, 30.9 and 43.5 for Mantech, BAAQMD, and AAC, respectively. The percentages of outliers for the background sample from Santa Monica are 12.7, 39.6, 23.5, and 23.5 for BRC, EPA, SDAPCD, and VCAPCD, respectively.

In general, the major peaks (i.e., most abundant peaks) are consistently identified by all of the laboratories. Larger discrepancies exist for olefins greater than C₄ and for hydrocarbon greater than C₈. Sample contamination is evident in some samples, especially those analyzed by EPA. The specific compounds that are inconsistently identified vary from group to group and from sample to sample depending on how the chromatographic data are processed. Although automated peak identification algorithms are commonly used, some manual data processing is used by most chromatographers for quality control purposes, and in some cases, is the primary method of peak identification. Because manual processing is used in varying degree to process large numbers of complex chromatograms, minor peaks can be easily misidentified.

Differences in the values reported by two laboratories can also be traced to differences in analytical methods. For example, some laboratories analyze light hydrocarbons (C₂-C₄) on a separate column, while others analyze the entire sample on one column. C₂ compounds are difficult to resolve completely with a single column, especially with excessive moisture in the

sample. Excessive moisture can also cause nonlinear shift in retention times that can complicate peak identification. Polar organic compounds complicate the chromatogram and can coelute with hydrocarbon species of interest (e.g., methanol coelutes with cis-2-butene). Use of dryers to remove water and polar organic compounds stabilize retention times and simplify the chromatogram, but can also partly remove olefins and aromatics.

Sums of Species

Values of total nonmethane hydrocarbons (tnmhc) depend on the sampling and analytical methods and procedures. Consequently tnmhc is operationally defined and reflects the methods that are employed. Table 5.2-2 compares sum of the PAMS target compounds and total nonmethane hydrocarbons in the PAMS region of the chromatogram (up to n-undecane) reported by the audited laboratory, including the identified (idnmhc) and unidentified (unid) portions of tnmhc. Subtotal for paraffins, olefins, and aromatic compounds are also shown. Additional samples analyzed by DRI include a total for identified oxygenated compounds (idoxy).

Comparisons of the sum of the PAM target compounds and total NMHC in the PAMS region of the chromatogram are consistent with the regression statistics developed for the calibration comparisons with the laboratories generally reporting values within 10 percent of the corresponding DRI values. Examination of the other difference between TNMHC and sum of PAMS species provide an indication of the relative importance of organic compounds that are not PAM target compounds and their possible origin. For the ambient audit samples from Los Angeles and Azusa, which reflects mostly motor vehicle emissions, this total represent 10 to 25 percent of the TNMHC (up to n-undecane). ManTech's values for total hydrocarbons are lower than other laboratories because their method did not measure C₂ or C₃ compounds. EPA's values for total NMHC are consistently higher than the average. These higher values appear to be associated with some sort of sampling artifact. All other groups produced similar sums for PAMS target species.

Storage Stability

The stability of samples upon storage is assessed by determining changes in the compound matrix and concentration of the sample with time. The interior surfaces of the stainless steel canisters are made passive to minimize surface reactivity and allows stable storage for many of the compounds of interest. A number of studies (Wagoner et al, 1993; McClenny et al, 1991; Fung et al, 1993; Holdren and Smith, 1986; Oliver et al, 1986) have shown that a wide range of VOC are stable in canisters for at least 30 days. Most of the reported studies were performed in SUMMA[®]-treated stainless steel canisters at pressures above atmospheric pressure and in the presence of water vapor. Various observations at several laboratories have indicated that the presence of water vapor is essential in maintaining sample integrity; it neutralizes active sites in the sampling/canister system (Pate et al, 1991; Coutant and McClenny, 1991; Kelly et al, 1993). Some studies indicate that many oxygenated hydrocarbons such as aldehydes, ketones, and alcohols have less desirable storage properties (Pate et al, 1991; Kelly et al, 1993). Generally, organic compounds that are soluble in water do not store well in canisters. Also, hydrocarbons with carbon numbers higher than C₁₁ are not recovered quantitatively from the canisters (Zielinska and Fung, 1992; Zielinska et al,

1993). In addition, the variable quality and SUMMA[®] treatment of the canisters, their previous history, age, and storage temperatures, etc, may effect a compound's stability upon storage.

For the NARTSO-Northeast hydrocarbon comparison, EPA analyzed each of the audit canisters before and after analysis of the samples by the audited laboratories, so that storage stability could be evaluated (Fujita et al., 1997). The time between initial and repeat analyses ranged from one to three months. Without exception, all of the species in the synthetic mixtures, once in the transfer canisters, were stable (within 5 percent of the original values) throughout the duration of the comparison study. Initial and repeat values for most species were also within 5 to 10 percent of the NIST-traceable values. Several unstable and higher-molecular weight species showed decreases from their reference values. Acetylene and 2-methyl-1-pentene values were less than 50 percent of the reference value. Styrene, n-propylbenzene, m- and p-diethylbenzene were less than 80 percent, and p- and o-ethyltoluene and n-undecane were less than 90 percent of the reference values. However, even these species remained stable for up to three months once the dry synthetic mixtures were transferred to humidified canister.

5.3 Performance Audit and Field Comparisons for Carbonyl Compounds

Performance audits and field comparisons were conducted for measurement of carbonyl compounds as part of an external quality assessment program for SCOS97-NARSTO. Details of the protocol for the performance audits and field measurement comparisons are given in Appendix C.

5.3.1 Audit Objectives, Approach, and Protocol

The purpose of these audits and comparisons are to document differences that may exist between measurement groups. The audit consists the following three components.

1. Review by Desert Research Institute (DRI) of standard operating procedures (SOPs) used by each measurement group. Aspects of SOPs reviewed by DRI include cleaning and certifying samplers, sample volume determination, type of substrate, DNPH loading and blank levels, reagent pH, breakthrough, ozone removal, sample handling and storage, extraction efficiency, analytical calibration methods and reference materials, and data processing and management.
2. Performance audit involving sampling from a standard mixture of carbonyl compounds under field condition for both surface- and aircraft-based sampling (see Section 5.3.3).
3. Field measurement comparisons involving collocated sampling at Azusa during a non-IOP day with anticipated ozone value of at least 0.15 ppm (see Section 5.3.4).

The Desert Research Institute coordinated the performance audits and field measurement comparisons with the assistance of the Research Division of the Air Resources Board.

5.3.2 Sampling and Analysis Methods

Derivation of carbonyl compounds by 2,4-dinitrophenylhydrazine (DNPH) followed by liquid chromatography and UV detection is currently the most widely used method for measurement of ambient carbonyl compounds. Two variations of this method were used during SCOS97-NARSTO. AAC, AtmAA, DRI, SCAQMD, and VCAPCD collected ambient carbonyl compounds using C₁₈ (octadecylsilane-bonded silica) Sep-Pak cartridges (Waters Associates, Milford, MA) impregnated with acidified DNPH reagent while SDAPCD used similarly impregnated silica Sep-Pak cartridges recommended by EPA Compendium Method TO-11, which is the standard method used nationally at Photochemical Assessment Monitoring Stations (PAMS). The PAMS variant of the DNPH method includes an ozone scrubber upstream of the impregnated cartridge since silica cartridges were found to have significant negative ozone artifacts (Arnst and Tejada, 1989). This artifact was not observed with C₁₈ cartridges in comparison of the method with spectroscopic measurements of formaldehyde (Fung and Wright, 1990; Lawson et al., 1990; and Fung, 1993), and ozone scrubbers were not used with C₁₈ cartridges. Despite the acceptance and widespread use of the DNPH method, questions still remain regarding interferences and sampling artifacts associated with the method.

Collection of carbonyl compounds by the DNPH method is based on the acid-catalyzed derivatization of carbonyls by nucleophilic addition of the DNPH to a C=O bond, followed by 1,2-elimination of water to form 2,4-dinitrophenylhydrazone. This method offers very high selectivity and sensitivity of analysis. The DNPH-hydrazones, formed during sampling, are non-volatile and remain on the reagent-impregnated cartridge. The yellow to deep-orange colored DNPH-hydrazones have UV absorption maxima in the 360-375 nm range and can be analyzed by high performance liquid chromatography (HPLC) coupled with UV detection. Although C₁-C₇ carbonyl compounds are typically reported with the method, the PAMS program require state and local agencies to report only formaldehyde, acetaldehyde and acetone.

Cartridge samples are taken using an automated sampler with multiple channels to collect samples sequentially on an event basis. The sampler may have an additional channel for taking either a duplicate sample concurrently with one of the active channels or a field blank. Since cartridges will passively adsorb carbonyl compounds from the surrounding air if left open, the sampler are 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. The typical sampling flow rate is about 1.0 liter/min with a precision of $\pm 5\%$ or less.

Measurement of carbonyl compounds in the ambient atmosphere poses challenges because of their trace concentrations and interferences arising from atmospheric copollutants. The analytical method is well established, and questions regarding the accuracy of the DNPH method are mainly concerned with sampling. The major concerns are: 1) incomplete collection of carbonyls, 2) loss of carbonyl compounds by physical processes such as adsorption or chemical reaction with copollutants such as ozone, 3) generation of carbonyl

compounds as sampling artifacts, and 4) variable blanks resulting from contamination of the reagent and sampling equipment.

The factors affecting carbonyl measurements by the DNPH method were reviewed by Fujita et al. (1997) for the NARSTO-Northeast 1995 Hydrocarbon and Carbonyl Measurement Audits in order to provide a perspective for interpreting the results from two field comparisons that were conducted during the study. Relevant parameters include the substrate (type, DNPH loadings, blank levels, and variability), sampling conditions (ambient ozone concentrations, temperature, relative humidity, sample volume measurements, breakthrough, type of sampling, line and ozone scrubber), sample storage, and handling (exposure to light and heat, type of storage, and duration of storage), sample preparation and analysis (extraction efficiency and instrument calibration, and peak resolution). Relevant sections of the review by Fujita et al (1997) are summarized below.

Substrate Type

While a number of DNPH-coated solid sorbents have been used as sampling media for gaseous carbonyl compound collection, commercially available Sep-Pak silica gel cartridges and Sep-Pak C18 (octadecylsilane-bonded silica) cartridges (both from Waters Associates, Milford, MA) have found the widest application. To prepare a sampling media, an acidified DNPH solution in acetonitrile is passed through a prewashed Sep-Pak cartridge. DNPH-coated ready-to-use silica Sep-Pak cartridges are commercially available (Waters Associates, Milford, MA).

Reagent Loading and Blank Levels

Blank levels are frequently related to the loading level of DNPH on the cartridges. Higher loading levels almost always lead to higher blank levels. Kleindienst et al. (1994) measured DNPH loading levels and formaldehyde blank levels for two commercial ready-to-use silica cartridges and DNPH-impregnated C₁₈ from an independent laboratory. The HCHO blank level for the Waters DNPH-coated ready-to-use silica Sep-Pak cartridges, which have a typical loading of 5 \mp mol of DNPH per cartridge (1 mg/cartridge) were 1.18 nmol/cartridge. Similar cartridges from Supelco Corporation (Bellefonte, PA) had formaldehyde blank value of 0.65 nmol/cartridge, but the DNPH loading level of these cartridges was substantially less. HCHO blank level for C₁₈ cartridges was found to be 2.38 ± 0.51 nmol/cartridge. While the absolute blank level was a factor of 1-2 times higher than the silica gel cartridges, the relative standard deviation was in the same range as that found for silica gel. The DNPH loadings for the C18 cartridges was 10 \mp mol/cartridge (2 mg/cartridge), which is twice that of the Waters silica gel cartridge.

Under the analytical conditions used by DRI and AtmAA, carbonyl compounds are routinely detected in samples and blanks at 0.03 \mp g/sample level. The lower quantifiable limit in a field program is controlled by the variability of the field blank, which is at least several times higher than the analytical detection limit. Thus, experience of the field personnel, sampler design, and analytical protocol collectively determine the detection limit achieved in the program.

Reagent pH

The effect of pH on reaction yields was studied for formaldehyde and acetaldehyde (Bicking et al., 1988). For formaldehyde, a smooth relationship was observed over the pH range of 1.7-7.0, with maximum around pH 4. The reaction yields did not change significantly over the 3-5 pH range. In contrast, for acetaldehyde, the maximum yield was observed at pH 1.7 and the yield was nearly constant between 3 and 5. Protonation of the carbonyl group at low pH promotes the nucleophilic addition, but concurrently reduces the amount of unprotonated DNPH, which is the reactive nucleophile. Because of these competing effects, the rate passes through a maximum at a characteristic pH.

Temperature and Relative Humidity

Tuss et al. (1982) studied the effect of temperature on reaction yield at pH 3 for formaldehyde. At 25 °C the reaction was nearly complete after 20 min. Similar results were obtained by Lowe et al. (1981). However, results obtained by Cofer and Edahl (1986) indicated that longer derivatization times (ca. 2 hr) were required for completion at pH 2. The reaction yield was also dependent on the molar ratio of DNPH to carbonyl compounds. The data by Tuss et al (1982) showed that a DNPH molar ratio in excess of 40 is required for quantitative derivatization. They also showed that when HCHO-DNP hydrazone was added to the DNPH solution, the added hydrazone dissociated to variable extent, forming HCHO and DNPH, if the DNPH was present in less than 40-m ratio. However, the added hydrazone was fully recovered at DNPH molar ratios greater than 40. In contrast to liquid-phase derivatization, the mechanism of carbonyl trapping with DNPH-coated solid sorbent is not well understood. The derivatization can take place in a liquid-phase film or as a gas-solid phase reaction. Past studies, which document collection efficiency using two cartridges in series, assumed complete derivatization immediately. Because of the high degree of DNPH enrichment on cartridges the derivatization may proceed faster on solid sorbents than in liquid medium. Furthermore, the reduced water activity on cartridges may facilitate equilibrium toward hydrazone formation.

Using cartridge (upstream)-impinger (downstream) sampling trains, Grosjean (1991) examined the C₁₈ collection efficiency for formaldehyde and acetaldehyde in air at RH \square 28%. Cartridge collection efficiencies were 96, 95, and 88% for formaldehyde and 99, 99, and 92% for acetaldehyde at RH = 71, 44 and 28%, respectively. More recently, Grojean (1996) examined the collection efficiency for twenty carbonyl compounds in dry air (RH = 3-7%) and in humid air (RH = 55 \pm 10%). No breakthrough was found for any of the carbonyl compounds with humid air. In dry air, there was good agreement between measured and nominal concentrations for ketones but not for aldehydes. The decrease in collection efficiency should only be of concern in a limited number of applications since DNPH-coated cartridge measurements of carbonyls are seldom made in very dry air.

Breakthrough

During the NARSTO-Northeast 1995 Ozone Study, 48 tandem C₁₈ cartridges were collected to assess breakthrough (Fung, 1996) in ambient samples. Collection efficiencies were determined from the ratio of a carbonyl species amount measured in the upstream

cartridge to the total amount in both up- and downstream cartridges. Except for acetone, all species up to C₆ carbonyls average 95% efficiency or greater. Acetone collection efficiency averaged approximately 79%, with most of the lower values (45 to 65%) corresponding to the night time period when 6-hour samples were collected rather than 3 hour samples during the daylight hours. Average collection efficiency for acetone during daytime periods was over 90%.

Ozone Artifacts

Many of the current questions about the DNPH method are in regard to the effect of ozone on sampling with DNPH-coated solid adsorbents. Arnts and Tejada (1989) reported that DNPH-coated silica gel cartridges showed a dramatic decrease in the apparent HCHO concentrations in the presence of ozone. In the same study, they also evaluated cartridges prepared with the C₁₈ substrate, and observed no interference for formaldehyde from ozone at the 120 ppb level used in the experiment. Arnts and Tejada (1989) suggested that, in the case of silica gel cartridges, a DNPH derivative, which largely forms at the front of the cartridge and is immobilized, is destroyed by ozone. In the case of C₁₈ cartridges, the radicals generated by the ozone attack can be scavenged by the C₁₈ phase, thus limiting further attack on DNPH or hydrazone.

The results obtained by Arnts and Tejada were subsequently reproduced by Kleindienst et al. (1994). In addition to formaldehyde, Kleindienst et al also made measurements of a four-component mixture containing acetaldehyde, propionaldehyde, acetone, and methyl ethyl ketone to determine the effect of ozone on these compounds when using both types of cartridges (Table on page 13). For formaldehyde, acetaldehyde, and propionaldehyde, collection on silica gel showed systematically lower values without the use of an ozone scrubber while values with the scrubber were within 10% of the assay values. With C₁₈, the three aldehydes showed good agreement with the assay values. Unlike silica gel, the presence of the scrubber makes little difference in the values observed for C₁₈ cartridges except for HCHO. With the C₁₈ cartridge, a positive ozone interference was detected with the formation of a peak which coelutes with the HCHO hydrazone. Several chromatographic conditions were used without success to separate the coeluting peak, which suggests the possibility that the artifact is the HCHO hydrazone itself. The magnitude of the interference is approximately 1.7% of the number of moles of ozone that pass through the cartridge. The presence of ozone in the system does not lead to formation of peaks that are coincident to the hydrazones for the acetaldehyde or propionaldehyde. Reactions of ozone with the ketone hydrazones were found to be considerably less than with the aldehyde hydrazones for both silica gel and C₁₈ cartridges. Assuming that the extent of derivatization of the ketones on the cartridges is rapid, the results indicate that the ketone-hydrazones are considerably less reactive to ozone than the aldehyde hydrazones.

**Effect of Added Ozone (120 ppbv) on Carbonyl Levels for Sample Collection
on Silica Gel and C₁₈ Cartridges ^a**

	Silica <u>w/o scrubber</u>	Silica <u>w/ scrubber</u>	C18 <u>w/o scrubber</u>	C18 <u>w/ scrubber</u>
Formaldehyde	46.3 ± 6.4%	93.3 ± 18.6%	97.6 ± 8.5%	80.1 ± 11.2%
Acetaldehyde	76.3 ± 8.4%	102.2 ± 4.7%	100.7 ± 5.2%	97.6 ± 3.3%
Propionaldehyde	62.7 ± 1.8%	95.6 ± 3.1%	89.2 ± 2.6%	94.7 ± 1.1%
Acetone	90.0 ± 1.3%	103.3 ± 5.6%	87.4 ± 11.4%	85.3 ± 12.2%
MEK	149.2 ± 35.4%	117.3 ± 11.9%	118.9 ± 11.9%	103.9 ± 18.1%

^a Averages calculated from data in Kleindienst et al. (1994).

Positive ozone artifacts have also been reported (Rodler and Birks, 1994) on formation of HCHO, methy vinyl ketone, and methacrolein from isoprene, and several higher carbonyls from the C₁₈ substrate. In the same paper, these authors noted that sample medium acidity greatly influenced the formation of the isoprene oxidation products. Thus, one can deduce that optimum acidity of the sampling medium is essential to minimize this isoprene artifact. The C₁₈ artifact observed by Rodler and Birks (1994) was based on laboratory experiments and is contrary to the field measurements made when daily ozone levels of 260 to 280 ppb were observed (Fung, 1993). Others have reported negative ozone artifacts with the C₁₈ cartridges (Sirju and Shepson, 1995). But these authors considered the interference was more relevant to HCHO measurements in clean air. An experiment in which atmospheric samples were collected by collocated C₁₈ and silica gel cartridges that were prepared at the same time under identical conditions gave comparable formaldehyde levels which also compared well to the Tunable Diode Laser Absorption Spectroscopy (TDLAS) measurements (Fung, 1993). These results suggest that the type of substrate (C₁₈ versus silica gel) is less critical than how the cartridge is prepared.

The U.S. EPA Method TO-11 currently recommends using the silica gel cartridge in conjunction with a KI scrubber to overcome the ozone artifact. The use of CuO cartridge in front of the sampling cartridge has also been reported (Vairavamurthy et al, 1993). However, the use of ozone scrubbers has not been sufficiently time-tested to ensure its reliability.

Ozone Removal

Tests were conducted by EPA and ManTech to examine the efficiency of ozone removal systems using both potassium iodide (KI) scrubbers and denuders (Kleindienst et al., 1994). Ozone scrubbers were obtained from Waters Corporation and contained KI inside a standard polyethylene cartridge. Ozone denuders were produced in-house using coiled one meter lengths of 6.4-mm copper tubing (outside diameter) coated with saturated KI solution, then dried under nitrogen. Tests were performed to evaluate both the efficiency of ozone (120 ppbv) removal and the passage of carbonyl compounds through the removal systems. Experiments were conducted at various levels of relative humidity from 2-75%. For RH less

than approximately 5%, the scrubber has extremely low capacity for ozone removal and breakthrough occurs within a few minutes at a flow of 1 L min⁻¹. Scrubbing efficiency increases substantially even at low levels of relative humidities (ca. 10%). For ozone denuders, even under dry conditions, the device showed a moderate capacity for removing ozone. Under dry condition, the denuders showed negligible breakthrough for 120 ppbv ozone at (2 L min⁻¹) for approximately 45 minutes. At moderate to high RH, the ozone denuders have high capacity for ozone removal. Results show an efficiency of at least 24,000 ppbv-h for these devices. For an average ozone concentration (day and night) of 60 ppbv the devices are expected to be effective for at least 16 days when used at a flow rate of 1 L min⁻¹.

Carbonyl compounds are generally quite soluble in water and KI is a highly hygroscopic chemical. In tests conducted at RH of 75%, there was no evidence of formaldehyde retention on KI scrubbers over a two-hour exposure (Kleindienst et al., 1994). Other carbonyls were not tested, and it is possible that carbonyl compounds with carbon number higher than C₄ might be retained by the scrubber or denuder in some cases. Method TO-11 specifies heating the KI denuders to approximately 50 °C to avoid formaldehyde loss.

Comparison of the DNPH Method with Spectroscopic Measurements

There are few measurement techniques which can be used to evaluate the accuracy of the ambient carbonyl species concentrations. Previous studies in California prior to and during the 1987 Southern California Air Quality Study (SCAQS) indicated that formaldehyde concentrations determined using C₁₈ DNPH cartridges similar to those used in NARSTO-Northeast compare well to those from continuous instruments such as long-path Fourier transform infrared detector (FTIR), differential optical absorption spectrometer (DOAS), and TDLAS.

In August 1986, during the 10-day Carbonaceous Species Methods Comparison Study (CSMCS) conducted by the California Air Resources Board in Glendora, CA, the efficiency of the C₁₈ cartridge collection method for formaldehyde was compared to more direct methods, such as long-path FTIR, DOAS, and the TDLAS. There was a small negative bias of 0.7 ppb, corresponding to -6.9% at the mean formaldehyde concentration (10.2 ppb) observed during the study (Fung and Wright 1990, Lawson et al 1990). The average peak ozone concentration for the ten day study was approximately 195 ppb (Lawson et al 1990).

During the 1987 Southern California Air Quality Study, formaldehyde measurements were made at the Claremont sampling site by TDLAS and DOAS and by both C₁₈ and silica gel DNPH cartridges. Measurements of HCHO by C₁₈ DNPH cartridges generally tracked ozone concentrations and were in reasonably good agreement with TDLAS and DOAS measurements (Fujita and Croes, 1990). In contrast, measurements of HCHO by silica gel DNPH cartridges were substantially lower during the middle of the day, when ozone reached maximum concentrations. These data indicate that the DNPH-coated C₁₈ cartridge collection method is reliable in the presence of higher ozone concentrations (the studies were conducted in southern California on days when ozone concentrations ranged from 200 to 300 ppb), at least as far as the formaldehyde measurements are concerned.

Also, the HCHO data showed good agreements between the C₁₈ DNPH cartridge and the TDLAS in the 1993 Los Angeles Atmospheric Free Radical Experiment (Mackay, 1994) and in the NCAR/SOS Formaldehyde Intercomparison Study (Calvert et al., 1996).

Sample Handling and Storage

An experiment was performed by Fung et al. (1995) to assess the effectiveness of various types of packaging used to protect the DNPH cartridges from contamination during storage and shipment. In general, the amount of exposure was reduced significantly by using a protective closure compared to an open cartridge. Even the PVC cap, the worst performer of the group, reduced formaldehyde exposure to approximately 2% of an open cartridge. For formaldehyde, a polyethylene cap provided about ten times more protection than PVC caps and about twice as much protection as plugs. Screw-capped vials offer additional protection.

As mentioned above, hydrazones of stable carbonyls, such as formaldehyde, acetaldehyde, propionaldehyde, acetone, etc, maintain their integrity on silica gel and C18 cartridges, as well as in impinger reagent solutions, for over a month under refrigerated storage (Fung et al, 1993; Vairavamurthy et al, 1993 and references therein). However, the olefinic aldehydes such as acrolein and crotonaldehyde degrade partially on the cartridges, either during sampling or storage, and form unknown products. Also, acrolein DNPH derivative is not stable in the strongly acidic DNPH solutions used in the impinger method. In order to preserve its integrity it has to be extracted from this solution immediately after sampling (Freeman, 1992)

Those usually stable hydrazone products were stable in the cartridge in this study as well. Duplicates were collected in the field. One sample from each of the duplicate pairs was retrieved and analyzed immediately after collection, while the original samples remained in the sampler until they were retrieved during the normal weekly visits by the technician. The excellent agreements between the pairs confirmed that after collection the samples were stable up to 7 days of holding time encountered in the study (Fung and Wright 1987).

Exposure to sunlight causes significant production of carbonyls which can be eliminated by wrapping the cartridges in aluminum foil during sampling and storage (Zhou and Mopper, 1990)

Sample Preparation and Analysis

Cartridges are eluted with 2-5 mL of acetonitrile by gravity feed into a graduated cylinder and diluted to the appropriate volumetric mark. An aliquot of the eluent is transferred into a septum vial and injected with an autosampler into a high performance liquid chromatograph for separation and quantification of the hydrazones. The derivatized carbonyl compounds are measured at 360 nm using UV absorption. An acetonitrile/water and acetonitrile/methanol/water mixtures are used as eluents or acetonitrile/THF/water and acetonitrile/water. Ambient air samples typically contain C₁-C₆ carbonyls and benzaldehyde, with formaldehyde, acetaldehyde, and acetone being most abundant. Higher carbonyls include MEK, pentanones, and hexanones. Aldehydes >C₃ are generally much lower in concentrations than corresponding ketones. State and local agencies are currently required under PAMS to report formaldehyde, acetaldehyde and acetone. Complete speciation of C₁-C₆

carbonyls is possible, but significantly increases the length of the analysis. For NARSTO-Northeast, individual species data were reported only for C₁-C₃ carbonyls, and combined concentrations were reported by carbon number for C₄ to C₆ carbonyls since higher carbonyls are routinely group together for modeling applications. The carbonyl concentrations, in ppb, are computed from the amounts measured after blank correction and the volume of air sampled. Combined uncertainties are determined from analytical uncertainty, blank variability, and the lower quantifiable limit.

Lower Quantifiable Limits and Measurement Precision

Factors that may cause a bias in this measurement, such as breakthrough, blank variability, hydrazone product stability were evaluated and conducted as part of the QA/QC activities in NARSTO-Northeast. Based on field blanks and their variability, lower quantifiable limits (LQL) for 3-hour samples were approximately 0.4 ppbv or less for all but the >C₆ carbonyls, which was estimated at 1 ppbv. The LQLs for 6-hour samples are half those values. Analytical precisions derived from repeat analysis range from 0.014 μg for propanal to 0.16 μg for >C₆ carbonyls, corresponding to a coefficient of variation (CV) of 3 to 4% for the major components such as formaldehyde, acetaldehyde, and acetone. There were 26 pairs of collocated samples, which provided an estimation of the carbonyl measurement precision. Most species had a CV of 4 to 8%, except propanal (10.6%), C₅ carbonyls (9%), and >C₆ carbonyls (15.0%).

Carbonyl Compound Measurement Comparison in Agawam, MA

Ambient measurements of carbonyl compounds by Atmospheric Assessment Associates (AtmAA), the principal carbonyl measurement laboratory for NARSTO-Northeast, and the State of Massachusetts Department of Environmental Protection (MADEP) were compared under field conditions at Agawam, MA. during August 8-11, 1995. AtmAA collected ambient carbonyl compounds using C₁₈ Sep-Pak cartridges impregnated with acidified DNPH reagent while MADEP used similarly impregnated silica Sep-Pak cartridges according to EPA Method TO-11. In order to examine the effect of ozone removal, MADEP collected silica gel cartridges with an unheated KI denuder, a heated KI denuder, uncoated copper tube, and with Teflon tubing. The following findings of the comparison were reported by Fujita et al. (1997).

- The average coefficient of variations of replicate analysis by AtmAA was better than 5% for all species with the exception of benzaldehyde and >C₆ carbonyl compounds, which were at or below the limit of detection. The method precision determined from duplicate samples were better than 10% for formaldehyde, acetaldehyde, acetone, and C₄ and C₅ carbonyls, 10-20% for propanal, m-tolualdehyde and C₆ carbonyls. Acetone was the only species that showed significant breakthrough with an average ratio of back cartridge to sum of front and back cartridges of 12.3% ± 5.0% for four 3-hour daytime samples. Breakthrough for acetone are correspondingly higher for 6-hour nighttime samples. Average breakthrough for the other species were within lower quantifiable limits.

- Cartridge extracts were exchanged between AtmAA and MADEP to determine whether systematic biases exist due to analytical methods. Values for the MADEP extracts reported by the two laboratories are generally well correlated. Both formaldehyde and propanal show a positive bias with average AtmAA to MADEP ratios of 1.27 ± 0.04 and 1.55 ± 0.20 , respectively. AtmAA's values are also higher for acetone in some samples. But, on average, were not significantly different from values reported by MADEP. In contrast, ratios of values reported by the two laboratories for the AtmAA extracts were highly variable, with MADEP reporting about a factor of 15 higher values for formaldehyde in half of the extracts. Ratios for the other half of the extracts were near one to one. Unusually large discrepancies were also found for acetaldehyde and acetone in half the samples. Check of data processing revealed no obvious errors. Comparisons of analysis of the extracts by AtmAA both before and after analysis by MADEP showed no significant changes in the extract during this time.
- Agreements between AtmAA and MADEP for the three major carbonyl compounds, formaldehyde, acetaldehyde and acetone, are remarkably good. Concentrations of propanal were at or below the detection limit. Concentrations were relatively low during the four-day sampling period, ranging from 2-5, 2-3, and 2-3 ppbv for formaldehyde, acetaldehyde and acetone, respectively. The average MADEP/AtmAA ratio for formaldehyde was 1.21 with an unheated KI denuder, 1.06 with a heated KI denuder, 1.02 with an uncoated copper tubing, and 1.10 with Teflon tubing. For acetaldehyde, the best agreement between MADEP and AtmAA (ratio of 1.00) was obtained when a heated KI denuder was used with the silica gel cartridges. The other three MADEP sampling configurations gave MADEP/AtmAA ratios of 0.74 to 0.82. MADEP and AtmAA values for acetone are in good agreement with the exception of the midnight to 6:00 a.m. samples due to greater breakthrough of acetone in C₁₈ cartridges.

Carbonyl Compound Measurement Comparison in Nashville, TN

During the summer of 1995, a carbonyl measurement comparison was conducted in Nashville, TN as part of the Nashville/Middle Tennessee Ozone Study. A major objective of the Nashville Study was to obtain high temporal resolution of ambient carbonyl compounds by gas chromatography/mass spectrometry systems, one operated by the University of Miami and a second system operated by Purdue University. The research-grade carbonyl measurements were compared to more common methods using DNPH-impregnated cartridges according to the protocol recommended by the Environmental Protection Agency for PAMS (ManTech Environmental Technology Inc.) and the variation of the DNPH method used by Atmospheric Assessment Associates (AtmAA) in the NARSTO-Northeast Study. Fujita et al. (1997) described the results of the comparison of DNPH-impregnated cartridge methods.

- To establish comparability of chemical analysis between ManTech and AtmAA, calibration standard and extracts for several samples were exchanged between the two laboratories. Regression statistics for each pair of analyses show good correlation between the two laboratories, with slopes and correlation coefficients both approaching unity for formaldehyde, acetaldehyde and acetone for both sets of extracts.

Concentrations of propanal were substantially lower than for the other carbonyl compounds, but also show good correlation between the two laboratories. Repeat analysis of the extracts by AtmAA after approximately one month show that the extracts were stable during the exchange of extract.

- During the first week of measurements (July 4-11), formaldehyde values were in the range of 1-5 ppbv. Substantial higher formaldehyde concentrations were detected during the July 13-15 period with ozone levels occasionally exceeding 135 ppbv. Unfortunately, for reasons that could not be explained, twenty-two AtmAA sample cartridges were not exposed during this high ozone period. Most of the direct comparisons between silica gel and C₁₈ cartridges were made during the period July 20-22, 27 and 29. Formaldehyde concentrations ranged from 10-20 ppbv during the first half of this period and from 2-5 ppbv during the latter half.
- Ratios of values for silica gel cartridges to corresponding C₁₈ cartridges were determined for three alternative configurations for ozone removal: KI-coated copper denuder tube, commercial packed KI scrubber, and no ozone removal. For formaldehyde, the silica gel/C₁₈ ratios averaged 0.98 ± 0.19 with the commercial KI scrubber, 0.87 ± 0.03 for the KI-coated copper denuder tube, and 0.59 ± 0.15 with no ozone removal. These results are consistent with the widely reported negative ozone artifact. Whether ozone was removed or not, the silica gel/C₁₈ ratios for acetaldehyde were about half and about 0.7 for acetone.
- The average coefficient of variations of replicate analysis by AtmAA were better than 5% for all species with the exception of benzaldehyde and >C₆ carbonyl compounds, which were at or below the limit of detection. The method precision determined from duplicate samples were better than 10% for the three major carbonyl compounds, formaldehyde, acetaldehyde, and acetone.

In summary, there are few measurement techniques that can be used to evaluate the accuracy of the carbonyl species concentrations made by the DNPH method. Previous studies in California prior to and during the Southern California Air Quality Study (SCAQS) indicated that formaldehyde concentrations determined using C₁₈ DNPH cartridges similar to those used in NARSTO-Northeast compare well to those from continuous instruments such as long-path FTIR, DOAS, and TDLAS. There was a small negative bias of 0.7 ppb, corresponding to -6.9% at the mean formaldehyde concentration (10.2 ppb) observed during the study (Fung and Wright 1990, Lawson et al 1990). The average peak ozone concentration for the ten day study was approximately 195 ppb (Lawson et al 1990). Measurements of HCHO by C₁₈ DNPH cartridges during SCAQS generally tracked ozone concentrations and were in reasonably good agreement with TDLAS measurements. Also, the HCHO data showed good agreements between the C₁₈ DNPH cartridge and the TDLAS in the 1993 Los Angeles Atmospheric Free Radical Experiment (Mackay, 1994) and in the NCAR/SOS Formaldehyde Intercomparison Study (Calvert et al., 1996). In contrast, SCAQS measurements of HCHO by silica gel DNPH cartridges were substantially lower in comparison to the TDLAS during the middle of the day, when ozone reached maximum concentrations. Arnts and Tejada (1989) reported significant ozone interference associated with EPA Method TO-11 using DNPH-coated silica gel cartridges. They observed a significant reduction in the level of formaldehyde measured in

the presence of ozone. In the same study, they also evaluated cartridges prepared with the C₁₈ substrate, and observed no interference for formaldehyde from ozone at the 120 ppb level used in the experiment. Arnts and Tejada concluded that the ozonolysis of formaldehyde hydrazone is apparently substrate dependent (silica gel vs C₁₈). These results were subsequently reproduced by Mantech (Kleindienst, 1994).

Positive ozone artifacts have also been reported (Rodler and Birks, 1994) on formation of HCHO, methyl vinyl ketone, and methacrolein from isoprene, and several higher carbonyls from the C₁₈ substrate. The C₁₈ artifact observed by Rodler and Birks (1994) is contrary to the field data collected from the studies cited above in which daily ozone levels of 260 to 280 ppb were observed. An experiment in which atmospheric samples were collected by collocated C₁₈ and silica gel cartridges that were prepared at the same time under identical conditions gave comparable formaldehyde levels which also compared well to the TDLAS measurements (Fung, 1993). These results suggest that the type of substrate (C₁₈ versus silica gel) is less critical than how the cartridge is prepared. Artifacts reported have been on the cartridges prepared by individual researchers, and the cartridge composition was not addressed in each case. The artifacts observed may not have been attributed solely to the substrate. Multiple factors, such as, among others, reagent formulation, loading, and acidity of the DNPH, are important in determining the extent of the artifacts that may occur.

With the exception of nighttime acetone values, it is likely that nominal accuracy of the DNPH carbonyl data is better than 20 percent for measured carbonyl species with concentrations above 2 ppb. Hydrocarbon sampling onboard aircraft is essentially the same as on the surface. However, because of the longer sampling times required for the DNPH-cartridge method, ambient samples are first collected in Tedlar bags. The air samples are transferred from the bags to cartridges soon after the flight has ended. Other than the transfer bag, the sampling procedures are identical to the collection of surface samples.

5.3.3 SCOS97-NARSTO Performance Audit for Carbonyl Compounds

The carbonyl performance audit consisted of sampling under field conditions with addition of a standard mixture of carbonyls from a 6-liter stainless steel canister to an ambient sample. The protocols for the audit and comparison are included in Appendix C. The standard audit protocol consisted of a 3-hour ambient sample using two DNPH cartridges in series (the same configuration as a breakthrough experiment) with addition of the standard mixture, with appropriate dilution, between the two cartridges. The front cartridge served to scrub ambient carbonyl compounds and ozone. Each group collected two samples. DRI analyzed the contents of the canister by DNPH/HPLC prior to shipment and upon its return.

The main supply of the standard mixture was prepared at the Desert Research Institute in a 33-liter tank. Carbonyl compounds were directly injected by microsyringe into a one-liter glass bulb. The mixture in the glass bulb was transferred into a 33-liter stainless steel canister by sweeping the contents of the bulb into the canister with humidified nitrogen gas to a pressure of 30 psi. Dry nitrogen gas was then added to the canister to bring the total canister pressure up to 80 psi. The mixture was prepared on May 19, 1997. The first sample from the standard mixture was collected onto C₁₈ DNPH cartridges during the week of June 15.

Aliquot of the standard mixture was withdrawn from the 33-liter canisters into 6-liter transfer canisters about ten days before the mixture was sent to an audited laboratory. After an equilibration period of one week, a sample was collected on DNPH C₁₈ cartridges for HPLC analysis at DRI. A second sample was collected after the standard mixture was returned to DRI.

The Desert Research Institute provided a dilution apparatus with the 6-liter canister containing the standard mixture of carbonyl compounds. The gas standard dilution and delivery system is designed to allow the addition of standard gas mixtures from a 6-liter canister at a constant flow of up to 20 sccm (standard cubic centimeter per second) (70° F and 29.92 in. Hg). It consists of a Sierra Instruments, Inc. Gas-Trak mass flow controller, model number 810C-SQR-249 (Serial No. C1261), a 6-liter stainless steel gas standard transfer canister, and a 3-way valve and tee assembly. The flow controller was preset to provide a flow of 5.0 mL per minute. Prior to shipment of the gas dilution and delivery system, the fittings and stainless steel sampling lines were cleaned with deionized water and baked at 170°C for 24 hours.

The following measurement groups participating in the audit: Atmospheric Analytical Consultants (Sucha Parmar), Atmospheric Assessment Associates (Kochy Fung), San Diego Air Pollution Control District (Mahmood Hossain), South Coast Air Quality Management District (Steve Barbosa), and Ventura County Air Pollution Control District (Jim Balders). Although the same laboratory performed the chemical analyses for AAC and VCAPCD, the use of different samplers require the collection of separate samples by each group.

Each group collected two replicate samples from the transfer canister according to their normal sampling protocol with the following modifications. The standard audit protocol consists of a 3-hour ambient sample using two DNPH cartridges in series (the same configuration as a breakthrough experiment) at a nominal flow rate of 1 liter of ambient air per minute. The standard mixture was added at a nominal flow rate of 5 mL per minute in between the two cartridges. If an ozone scrubber was normally used in sampling, the scrubber was placed upstream of the sample cartridge and downstream of the gas addition. The front cartridge serves to scrub ambient carbonyl compounds and ozone. Data were reported for both sample and scrubber cartridges. The loadings on the scrubber cartridge were used to characterize the incoming ambient. A third cartridge was placed downstream of the sample cartridge to quantify any breakthrough that may occur. This step was left out if it resulted in excessive pressure drop.

A minimum of two field blanks was collected during the audit. During the audit, cartridge end-caps for the blank cartridges were removed and left off for the time required to place new cartridges in the sampler (typically a few minutes). After this brief exposure the blank cartridges were sealed again with the end-caps, checked that plugs were tight, and placed inside the sampler until the sample cartridges were removed from the sampler and placed in coolers for transport to the laboratory.

The performance audits for the aircraft sampling of carbonyl compounds were similar to surface-based measurements. The main procedural difference is that the Tedlar bags were filled with zero-air with addition of the standard carbonyl mixture. SDAPCD and AtmAA

collected one sample from a Tedlar bag by first filling the bag with the standard mixture diluted with scrubbed ambient air or zero air (also with inline scrubber). Samples were transferred from the bag to the cartridge in accordance with the procedures used during SCOS.

The groups were instructed to return the gas dilution system and 6-liter canister (with a minimum pressure of 10 psig) to DRI within five working days after receipt of the equipment. A new supply of the standard mixture was sent to the next laboratory. Each analytical laboratory processed and analyzed all samples for this audit within five working days after sample collection. Each laboratory performed two replicate measurements for each of the two samples in order to determine analytical precision. Data were reported to the ARB and were forwarded to DRI for analysis once DRI's data for the initial and final standard concentrations were sent to ARB.

Results of the performance audits are summarized in Table 5.3-1 and Figure 5.3-1. Table 5.3-2 shows the ratio of the average values reported by each group to DRI's pre and post analysis of the 6-liter transfer canisters. The values in the table are in \bar{x} g/sample and are normalized to the volume of standard delivered to the cartridge. AAC and VCAPCD values differ substantially from DRI values for formaldehyde and acetaldehyde (almost 2 times DRI) [methyl ethyl ketone results are not shown]. With the exception of AAC and VCAPCD, the values obtained by the audited laboratories were in reasonable agreement with those obtained by the reference laboratory. Relative comparisons to DRI's pre and post analysis of the 6-liter transfer canisters show losses of up to half of the acetone in the canisters during the period of the audit and up to 30 percent loss for formaldehyde. The other three carbonyls in the standard mixture (acetaldehyde, butanal and benzaldehyde) are stable in comparison.

5.3.4 Field Comparison Study

The collocated ambient sampling was intended to examine variations among measurement groups in reported values of carbonyl compounds under actual field conditions when ozone levels are comparable to those encountered during SCOS97 Intensive Operational Periods. One of the objectives of the collocated sampling was to compare values obtained for samples collected by DNPH-impregnated silica gel cartridges with KI denuder versus DNPH-impregnated C₁₈ cartridges without an ozone scrubber. However, this objective was not achieved because all groups used C₁₈ cartridges. The comparison also examined amounts of breakthrough by collecting duplicate cartridges in series, and levels and variability of field blanks.

The field measurement comparisons were conducted at Azusa during September 23 and 24 in accordance with the protocol in Appendix C. Participants included DRI, AtmAA, and VCAPCD. The comparisons consisted of collocated samplings at the Azusa monitoring station through a common sampling manifold that was provided at the site. Collocated sampling was conducted on two consecutive non-IOPs days [the goal had been to select days with ozone levels comparable to IOP days that proved difficult to do during SCOS97]. A total of four 3-hour samples were collected according to the following schedule: first day - 1300 to 1600, and 1700 to 2000 PDT; second day - 0600 to 0900 and 0900 to 1200. A duplicate sample was collected during the 0900-1200 sampling period of the second day by groups that have the

ability to collect parallel samples. A backup cartridge, placed in series with the primary sample, was collected during the 1300 to 1600 period of the first sampling day and 0600 to 0900 period of the second day of sampling. A minimum of two field blanks was collected during the comparison, one for each day of sampling.

Each analytical laboratory processed and analyzed all comparison samples within ten working days after collection, and performed replicate analyses for all four samples in order to determine analytical precision. Each laboratory reported their data to the Air Resources Board within four week of field sampling. The submittal included: concentration data and associated uncertainties for individual C₁ to C₇ carbonyl compounds; field data needed to calculate sample volumes including temperature and pressure if volume adjustments are made and nominal volume uncertainty; and laboratory data (mass of analyte per sample, extraction volume and correction for extraction efficiency and uncertainty if applicable, and all blank samples used in deriving the mean blank subtractions). Data were forwarded to DRI for analysis after ARB had received the data from all participants. The comparison data are shown in Table 5.3-3.

Results of the field measurement comparison were as expected with variation among the three groups ranging from 10 to 25 percent for C₁ to C₃ carbonyl compounds. The average relative standard errors for the four sampling periods are 22.2, 10.7, 20.5, 15.2, and 18.4 percent for formaldehyde, acetaldehyde, acetone, propionaldehyde, and methyl ethyl ketone, respectively. DRI reported consistently lower values than AtmAA and VCAPCD for formaldehyde and higher values for benzaldehyde. There is generally good agreement among the three groups for the other carbonyl compounds.

5.4 Measurement Comparisons for Halogenated Compounds

Halogenated compounds can be quantified from canister samples, with the same column as used for C₃-C₁₁ hydrocarbons. However, electron capture detection is used rather than flame ionization due to the weaker and variable response of the FID for halogenated compounds. This method was used by DGA to measure peroxyacetylnitrate (PAN) as well as perchloroethylene and methylchloroform at Azusa and Simi Valley and by Desert Research Institute (Schorran) to measure halogenated "tracers of opportunity" at Lancaster and Barstow.

Field and laboratory comparisons of halogenated hydrocarbon measurements were conducted as part of an external quality assessment program for the SCOS97-NARSTO. Appendix D documents the protocol for the comparison study.

The two canister samples that were used in this laboratory comparison were those collected by CE-CERT at the Azusa sampling site during the second SCOS intensive operational periods, and analyzed by Biospheric Research Corporation for speciated hydrocarbons. After speciated hydrocarbon analysis, BRC also analyzed the two comparison samples for halogenated hydrocarbons. These samples were then sent to DRI (Zielinska), DRI (Schorran) and Mantech, in round-robin fashion in that order, for analysis of halogenated hydrocarbons. Continuous measurements of halogenated hydrocarbons that were made at Azusa by DGA, Inc. are also included in the comparison. Each laboratory submitted their data to Air Resources Board, which then forwarded the data to DRI for evaluation.

Table 5.4-1 shows the results of the measurement intercomparisons for F12, methylbromide, F11, F114, chloroform, methyl chloroform, carbon tetrachloride, trichloroethylene, chlorodibromomethane, perchloroethylene, m-dichlorobenzene, p-dichlorobenzene, and o-dichlorobenzene. The coefficient of variation for the two tracers of opportunity were 18.2 and 3.7 percent for methyl chloroform and perchloroethylene, respectively. [Carbon Tetrachloride CV was significantly higher than any others]. The average CV for all reported halogenated compounds was 12.4 percent.

5.5 Measurement Comparisons for Biogenic Hydrocarbons

Appendix E documents the protocol for the field and laboratory comparisons of biogenic hydrocarbon measurements that were conducted as part of an external quality assessment program for the SCOS97-NARSTO. The participating laboratories include the University of California, Riverside (Arey), Biospheric Research Corporation (Rasmussen), Desert Research Institute (Zielinska) and ManTech Environmental Technology, Inc. (Daughtrey). The purpose of these comparisons was to document differences that may exist between measurement groups, and to compare isoprene values obtained from canister samples and solid adsorbent samples. Isoprene was the main compound of interest for this comparison. Although some questions exist concerning the analysis of terpenes from canisters samples, these compounds were also reported if observed in the sample.

UC, Riverside collected two canister samples along with adsorbent tube samples on the campus of UC, Riverside on August 1, 1997 from 2:30 to 6:15 pm. The two canisters, one supplied by Biospheric Research Corporation and one by Desert Research Institute, were collected simultaneously using a DRI sampler to a minimum of 15 psig. BRC and DRI analyzed their respective canisters. DRI sent their canister to Mantech after completing their analysis. Each laboratory submitted their data to the Air Resources Board, which forwarded the data to DRI for evaluation.

Table 5.5-1 show that the average isoprene mixing ratios reported by the four laboratories ranged from 22.05 to 26.79 ppbC with an overall average of 24.00 ± 2.05 . The average of the adsorbent tube samples analyzed by GC/MS were 13 percent higher than the average of the DRI and BRC analysis of canister samples by GC/FID. Although ManTech's replicate analysis of the canister samples by GC/MS were widely varying, the average of the two analyses was only 7 percent lower than the average of the GC/FID analyses.

**Table 5.1-1
Summary of SCOS97-NARSTO VOC Measurements**

Site Location	Sample		Chemical		Type of Site	Measurement	Times	Sampling Schedule	
	Collection	Analysis	DRI	Analysis				Frequency	Period
South Central Coast/Ventura Co.									
Point Conception	Cal Poly SLO	DRI	SCOS97	SCOS97	CO, CO ₂ , CH ₄ , MTBE, C ₂ -C ₁₁ HC, halocarbons, C ₁ -C ₇ carbonyls	B	IOP	after 8/15	
Ventura - Emma Wood	VCAPCD	VCAPCD/AAC	PAMS Type 1	PAMS Type 1	C ₂ -C ₁₁ HC, C ₁ -C ₇ carbonyls	B	3, IOP	6/16 to last IOP	
El Rio	VCAPCD	VCAPCD/AAC	PAMS Type 2	PAMS Type 2	C ₂ -C ₁₁ HC, C ₁ -C ₇ carbonyls	B	3, IOP	6/16 to last IOP	
Simi Valley	VCAPCD	VCAPCD	PAMS Type 3	PAMS Type 3	C ₂ -C ₁₁ HC	B	3, IOP	6/16 to last IOP	
Simi Valley	DGA	DGA	SCOS97	SCOS97	PAN, PPN, Perc	E	IOP		
South Coast Air Basin									
Burbank	SCAQMD	SCAQMD	PAMS Type 1, 2	PAMS Type 1, 2	C ₂ -C ₁₁ HC, carbonyls ^a	A	1	7/15 to last IOP	
Burbank	SCAQMD	DRI	SCOS97	SCOS97	CO, CO ₂ , CH ₄ , MTBE, C ₂ -C ₁₁ HC, halocarbons, C ₁ -C ₇ carbonyls	C	IOP	after 7/15	
San Nicolas Island	CE-CERT	DRI	SCOS97	SCOS97	CO, CO ₂ , CH ₄ , MTBE, C ₂ -C ₁₁ HC, halocarbons, C ₁ -C ₇ carbonyls	F	IOP		
Santa Catalina Island	USC	DRI	SCOS97	SCOS97	CO, CO ₂ , CH ₄ , MTBE, C ₂ -C ₁₁ HC, halocarbons, C ₁ -C ₇ carbonyls	F	IOP	after 7/15	
Hawthorne	SCAQMD	SCAQMD	PAMS Type 1	PAMS Type 1	C ₂ -C ₁₁ HC	A	3	7/6 to 9/28	
Los Angeles - North Main	ARB	ARB	NMOC/HAPs	NMOC/HAPs	C ₂ -C ₁₁ HC	C	3	7/3 to 9/28	
Los Angeles - North Main	CE-CERT	BRC	SCOS97	SCOS97	CO, CO ₂ , CH ₄ , MTBE, C ₂ -C ₁₁ HC	B	IOP		
Los Angeles - ARCO Plaza	CE-CERT	BRC	SCOS97	SCOS97	CO, CO ₂ , CH ₄ , MTBE, C ₂ -C ₁₁ HC	B	IOP		
Pine Mountain	UCR	DRI	SCOS97	SCOS97	CO, CO ₂ , CH ₄ , MTBE, C ₂ -C ₁₁ HC, halocarbons, C ₁ -C ₇ carbonyls	B	IOP		
Pine Mountain	UCR	UCR	SCOS97	SCOS97	Biogenic HC & oxidation product	B	IOP		
Anaheim	CE-CERT	DRI	SCOS97	SCOS97	CO, CO ₂ , CH ₄ , MTBE, C ₂ -C ₁₁ HC, halocarbons, C ₁ -C ₇ carbonyls	D			
Pico Rivera	SCAQMD	SCAQMD	PAMS Type 2	PAMS Type 2	C ₂ -C ₁₁ HC, carbonyls ^a	A	1	7/6 to last IOP	
Upland	SCAQMD	SCAQMD	PAMS Type 1, 4	PAMS Type 1, 4	C ₂ -C ₁₁ HC	A	3	7/6 to 9/28	

**Table 5.1-1 (continued)
Summary of SCOS97-NARSTO VOC Measurements**

Site Location	Sample		Chemical		Type of Site	Measurement	Times	Sampling Schedule	
	Collection	Analysis	Analysis	Frequency				Period	
Azusa	SCAQMD	SCAQMD	SCAQMD	PAMS Type 3	C ₂ -C ₁₁ HC	A	3	7/6 to 9/28	
Azusa	CE-CERT	BRC	BRC	SCOS97	CO, CO ₂ , CH ₄ , MTBE, C ₂ -C ₁₁ HC	B	IOP		
Azusa	DGA	DGA	DGA	SCOS97	PAN, PPN, Perc	E	IOP		
Azusa	UCD	UCD	UCD	SCOS97	Multi-functional carbonyls		IOP	September IOPs	
Azusa	UCLA	UCLA	UCLA	SCOS97	Total reactive carbon and HC		IOP	September IOPs	
Azusa	UCR	UCR	UCR	SCOS97	Biogenic HC & oxidation product	B	IOP		
Azusa	EPA/ManTech	EPA/ManTech	EPA/ManTech	SCOS97	PAMS HC, HAPs, biogenic HC, MVK, methacrolein, and C ₄ -C ₁₀ carbonyls	E	IOP	9/1 to 9/30	
Banning	SCAQMD	SCAQMD	SCAQMD	PAMS Type 2	C ₂ -C ₁₁ HC, carbonyls ^a	A	3	7/6 to 9/28	
Banning	UCR	UCR	UCR	SCOS97	Biogenic HC & oxidation product	B	IOP		
Mohave Desert Air Basin									
Twenty-Nine Palms	AAC	AAC	AAC	SCOS97	CO, CO ₂ , CH ₄ , MTBE, C ₂ -C ₁₁ HC, C ₁ -C ₇ carbonyls	B	IOP		
Barstow	DRI (Schorran)	DRI (Zielinska)	DRI (Zielinska)	SCOS97	CO, CO ₂ , CH ₄ , MTBE, C ₂ -C ₁₁ HC, halocarbons, C ₁ -C ₇ carbonyls	B + 2100	Type 1 and 3 IOPs	7/15 to 10/15	
Barstow	DRI (Schorran)	DRI (Schorran)	DRI (Schorran)	SCOS97	Continuous halocarbon	E	Type 1 and 3 IOPs	7/15 to 10/15	
Lancaster	DRI (Schorran)	DRI (Schorran)	DRI (Schorran)	SCOS97	Continuous halocarbon	E	Type 1 and 3 IOPs	7/15 to 10/15	
San Diego Air Basin									
El Cajon	SDAPCD	SDAPCD	SDAPCD	PAMS Type 2	C ₂ -C ₁₁ HC, carbonyls ^a	B	3, IOP	7/3 to 9/28	
Alpine	SDAPCD	SDAPCD	SDAPCD	PAMS Type 3	C ₂ -C ₁₁ HC	B	3, IOP	7/3 to 9/28	
Mount Soledad	SDAPCD	SDAPCD	SDAPCD	PAMS Type 1	C ₂ -C ₁₁ HC, carbonyls ^a	B	3, IOP	7/3 to 9/28	
San Diego - 12th Street	ARB	ARB	ARB	NMOC/HAPs	C ₂ -C ₁₁ HC	C	3	7/3 to 9/28	
San Diego - Overland	SDAPCD	SDAPCD	SDAPCD	PAMS Type 2	C ₂ -C ₁₁ HC, carbonyls ^a	B	3, IOP	7/3 to 9/28	

**Table 5.1-1 (continued)
Summary of SCOS97-NARSTO VOC Measurements**

Site Location	Sample		Chemical Analysis	Type of Site	Measurement	Times	Sampling Schedule	
	Collection						Frequency	Period
Mexico								
Mexicali-ITM	Tracer ES&T	DRI	SCOS97	CO, CO ₂ , CH ₄ , MTBE, C ₂ -C ₁₁ HC, halocarbons, C ₁ -C ₇ carbonyls	H	IOP		
Tijuana-Rosarito	Tracer ES&T	DRI	SCOS97	CO, CO ₂ , CH ₄ , MTBE, C ₂ -C ₁₁ HC, halocarbons, C ₁ -C ₇ carbonyls	J	IOP		
Aircraft								
STI Aztec	STI/CE-CERT	BRC	SCOS97	CO, CO ₂ , CH ₄ , MTBE, C ₂ -C ₁₁ HC	K	IOP		
STI Aztec	STI/CE-CERT	AtmAA	SCOS97	C ₁ -C ₇ carbonyls	K	IOP		
UCD Cessna	UCD/CE-CERT	BRC	SCOS97	CO, CO ₂ , CH ₄ , MTBE, C ₂ -C ₁₁ HC	L	IOP		
UCD Cessna	UCD/CE-CERT	AtmAA	SCOS97	C ₁ -C ₇ carbonyls	L	IOP		
EOPACE Navajo	SDAPCD	SDAPCD	SCOS97	C ₂ -C ₁₁ HC, C ₁ -C ₇ carbonyls	M	IOP		
Gibbs Cessna	SDAPCD	SDAPCD	SCOS97	C ₂ -C ₁₁ HC, C ₁ -C ₇ carbonyls	N	IOP		

Type 1 - Upwind background.

Type 2 - Maximum precursor emissions (typically located immediately downwind of the central business district).

Type 3 - Maximum ozone concentration.

Type 4 - Extreme downwind transported ozone area that may contribute to overwhelming transport in other areas.

a formaldehyde, acetaldehyde and acetone.

A. Eight 3-hour samples beginning at 0000, 0300, 0600, 0900, 1200, 1500, 1800, and 2100, PDT.

B. Four 3-hour samples beginning at 0300, 0600, 1300, and 1700 PDT.

C. Two 3-hour samples beginning at 0600 and 1300 PDT.

D. 3-hour sample at 0600 PDT

E. Continuous

F. Two 12-hour samples at 0600 and 1800.

G. Two 3-hour samples at 1000 and 1300.

H. Two 3-hour samples at 0600 and 1500.

J. Two 3-hour samples at 1000 and 1300.

K. Four grab samples per morning flight and 2 grab samples per afternoon flight (6 samples per IOP day)

L. Two grab samples per flight (6 samples per IOP day)

M. Five grab samples per flight (10 samples per IOP day)

N. Four grab samples per flight (8 samples per IOP day)

I. daily; 3. every third day; IOP. 1.5 intensive operational period days

**Table 5.1-2
PAMS Target Compounds**

No.	Mnemonics ¹	Names	Formula	AIRS Code	MW	Group	k_{OH} at 298	
							K	hours
1	ETHENE	ethene	C2H4	43203	28.05	O	8.52	6.52
2	ACETYL	acetylene	C2H2	43206	26.04	Y	0.90	61.73
3	ETHANE	ethane	C2H6	43202	30.07	P	0.27	207.30
4	PROPE	Propene	C3H6	43205	42.08	O	26.30	2.11
5	N_PROP	n-propane	C3H8	43204	44.10	P	1.15	48.31
6	I_BUTA	isobutane	C4H10	43214	58.12	P	2.34	23.74
7	LBUT1E	1-butene	C4H8	43280	56.11	O	31.40	1.77
8	N_BUTA	n-butane	C4H10	43212	58.12	P	2.54	21.87
9	T2BUTE	t-2-Butene	C4H8	43216	56.11	O	64.00	0.87
10	C2BUTE	c-2-butene	C4H8	43217	56.11	O	56.40	0.99
11	IPENTA	isopentane	C5H12	43221	72.15	P	3.90	14.25
12	PENTE1	1-pentene	C5H10	43224	70.13	O	31.40	1.77
13	N_PENT	n-pentane	C5H12	43220	72.15	P	3.94	14.10
14	I_PREN	isoprene	C5H8	43243	68.11	O	101.00	0.55
15	T2PENE	t-2-Pentene	C5H10	43226	70.13	O	67.00	0.83
16	C2PENE	c-2-pentene	C5H10	43227	70.13	O	65.00	0.85
17	BU22DM	2,2-dimethylbutane	C6H14	43244	86.17	P	2.32	23.95
18	CPENTA	cyclopentane	C5H10	43242	70.13	P	5.16	10.77
19	BU23DM	2,3-dimethylbutane	C6H14	43284	86.17	P	6.20	8.96
20	PENA2M	2-methylpentane	C6H14	43285	86.17	P	5.60	9.92
21	PENA3M	3-methylpentane	C6H14	43230	86.17	P	5.70	9.75
22	P1E2ME	2-methyl-1-pentene	C6H12	43246	84.16	O	31.40	1.77
23	N_HEX	n-hexane	C6H14	43231	86.17	P	5.61	9.90
24	MCYPNA	Methylcyclopentane	C6H12	43262	84.16	P	8.81	6.31
25	PEN24M	2,4-dimethylpentane	C7H16	43247	100.20	P	5.10	10.89
26	BENZE	benzene	C6H6	45201	78.11	A	1.23	45.17
27	CYHEXA	cyclohexane	C6H12	43248	84.16	P	7.49	7.42
28	HEXA2M	2-methylhexane	C7H16	43263	98.19	P	6.79	8.18
29	PEN23M	2,3-dimethylpentane	C7H16	43291	100.20	P	4.87	11.41
30	HEXA3M	3-methylhexane	C7H16	43249	100.20	P	7.16	7.80
31	PA224M	2,2,4-trimethylpentane	C8H18	43250	114.23	P	3.68	15.10
32	N_HEPT	n-heptane	C7H16	43232	100.20	P	7.15	7.77
33	MECYHX	methylcyclohexane	C7H14	43261	98.19	P	10.40	5.34
34	PA234M	2,3,4-trimethylpentane	C8H18	43252	114.23	P	7.00	7.94
35	TOLUE	toluene	C7H8	43202	92.14	A	5.96	9.32
36	HEP2ME	2-methylheptane	C8H18	43260	114.23	P	8.18	6.80
37	HEP3ME	3-methylheptane	C8H18	43253	114.23	P	8.56	6.49
38	N_OCT	n-octane	C8H18	43233	114.22	P	8.68	6.40
39	ETBZ	ethylbenzene	C8H10	45203	106.16	A	7.10	7.82
40	MP_XYL	mp-xylene	C8H10	45109	106.16	A	18.95	4.71
41	STYR	styrene	C8H8	45220	104.14	A	58.00	0.96
42	O_XYL	o-xylene	C8H10	45204	106.17	A	13.70	4.06
43	N_NON	n-nonane	C9H20	43235	128.26	P	10.20	5.45
44	IPRBZ	isopropylbenzene	C9H12	45210	120.20	A	6.50	8.55
45	N_PRBZ	n-propylbenzene	C9H12	45209	120.20	A	6.00	9.26
46	M_ETOL	m-ethyltoluene	C9H12	45212	120.20	A	19.20	2.89
47	P_ETOL	p-ethyltoluene	C9H12	45213	120.20	A	12.10	4.59
48	BZ135M	1,3,5-trimethylbenzene	C9H12	45207	120.20	A	57.50	0.97
49	O_ETOL	o-ethyltoluene	C9H12	45211	120.20	A	12.30	4.52
50	BZ124M	1,2,4-trimethylbenzene	C9H12	45208	120.20	A	32.50	1.71
51	N_DEC	n-decane	C10H22	43238	142.29	P	11.60	4.79
52	BZ123M	1,2,3-trimethylbenzene	C9H12	45225	120.20	A	32.70	1.70
53	DETBZ1	m-diethylbenzene	C10H14	45218	134.22	A	14.20	3.90
54	DETBZ2	p-diethylbenzene	C10H14	45219	134.22	A	14.20	3.90
55	N_UNDE	n-undecane	C11H24	43954	156.30	P	13.20	4.20
	TNMOC	total non-methane organic compounds						

A = aromatic, AL = Aldehyde, O = alkene (olefin), P = paraffin, Y = alkyne, K = ketone, E = ether, X = haogenated, OH = alcohol

Note: Rate constants k at 298 K for the reaction of OH radicals with VOCs.

Unit: 1012 x k cm³ molecule⁻¹ s⁻¹

Table 5.2-1
SCOS97-NARSTO Hydrocarbon Measurement Comparison – PAMS Target Compounds

Lab	Sample	Slope	Intercept	R-sq	Lab/DRI Average	Lab/DRI StdDev	Number Obs.	Number < detection	Species not reported	Number Outliers	Outlier Species (lab value/DRI value)
ARB	Azusa	0.96	0.1	0.99	1.03	0.17	36	10	p_etoI, bz123m, n_prbz, i_pren, detbz2, iprbz, t2but, c2but, t2pene, ple2me	9	detbz1 (0.0/1.0), c2pene (0.0/1.1), hexa3m (0.0/2.3), bz135m (0.0/2.5), styr (0.0/4.2), pente1 (1.4/0.1), acetyl (12.0/17.9), mecyhx (2.3/4.0), beaby1 (3.8/2.6)
ARB	Los Angeles	0.93	0.2	0.97	0.99	0.15	42	10	i_pren, detbz2, iprbz, t2but, c2but, t2pene, ple2me, detbz1, pente1, c2pene	3	hexa3m(0.0/3.8), styr(0.0/1.3), n_unde(3.0/1.1)
BRC	Azusa	0.98	0.1	0.95	1.02	0.19	45	9	n_unde, hep3me, bz123m, detbz2, iprbz, ple2me, detbz1, pente1, styr	1	bz135m(1.2/2.5)
BRC	Los Angeles	0.95	0.1	0.99	0.99	0.11	44	4	detbz2, iprbz, ple2me, detbz1	7	n_dec (2.3/1.6), styr (0.0/1.3), n_unde (0.0/1.1), hep3me (0.0/1.6), bz123m (0.0/1.4), p_etoI (4.0/1.4), o_etoI (1.6/1.1)
BRC	Santa Monica	0.81	0.1	0.91	1.02	0.27	31	17	mecyhx, n_dec, m_etoI, hep2me, n_non, n_unde, hep3me, p_etoI, bz123m, n_prbz, detbz2, o_etoI, iprbz, t2pene, detbz1, pente1, c2pene	3	bz124m (0.0/1.2), bz135m (0.0/1.3), styr (0.0/1.1)
SCAQMD-lab	Azusa	1.02	-0.2	0.99	0.95	0.13	37	12	bz123m, n_prbz, detbz2, o_etoI, iprbz, t2but, c2but, t2pene, ple2me, detbz1, pente1, c2pene	6	acetyl (8.4/17.9), beaby1 (0.0/2.6), bz135m (0.9/2.5), i_pren (0.7/0.8), cpenta (2.4/0.8), styr (0.0/2.3)
SCAQMD-lab	Los Angeles	1.06	-0.1	0.99	1.04	0.14	43	8	i_pren, iprbz, t2but, c2but, t2pene, ple2m, edetbz1, c2pene	4	acetyl(8.4/16.9), hexa3m(6.0/3.8), beaby1(0.0/4.3), styr(0.7/1.3)

Table 5.2-1 (continued)
SCOS97-NARSTO Hydrocarbon Measurement Comparison – PAMS Target Compounds

Laboratory	Sample Type	Slope	Intercept	R-sq	Lab/DRI Average	Lab/DRI StdDev	Number Obs.	Number < detection	Species not reported a	Number Outliers	Outlier Species (lab value/DRI value)
SCAQMD Auto-GC	Azusa	1.08	-0.4	0.98	1.00	0.15	46	0		9	acetyl (5.0/17.9), n_dec (4.0/2.7), beabyl (0.8/2.6), bz135m (0.9/2.5), styr (0.6/2.3), bu23dm (3.2/2.2), m_etol (3.3/1.8), detbz1 (1.0/0.1), pente1 (3.1/0.1)
SCAQMD- Aut	Los Angeles	1.14	-0.3	0.98	1.08	0.21	46	0		9	acetyl (4.9/16.9), n_dec (3.3/1.6), beabyl (1.5/4.3), m_etol (4.6/3.0), n_unde (2.0/1.1), p_etol (2.5/1.4), n_prbz (1.8/1.0), detbz1 (1.6/0.2), pente1 (3.4/0.3)
EPA	Azusa	0.95	0.4	0.96	1.05	0.14	47	3	p_etol, c2bute, mecyhx	5	beabyl (6.9/2.6), bz135m (6.0/2.5), etbz (3.7/2.5), styr (3.3/2.3), ple2me (5.0/0.2)
EPA	Los Angeles	1.00	0.1	0.95	1.04	0.16	44	2	iprbz, t2bute	9	hexa2m (4.5/3.1), beabyl (8.6/4.3), styr (4.9/1.3), n_oct (3.2/2.1), bu22dm (5.8/2.1), m_etol (4.5/3.0), bz123m (2.2/1.4), detbz2 (1.8/1.0), ple2me (5.4/0.2)
EPA	Santa Monica	0.87	0.1	0.90	1.18	0.36	26	3	hep2me, iprbz, detbz1	19	tolue (2.9/2.1), ethane (10.5/4.0), ethene (2.1/1.1), pa224m (1.0/0.6), bz124m (1.8/1.2), n_hept (0.7/0.2), n_dec (1.1/0.1), beabyl (4.6/0.6), bz135m (0.0/1.3), etbz (0.5/0.4), styr (0.1/1.1), prope (1.3/0.5), n_oct (3.7/0.3), bu22dm (15.9/0.4), m_etol (1.2/0.4), pa234m (0.8/0.2), n_unde (0.7/0.2), hep3me (0.5/0.2), bz123m (1.0/0.2), n_prbz (0.7/0.2), detbz2 (6.4/0.4), o_etol (0.5/0.2), ple2me (4.7/0.0)

Table 5.2-1 (continued)
SCOS97-NARSTO Hydrocarbon Measurement Comparison – PAMS Target Compounds

Laboratory	Sample Type	Slope	Intercept	R-sq	Lab/DRI Average	Lab/DRI StdDev	Number Obs.	Number < detection	Species not reported a	Number Outliers	Outlier Species (lab value/DRI value)
Mantech	Azusa	1.00	-0.1	0.95	0.97	0.16	32	8	bz123m, iprbz, t2bute, t2pene, p1e2me, detbz1, pente1, c2pene	15	ipenta (35.7/22.1), acetyl (0.0/17.9), n_prop (0.0/12.5), ethane (0.0/9.0), ethene (0.0/7.8), benze (6.9/4.7), hexa3m (0.0/4.2), beabyl (6.0/2.6), bz135m (1.3/2.5), styr (0.0/2.3), bu23dm (0.0/2.2), prope (0.0/2.1), m_eto1 (2.7/1.8), n_unde (2.6/1.4), detbz2 (2.1/0.8)
Mantech	Los Angeles	1.12	-0.6	0.95	1.00	0.18	37	5	iprbz, t2pene, p1e2me, detbz1, c2pene	13	acetyl (0.0/16.9), n_prop (0.0/19.7), ethane (0.0/17.4), ethene (0.0/11.7), hexa3m (0.0/3.8), beabyl (7.7/4.3), styr (0.0/1.3), bu23dm (0.0/2.7), prope (0.0/4.7), n_unde (2.3/1.1), i_pren (0.8/0.3), cpenta (0.0/1.4), detbz2(2.6/1.0)
BAAQMD	Asuza	0.90	0.2	0.97	0.96	0.18	30	7	n_prbz, i_pren, iprbz,t2bute, c2bute, detbz1, c2pene	18	acetyl (6.3/17.9), pena2m (4.2/7.6), i_buta (1.5/3.6), bz124m (0.0/3.5), hexa2m (1.6/3.0), pen23m (0.0/2.7), bz135m (6.4/2.5), cyhexa (4.1/2.1), m_eto1 (0.8/1.8), pen24m (0.0/1.7), n_non (0.6/1.4), hep3me (1.9/1.1), p_eto1 (0.5/1.1), bz123m (0.6/1.0), detbz2 (1.4/0.8), o_eto1 (5.7/0.7), p1e2me (1.6/0.2), pente1 (4.5/0.1)
BAAQMD	Los Angeles	0.90	0.3	0.97	0.95	0.20	34	5	i_pren, iprbz, t2bute, t2pene, c2pene	16	acetyl (6.4/16.9), bz124m (0.0/6.5), pen23m (0.0/3.5), n_dec (7.0/1.6), beabyl (6.8/4.3), bz135m (0.8/2.2), cyhexa (5.1/2.8), pen24m (0.0/2.0), n_unde (1.6/1.1), hep3me (2.8/1.6), bz123m (0.7/1.4), detbz2 (6.7/1.0), o_eto1 (5.0/1.1), p1e2me (1.2/0.2), detbz1 (5.4/0.2), pente1 (4.6/0.3)

Table 5.2-1 (continued)
SCOS97-NARSTO Hydrocarbon Measurement Comparison – PAMS Target Compounds

Laboratory	Sample Type	Slope	Intercept	R-sq	Lab/DRI Average	Lab/DRI StdDev	Number Obs.	Number < detection	Species not reported a	Number Outliers	Outlier Species (lab value/DRI value)
SDAPCD	Azusa	0.88	0.3	0.93	0.95	0.17	38	11	bz123m, n_prbz, detbz2, iprbz, t2bute, c2bute, t2pene, p1e2me, detbz1, penta1, c2pene	6	ipenta (55.1/22.1), ethane (2.9/9.0), pena2m (15.3/7.6), bz135m (4.2/2.5), m_eto1 (2.6/1.8), o_eto1(1.5/0.7)
SDAPCD	Los Angeles	0.94	0.1	0.96	0.96	0.15	40	10	i_pren, detbz2, iprbz, t2bute, c2bute, t2pene, p1e2me, detbz1, penta1, c2pene	5	ipenta (41.0/23.9), ethane (6.1/17.4), pena2m (17.5/8.6), n_dec (2.5/1.6), bz135m (1.1/2.2)
SDAPCD	Santa Monica	0.72	0.4	0.66	1.06	0.20	9	30	pena3m, m_cypna, n_hex, mecylx, i_buta, hexa2m, n_hept, o_xyl, pen23m, etbz, bu23dm, cyhexa, n_oct, bu22dm, pen24m, hep2me, pa234m, n_non, hep3me, p_eto1, bz123m, n_prbz, cpenta, detbz2, o_eto1, iprbz, t2pene, detbz1, penta1, c2pene	12	ipenta (63.7/2.0), acetyl (1.3/2.3), ethane (1.3/4.0), pena2m (2.8/0.9), pa224m (0.0/0.6), bz124m (0.7/1.2), n_dec (2.0/0.1), beabyl (1.3/0.6), bz135m (2.2/1.3), prope (0.8/0.5), m_eto1 (1.2/0.4), n_unde (2.0/0.2)
VCAPCD	Azusa	1.05	-0.1	0.98	1.00	0.13	32	11	n_prbz, i_pren, detbz2, o_eto1, iprbz, c2bute, t2pene, p1e2me, detbz1, penta1, c2pene	12	acetyl (52.3/17.9), ethane (2.9/9.0), ethene (0.0/7.8), beabyl (15.0/2.6), bz135m (1.0/2.5), styr (1.0/2.3), bu23dm (3.5/2.2), prope (3.3/2.1), hep2me (2.3/1.5), hep3me (2.1/1.1), cpenta (1.5/0.8), t2bute (3.5/0.3)
VCAPCD	Los Angeles	1.17	-0.4	0.97	1.04	0.16	39	8	i_pren, iprbz, t2bute, c2bute, t2pene, p1e2me, detbz1, c2pene	8	acetyl (59.8/16.9), ethane (0.0/17.4), ethene (19.3/11.7), beabyl (14.0/4.3), penta1 (1.2/0.3)styr (4.7/1.3)prope (9.7/4.7)n_oct (3.0/2.1)

Table 5.2-1 (continued)
 SCOS97-NARSTO Hydrocarbon Measurement Comparison – PAMS Target Compounds

Laboratory	Sample Type	Slope	Intercept	R-sq	Lab/DRI Average	Lab/DRI StdDev	Number Obs.	Number < detection	Species not reported a	Number Outliers	Outlier Species (lab value/DRI value)
VCAPCD	Santa Monica	0.96	0.1	0.81	1.11	0.22	8	31	n_hex, mecylhx, i_buta, hexa2m, n_hept, o_xyl, pen23m, n_dec, bz135m, etbz, styr, propc, cyhexa, n_oct, bu22dm, m_etol, hep2me, pa234m, n_non, n_unde, hep3me, p_etol, n_prbz, cpenta, detbz2, o_etol, iprbz, t2pene, detbz1, pente1,	12	acetyl (27.2/2.3), n_prop (0.0/1.3), ethane (0.0/4.0), ethene (2.0/1.1), mp_xyl (2.3/1.3), pa224m (0.0/0.6), pena3m (0.0/0.7), mecpna (1.4/0.6), beabyl (3.2/0.6), bu23dm (1.9/0.3), pen24m (1.1/0.2), bz123m (1.4/0.2)
AAC	Azusa	0.90	0.6	0.94	1.01	0.20	20	8	i_pren, cpenta, iprbz, t2bute, c2pene, t2pene, p1e2me, detbz1	27	ethane (5.0/9.0), ethene (3.0/7.8), pena2m (17.0/7.6), pena3m (7.0/4.3), bz124m (7.0/3.5), beabyl (0.0/2.6), etbz (4.0/2.5), styr (5.0/2.3), bu23dm (4.0/2.2), propc (3.0/2.1), cyhexa (0.0/2.1), n_oct (3.0/2.1), bu22dm (8.0/1.9), m_etol (4.0/1.8), pen24m (0.0/1.7), hep2me (4.0/1.5), pa234m (2.0/1.4), n_non (0.0/1.4), n_unde (2.0/1.4), hep3me (0.0/1.1), p_etol (0.0/1.1), bz123m (4.0/1.0), n_prbz (4.0/0.9), detbz2 (2.0/0.8), o_etol (3.0/0.7), pente1 (6.0/0.1), c2pene (2.0/0.1)
AAC	Los Angeles	0.76	0.7	0.92	0.94	0.23	24	7	i_pren, iprbz, t2bute, c2bute, t2pene, p1e2me, detbz1	19	ethane (6.0/17.4), ethene (3.0/11.7), pena2m (16.0/8.6), pena3m (7.0/5.0), o_xyl (2.0/4.1), beabyl (0.0/4.3), styr (5.0/1.3), cyhexa (0.0/2.8), n_oct (3.0/2.1), bu22dm (8.0/2.1), pen24m (0.0/2.0), hep2me (4.0/1.8), n_non (0.0/1.2), n_unde (2.0/1.1), hep3me (0.0/1.6), p_etol (0.0/1.4), bz123m (4.0/1.4), n_prbz (4.0/1.0), cpenta (0.0/1.4), detbz2 (2.0/1.0), o_etol (3.0/1.1), pente1 (5.0/0.3), c2pene(1.0/0.2)

Table 5.2-2
SCOS97-NARSTO Hydrocarbon Measurement Comparison – Total and Subtotals

Laboratory	Flag	Location	idnmhc	unid	nmhc	idoxy	PAMS	paraffin	olefin	aromatic
Mantech		Azusa					164.4	107.1	6.4	50.9
Mantech		Azusa					160.2	101.4	8.6	50.2
SCAQMD-lab		Azusa	173.7		241.7		181.9	120.5	19.4	42.0
SCAQMD-Aut		Azusa	198.1		330.4		198.1	126.1	21.0	51.0
SDAPCD		Azusa	232.9	76.3	309.2		233.1	158.0	27.0	48.1
BRC		Azusa	205.3	57.2	262.5		198.3	130.5	27.6	44.7
EPA		Azusa			409.0		229.2	150.9	52.0	57.0
EPA	d	Azusa			470.2		237.2	178.2	65.0	50.1
VCAPCD		Azusa					246.0	127.7	74.1	44.2
BAAQMD		Asuza	303.0				196.3	118.5	29.8	67.5
DRI		Azusa	237.4	24.7	262.1	25.0	207.3	135.4	39.8	52.9
DRI	d	Azusa	234.3	22.2	256.5	19.4	204.5	133.7	38.9	51.5
DRI	d,r	Azusa	238.2	22.2	260.4	28.0	209.7	135.1	39.3	55.0
DRI	r	Azusa	234.3	21.1	255.4	30.6	205.1	133.0	38.6	53.6
AAC		Azusa	236.0				236.0	142.0	29.0	65.0
ARB		Azusa	202.0	48.1	291.0		186.0	114.8	29.8	41.4
ARB		Azusa	197.0	55.4	305.0		186.3	117.2	30.2	39.9
Mantech		LA					190.0	111.1	10.2	68.7
SCAQMD-lab		LA	240.5		357.4		258.1	161.4	28.7	68.0
SCAQMD-Aut		LA	276.4		448.4		276.5	172.0	31.7	72.8
SDAPCD		LA	264.0	60.8	324.8		264.2	170.0	34.2	60.0
BRC		LA	259.0	99.9	358.9		250.8	156.8	38.0	61.5
BRC	d	LA	256.5	62.9	319.4		248.1	155.1	36.8	61.8
EPA		LA	0.0		593.2		285.7	199.8	103.3	73.2
VCAPCD		LA	0.0				329.4	157.4	104.0	68.0
BAAQMD		LA	349.0				259.6	157.4	40.7	79.7
DRI		LA	300.9	21.2	322.1	16.2	261.0	169.6	49.3	69.3
DRI	d	LA	294.8	20.2	315.0	9.7	261.1	169.6	49.1	67.9
DRI	d,r	LA	293.8	21.4	315.2	11.3	257.5	167.4	47.9	67.5
DRI	r	LA	300.1	21.3	321.4	18.3	260.8	168.8	49.0	70.0
AAC		LA	234.0				234.0	142.0	27.0	65.0
ARB		LA	255.5	34.2	363.0		245.0	152.5	35.5	59.2
ARB	d	LA	260.6	48.6	355.0		245.5	149.6	36.8	60.3
BRC		SM	26.1	28.7	54.8		24.8	15.7	3.3	5.8
Mantech		SM					28.9	5.6	4.4	18.9
SDAPCD		SM	90.4	76.1	166.5		90.5	76.4	4.5	9.6
EPA		SM			381.6		80.8	66.7	111.5	19.0
VCAPCD		SM					51.5	11.2	32.4	7.9
DRI		SM	45.8	6.0	51.8	10.4	33.3	19.7	16.8	11.1
DRI	r	SM	47.8	4.7	52.5	14.3	33.5	18.7	16.3	13.0

Azusa: 6/10/97 beginning at 12:23, PDT for 283 minutes.

Los Angeles-N. Main: 6/10/97 beginning at 8:00, PDT for 240 minutes.

Santa Monica: 6/10/97 beginning at 16:30, PDT for 70 minutes.

Flag with "d" are duplicates and "r" are analytical replicates.

ManTech's values for total hydrocarbons are lower than other laboratories because their method did not measure C₂ or C₃ compounds.

Idnmhc=identified nmhc; unid=unidentified nmhc; idoxy=identified oxygenated nmhc; PAMS=PAMS species

Table 5.3-1
SCOS97-NARSTO Performance Audit for Measurement of Carbonyl Compounds

Group	Canister	Sample	formal	acetal	acetone	MEK	propanal	butanal	benzal
DRI		Average Blank	0.08	0.06	0.40				
DRI	79077	Pre -blank	0.48	0.58	4.87				
DRI	79077	Pre/ Backup - blank	0.22	0.09	0.13				
DRI	79077	Post - blank	0.37	0.57	2.77				
DRI	79077	Average of Pre and Post	0.42	0.58	3.82				
SCAQMD		Average Blank	0.07	0.61	0.15				
SCAQMD	79077	Run #1 - blank	0.56	0.57	3.56				
SCAQMD	79077	Run #2 - blank	0.41	0.56	3.56				
SCAQMD	79077	Average	0.48	0.57	3.56				
SDAPCD		Average Blank	0.04	0.03	0.15				
SDAPCD	79077	Run #1	0.43	0.48	2.56				
SDAPCD	79077	Run #2	0.40	0.49	2.76				
SDAPCD	79077	Average # 1 & 2	0.42	0.48	2.66				
SDAPCD	79077	Bag #168	0.50	0.48	2.38				
SDAPCD	79077	Bag #127	0.48	0.49	2.72				
SDAPCD	79078	Average # 168 & 127	0.49	0.49	2.55				
DRI	X082	Pre - blank	0.67	0.62	5.17	0.30	0.05	1.97	2.31
DRI	X082	Pre - blank, replicate	0.67	0.62	5.23	0.28	0.08	1.98	2.29
DRI	X082	Post - blank	0.69	0.64	2.75	0.01	0.05	2.29	2.05
DRI	X083	average	0.68	0.63	3.96	0.16	0.05	2.13	2.18
AtmAA	X082	Q7	0.63	0.60	2.17	0.00	0.00	2.45	2.65
AtmAA	X082	Q7 R	0.63	0.59	2.14	0.00	0.00	2.41	2.58
AtmAA	X082	Q9	0.66	0.64	2.35	0.00	0.00	2.57	2.83
AtmAA	X083	Average Q7 and Q9	0.65	0.62	2.26	0.00	0.00	2.51	2.74
AtmAA	X082	Q13, bag	0.63	0.49	2.93	0.00	0.00	2.60	2.03
AtmAA	X082	Q13, replicate	0.64	0.48	2.92	0.00	0.00	2.55	1.99
AtmAA	X082	Q14, bag	0.58	0.46	2.81	0.00	0.00	2.80	2.15
AtmAA	X083	Average Q13 and Q14	0.60	0.47	2.87	0.00	0.00	2.70	2.09
DRI		Average Blank	0.08	0.06	0.40	0.09	0.00	0.00	0.00
DRI	X056	Pre - blank	0.37	0.59	2.56	-0.06	0.00	2.06	1.74
DRI	X056	Post - blank	0.23	0.56	2.70	0.07	0.00	1.90	1.23
DRI	X056	Average of Pre and Post	0.30	0.57	2.63	0.00	0.00	1.98	1.49
AAC	X056	Audit #1	1.97	0.92	1.84	1.90	0.14	0.00	1.55
AAC	X056	Audit #2	2.64	1.22	5.14	2.05	0.14	0.00	1.75
AAC	X056	Audit #3	3.26	1.06	3.45	2.22	0.15	0.00	2.02
AAC	X057	Average	2.62	1.07	3.48	2.06	0.14	0.00	1.78
DRI		Average Blank	0.08	0.07	0.41	0.06	0.01	0.00	0.00
DRI	X082	Pre - blank	0.39	0.42	2.34	0.08	0.03	2.11	2.39
DRI	X082	Post blank	0.47	0.53	2.39	0.00	0.05	1.99	2.22
DRI	X082	Average of Pre and Post	0.43	0.48	2.37	0.04	0.04	2.05	2.30
VCAPCD		Average Blank	0.02	0.07	0.06	0.00	0.00	0.00	0.00
VCAPCD	X082	El Rio Audit - blank	1.97	0.85	2.89	0.38	0.10	2.26	3.13

Table 5.3-2
SCOS97-NARSTO Performance Audit for Measurement of Carbonyl Compounds
Ratio to DRI Pre and Post Analysis of Transfer Standards

Group	Canister	Ratios to DRI	formal	acetal	acetone	MEK	propanal	butanal	benzal
SCAQMD	79077	Average to DRI Pre	1.01	0.97	0.73				
SCAQMD	79077	Average to DRI Post	1.29	0.98	1.28				
SCAQMD	79077	Average to DRI Average	1.13	0.98	0.93				
SDAPCD	79077	Average to DRI Pre	0.87	0.83	0.55				
SDAPCD	79077	Average to DRI Post	1.12	0.84	0.96				
SDAPCD	79077	Average to DRI Average	0.98	0.84	0.70				
SDAPCD	79077	Ave Bags to DRI Pre	1.03	0.83	0.52				
SDAPCD	79077	Ave Bags to DRI Post	1.31	0.85	0.92				
SDAPCD	79078	Ave Bags to DRI Average	1.15	0.84	0.67				
AtmAA	X082	Average to DRI Pre	0.96	1.00	0.44			1.27	1.19
AtmAA	X082	Average to DRI Post	0.93	0.96	0.82			1.10	1.34
AtmAA	X082	Average to DRI Average	0.95	0.98	0.57			1.18	1.26
AtmAA	X082	Ave Bags to DRI Pre	0.90	0.76	0.56			1.37	0.90
AtmAA	X082	Ave Bags to DRI Post	0.87	0.74	1.04			1.18	1.02
AtmAA	X082	Ave Bags to DRI Average	0.88	0.75	0.73			1.27	0.96
AAC	X056	Average to DRI Pre	7.03	1.82	1.36	-33.53			1.02
AAC	X056	Average to DRI Post	11.55	1.90	1.29	29.28			1.44
AAC	X056	Average to DRI Average	8.74	1.86	1.32	*			1.20
VCAPCD	X082	Average to DRI Pre	5.04	2.02	1.23			1.07	1.31
VCAPCD	X082	Average to DRI Post	4.20	1.59	1.21			1.13	1.41
VCAPCD	X082	Average to DRI Average	4.58	1.78	1.22			1.10	1.36

* Peaks were misidentified and no proper assessment was possible.

Table 5.3-3
SCOS97-NARSTO Field Comparisons for Measurement of Carbonyl Compounds at Azusa

Group	Date	Start Hour	Dur (min)	Type	formal	acetal	aceto	proal	mek	butal	benzal
DRI	9/23/97	1300	182.2	sample	3.00	2.31	6.35	0.54	1.77	0.29	1.51
DRI	9/23/97	1300	182.2	backup	0.16	0.00	0.00	0.05	0.00	0.00	0.00
AtmAA	9/23/97	1300	180	sample	5.98	3.73	5.69	0.84	0.85	0.79	0.02
AtmAA	9/23/97	1300	180	backup	0.21	0.10	0.11	0.03	0.03	0.04	0.00
VCPACD	9/23/97	1300	180	sample	7.31	4.51	4.03	1.02	1.57	0.89	0.30
DRI	9/23/97	1700	183.3	sample	3.60	4.18	7.33	1.01	2.02	0.22	1.76
AtmAA	9/23/97	1700	180	sample	7.29	3.74	6.70	0.79	1.43	0.67	0.06
AtmAA	9/23/97	1700	180	replicate	7.25	3.80	6.68	0.81	1.43	0.71	0.04
VCPACD	9/23/97	1700	180	sample	5.65	3.62	3.65	0.70	1.07	0.60	0.32
DRI	9/24/97	0600	179	sample	2.15	1.65	8.03	0.28	2.72	0.14	1.59
DRI	9/24/97	0600	179	backup	0.51	0.00	0.00	0.00	0.00	0.00	0.00
AtmAA	9/24/97	0600	180	sample	4.95	2.05	8.22	0.36	2.02	0.39	0.05
AtmAA	9/24/97	0600	180	backup	0.20	-0.05	-0.11	0.00	-0.02	-0.01	-0.03
VCPACD	9/24/97	0600	180	sample	5.50	3.04	3.50	0.69	1.39	0.84	0.16
DRI	9/24/97	0905	178	sample	2.79	2.64	8.26	0.66	1.45	0.20	1.20
DRI	9/24/97	0905	178.5	collocated	3.38	2.53	7.94	0.40	1.42	0.21	1.16
AtmAA	9/24/97	0900	180	sample	6.20	2.61	7.87	0.57	1.05	0.52	0.12
AtmAA	9/24/97	0900	180	duplicate	5.85	2.63	7.85	0.58	1.01	0.50	0.10
VCPACD	9/24/97	0900	180	sample	5.23	2.74	3.00	0.61	0.82	0.46	0.16
VCPACD	9/24/97	0900	180	backup	0.44	0.60	2.52	0.09	0.41	0.08	0.09
	9/23/97	1300	average	sample	5.43	3.52	5.36	0.80	1.40	0.66	0.61
			std error		1.27	0.64	0.69	0.14	0.28	0.18	0.46
	9/23/97	1700	average	sample	5.51	3.85	5.89	0.83	1.51	0.50	0.71
			std error		1.07	0.17	1.14	0.09	0.28	0.14	0.53
	9/24/97	0600	average	sample	4.20	2.25	6.58	0.44	2.04	0.46	0.60
			std error		1.04	0.41	1.54	0.13	0.38	0.21	0.50
	9/24/97	0900	average	sample	4.74	2.66	6.38	0.61	1.11	0.39	0.49
			std error		1.01	0.04	1.69	0.02	0.18	0.10	0.35
	All samples				22.2%	10.7%	20.5%	15.2%	18.4%	31.6%	75.8%
	mean relative std error										

Table 5.4-1
SCOS97-NARSTO Halocarbon Measurement Comparison

Species	Formula	BRC	DRI OAL	DRI Schorran	DGA	Average	Std Dev	CV
F12 (dichlorodifluoromethane)	CCl ₂ F ₂	884	780			832	74	8.8%
methylbromide	CH ₃ Br		100					
F11 (trichlorofluoromethane)	CCl ₃ F	352	330	366		349	18	5.2%
F113 (trichlorotrifluoroethane)	Cl ₃ CCF ₃	1110	1410	1126		1215	169	13.9%
chloroform	CCl ₃	56	50			53	4	8.0%
methyl chloroform	CH ₃ CCl ₃	654	630	868		717	131	18.2%
carbon tetrachloride	CCl ₄	103	90	176		123	46	37.7%
trichloroethylene	Cl ₂ CCHCl	53	50	53		52	2	3.4%
chlorodibromomethane	ClCHBr ₂		10					
perchloroethylene (tetra)	Cl ₂ CCCl ₂	775	770	823	434 ^a	789	29	3.7%
m-dichlorobenzene	1,3-Cl ₂ C ₆ H ₄		40					
p-dichlorobenzene	1,4-Cl ₂ C ₆ H ₄		390					
o-dichlorobenzene	1,2-Cl ₂ C ₆ H ₄		30					
								12.4%

a Not included in average.

**Table 5.5-1
SCOS97-NARSTO Biogenic Hydrocarbon Measurement Comparison**

Laboratory	Analysis Date	Sample Type	Analysis Method	Sample ID	Isoprene (ppbC)	Ratio to Grand Ave.
Mantech	9/12/97	Canister	GC/MS	X098	16.86	0.70
Mantech	9/12/97	Canister	GC/MS	X098r	27.24	1.13
DRI	8/7/97	Canister	GC/FID	X098	24.02	1.00
DRI	8/12/97	Canister	GC/FID	X098r	24.30	1.01
BRC	8/13/97	Canister	GC/FID	4	23.00	0.96
UCR	8/97	Carbotrap	GC/MSD-SIM	1	25.95	1.08
UCR	8/97	Carbotrap	GC/MSD-SIM	2	24.40	1.02
UCR	8/97	Carbotrap	GC/MSD-SIM	3	27.49	1.15
UCR	8/97	Carbotrap	GC/MSD-SIM	4	27.26	1.14
UCR	8/97	Carbotrap	GC/MSD-SIM	5	28.87	1.20
Averages						
Mantech					22.05	0.92
DRI					24.16	1.01
BRC					23.00	0.96
UCR					26.79	1.12
Grand Average					24.00	
Standard Deviation					2.05	
Relative Percent Difference					8.6%	

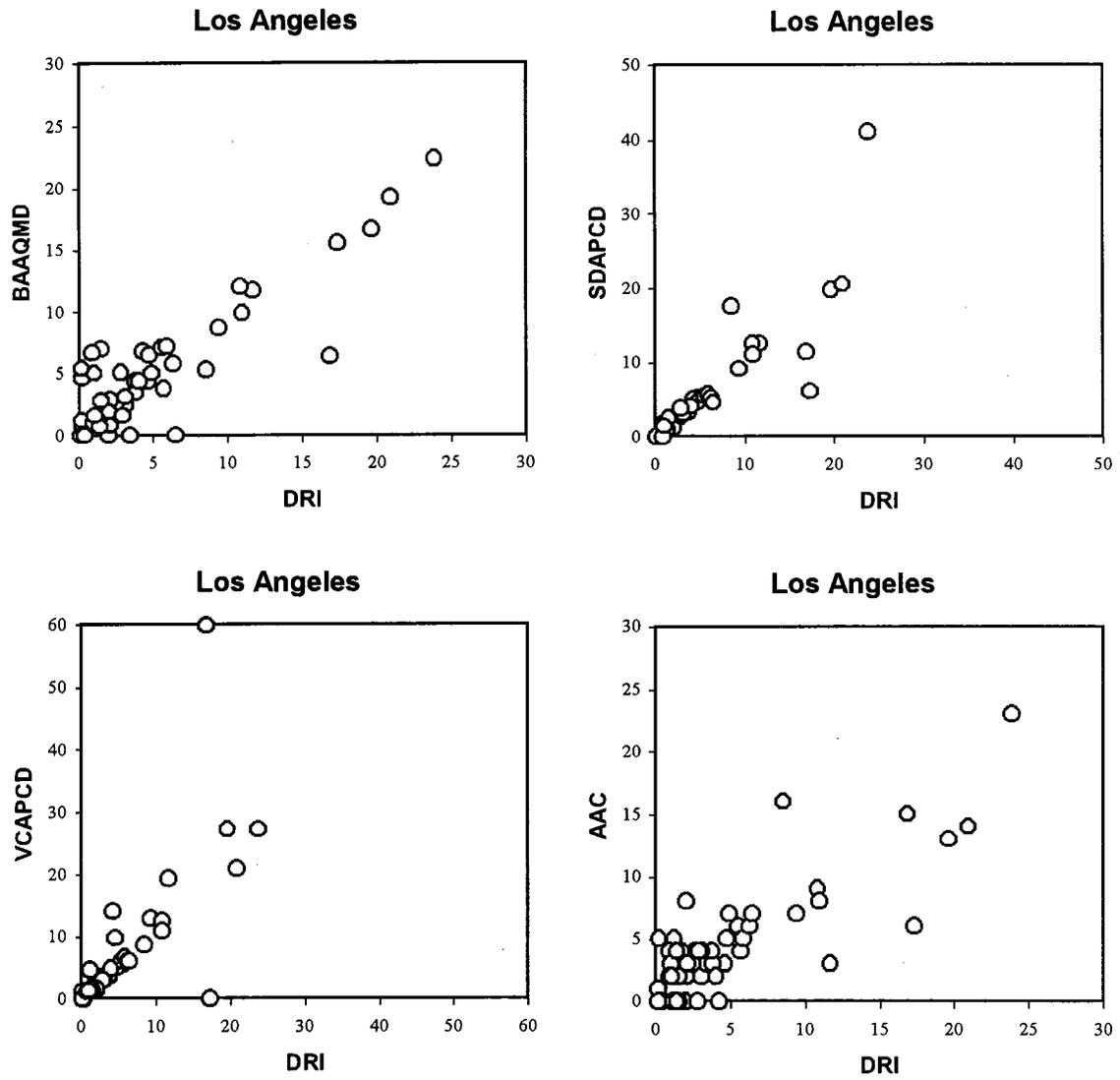


Figure 5.2-1 (continued). Scatterplots of values for PAMS compounds for the Los Angeles comparison sample.

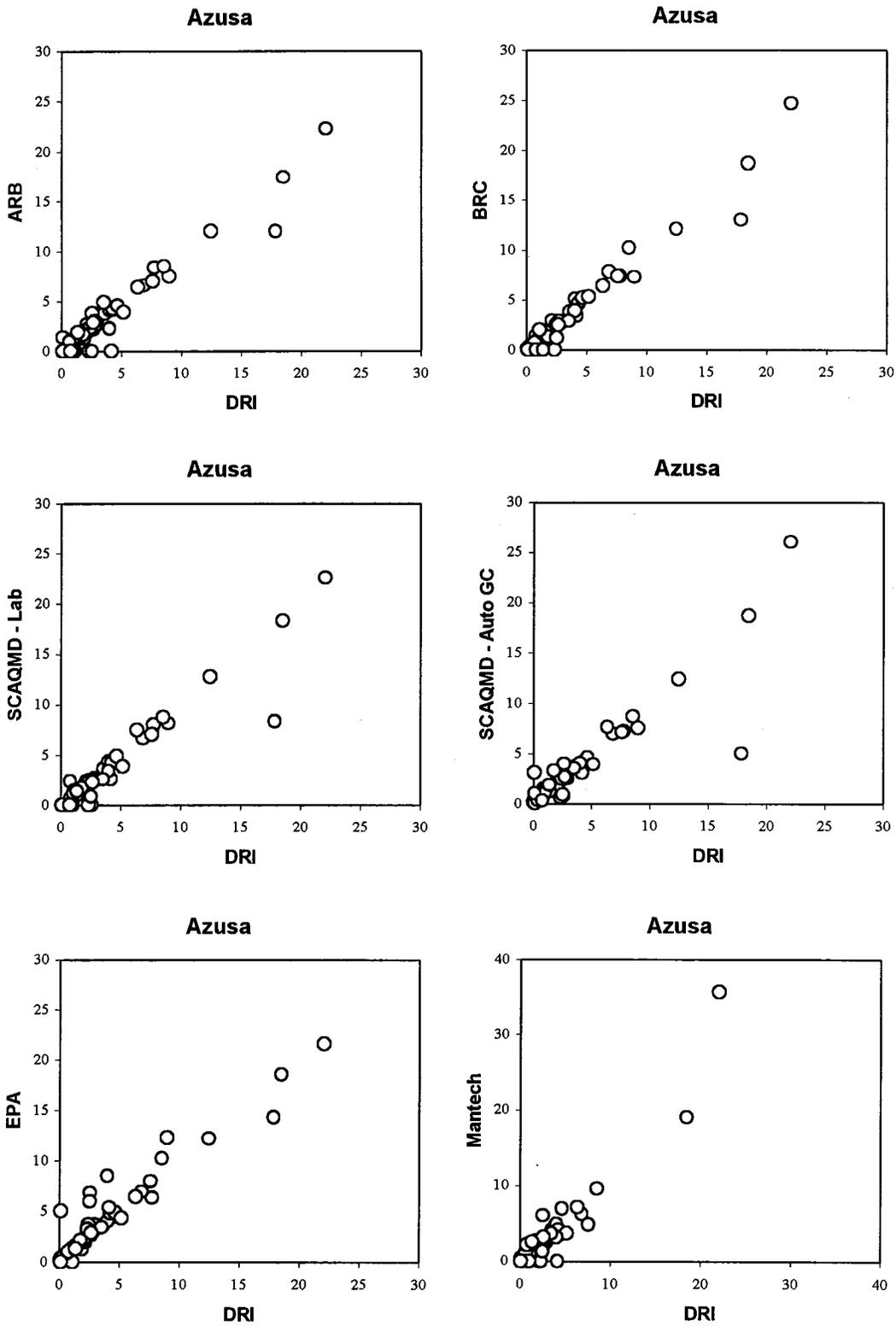


Figure 5.2-2. Scatterplots of values for PAMS compounds for the Azusa comparison sample.

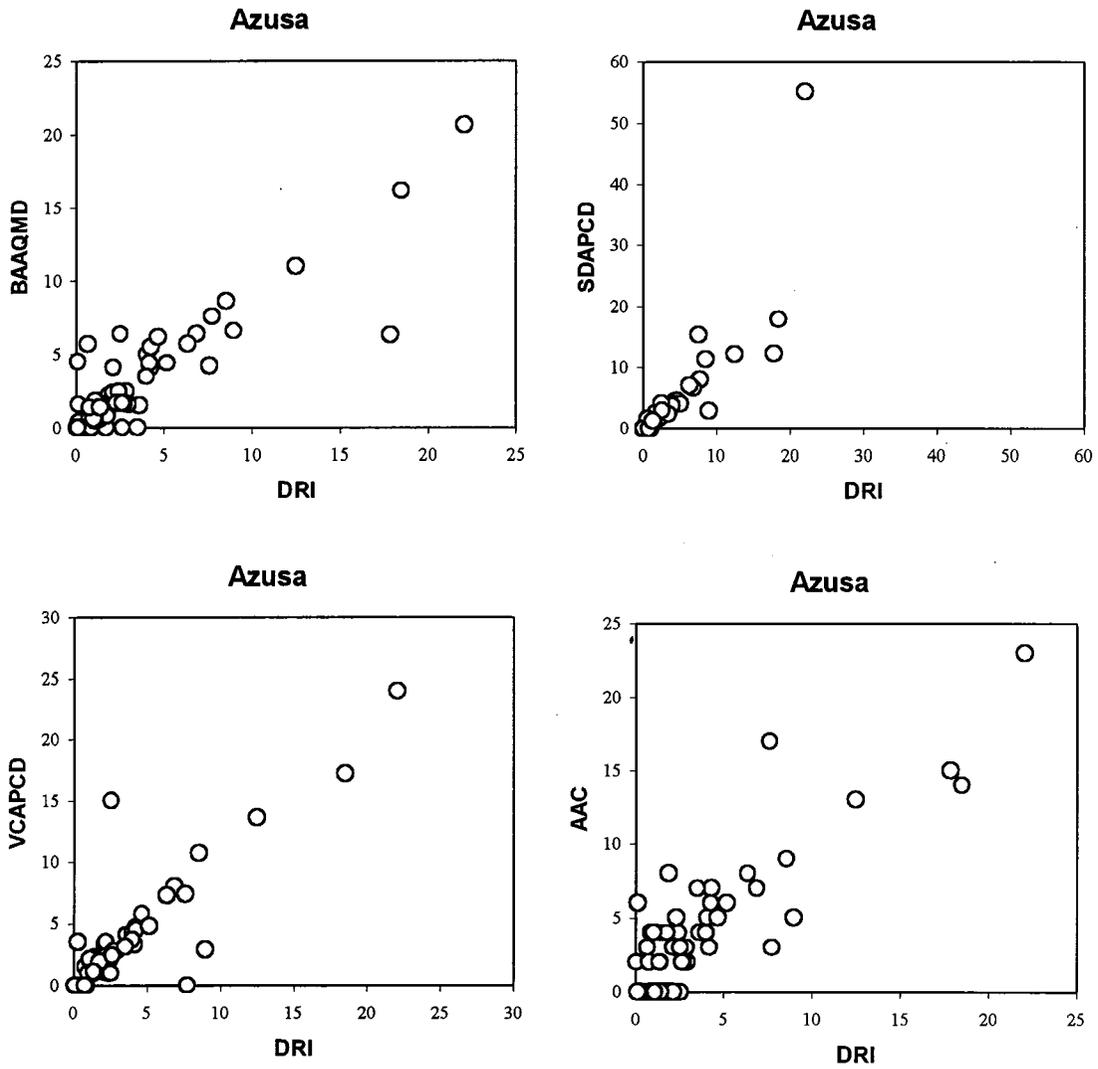


Figure 5.2-2 (continued). Scatterplots of values for PAMS compounds for the Azusa comparison sample.

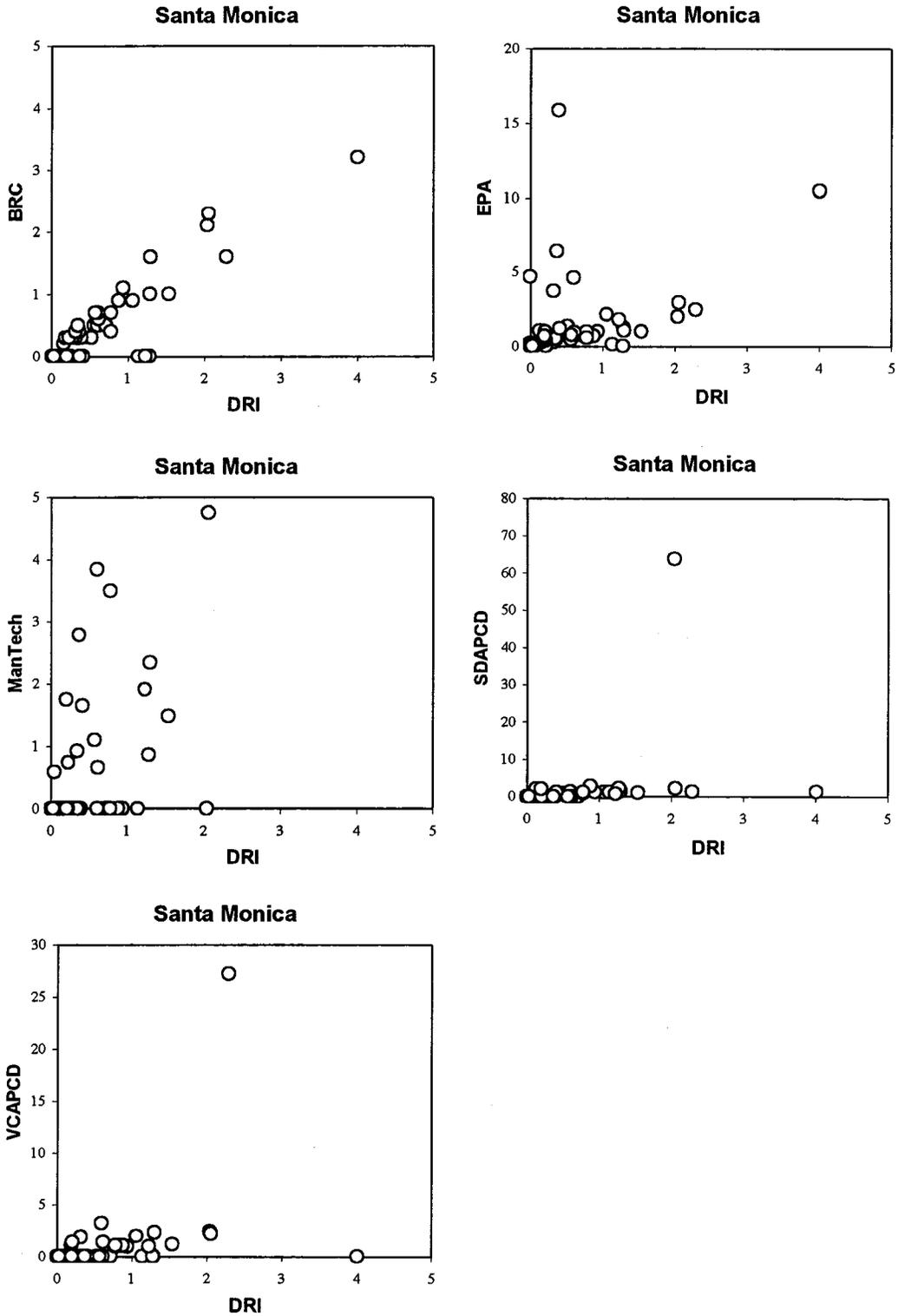


Figure 5.2-3a. Scatterplots of values for PAMS compounds for the Santa Monica comparison sample.

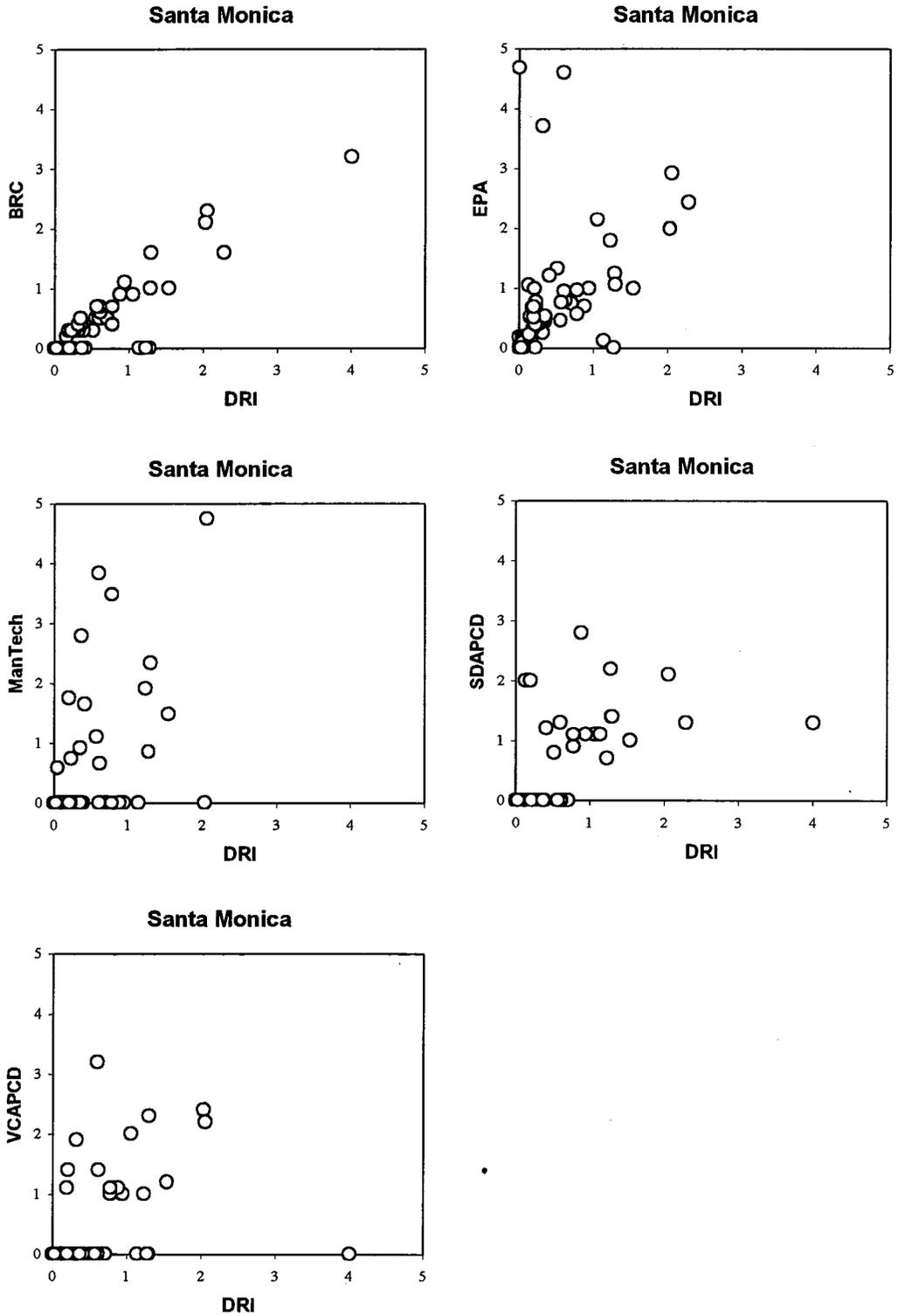


Figure 5.2-3b. Scatterplots of values for PAMS compounds for the Santa Monica comparison sample with common scaling.

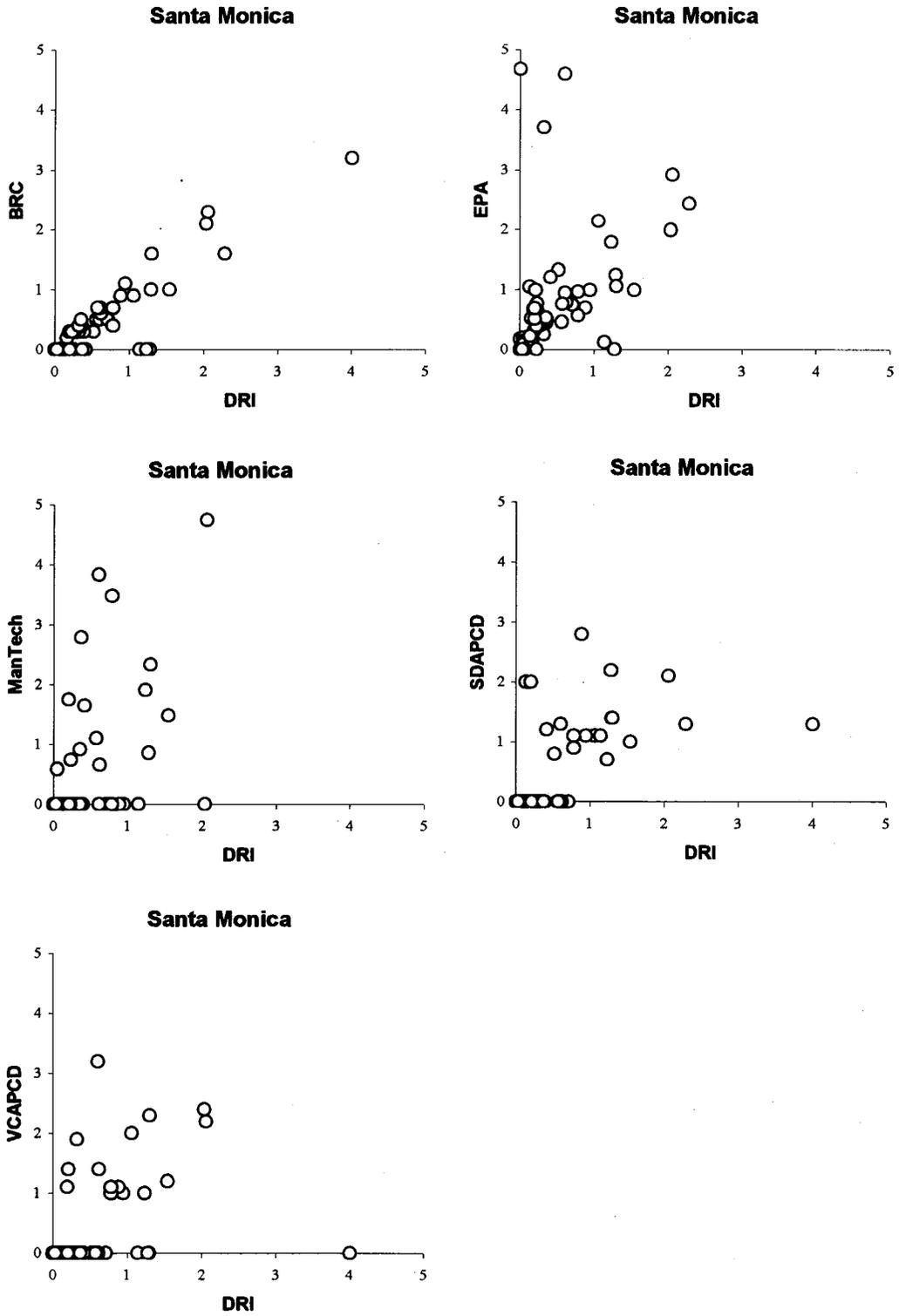


Figure 5.2-3b. Scatterplots of values for PAMS compounds for the Santa Monica comparison sample with common scaling.

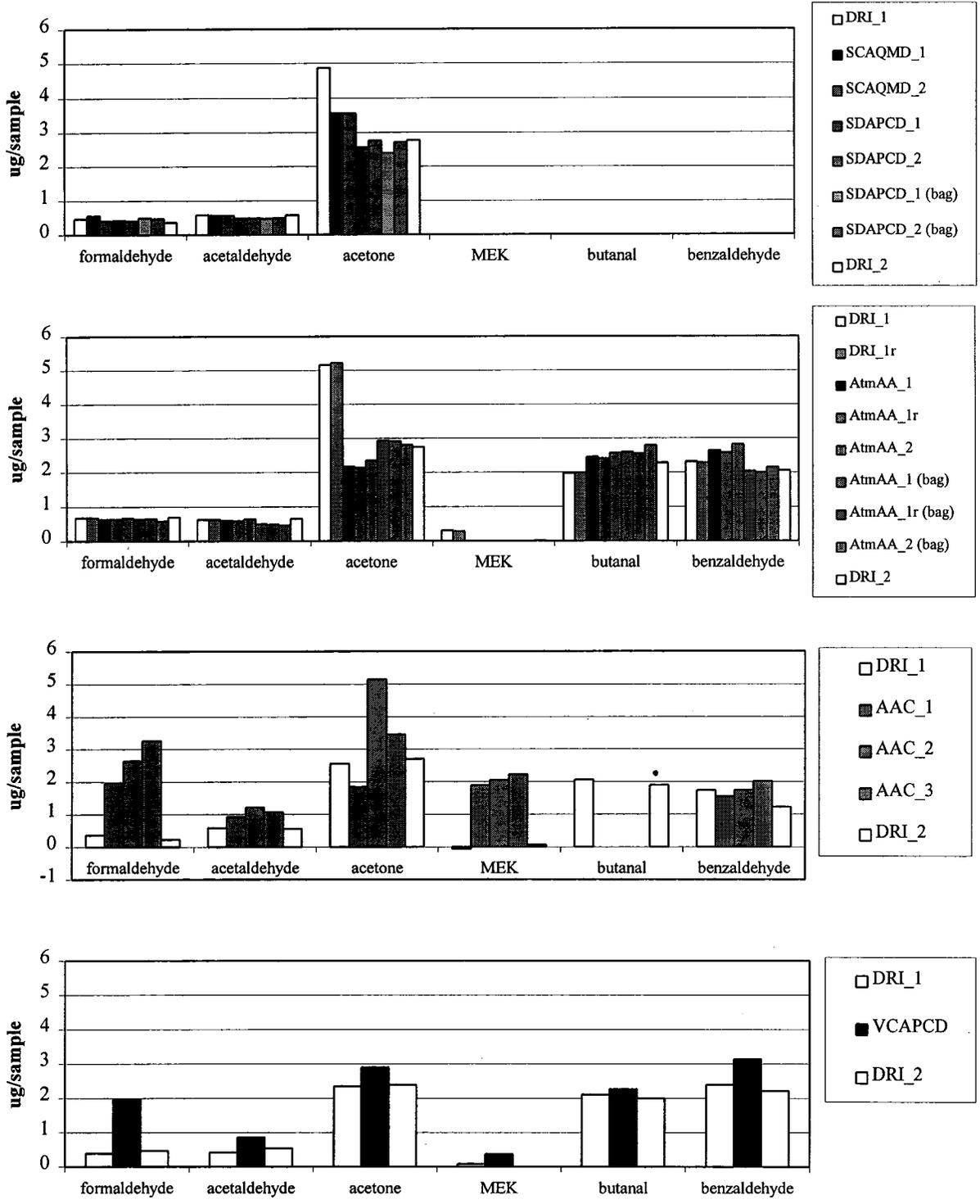


Figure 5.3-1. SCOS97-NARTSTO performance audits for measurement of carbonyl compounds by EPA Method TO-11.

6. PARTICULATE MATTER SAMPLER FLOW AUDITS

6.1 Introduction: Background and Motivation for Audits

The 1997 Southern California Ozone Study, North American Strategy for Tropospheric Ozone (SCOS97-NARSTO) Aerosol Program involved research instruments deployed with the purpose of improving our understanding of gaseous aerosol precursors and important aerosol constituents, such as nitrate compounds. It was an intensive study of limited duration, with a high rate of data return anticipated (California Air Resources Board, 1997). The external audit was intended as a collegial effort of minimum intrusion, focussing on critical aspects of instrument operation. The overall goal of this audit was to provide an external assurance of data quality. Even though some of the measurement methods involved new, state-of-the-art approaches, an external audit of selected operating conditions and parameters will provide additional checks and inputs to the assessment of data quality.

Watson, et al., (1983) have defined the quality of data according to criteria which have found widespread acceptance. Those criteria are as follows:

- Accuracy: a measure of the deviation of a measurement from the true value (e.g., as given by a standard);
- Precision: the standard deviation of repeated measurements of the same observable with the same instrument (i.e., a measure of the width of the interval into which repeated measurements would fall);
- Validity: a judgement of the degree to which the assumptions of the measurement have been met (e.g., a measurement is invalid if critical operating requirements of the instrument are not satisfied).

Audits performed by an independent, external organization contribute to the quality of the data in regard to all three of these criteria. The aerosol sampler flow audit conducted for the SCOS97-NARSTO Aerosol Program is concerned with the samplers and operators shown in Table 6.1-1.

Table 6.1-1. Aerosol Samplers, Sites, and Operators in the SCOS97-NARSTO Aerosol Program Audit

Aerosol Sampler Type	Sampling Sites	Sampler Operators
CIT ⁽¹⁾ PM2.5, PM10, and ammonia samplers	<ol style="list-style-type: none"> 1. UC Riverside, Pierce Hall 2. Azusa (“secondary”) 3. Los Angeles North Main 	California Institute of Technology
CIT MOUDI ⁽²⁾ samplers	<ol style="list-style-type: none"> 1. UC Riverside, Pierce Hall 2. Azusa (“secondary”) 3. Los Angeles North Main 	California Institute of Technology
Federal Reference Sampler Prototype, R&P ⁽³⁾	<ol style="list-style-type: none"> 1. UC Riverside, ”Ag Ops” 	R&P, on-site maintenance by HSPH and BYU ⁽⁴⁾
Federal Reference Sampler Prototype, Graseby ⁽⁵⁾	<ol style="list-style-type: none"> 1. Azusa (“primary”) 2. Los Angeles North Main 	South Coast Air Quality Management District
CADMP Sampler ⁽⁶⁾	<ol style="list-style-type: none"> 1. Azusa (“primary”) 2. Los Angeles North Main 	South Coast Air Quality Management District

Notes:

1. California Institute of Technology
2. Micro-Orifice Uniform Deposit Impactor
3. Rupprecht and Patashnick, Inc., Albany, NY
4. Harvard School of Public Health and Brigham Young University
5. Graseby-Andersen, Atlanta, GA
6. California Acid Deposition Monitoring Program

6.2 Field Performance Audits

Aerosol sampler flows are commonly-audited parameters for which standard field performance audit procedures have been developed at Desert Research Institute and many other laboratories. The filter-based measurements in the SCOS97-NARSTO Aerosol Program were audited in the following priority:

- the sample flow rates of all filter samplers which are intended to provide the volumetric concentrations of particles or gases, or of particulate composition;
- the volumetric flow rates of all fine particle inlet flows that require given setpoints in order to establish fine particle size cut-points.

The field performance audit included two principal activities, conducted in the period August 6 to August 20, 1997:

1. Prepare Field Audit Transfer Standards: With the assistance of the DRI-EEEC Quality Assurance (QA) Laboratory, the auditors prepared flow standards appropriate to the operating ranges of the SCOS97-NARSTO Aerosol Program filter samplers. The flow standards were calibrated against QA Laboratory Primary Standards, including Roots Meters and piston-style standards. The DRI field audit standards deployed for the SCOS97-NARSTO Aerosol Program are listed in Table 6.2-1.
2. Field Performance Audits: The flow audit standards were applied to the aerosol samplers summarized in Table 6.1-1. Discrepancies identified in the initial audit were quantified and reported. The auditors worked in a collegial way with the sampler operators, with the common goal of assuring that the instrument is correctly prepared for the onset of measurements.

The results of the field audits are presented in Section 6.3 of this report, and recommendations are given in Section 6.4. Comments on the first draft version of section 6 (Particulate Matter Sampler Flow Audits) were provided by four reviewers who were contacted by the California Air Resources Board. These comments together with DRI responses are included in Section 6.5. Section 6.6 contains copies of two e-mail messages sent from the field sites, giving details concerning the audit findings and recommendations.

Table 6.2-1.

SCOS97-NARSTO Aerosol Program Audit Standards for Aerosol Sampler Flows

Audit Standard Instrument	Parameter Range or Value of Standard	Instrument to Which Standard Applied
"Gilibrator" (1)	0.001 to 30 liters/minute	CIT filter flows; Federal Reference prototypes
Dwyer 10-100 SCFH Rotameter	10 to 50 liters/minute	CIT Inlet flows; MOUDI, CADMP
Dwyer 40-400 SCFH Rotameter	30 to 200 liters/minute	CADMP
Dichotomous Sampler Orifice	16.7 liters/minute	Federal Reference prototypes

Notes:

1. Gilian Instrument Corp., Wayne, NJ

6.3 Audit Results

6.3.1 California Institute of Technology Samplers

The comparisons between the on-site investigator's flow determinations and those of the auditors are shown in Tables 6.3-1a, 6.3-1b, and 6.3-1c, for the UC Riverside, Azusa Secondary, and Los Angeles-North Main sites, respectively. The individual filter flows and the combined inlet flows were measured, using the audit standards. The audit determinations of the inlet flows were compared to the sums of the investigator's individual filter flows. In all cases, and for all flows, the CIT sampler audit indicated discrepancies not exceeding 5%; this is a commonly-applied flow audit criterion. The agreement found for the inlet vs. individual flow comparison indicated that no leaks are present in the CIT sampler inlets, cyclones, and sampling trains.

6.3.2 Micro-Orifice Uniform Deposit Impactor (MOUDI) Samplers

The MOUDI sampler flow audit results are also shown in Tables 6.3-1a, 6.3-1b, and 6.3-1c, for the UC Riverside, Azusa Secondary, and Los Angeles-North Main sites, respectively. The MOUDI units were operated on site by the California Institute of Technology (Jonathan Allen). Their flows had been set according to pressure drop criteria supplied by the manufacturer. This procedure was adopted by CIT, on the basis of the manufacturer's recommendations, to precisely set the particle size cut-points of the MOUDI stages. In all cases, the resulting audit determinations indicate that the volumetric flow rates at site conditions were lower than the nominal 30 liter/minute flow rate of the MOUDI. These discrepancies range from about 5% to about 12%, and are shown in bold type. The flow rate criteria were well-understood by the investigator, and a recommendation (Section 6.4) for resolution of the discrepancies was developed in discussions between the auditors and the investigator.

6.3.3 Federal Reference Method Prototype Samplers

Two types of Federal Reference Method (FRM) sampler prototypes were included in this audit: (a) the Graseby-Andersen version; and (b) the Rupprecht and Patashnick version. The results of their flow audits are shown in Table 6.3-2. Note that the nominal flow rate for all FRM prototypes is 16.7 liters/minute.

All audited FRM prototypes met the 5% audit flow criterion, although the discrepancies were greater at Azusa Primary than at the other sites. The displays of both FRM samplers at Azusa indicated near-nominal flow rates while lower values were measured by both the auditor and by the South Coast Air Quality Management District (SCAQMD).

Graseby-Andersen FRM samplers were also located at the Los Angeles-North Main site, but could not be audited because filter holders were not available at the time of the audit.

6.3.4 California Acid Deposition Monitoring Program (CADMP) Samplers

The CADMP flow audit results are shown in Table 6.3-3; discrepancies exceeding the 5% criterion were found at both sites, and are shown in bold type. It is apparent that the Los Angeles-North Main unit requires recalibration. Recommendations regarding the CADMP samplers will be given in Section 6.4 of this report.

Table 6.3-1a.

Field Flow Audit Results for California Institute of Technology Samplers
Deployed in SCOS97-NARTSO Aerosol Program

Site: UC Riverside, Pierce Hall
Date: 8/18/97

Sampler	Filter	Investigator's Flow (1)	Audit Flow (1)	Difference, Percent (2)	
PM2.5	FQ2	13.4	13.4	0.0	
	FQ3	13.6	13.5	0.7	
	Inlet (3)		26.1	3.4	
PM2.5	FQ1	13.3	13.5	-1.5	
	FT2	14.0	14.4	-2.8	
	Inlet (3)		26.8	1.9	
PM2.5	FT1	14.0	14.3	-1.9	
	FN1	7.2	7.4	-3.2	
	FN2	7.1	7.2	-1.1	
	Inlet (3)		27.8	1.8	
PM10	CT1	5.6	5.7	-1.1	
	CT2	5.6	5.7	-1.1	
	CQ1	5.2	5.3	-1.5	
	Inlet (3)		16.3	0.4	
"Total"	Ammonia	Total	10.7	11.2	-4.1
MOUDI MDI-110 (4)		30.0	28.5	5.3	
MOUDI MDI-072 (4)		30.0	27.6	8.7	

Notes:

(1) All flows are liters/minute at site conditions.

(2) Differences are investigator's flow minus audit determination, divided by the audit determination, and expressed as a percentage.

(3) Inlet audit results are expressed the sum of the investigator's filter flow determinations minus the audit determination, divided by the audit determination and expressed as a percentage.

(4) Investigator's determination of MOUDI flow is given as nominal value of 30 liters/minute.

Table 6.3-1b.

**Field Flow Audit Results for California Institute of Technology Samplers
Deployed in SCOS97-NARTSO Aerosol Program**

Site: Azusa "Secondary"
Date: 8/19/97

Sampler	Filter	Investigator's Flow (1)	Audit Flow (1)	Difference, Percent (2)
PM2.5	FQ2	13.9	14.1	-1.4
	FQ3	13.7	13.8	-0.8
	Inlet (3)		26.9	2.6
PM2.5	FQ1	13.3	13.4	-0.8
	FT2	14.0	14.1	-0.9
	Inlet (3)		26.7	2.2
PM2.5	FT1	14.0	14.1	-1.0
	FN1	7.2	7.2	-0.6
	FN2	7.1	7.1	0.4
	Inlet (3)		27.4	3.3
PM10	CT1	5.7	5.9	-2.9
	CT2	5.0	5.1	-1.6
	CQ1	5.7	5.8	-1.2
	Inlet (3)		16.5	-0.7
"Total"	Ammonia	11.2	11.7	-4.5
MOUDI MDI-109 (4)		30.0	27.2	10.3
MOUDI MDI-071 (4)		30.0	26.7	12.4

Notes:

- (1) All flows are liters/minute at site conditions.
- (2) Differences are investigator's flow minus audit determination, divided by the audit determination, and expressed as a percentage.
- (3) Inlet audit results are expressed the sum of the investigator's filter flow determinations minus the audit determination, divided by the audit determination and expressed as a percentage.
- (4) Investigator's determination of MOUDI flow is given as nominal value of 30 liters/minute.

Table 6.3-1c.
Field Flow Audit Results for California Institute of Technology Samplers
Deployed in SCOS97-NARTSO Aerosol Program

Site: Los Angeles-North Main
Date: 8/19/97

Sampler	Filter	Investigator's Flow (1)	Audit Flow (1)	Difference, Percent (2)
PM2.5	FQ2	13.1	13.7	-4.7
	FQ3	12.6	13.2	-4.6
	Inlet (3)		25.9	-0.8
PM2.5	FQ1	14.1	14.6	-3.2
	FT2	12.8	13.1	-2.2
	Inlet (3)		26.9	0.0
PM2.5	FT1	12.8	13.3	-3.6
	FN1	7.2	7.4	-2.2
	FN2	6.8	6.9	-1.0
	Inlet (3)		25.8	3.9
PM10	CT1	5.2	5.4	-3.8
	CT2	5.6	5.8	-3.4
	CQ1	5.3	5.6	-4.7
	Inlet (3)		16.4	-2.1
"Total"	Ammonia	10.3	10.5	-1.6
MOUDI MDI-108 (4)		30.0	27.6	8.7
MOUDI MDI-107 (4)		30.0	27.6	8.7

Notes:

- (1) All flows are liters/minute at site conditions.
- (2) Differences are audit flow minus investigator's determination, expressed as percentage of the mean of the two determinations.
- (3) Inlet audit results are expressed as audit inlet flow determination minus the sum of the investigator's filter flow determinations, expressed as a percentage of the mean of the two inlet flow estimates.
- (4) Investigator's determination of MOUDI flow is given as nominal value of 30 liters/minute.

Table 6.3-2. Field Flow Audit Results for Federal Reference Method Samplers

Deployed in SCOS97-NARSTO Aerosol Program

Sampler	Indicated Flow (1)	Audit Flow (1)	Difference, Percent (2)
Site: UC Riverside "Ag Ops" Date: 8/17/97			
R&P (3), Harvard/ADI Shelter	16.7	16.86	-0.9
R&P (3), BYU Shelter	16.7	16.77	-0.4
Site: UC Riverside Pierce Hall Rooftop, Date: 8/16/97			
Graseby (4)	16.63	16.71	-0.5
Graseby (4)	16.66	16.74	-0.5
Site: Azusa Primary, Date: 8/20/97			
Graseby (4) #0014 (Azusa)	16.48	15.71	4.9
Graseby (4) #0015 (Azusa)	16.67	16.17	3.1
Graseby (4) #0015 (Azusa)	16.65	16.26	2.4

Notes:

- (1) All flows are given in liters/minute at site conditions.
- (2) Differences are investigator's flow minus audit determination, expressed as percentage of the audit determination.
- (3) Rupprecht and Patashnick, Albany, NY
- (4) Graseby-Andersen, Atlanta, GA

**Table 6.3-3. Field Flow Audit Results for CADMP ⁽¹⁾ Samplers
Deployed in SCOS97-NARSTO Aerosol Program**

Site	Nominal Flow (2)	Audit Flow (2)	Difference Percent (3)
Azusa Primary			
Filter Flow	20.0	18.9	5.8
Black Makeup Flow	46.5	46.7	-0.4
Blue Makeup Flow	46.5	45.9	1.3
Inlet Flow	113.0	111.5	1.3
Los Angeles-North Main			
Filter Flow	20.0	21.5	-7.0
Black Makeup Flow	46.5	52.2	-10.9
Blue Makeup Flow	46.5	49.5	-6.1
Inlet Flow	113.0	123.2	-8.3

Notes:

- (1) California Acid Deposition Monitoring
- (2) All flows are given in liters/minute at site
- (3) Differences are investigator's flow minus audit determination, expressed as percentage Of audit

6.4 Recommendations

The recommendations resulting from each case of audit flow discrepancies are summarized in the following subsections. Details concerning the audit findings were issued from the field as e-mail communications on 8/20/97 and 8/21/97; these field advisories are included in Section 6.6 of this report.

6.4.1 MOUDI Samplers

It was recommended that California Institute of Technology measure the MOUDI flow rates before and after each sampling run. Use of a lower flow rate based on pressure drop criteria would not be a problem as long as that flow rate was determined accurately.

6.4.2 FRM Samplers

It was recommended that the FRM samplers at Azusa and Los Angeles-North Main be recalibrated. The FRM sampler displays at Azusa appeared to give erroneous flow indications. Preliminary indications obtained on August 20 suggested that the SCAQMD Dry Cal meter and the DRI audit standards agreed within 5%. Our understanding was that SCAQMD used that device to calibrate the Los Angeles-North Main FRM samplers.

6.4.3 CADMP Samplers

It was recommended that the CADMP samplers at both Azusa and Los Angeles-North Main be recalibrated. The operator (Ms. Yoosephiance) was given suggestions as to use of the site flow meters to directly determine the CADMP sampler's differential pressure gauge readings for desired flow rates, in lieu of a full sampler calibration. Later information provided by the operator indicated that the CADMP samplers had been meeting a 10% field flow check criterion established by the California Air Resources Board.

6.4.4 Time Convention for Data Base

Pacific Daylight Time was the operational standard for the SCOS97-NARSTO Aerosol Program, but the CADMP sampler clocks were set to indicate Pacific Standard Time (PST). This offers the potential for confusion. The On and Off times of all samplers appeared to be set correctly for PST, but care must be taken in the reporting of the data.

6.5 Draft Audit Report Reviews And Responses

6.5.1 Comments From Reviewers Of The Draft Audit Report

On October 9, 1997, Dr. Motallebi sent the following comments, which are repeated verbatim from reviewers whose inputs were solicited by the California Air Resources Board:

A) Dr. Jonathan Allen of California Institute of Technology

I have reviewed the draft report of the aerosol flow audit conducted by DRI and have the following comments:

1. Recommendation 3.4 does not apply to the Caltech samplers. There were no clocks on the Caltech samplers. As agreed with the SCOS97-Aerosol project management, all times were recorded as PDT during the project.
2. Regarding recommendation 3.1, we believe that the pressure drop criterion used to set the MOI flows is stable, although the flows might not be the nominal 30 L/min. Therefore, we did not measure the flows directly during the sampling events. We will measure these flows in the laboratory at the conclusion of the study. We will take into account the flow audit results and laboratory measurements when reporting our data.

B) Mr. Solomon Teffera of South Coast Air Quality Management District

We were surprised at the flow measurements John (Bowen) did which showed more than 5 % discrepancy from our own. This is because we had calibrated the new DRI-cal meter at the District instrument lab. As you know the calibrator we have is really a primary standard, the accuracy of which is traceable to NIST only through the physical measurement attributes of the tube such as diameter. However we did notice that when we rechecked the flow only days after the calibration, they were off as John indicated. I agree with him that for some yet unknown reason the samplers do not hold their calibrated flow rate well and may need recalibrating often. This is a question we are planning to address with the manufacturer and EPA?

Overall, we believe we have met the minimum 5% flow rate variation for the study. But the fact that the FRM samplers required frequent recalibration is an issue we should investigate further.

C) Ms. Thelma Yoosephiance of ARB/Monitoring Laboratory Division - El Monte

In the Final Field Audit Report from Desert Research Institute (DRI), dated September 12, 1997, the audit results indicate that the California Acid Deposition Monitoring Program (CADMP) samplers located at the Azusa and Los Angeles - North Main Street sites did not pass their audit criteria. The audits of both sites were performed on August 19, 1997.

The audit results for the Los Angeles site indicate a percent (%) difference of -7.0% for the sample flow, -10.9% and -6.1% for the make-up flows, and -8.3% for the inlet flow. The sample flow results, at the Azusa site, indicated a difference of +5.8%. It should be noted that DRI uses a 5% discrepancy as their audit criteria. The discrepancy defined in the ARB's standard operating procedures (SOP) is 10% for instruments that use size selective inlets. An error of more than 10% would render ineffective the size selectivity of the inlet.

On September 23, 1997 the flows were checked using an ARB certified transfer standard and the flow rates were found to be within 2% of true value. The audit was conducted on a hot summer day when ambient temperatures ranged from 98 to 108 degrees Fahrenheit (F). The accuracy of the rotameter used and the extreme ambient weather conditions at the time of the audit may explain the difference in results. We believe that the ARB transfer standard used in checking DRI's audit provides a higher level of traceability and accuracy.

Additionally, in an E-mail message (dated August 20, 1997) attached to the report, DRI states that "the samplers have not been calibrated for some time...for the near term the sample flow rates can be reset using a direct measurement of the flow rates and noting the corresponding flow..." The CADMP samplers are calibrated twice a year, in accordance with ARB's SOP. The samplers at Azusa and Los Angeles - North Main were last calibrated on March 26, 1997 and April 29, 1997, respectively. The audit was performed within two months of the next scheduled calibrations. Based on the results of our confirmatory flow checks, the samplers were found to be operating properly. Therefore, no adjustments were made to the instruments.

D) Mr. Fred Burriell of ARB/Monitoring Laboratory Division - Sacramento

I finished reviewing the Draft Report for the SCOS97-NARSTO Aerosol Sampler Unit, and I have the following suggestions/recommendations:

If the Federal Reference Methods are designated as Dichots or TEOM's, total flow is not a good indicator of the sampler's ability to measure PM10 or PM2.5. In the case of the dichot, it is necessary to measure the coarse flow, the fine flow, and the total flow. In the case of the TEOM, it is necessary to measure the main flow, the auxiliary flow, and the total flow. Only by measuring the different component flows can you be sure that the sampler is actually measuring PM10 or PM2.5, or both. If the flows are not within the cut-points for PM10 or PM2.5, the sampler can not properly measure these particulates, and you may be collecting particles that are not of the correct size. Both samplers have a total flow rate, but also designed flow rates to insure that the particles collected are of the correct size. Without measuring the other flows, the data may be jeopardized.

6.5.2 Desert Research Institute Responses To Reviewer's Comments

First, we thank the reviewers for their comments. Our responses are as follows:

- A) Regarding Dr. Allen's comments, we will correct the statement concerning sampler clocks.
- B) Regarding Mr. Teffara's comments, it appears that he concurs with our findings. We would support his plan to contact the FRM manufacturer and the EPA, concerning flow variations.

- C) Regarding Ms. Yoosephiance's comments, we understand that ARB applies a 10% pass/fail criterion for flow audits. The auditors can insert this comment into the report, but it is up to the ARB to decide whether or not corrective action is required when flows differ from audit standards by more than 5%. Based on our experience with the CADMP samplers, we believe that a 5% criterion is reasonable. As regards possible differences between DRI and ARB flow standards, we do not have any indication that our standards are in error. Also, during the Riverside/SCOS audits, the DRI standards agreed very well with standards used by EPRI and Cal Tech participants, as well as many of the FRM samplers.
- D) Regarding Mr. Burriell's comments, his points are well-taken, but they do not apply to the single-channel FRM prototypes to which our audits pertain.

6.6 Field Advisories Concerning Moudi, Frm, and Cadmp Sampler Flow Audit Discrepancies (e-mails 8/20/97 AND 8/21/97)

Subject: Summary of findings during audits of aerosol instruments
Date: Wed, 20 Aug 1997 08:31:08 -0700 (PDT)
From: John Bowen <johnb@sage.dri.edu>
To: bcroes@arb.ca.gov
CC: nmotalle@cleanair.arb.ca.gov, fredr@sage.dri.edu

Bart/Nehzat

Flow audits were conducted at three sites: Riverside (Pierce Hall), Azusa, and Central Los Angeles. Audited instruments included:

All sites: Cal Tech samplers - 3 PM_{2.5} inlets with a total of 7 filter flows, 1 PM₁₀ inlet with 3 filter flows and one open-faced filter, 2 MOUDI's.

All sites: 2 FRM PM_{2.5} samplers

Azuza and CELA: PM_{2.5} CADMP samplers

Preliminary results (subject to possible minor changes following checks of audit equipment):

Cal Tech sample and inlet flow rates agreed with audit flow rates to within +/-5% except for MOUDI inlet flow rate. MOUDI's were set using manufacturer's pressure drop. Flow rates on all MOUDI inlets were 26-28 lpm (should be 30 lpm).

Results of Cal Tech audits were discussed with Jonathan Allen as the audits progressed. He will be determining what to do with the MOUDI flow rates. We recommended that flow rates be set on site using external measurement device. We also recommended that additional filters be placed on exhaust ports of carbon-vane pumps to prevent generation of carbon particles while sampling.

FRM: Instruments at Riverside were operational and flow rates within limits. Instruments at Azusa both had low flow rates:

SN 0014: Audit flows were approximately 15.4 lpm. Instrument flows were displayed as about 16.4 lpm but highly variable (15.8-17.0 lpm)

SN 0015: Audit flows were approximately 15.8 lpm. Instrument flows were displayed as 16.6 lpm.

Instruments at CELA: Filter holders were not available at site. It was not possible to audit instruments.

Recommendation for FRM's at Azusa and CELA: Flow rates should be recalibrated using a known flow standard such as a orifice meter or portable bubble meter.

CADMP samplers:

Azusa: Sample flow rate was 18.9 lpm (nominally 20 lpm). This is slightly outside the 5% limit. Total inlet flows are 111 lpm (nominally 113 lpm).

CELA: Sample flow rate was 21.5 lpm (nominally 20 lpm). This 7.5 % high. Total inlet flows were 123 (8% higher than nominal).

We discussed findings with Thelma Yoosephiance. The samplers have not been calibrated for some time. We suggested that for the near term the sample flow rates can be reset using a direct measurement of the flow rates and noting the corresponding flow indicators (Magnehelic pressure drops). Then the samplers can be set to this indicator reading before each sample. The indicator reading at the end of the sample period can be used to determine possible change of flow during the sampling. Some additional discussions on how to do the flow setting may be necessary.

One other issue is the time of samplers: Cal Tech and CADMP samplers are run on PST. FRM's were set to PDT. All sampling should be on same time.

John Bowen/Fred Rogers
Desert Research Institute

Subject: FRM flow rates at Azusa
Date: Thu, 21 Aug 1997 10:48:54 -0700 (PDT)
From: John Bowen <johnb@sage.dri.edu >
To: bcroes@arb.ca.gov
CC: fredr@sage.dri.edu

Bart,

I met Salomon Tehboua at the Azusa site at about 4:30 PM on Wed, Aug 20 and was able to recheck the flows on the FRM's.

My first check of sampler designated Azusa01 (SN 0015) using my Gilibrator bubble meter gave a flow rate of 16.17 lpm with a displayed instrument average of 16.67 lpm. A second check about half an hour later gave a measured flow rate of 16.26 lpm with an instrument average of 16.65 lpm.

My check of sampler designated Azusa02 (SN 0014) with my Gilibrator bubble meter gave a flow rate of 15.71 lpm with a displayed instrument average of 16.48 lpm.

A check of Azusa02 with the District's Dry Cal flow meter resulted in an inlet flow rate in the range 15.7 - 15.8 lpm, indicating that we were getting similar results with the two different devices. A calibration procedure was started on the sampler. Because of time constraints on my schedule, I was not able to remain at the site to re-audit. After the recalibration, the flow rates were to be re-measured with the Dry Cal meter.

A check of Azusa01 with the Dry Cal flow meter gave inlet flows near 16.5 lpm or higher than I measured with the Gilibrator.

For both samplers, I found the measured flow rates to be less than those displayed on the instrument by 0.5 - 0.6 lpm. I cannot at this point explain why the District found better comparison between their inlet measurements and the instrument flows during their previous checks of the samplers' calibrations. There seems to be some long-term variation in the flow rates that causes differences in spot check measurements.

I still have Fred's cell phone if you want to talk to me further or you may be able to reach me at DRI in Las Vegas at (702) 895-0417. I will be returning to Reno on Saturday, Aug 23.

John Bowen

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Appendix A

**Protocol for SCOS97-NARSTO
Performance Audit and Laboratory Comparison
for Speciated Hydrocarbon Measurements**

(Revised May 28, 1997)

**Protocol for SCOS97-NARSTO
Performance Audit and Laboratory Comparison
for Speciated Hydrocarbon Measurements**

1.0 Purpose and Overview

- 1.1 Performance audits of hydrocarbon measurements are being conducted as part of an external quality assessment program for the SCOS97-NARSTO Study. The purpose of the audits is to document differences that may exist between laboratories in the SCOS study area (greater than 30% for concentrations of individual species above 1.0 ppbC).
- 1.2 The audits will consist of a review by Desert Research Institute (DRI) of standard operating procedures (SOPs) used by each measurement group, and performance audits consisting of two to five ambient samples.

2.0 Participants

2.1 Coordination, Data Compilation and Analysis

Desert Research Institute (Dr. Eric Fujita, ericf@sage.dri.edu, 702/677-3311 Fax - 702/677-3157) P.O. Box 60220 (Street Address: 5625 Fox Ave.) Reno, NV 89506

California Air Resources Board (Mike Miguel, mmiguel@arb.ca.gov, 916/322-7054 Fax - 916/322-8217) P.O. Box 2815 Sacramento, CA 95812

2.2 Collection of Ambient Audit Samples

Air Resources Board, Monitoring and Laboratory Division (Pat Harrington, 818/575-6993 Fax - 818/350-6468) 9480 Telstar Ave Suite 4 El Monte, CA 91731.

2.3 Participating Laboratories

(1.) California Air Resources Board, Monitoring and Laboratory Division (Hieu Le, 916/323-4398; Fax - 916/327-8217) 1309 T Street Sacramento, CA 95812

(2.) U.S. EPA National Exposure Research Laboratory (Bill Lonneman, 919/541-3895; Fax - 919/541-4787) mailing address: MailDrop 84 Research Triangle Park, NC 27711 shipping address for canisters: EPA Tech Center Alexander Drive & Highway 54 Research Triangle Park, NC 27711

(3.) Biospheric Research Corporation (Dr. Rei Rasmussen, rrasmus@ese.ogi.edu, 503/690-1077; Fax - 503/690-1669) 17010 N.W. Skyline Blvd. Portland, Oregon 97231

(4.) Desert Research Institute (Dr. Barbara Zielinska, e-mail: barbz@sage.dri.edu, 702/6773198; Fax - 702/677-3157) mailing address: P.O. Box 60220 Reno, NV 89506 shipping address: 5625 Fox Avenue Reno, NV 89506

(5.) San Diego Air Pollution Control District (Mahmood Hossain, mhossain@sdapcd.co.san-diego.ca.us, 619/694-3358 Fax 619/694-2730) 9150 Chesapeake Dr. San Diego, CA 92123-1026.

(6.) South Coast Air Quality Management District (Steve Barbosa, sbarbosa@aqmd.gov, 909/396-2171, Fax 909/396-2175) 21865 E. Copley Dr. Diamond Bar, CA 91765-4182.

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(7.) Ventura County Air Pollution Control District (Doug Tubbs, doug@vcmtss.mhs.compuserve.com, 805/662-6950, Fax 805/645-1444) .669 County Square Dr. 2nd floor Ventura, CA 93003-5417.

(8.) Bay Area Air Quality Management District (Rudy Zurrudo, rvz@merkle.baqmd.gov, 415/749-4629, Fax 415/749-5101) 939 Ellis Street San Francisco, CA 94109.

(9.) ManTech Environmental Technology, Inc. (Dr. Hunter Daughtrey, Hunter@epamail.epa.gov, 919/541-4540, Fax 919/541-3566) 2 Triangle Dr. Research Triangle Park, NC 27709. *Analyze canisters supplied by EPA.*

(10.) UCLA (Dr. Susanne Paulson, paulson@atmos.ucla.edu, 310/206-4442, Fax 310/206-5219) Department of Atmospheric Sciences, University of California, Los Angeles Los Angeles, CA 90095-1565. *Analyze canisters supplied by Desert Research Institute.*

(11.) Atmospheric Analytical Consultants (Dr. Sucha Parmar, sparmar@aol.com, 805/650-1642, Fax 805/650-1644) Ventura, CA

3.0 Specific Objectives and Approach

- 3.1 Review SOPs to identify differences in analytical methods and procedures that may cause differences in the data produced by participating laboratories. Aspects of SOPs to be reviewed by DRI will include cleaning and certifying canisters and samplers, calibration methods and reference materials, use and maintenance of dryers for water management, sample trapping and injection methods, choice of chromatographic column and operating conditions, peak integration procedure and selection of threshold, peak identification procedures, and data processing and management.
- 3.2 Assess stability of specific compounds in canisters over a time period comparable to the average holding time during the field study.
- 3.3 Determine significant systematic biases (greater than 30% for concentrations above 1.0 ppbC for individual compounds and greater than 20% for total non-methane hydrocarbons) due to analytical methods and procedures. DRI will determine consistency in peak identification for individual species, total NMHC, and fraction of unidentified NMHC.

4.0 Management and Communication Protocol

- 4.1 Air Resources Board, Monitoring and Laboratory Division will arrange for collection of ambient samples.
- 4.2 Mike Miguel of the ARB will receive and forward data from participants to DRI for analysis.
- 4.2 Eric Fujita of DRI will prepare a summary report for review by participants.

5.0 Documentation

Each laboratory is to submit the following documentation to Eric Fujita: 1) description of collection and analysis methods and standard operating procedures for canister and sampler cleaning and certification, sample collection, sample analysis, data processing and management, quality control and assessment; 2) list of compounds in the retention time library; and 3) definition of minimum detection limits and measurement precision.

6.0 Performance Audit Samples

- 6.1 Each participating laboratory, except ManTech and UCLA, will supply cleaned, evacuated 6-liter canisters to ARB in El Monte, CA by May 30, 1997. Canisters are to be shipped to Pat Harrington at 9480 Telstar Avenue, Suite 4 El Monte, CA 91731. The following numbers of canisters are to be supplied by each laboratory.

2 canisters: AAC, BAAQMD, SCAQMD

3 canisters: BRC, SDAPCD, VCAPCD

4 canisters: ARB

5 canisters: DRI, EPA

Canisters should be labeled by each laboratory with an internal identification number. ARB will tag each canister with the following sampling information: laboratory, canister identification number, sampling site, date, start and end times, and sampling port number.

- 6.2 ARB will fill the canisters to 20-25 psi with ambient air from the Los Angeles area using the twelve-port manifold sampling system supplied by the Desert Research Institute. One set of canisters will be collected in the morning (after 6:00 a.m. and before 9:00 a.m., PDT) at the Los Angeles N. Main monitoring station to represent an area heavily influenced by mobile source emissions. The other set will be collected in the afternoon (after 1:00 p.m. and before 4:00 p.m., PDT) at the Azusa monitoring station to represent a downwind area with maximum ozone levels. In addition, a set of evening samples (after 6:00 p.m. and before 8:00 p.m.) will be collected at Santa Monica Beach to represent a background sample. The following sampling list indicates the relative positions of the samples to be collected by ARB.

LA, N. Main: AAC, ARB, BAAQMD, BRC, DRI, EPA, SCAQMD, SDAPCD, VCAPCD, ARB (duplicate), DRI (duplicate), EPA (duplicate)

Azusa: AAC, ARB, BAAQMD, BRC, DRI, EPA, SCAQMD, SDAPCD, VCAPCD, ARB (duplicate), DRI (duplicate), EPA (duplicate)

Santa Monica: BRC, DRI, EPA, SDAPCD, VCAPCD

- 6.3 Pat Harrington will send the tagged ambient audit samples to participating laboratory by June 4, 1997.
- 6.4 Each laboratory will analyze the audit samples within ten working days after receiving the audit canisters. EPA, ARB and DRI will reanalyze their primary samples after one and two months to monitor the stability of the audit samples. Upon completion of analysis, the two duplicate samples collected by DRI and EPA will be forwarded to UCLA and ManTech, respectively by June 20, 1997.

7.0 Data Submittal and Analysis

- 7.1 Each laboratory will send hardcopies of chromatograms and a data report (species identification, retention times, individual species concentrations in ppbC, and total non-methane organic gases including unidentified hydrocarbons) to Mike Miguel by July 9, 1997 (by July 25 for UCLA and ManTech). The data should also be sent electronically in a spreadsheet or database format. To expedite and facilitate compilation and comparison of data, use the 6-character mnemonic shown in Table C-1 for species field names. The table of field names will be sent to each participating laboratory in both Excel and ASCII

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files for use in constructing the database/spreadsheet. The list of identified compounds should be those normally reported by each group (PAMS target list in most cases), or specified by contract. UCLA will report "total reactive carbon." Mike Miguel will forward the data to DRI for analysis after receiving DRI's analytical data.

- 7.2 Corrections to originally submitted data must be accompanied by sufficient documentation of the reasons.
- 7.3 Analysis of the data by DRI will include linear regression of data for each participating laboratory versus the average values (individual values exceeding two standard deviations of the mean of all values will be removed from the average). Differences in species concentrations of greater than 30% (for concentrations above 1 ppbC) between individual laboratories versus the adjusted mean values. Chromatograms will be examined to identify possible discrepancies in species identification.
- 7.4 Results will be sent to all participants for review and comments within three weeks after all data reports have been submitted. Each of the laboratories will be identified in the report by code only (letter code selected at random) in the draft report. The final report will contain the letter code key as an appendix.

Table 1
SCOS97 VOC Data Field Names (Mnemonics)

Sort No.	Compound Name ^a	Mnemonic	Flag	C_no	mw	convert to ug/m3
1	carbon monoxide (ppmv)	CO_PPM		1	28.01	1145.609
2	carbon dioxide (ppmv)	CO2PPM		1	44.01	1800.009
3	methane (ppmv)	METHAN		1	16.04	656.036
4	ethane	ETHANE	p	2	30.07	0.6149
5	ethene	ETHENE	p	2	28.05	0.5736
6	acetylene	ACETYL	p	2	26.04	0.5325
7	propene	PROPE	p	3	42.08	0.5737
8	propane	N_PROP	p	3	44.1	0.6012
9	Freon 12	FRE12	n	1	120.91	4.9452
10	isobutane	I_BUTA	p	4	58.12	0.5943
11	1-butene	LBUT1E	p	4	56.11	0.5737
12	iso-butene	LIBUTE	p	4	56.11	0.5737
13	1-butene&1-butene	BEABYL	p	4	56.11	0.5737
14	1,3-butadiene	BUDI13		4	54.09	0.5531
15	acetaldehyde	ACETAL	o	2	44.05	0.9008
16	n-butane	N_BUTA	p	4	58.12	0.5943
17	methanol (ppbv)	METOH	o	0.58	32.04	1.3104
18	t-2-butene	T2BUTE	p	4	56.11	0.5737
19	1&2-butyne	BUTYN		4	54.09	0.5531
20	c-2-butene	C2BUTE	p	4	56.11	0.5737
21	3-methyl-1-butene	B1E3ME		5	70.13	0.5737
22	ethanol (ppbv)	ETHOH	o	1.18	46.07	1.8843
23	acetonitrile	ACN	n	2	41.05	0.8395
24	isopentane	IPENTA	p	5	72.15	0.5902
25	acetone	ACETO	o	3	58.08	0.7918
26	1-pentene	PENTE1	p	5	70.13	0.5737
27	2-methyl-1-butene	B1E2M		5	70.13	0.5737
28	n-pentane	N_PENT	p	5	72.15	0.5902
29	isoprene	I_PREN	p	5	68.11	0.5571
30	t-2-pentene	T2PENE	p	5	70.13	0.5737
31	c-2-pentene	C2PENE	p	5	70.13	0.5737
32	2-methyl-2-butene	B2E2M		5	70.13	0.5737
33	F113	F113	n	2	187.38	3.8319
34	2,2-dimethylbutane	BU22DM	p	6	86.17	0.5874
35	2-methylpropanal	PRAL2M	o	4	72.07	0.7369
36	cyclopentene	CPENTE	p	5	68.11	0.5571
37	methacrolein	MEACRO	o	2	28.05	0.5736
38	4-methyl-1-pentene	P1E4ME		6	84.16	0.5737
39	3-methyl-1-pentene	P1E3ME		6	84.16	0.5737
40	cyclopentane	CPENTA	p	5	70.13	0.5737
41	2,3-dimethylbutane	BU23DM	p	6	86.17	0.5874
42	MTBE (ppbv)	MTBE	o	4.37	88.14	3.6049
43	2-methylpentane	PENA2M	p	6	86.17	0.5874
44	butanal	BUAL	o	4	72.12	0.7374
45	butanone	BUONE	o	4	72.12	0.7374
46	3-methylpentane	PENA3M	p	6	86.17	0.5874
47	2-methyl-1-pentene	P1E2ME	p	6	84.16	0.5737
48	1-hexene	HEX1E		6	84.16	0.5737
49	C6 olefin	C6OLE1		6	84.16	0.5737
50	n-hexane	N_HEX	p	6	86.17	0.5874
51	t-3-hexene + chloroform	T3HEXE		6	84.16	0.5737
52	c-3-hexene	C3HEXE		6	84.16	0.5737
53	t-2-hexene	T2HEXE		6	84.16	0.5737
54	2-methyl-2-pentene	P2E2ME		6	84.16	0.5737
55	c-2-hexene	C2HEXE		6	84.16	0.5737
56	cis-3-methyl-2-pentene	P2E3MC		6	84.16	0.5737
57	trans-3-methyl-2-pentene	P2E3MT		6	84.16	0.5737
58	3-methyl-2-pentene	P2E3ME		6	84.16	0.5737

59	2,2-dimethylpentane	PEN22M		7	100.2	0.5855
60	methylcyclopentane	MCYPNA	p	6	84.16	0.5737
61	2,4-dimethylpentane	PEN24M	p	7	100.2	0.5855
62	mechloroform	MECLOR	n	2	133.9	2.7383
63	2,2,3-trimethylbutane	BU223M		7	100.2	0.5855
64	1-methylcyclopentene	CPENE1		6	82.15	0.56
65	benzene	BENZE	p	6	78.11	0.5324
66	3,3-dimethylpentane	PEN33M		7	100.2	0.5855
67	cyclohexane	CYHEXA	p	6	84.16	0.5737
68	4-methylhexene	HEXE4M		7	98.19	0.5737
69	2-methylhexane	HEXA2M	p	7	98.19	0.5737
70	2,3-dimethylpentane	PEN23M	p	7	100.2	0.5855
71	cyclohexene	CYHEXE		6	82.15	0.56
72	3-methylhexane + pentanal	HEXA3M	p	7	100.2	0.5855
73	C7 olefin	C7OLE1		7	98.19	0.5737
74	1,3-dimethylcyclopentane	CPA13M		7	98.19	0.5737
75	3-ethylpentane	PA3ET		8	114.23	0.584
76	2,2,4-trimethylpentane	PA224M	p	8	114.23	0.584
77	C7 olefin	C7OLE2		7	98.19	0.5737
78	t-3-heptene	T3HEPE		7	98.19	0.5737
79	n-heptane	N HEPT	p	7	100.2	0.5855
80	C8 olefin	C8OLE1		8	112.21	0.5737
81	C8 olefin	C8OLE2		8	112.21	0.5737
82	C8 olefin	C8OLE3		8	112.21	0.5737
83	2,4,4-trimethyl-1-pentene	P1E244		8	112.21	0.5737
84	methylcyclohexane	MECYHX	p	7	98.19	0.5737
85	C8 paraffin	C8PA1		8	114.23	0.584
86	2,5-dimethylhexane	HEX25M		8	114.23	0.584
87	2,4-dimethylhexane	HEX24M		8	114.23	0.584
88	C8 paraffin	C8PA2		8	114.23	0.584
89	2,3,4-trimethylpentane	PA234M	p	8	114.23	0.584
90	toluene	TOLUE	p	7	92.14	0.5384
91	2,3-dimethylhexane	HX23DM		8	114.23	0.584
92	2-methylheptane	HEP2ME	p	9	128.26	0.5829
93	4-methylheptane	HEP4ME		9	128.26	0.5829
94	C8 paraffin	C8PA3		8	114.23	0.584
95	3-methylheptane	HEP3ME	p	8	114.23	0.584
96	hexanal	HEXAL	o	6	100.16	0.6828
97	2,2,5-trimethylhexane	HEX225		9	128.26	0.5829
98	octene-1	OCT1E		8	112.21	0.5737
99	1,1-dimethylcyclohexane	CHX11M		8	112.21	0.5737
100	n-octane	N OCT	p	8	114.23	0.584
101	2,3,5-trimethylhexane	HEX235		9	128.26	0.5829
102	2,4-dimethylheptane	HEP24D		9	128.26	0.5829
103	4,4-dimethylheptane	HEP44D		9	128.26	0.5829
104	2,6-dimethylheptane	HEP26D		9	128.26	0.5829
105	2,5-dimethylheptane	HEP25D		9	128.26	0.5829
106	3,3-dimethylheptane	HEP33D		9	128.26	0.5829
107	C9 olefin	C9OLE1		9	126.24	0.5737
108	C9 olefin	C9OLE2		9	126.24	0.5737
109	ethylbenzene	ETBZ	p	8	106.16	0.5427
110	C9 olefin	C9OLE3		9	126.24	0.5737
111	m- & p-xylene	MP_XYL	p	8	106.16	0.5427
112	2-methyloctane	OCT2ME		9	128.26	0.5829
113	3-methyloctane	OCT3ME		9	128.26	0.5829
114	C9 paraffin	C9PAR1		9	128.26	0.5829
115	styrene + heptanal	STYR	p	8	104.14	0.5324
116	o-xylene	O_XYL	p	8	106.17	0.5428
117	nonene-1	NONE1		9	126.24	0.5737
118	C9 paraffin	C9PAR2		9	128.26	0.5829
119	n-nonane	N NON	p	9	128.26	0.5829
120	C9 paraffin	C9PAR3		9	128.26	0.5829

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121	C9 olefin	C9OLE4		9	126.24	0.5737
122	C9 paraffin	C9PAR4		9	128.26	0.5829
123	isopropylbenzene	IPRBZ	p	9	120.2	0.5462
124	isopropylcyclohexane	IPCYHX		9	126.24	0.5737
125	alpha-pinene	A PINE		10	136.23	0.5572
126	benzaldehyde	BZALDE	o	7	106.1	0.6199
127	2,6-dimethyloctane	OCT26D		10	142.29	0.582
128	C10 olefin	C10OL1		10	140.27	0.5737
129	3,6-dimethyloctane	OCT36M		10	142.29	0.582
130	n-propylbenzene	N_PRBZ	p	9	120.2	0.5462
131	m-ethyltoluene	M_ETOL	p	9	120.2	0.5462
132	p-ethyltoluene	P_ETOL	p	9	120.2	0.5462
133	1,3,5-trimethylbenzene	BZ135M	p	9	120.2	0.5462
134	C10 paraffin	C10P_A		10	142.29	0.582
135	o-ethyltoluene	O_ETOL	p	9	120.2	0.5462
136	octanal	OCTAL	o	8	128	0.6544
137	beta-pinene	B_PINE		10	136.23	0.5572
138	1,2,4-trimethylbenzene	BZ124M	p	9	120.2	0.5462
139	n-decane	N_DEC	p	10	142.29	0.582
140	C10 aromatic	C10AR1		10	134.22	0.549
141	isobutylbenzene	I_BUBZ		10	134.22	0.549
142	sec-butylbenzene	S_BUBZ		10	134.22	0.549
143	C10 olefin	C10OL2		10	140.27	0.5737
144	1,2,3-trimethylbenzene	BZ123M	p	9	120.2	0.5462
145	C10 paraffin	C10P_C		10	142.29	0.582
146	limonene	LIMON		10	136.24	0.5572
147	indan	INDAN		9	118.17	0.537
148	indene	INDENE		9	116.15	0.5278
149	m-diethylbenzene	DETBZ1	p	10	134.22	0.549
150	C10 aromatic	C10AR2		10	134.22	0.549
151	p-diethylbenzene	DETBZ2	p	10	134.22	0.549
152	n-butylbenzene	N_BUBZ		10	134.22	0.549
153	o-diethylbenzene	DETBZ3	p	10	134.22	0.549
154	C10 aromatic	C10AR3		10	134.22	0.549
155	1,3-dimethyl-4-ethylbenzene	BZDME		10	134.22	0.549
156	C10 aromatic	C10AR4		10	134.22	0.549
157	isopropyltoluene	IPRTOL		10	134.22	0.549
158	nonanal	NONAL	o	9	142	0.6453
159	n-undecane	N_UNDE	p	11	156.3	0.5812
160	C10 aromatic	C10AR5		10	134.22	0.549
161	C10 aromatic	C10AR6		10	134.22	0.549
162	C11 paraffin	C11P_A		11	156.32	0.5812
163	1,2,4,5-tetramethylbenzene	BZ1245		10	134.22	0.549
164	1,2,3,5-tetramethylbenzene	BZ1235		10	134.22	0.549
165	C11 paraffin	C11P_B		11	156.32	0.5812
166	2-methylindan	IND_2M		10	132.21	0.5407
167	1-methylindan	IND_1M		10	132.21	0.5407
168	C11 aromatic	C11AR1		11	148.22	0.5511
169	C11 aromatic	C11AR3		11	148.22	0.5511
170	naphthalene	NAPHTH		10	128.16	0.5242
171	n-dodecane	N_DODE		12	170.34	0.5806
	Total Identified NMHC	IDNMHC		1		
	Unidentified ^b	UNID		1	13.85	0.5665
	Total NMHC	TNMHC				
	Identified oxygenated (ppbv) ^c	IDOXY		1		

a. Unless otherwise indicated, conversions to ug/m3 assume data are in ppbC.

b. Sum of unidentified hydrocarbons. Excludes halogenated and oxygenated compounds.

c. Sum of MTBE, methanol, and ethanol.

Flags: p - PAMS target list; o - oxygenated compounds; n - non-hydrocarbon compounds.

Appendix A.1

**SCOS97-NARSTO Hydrocarbon Measurement
Comparison Data**

Appendix A.1 - SCOS97-NARSTO Hydrocarbon Measurement Comparison Data

Mnemonic	Parameter	Type	Sort	C#	ARB	ARB	AAC	BAAQMD
Sample								
Site	Sampling Location				Azusa	Azusa	Azusa	Asuza
Date	Date				970610	970610	970610	970610
Start	Start Time (PDT)				1223	1223	1223	1223
Dur	Duration (min)				283	283	283	283
Can ID	Can ID				22865	22891		
Flag	Sampling and Analysis Flag					d		
Total								
PAMS	Sum of PAM Species				184.5	184.4	236.0	183.8
other id	Other identified hydrocarbons				9.5	9.2		33.7
unid	Unidentified compounds				60.4	55.4		25.0
tnmhc	Total non-methane hydrocarbons				254.4	305.0		242.5
idoxy	Identified oxygenated compounds					0.0		40.5
PAMS								
ethene	ethene	ole	p01	2	8.4	8.5	3	7.6
acetyl	acetylene	ole	p02	2	12.0	12.2	15	6.3
ethane	ethane	par	p03	2	7.5	7.4	5	6.6
prope	propene	ole	p04	3	2.7	2.6	3	2.2
n_prop	propane	par	p05	3	12.0	11.9	13	11.0
i_buta	isobutane	par	p06	4	3.8	3.8	4	1.5
lbut1e	1-butene	ole	p07	4				
libute	iso-butene	ole	p07a	4	3.8	3.9		
beabyl	1-butene&i-butene	ole	p07b	4				2.0
n_buta	n-butane	par	p08	4	6.6	6.6	7	6.4
t2bute	t-2-butene	ole	p09	4				
c2bute	c-2-butene	ole	p10	4				
ipenta	isopentane	par	p11	5	22.3	22.0	23	20.6
pente1	1-pentene	ole	p12	5	1.4	1.1	6	4.5
n_pent	n-pentane	par	p13	5	8.5	8.8	9	8.6
i_pren	isoprene	ole	p14	5				
t2pene	t-2-pentene	ole	p15	5				0.4
c2pene	c-2-pentene	ole	p16	5			2	
bu22dm	2,2-dimethylbutane	par	p17	6	1.3	1.3	8	2.2
cpenta	cyclopentane	par	p18	5	1.1	1.2		0.6
bu23dm	2,3-dimethylbutane	par	p19	6	2.2	2.3	4	2.0
pena2m	2-methylpentane	par	p20	6	7.0	7.5	17	4.2
pena3m	3-methylpentane	par	p21	6	4.2	4.4	7	4.1
p1e2me	2-methyl-1-pentene	ole	p22	6				1.6
n_hex	n-hexane	par	p23	6	4.1	4.6	5	5.0
mcypna	methylcyclopentane	par	p24	6	4.3	4.3	6	5.5
pen24m	2,4-dimethylpentane	par	p25	7	1.8	1.8		
benze	benzene	aro	p26	6	4.6	4.6	5	6.2
cyhexa	cyclohexane	par	p27	6	1.9	2.0		4.1
hexa2m	2-methylhexane	par	p28	7	2.7	2.6	2	1.6
pen23m	2,3-dimethylpentane	par	p29	7	2.2	2.4	3	
hexa3m	3-methylhexane + pentanal	par	p30	7			3	4.4
pa224m	2,2,4-trimethylpentane	par	p31	8	3.9	4.0	6	4.4
n_hept	n-heptane	par	p32	7	2.6	2.6	3	2.5
mecyhx	methylcyclohexane	par	p33	7	2.3	3.5	4	3.5
pa234m	2,3,4-trimethylpentane	par	p34	8	1.3	1.3	2	1.6
tolue	toluene	aro	p35	7	17.4	17.4	14	16.2
hep2me	2-methylheptane	par	p36	9	1.3	1.3	4	1.4
hep3me	3-methylheptane	par	p37	8	1.4	1.3		1.9
n_oct	n-octane	par	p38	8	2.2	2.2	3	2.4

Appendix A.1 - SCOS97-NARSTO Hydrocarbon Measurement Comparison Data

Mnemonic	Parameter	Type	Sort	C#	ARB	ARB	AAC	BAAQMD
etbz	ethylbenzene	aro	p39	8	2.4	2.4	4	2.5
mp_xyl	m- & p-xylene	aro	p40	8	6.4	6.3	8	5.7
styr	styrene + heptanal	aro	p41	8			5	1.7
o_xyl	o-xylene	aro	p42	8	3.0	3.9	2	1.7
n_non	n-nonane	par	p43	9	1.5	1.3		0.6
iprbz	isopropylbenzene	aro	p44	9				
n_prbz	n-propylbenzene	aro	p45	9			4	
m_etol	m-ethyltoluene	aro	p46	9	1.7	1.6	4	0.8
p_etol	p-ethyltoluene	aro	p47	9				0.5
bz135m	1,3,5-trimethylbenzene	aro	p48	9			3	6.4
o_etol	o-ethyltoluene	aro	p49	9	1.0		3	5.7
bz124m	1,2,4-trimethylbenzene	aro	p50	9	4.9	3.7	7	
n_dec	n-decane	par	p51	10	2.9	2.4	2	1.7
bz123m	1,2,3-trimethylbenzene	aro	p52	9			4	0.6
detbz1	m-diethylbenzene	aro	p53	10				
detbz2	p-diethylbenzene	aro	p54	10			2	1.4
n_unde	n-undecane	par	p55	11	1.9	1.4	2	1.4
Other ID								
budi13	1,3-butadiene	ole	id001	4				
butyn	1&2-butyne	ole	id002	4				
b1e3me	3-methyl-1-butene	ole	id003	5				1.4
b1e2m	2-methyl-1-butene	ole	id004	5				
b2e2m	2-methyl-2-butene	ole	id005	5				1.4
cpente	cyclopentene	ole	id006	5	1.5	1.9		
p1e4me	4-methyl-1-pentene	ole	id007	6				
p1e3me	3-methyl-1-pentene	ole	id008	6				
hex1e	1-hexene	ole	id009	6				0.8
c6ole1	C6 olefin	ole	id010	6				
t3hexe	t-3-hexene + chloroform	ole	id011	6				
c3hexe	c-3-hexene	ole	id012	6				
t2hexe	t-2-hexene	ole	id013	6				
p2e2me	2-methyl-2-pentene	ole	id014	6				
c2hexe	c-2-hexene	ole	id015	6				
p2e3mc	cis-3-methyl-2-pentene	ole	id016	6				
p2e3mt	trans-3-methyl-2-pentene	ole	id017	6				
p2e3me	3-methyl-2-pentene	ole	id018	6				
pen22m	2,2-dimethylpentane	par	id019	7				
bu223m	2,2,3-trimethylbutane	par	id020	7				
cpene1	1-methylcyclopentene	ole	id021	6				
pen33m	3,3-dimethylpentane	par	id022	7				
hexe4m	4-methylhexene	ole	id023	7				
hep1e	1-Heptene	ole	id024	7				0.6
cyhexe	cyclohexene	ole	id025	6				
c7ole1	C7 olefin	ole	id026	7				
cpa13m	1,3-dimethylcyclopentane	par	id027	7		1.0		
pa3et	3-ethylpentane	par	id028	8				
c7ole2	C7 olefin	ole	id029	7				
t3hepe	t-3-heptene	ole	id030	7				
h2e2me	2-methyl-2-hexene	ole	id031	7				1.0
c8ole1	C8 olefin	ole	id032	8				
c8ole2	C8 olefin	ole	id033	8				
c8ole3	C8 olefin	ole	id034	8				
p1e244	2,4,4-trimethyl-1-pentene	ole	id035	8				
c8pa1	C8 paraffin	par	id036	8				
hex25m	2,5-dimethylhexane	par	id037	8				0.5

Appendix A.1 - SCOS97-NARSTO Hydrocarbon Measurement Comparison Data

Mnemonic	Parameter	Type	Sort	C#	ARB	ARB	AAC	BAAQMD
hex24m	2,4-dimethylhexane	par	id038	8				
c8pa2	C8 paraffin	par	id039	8				
hx23dm	2,3-dimethylhexane	par	id040	8				0.4
hep4me	4-methylheptane	par	id041	9				2.5
c8pa3	C8 paraffin	par	id042	8				
hex3et	3-Ethylhexane	par	id043	7	4.9	6.3		0.4
hex225	2,2,5-trimethylhexane	par	id044	9				
oct1e	octene-1	ole	id045	8				
chx11m	1,1-dimethylcyclohexane	par	id046	8				
hex235	2,3,5-trimethylhexane	par	id047	9				
hep24d	2,4-dimethylheptane	par	id048	9				2.9
hep44d	4,4-dimethylheptane	par	id049	9				
hep26d	2,6-dimethylheptane	par	id050	9				
hep25d	2,5-dimethylheptane	par	id051	9				2.4
hep33d	3,3-dimethylheptane	par	id052	9				
c9ole1	C9 olefin	ole	id053	9				
c9ole2	C9 olefin	ole	id054	9				
c9ole3	C9 olefin	ole	id055	9				
oct2me	2-methyloctane	par	id056	9				
oct4me	4-methyloctane	par	id057	9				
oct3me	3-methyloctane	par	id058	9				0.7
c9par1	C9 paraffin	par	id059	9				
none1	nonene-1	ole	id060	9				
c9par2	C9 paraffin	par	id061	9				
c9par3	C9 paraffin	par	id062	9				
c9ole4	C9 olefin	ole	id063	9				
c9par4	C9 paraffin	par	id064	9				
ipcyhx	isopropylcyclohexane	par	id065	9				
a_pine	alpha-pinene	ole	id066	10				
oct26d	2,6-dimethyloctane	par	id067	10				
c10ol1	C10 olefin	ole	id068	10				
oct36m	3,6-dimethyloctane	par	id069	10				
c10p_a	C10 paraffin	par	id070	10				
b_pine	beta-pinene	ole	id071	10				
c10ar1	C10 aromatic	aro	id072	10				1.7
i_bubz	isobutylbenzene	aro	id073	10				
s_bubz	sec-butylbenzene	aro	id074	10				3.9
c10ol2	C10 olefin	ole	id075	10				
c10p_c	C10 paraffin	par	id076	10				
limon	limonene	ole	id077	10				
indan	indan	par	id078	9				
indene	indene	ole	id079	9				
c10ar2	C10 aromatic	aro	id080	10				
n_bubz	n-butylbenzene	aro	id081	10				
detbz3	o-diethylbenzene	aro	id082	10				12.5
c10ar3	C10 aromatic	aro	id083	10				
bzdme	1,3-dimethyl-4-ethylbenzene	aro	id084	10				
c10ar4	C10 aromatic	aro	id085	10				
iprtol	isopropyltoluene	aro	id086	10				
c10ar5	C10 aromatic	aro	id087	10				
c10ar6	C10 aromatic	aro	id088	10				
c11p_a	C11 paraffin	par	id089	11				
bz1245	1,2,4,5-tetramethylbenzene	aro	id090	10				
bz1235	1,2,3,5-tetramethylbenzene	aro	id091	10				
c11p_b	C11 paraffin	par	id092	11				

Appendix A.1 - SCOS97-NARSTO Hydrocarbon Measurement Comparison Data

Mnemonic	Parameter	Type	Sort	C#	ARB	ARB	AAC	BAAQMD
ind_2m	2-methylindan	par	id093	10				
ind_1m	1-methylindan	par	id094	10				
c11ar1	C11 aromatic	aro	id095	11				
c11ar3	C11 aromatic	aro	id096	11				
naphth	naphthalene	aro	id097	10				
n_dode	n-dodecane	par	id098	12				0.6
Oxygenated								
metoh	methanol (ppbv)	oxy	oxy01	0.58				
ethoh	ethanol (ppbv)	oxy	oxy02	1.18				
mtbe	MTBE	oxy	oxy03	4.37				14.5
aceto	acetone	carb	oxy04	3				18.0
acetal	acetaldehyde	carb	oxy05	2				8.0
pral2m	2-methylpropanal	carb	oxy06	4				
bual	butanal	carb	oxy07	4				
buone	butanone (MEK)	carb	oxy08	4				
pental	pentanal	carb	oxy09	5				
pe2one	2-pentanone	carb	oxy10	5				
hexal	hexanal	carb	oxy11	6				
heptal	heptanal	carb	oxy12	7				
octal	octanal	carb	oxy13	8				
nonal	nonanal	carb	oxy14	9				
bzalde	benzaldehyde	carb	oxy15	7				
Subtotals Type and Carbon Number								
par	Sum of paraffins				114.8	117.2	142	118.5
ole	Sum of olefins				29.8	30.2	29	29.8
aro	Sum of aromatics				41.4	39.9	65	67.5
C2par	C2 paraffins	par		2	7.5	7.4	5	6.6
C2ole	C2 olefins	ole		2	20.4	20.7	18	13.9
C3par	C3 paraffins	par		3	12.0	11.9	13	11.0
C3ole	C3 olefins	ole		3	2.7	2.6	3	2.2
C4par	C4 paraffins	par		4	10.4	10.4	11	7.9
C4ole	C4 olefins	ole		4	3.8	3.9	0	2.0
C5par	C5 paraffins	par		5	31.9	32.0	32	29.8
C5ole	C5 olefins	ole		5	2.9	3.0	8	7.7
C6par	C6 paraffins	par		6	25.0	26.4	47	27.1
C6ole	C6 olefins	ole		6	0.0	0.0	0	2.4
C6aro	C6 aromatics	aro		6	4.6	4.6	5	6.2
C7par	C7 paraffins	par		7	11.6	13.9	15	12.0
C7ole	C7 olefins	ole		7	0.0	0.0	0	1.6
C7aro	C7 aromatics	aro		7	17.4	17.4	14	16.2
C8par	C8 paraffins	par		8	8.8	8.8	11	11.2
C8ole	C8 olefins	ole		8	0.0	0.0	0	0.0
C8aro	C8 aromatics	aro		8	11.8	12.6	19	11.6
C9par	C9 paraffins	par		9	2.8	2.6	4	9.8
C9ole	C9 olefins	ole		9	0.0	0.0	0	0.0
C9aro	C9 aromatics	aro		9	7.6	5.3	25	14.0
C10par	C10 paraffins	par		10	2.9	2.4	2	1.7
C10ole	C10 olefins	ole		10	0.0	0.0	0	0.0
C10aro	C10 aromatics	aro		10	0.0	0.0	2	19.5
C11par	C11 paraffins	par		10	1.9	1.4	2	1.4

Sampling and analysis flags: d-duplicate sample, r-replicated analysis

Appendix A.1 - SCOS97-NARSTO Hydrocarbon Measurement Comparison Data

Mnemonic	BRC	DRI	DRI	DRI	DRI	EPA	EPA	Mantech	Mantech
<u>Sample</u>									
Site	Azusa	Azusa							
Date	970610	970610	970610	970610	970610	970610	970610	970610	970610
Start	1223	1223	1223	1223	1223	1223	1223	1223	1223
Dur	283	283	283	283	283	283	283	283	283
Can ID	A-121	79061	79061	X110	X110	MTC5	MTC53		
Flag			r	d	d,r		d		d
<u>Total</u>									
PAMS	198.3	206.94	204.64	204.24	209.39	228.99	237.24	164.4	160.2
other id	7.0	24.37	23.48	22.94	23.07	40.01	66.61		
unid	57.2	24.74	21.08	22.21	22.22	104.04			
tnmhc	262.5	262.09	255.38	256.46	260.44	373.04	470.18		
idoxy	10.2	38.23	43.94	30.97	41.60	35.95	40.88	112.6	
<u>PAMS</u>									
ethene	7.4	7.75	7.56	7.64	7.75	6.36	6.09		
acetyl	13.0	17.87	17.78	17.66	17.65	14.27	13.67		
ethane	7.3	8.98	7.85	7.98	7.65	12.29	12.25		
prope	2.1	2.13	2.35	2.40	2.29	2.35	2.36		
n_prop	12.1	12.49	12.27	12.84	12.94	12.21	12.11		
i_buta	3.8	3.62	3.80	3.71	3.88	3.56	3.56	4.2	3.4
lbute		0.49	0.49	0.52	0.63			6.0	6.7
libute	2.6	2.07	1.87	2.05	2.06	6.86	8.46		
beabyl									
n_buta	7.8	6.87	7.22	6.87	7.15	6.95	7.35	6.2	5.1
t2bute	0.4	0.29	0.23	0.34	0.27	0.32	0.03		0.4
c2bute	0.2	0.16	0.17	0.17	0.19			0.4	
ipenta	24.7	22.07	21.99	21.97	22.06	21.58	21.10	35.7	33.4
pente1		0.12	0.14	0.11	0.12	0.38	0.37		0.5
n_pent	10.2	8.55	8.49	8.63	8.66	10.22	9.59	9.6	7.8
i_pren	0.6	0.83	0.63	0.71	0.83	0.74			1.0
t2pene	0.2	0.15	0.14	0.17	0.17	0.20	0.18		
c2pene	0.1	0.07	0.10	0.12	0.08	0.13	0.07		
bu22dm	1.5	1.88	1.59	1.49	1.54	1.29	21.83	1.6	1.2
cpenta	1.4	0.80	0.89	0.98	0.89	1.01	1.01	1.1	
bu23dm	2.3	2.20	2.08	2.16	2.12	1.99	1.89		
pena2m	7.4	7.61	7.39	7.82	7.96	7.97	8.21	4.8	5.4
pena3m	4.6	4.29	4.21	4.33	4.28	4.33	4.30	3.4	3.6
p1e2me		0.15	0.11	0.15	0.13	5.03	7.00		
n_hex	5.1	4.06	3.90	4.05	4.15	4.03	3.95	4.9	5.0
mcypna	4.6	4.28	4.14	4.24	4.25	4.79	4.34	4.2	4.3
pen24m	1.7	1.71	1.63	1.65	1.75	1.93	1.76	1.4	1.5
benze	5.2	4.67	4.60	4.70	4.82	4.86	4.62	6.9	6.8
cyhexa	2.1	2.13	2.06	2.25	2.13	2.23	2.01	1.9	2.0
hexa2m	2.8	2.96	3.00	2.85	2.96	3.67	4.86	2.5	2.6
pen23m	2.6	2.65	2.57	2.65	2.70	2.62	3.03	2.4	2.5
hexa3m	3.4	4.19	4.07	3.56	3.95	5.37	3.35		
pa224m	5.3	5.18	4.97	5.13	5.05	4.31	5.68	3.7	3.7
n_hept	2.8	2.87	2.78	2.86	2.86	3.04	2.81	3.1	3.3
mecyhx	3.9	4.02	3.96	3.94	4.06	8.50	3.30	3.2	3.3
pa234m	1.4	1.41	1.41	1.44	1.41	1.66	1.55	1.2	1.3
tolue	18.7	18.50	18.39	18.61	18.89	18.56	18.91	19.0	19.1
hep2me	1.4	1.45	1.48	1.39	1.43	1.57	1.43	1.6	1.5
hep3me		1.14	1.38	1.15	1.34	1.37	1.33	1.3	1.1
n_oct	2.9	2.13	1.98	2.02	2.09	2.31	2.35	2.0	1.9

Appendix A.1 - SCOS97-NARSTO Hydrocarbon Measurement Comparison Data

Mnemonic	BRC	DRI	DRI	DRI	DRI	EPA	EPA	Mantech	Mantech
etbz	2.5	2.45	2.40	2.44	2.49	3.68	2.97	2.3	2.3
mp_xyl	6.4	6.37	6.27	6.31	6.45	6.45	4.42	7.1	7.7
styr		2.34	2.20	1.93	2.12	3.28			
o_xyl	2.9	2.74	2.63	2.63	2.78	2.91	2.78	3.0	3.0
n_non	1.4	1.40	1.30	1.38	1.42	1.58	1.37	1.6	1.6
iprbz		0.37	0.28	0.31	0.40	0.59	0.88		
n_prbz	0.9	0.89	0.83	0.83	0.73	0.82	0.82	0.9	0.9
m_etol	1.3	1.79	1.81	1.74	1.80	2.19	2.36	2.7	2.6
p_etol	2.0	1.11	1.19	1.06	1.17			0.9	1.0
bz135m	1.2	2.53	4.16	2.42	4.91	5.97	3.17	1.3	1.2
o_etol	0.7	0.68	0.72	0.68	0.70	0.89	0.48	1.0	0.9
bz124m	2.9	3.52	3.45	3.45	3.50	3.44	3.02	3.7	3.6
n_dec	2.5	2.65	2.47	2.58	2.57	2.87	2.43	3.2	3.5
bz123m		1.02	0.99	0.99	1.00	1.15	1.19		
detbz1		0.13	0.11	0.07	0.07				
detbz2		0.78	0.77	0.72	0.78	1.02	3.31	2.1	1.3
n_unde		1.38	1.39	1.39	1.36	1.29	1.33	2.6	2.6
Other ID									
budi13	0.3	0.75	0.60	0.76	0.57	0.80			
butyn									
b1e3me		0.06	0.08	0.07	0.09	0.10	0.08		
b1e2m		0.19	0.20	0.24	0.21	0.25	0.06		
b2e2m	0.7	0.37	0.33	0.30	0.38	0.27			
cpente		0.17	0.22	0.06	0.12	0.16			
p1e4me									
p1e3me						0.52	0.50		
hex1e		0.12	0.08	0.10	0.10	0.24	0.40		
c6ole1						0.29	0.35		
t3hexe		0.06	0.02			0.91	0.97		
c3hexe									
t2hexe		0.03	0.04	0.14	0.12				
p2e2me		0.07	0.03	0.04	0.04				
c2hexe		0.06	0.03	0.04	0.05	0.18	0.16		
p2e3mc		0.10	0.05			0.46	2.42		
p2e3mt		1.02	1.07	0.86	0.98				
p2e3me									
pen22m						0.57	1.33		
bu223m						0.44	0.48		
cpene1						0.26	1.91		
pen33m		0.27	0.32	0.30	0.37				
hexe4m						0.19			
hep1e									
cyhexe		0.36	0.36	0.36	0.39		2.95		
c7ole1				0.19	0.20	1.20	0.99		
cpa13m		1.10	1.04	1.07	1.06				
pa3et		1.33	1.26	1.31	1.25	1.45	1.25		
c7ole2						0.25	0.29		
t3hepe		0.19	0.10	0.12	0.10				
h2e2me									
c8ole1						0.46	2.52		
c8ole2						0.74	0.28		
c8ole3		0.31	0.26	0.11	0.09	0.48	0.27		
p1e244	0.8					2.32	1.94		
c8pa1		0.09	0.12	0.08	0.05	0.26	0.37		
hex25m	1.3	0.64	0.65	0.69	0.68	0.62	0.61		

Appendix A.1 - SCOS97-NARSTO Hydrocarbon Measurement Comparison Data

Mnemonic	BRC	DRI	DRI	DRI	DRI	EPA	EPA	Mantech	Mantech
hex24m	1.2	1.65	1.61	1.67	1.63	1.61	1.22		
c8pa2		0.62	0.61	0.56	0.67	0.59	0.63		
hx23dm	1.0	0.51	0.59	0.55	0.54	1.11	1.37		
hep4me		0.47	0.71	0.48	0.44	1.12	2.19		
c8pa3		0.20	0.21	0.22	0.18	0.18	0.21		
hex3et	1.7								
hex225		0.23	0.27	0.24	0.27	0.84	0.97		
oct1e		0.76	0.76	0.77	0.81	0.31	0.66		
chx11m		0.08	0.09	0.06	0.06				
hex235							0.69		
hep24d						0.23	0.28		
hep44d		0.27	0.27	0.27	0.26	0.53	0.57		
hep26d		0.40	0.30	0.34	0.35	0.32	4.80		
hep25d		1.08	1.00	0.91	0.91	1.24	1.20		
hep33d		0.38	0.34	0.37	0.38	0.68			
c9ole1		0.23	0.11	0.05	0.13	0.26			
c9ole2						0.35	0.98		
c9ole3		0.70	0.70	0.65	0.69	0.87	0.97		
oct2me		0.82	1.03	0.94	0.94				
oct4me						1.32	1.74		
oct3me		0.69	0.68	0.71	0.73	0.66	1.51		
c9par1		0.06	0.06	0.07	0.06	1.60	2.51		
none1		0.31	0.32	0.30	0.36	0.58	0.43		
c9par2		0.16	0.15	0.17	0.19		3.41		
c9par3		0.16	0.10	0.15	0.16	0.53	0.27		
c9ole4		0.09	0.07	0.07	0.08	0.21	2.04		
c9par4						0.62	1.10		
ipcyhx							1.65		
a_pine		0.37	0.34	0.30	0.29	0.37	0.35		
oct26d						2.02	2.30		
c10o11						1.77	4.52		
oct36m		0.44	0.37	0.39	0.39	0.53	1.80		
c10p_a		0.30	0.30	0.32	0.38	0.47	1.04		
b_pine									
c10ar1						0.51	0.44		
i_bubz		0.42	0.34	0.31	0.31	0.42	0.52		
s_bubz		0.21	0.18	0.09	0.10	0.21	0.19		
c10o12		0.35	0.33	0.35	0.34	2.65	2.56		
c10p_c		0.67	0.67	0.70	0.69	0.83	0.72		
limon		0.44	0.39	0.42	0.42	0.71	0.64		
indan		0.58	0.47	0.51	0.53				
indene		0.64	0.50	0.52	0.53				
c10ar2		0.51	0.44	0.44	0.42				
n_bubz									
detbz3		0.21	0.22	0.21	0.18				
c10ar3									
bzdme									
c10ar4		0.32	0.38	0.40	0.33				
iprtol		0.32	0.26	0.30	0.31				
c10ar5		0.10	0.13	0.11	0.11				
c10ar6									
c11p_a									
bz1245		0.23	0.20	0.22	0.21				
bz1235		0.16	0.18	0.20	0.14				
c11p_b									

Appendix A.1 - SCOS97-NARSTO Hydrocarbon Measurement Comparison Data

Mnemonic	BRC	DRI	DRI	DRI	DRI	EPA	EPA	Mantech	Mantech
ind_2m									
ind_1m									
c11ar1									
c11ar3									
naphth		0.49	0.49	0.36	0.29				
n_dode		0.45	0.45	0.40	0.41				
<u>Oxygenated</u>									
metoh									
ethoh						1.01	0.97	22.5	
mtbe	10.2	13.25	13.30	12.90	13.65	13.30	12.92	10.7	
aceto		9.80	12.40	7.28	13.12	21.63	27.96	38.3	
acetal									
pral2m		0.55	0.28	0.34	0.29	1.02			
bual		1.23	0.94	0.81	0.86			9.6	
buone		3.30	3.76	2.58	3.67			5.6	
pental								9.5	
pe2one								3.2	
hexal		1.95	1.84	1.31	1.44			6.1	
heptal								4.1	
octal		3.34	3.31	2.67	3.02			7.0	
nonal		3.32	6.41	2.89	5.05			18.5	
bzalde		1.49	1.70	0.19	0.50				
<u>Subtotals</u>									
par	130.5	135.41	132.96	133.71	135.06	150.87	178.23	107.1	101.4
ole	27.6	39.83	38.56	38.86	39.26	51.96	65.03	6.4	8.6
aro	44.7	52.86	53.62	51.53	55.01	56.95	50.08	50.9	50.2
C2par	7.3	8.98	7.85	7.98	7.65	12.29	12.25		
C2ole	20.4	25.62	25.34	25.30	25.40	20.63	19.76		
C3par	12.1	12.49	12.27	12.84	12.94	12.21	12.11		
C3ole	2.1	2.13	2.35	2.40	2.29	2.35	2.36		
C4par	11.6	10.49	11.02	10.58	11.03	10.51	10.91	10.3	8.5
C4ole	3.5	3.76	3.36	3.84	3.72	7.98	8.49	6.4	7.1
C5par	36.3	31.42	31.37	31.58	31.61	32.81	31.70	46.4	41.3
C5ole	1.6	1.96	1.84	1.78	2.00	2.23	0.76	0.0	1.5
C6par	27.6	26.45	25.37	26.34	26.43	26.63	46.53	20.8	21.4
C6ole	0.0	1.97	1.79	1.69	1.81	7.37	16.16	0.0	0.0
C6aro	5.2	4.67	4.60	4.70	4.82	4.86	4.62	6.9	6.8
C7par	17.2	19.77	19.37	18.88	19.71	26.14	20.92	12.6	13.1
C7ole	0.0	0.19	0.10	0.31	0.30	1.64	1.28	0.0	0.0
C7aro	18.7	18.50	18.39	18.61	18.89	18.56	18.91	19.0	19.1
C8par	13.1	14.98	14.88	14.88	14.95	15.47	16.57	8.1	8.0
C8ole	0.0	1.07	1.02	0.88	0.90	1.99	3.73	0.0	0.0
C8aro	11.8	13.90	13.50	13.31	13.84	16.32	10.17	12.4	12.9
C9par	2.8	6.50	6.67	6.34	6.43	10.18	22.44	3.2	3.1
C9ole	0.0	1.97	1.70	1.59	1.79	2.27	4.42	0.0	0.0
C9aro	9.0	11.91	13.43	11.48	14.21	15.05	11.92	10.4	10.1
C10par	2.5	2.95	2.77	2.90	2.95	3.34	3.47	3.2	3.5
C10ole	0.0	1.16	1.06	1.07	1.05	5.50	8.07	0.0	0.0
C10aro	0.0	3.88	3.70	3.43	3.25	2.16	4.46	2.1	1.3
C11par	0.0	1.38	1.39	1.39	1.36	1.29	1.33	2.6	2.6

Sampling an

Appendix A.1 - SCOS97-NARSTO Hydrocarbon Measurement Comparison Data

Mnemonic	SCAQMD lab	SCAQMD Auto-GC	SDAPCD	VCAPCD	ARB	ARB	AAC	BAAQMD	BRC
Sample									
Site	Azusa	Azusa	Azusa	Azusa	LA	LA	LA	LA	LA
Date	970610	970610	970610	970610	970610	970610	970610	970610	970610
Start	1223	1223	1223	1223	810	810	810	810	810
Dur	283	283	283	283	240	240	240	240	240
Can ID	54129	54129	AMB-083		22869	22899			S-77
Flag						d			
Total									
PAMS	181.91	198.10	233.1	246.0	243.7	244.1	234.0	254.0	250.8
other id					11.8	8.0		26.8	8.3
unid	59.83	132.34	76.3		43.8	48.6		7.9	99.9
tmhc	241.74	330.44	309.2		299.3	355.0		288.7	358.9
idoxy					0.0	0.0		39.3	10.0
PAMS									
ethene	8.03	7.26	8.0		12.8	12.7	3.0	11.7	11.8
acetyl	8.35	5.04	12.2	52.3	11.4	11.4	15.0	6.4	13.0
ethane	8.17	7.56	2.9	2.9	16.7	16.6	6.0	15.5	16.3
prope	2.34	2.65	2.5	3.3	5.4	5.2	3.0	4.4	5.0
n_prop	12.74	12.38	12.1	13.6	19.7	19.6	13.0	16.6	19.7
i_buta	3.62	3.72	3.5	4.1	5.7	5.8	4.0	3.8	5.3
lbutle		0.78	3.5	15.0					
libute					4.6	5.1			4.2
beabyl								6.8	
n_buta	6.64	6.99	6.6	8.0	9.0	9.0	7.0	8.7	9.0
t2bute		0.36		3.5					0.6
c2bute		0.39						0.8	0.3
ipenta	22.59	26.05	55.1	24.0	23.2	24.0	23.0	22.3	23.5
pente1		3.11				1.0	5.0	4.6	0.5
n_pent	8.77	8.74	11.3	10.7	10.5	10.5	9.0	12.0	11.4
i_pren	0.68	0.82	0.8						0.3
t2pene		0.32							0.3
c2pene		0.15					1.0		0.3
bu22dm	1.36	1.35	1.5	1.8	1.7	1.6	8.0	2.1	2.1
cpenta	2.38	0.93	1.0	1.5	1.5	1.6		1.5	1.7
bu23dm	2.30	3.24	2.1	3.5	2.5	2.6	4.0	2.0	2.6
pena2m	7.05	7.13	15.3	7.4	7.9	8.0	16.0	5.3	8.1
pena3m	4.18	4.16	4.4	4.7	5.1	5.2	7.0	5.0	4.9
p1e2me		0.07						1.2	
n_hex	4.32	3.92	4.0	4.3	5.0	4.8	5.0	6.5	5.2
mcpyna	4.27	4.00	4.4	4.5	5.5	5.4	6.0	7.1	5.5
pen24m	1.50	1.64	1.6	2.0	2.2	2.1			2.1
benze	4.88	4.61	4.6	5.8	5.5	5.5	5.0	7.2	6.0
cyhexa	2.12	2.03	1.9	2.2	2.6	2.7		5.1	2.8
hexa2m	2.53	2.56	2.7	2.8	2.7	3.0	2.0	2.4	3.1
pen23m	2.49	2.55	2.6	2.7	3.2	2.9	3.0		3.5
hexa3m	2.61	3.07	3.9	3.3			3.0	4.4	3.7
pa224m	3.87	3.94	4.0	4.8	5.1	5.0	6.0	5.8	6.3
n_hept	2.72	2.74	2.7	2.8	2.6	2.6	3.0	2.7	2.7
mecyhx	3.42	4.04	3.7	3.7	3.2	3.1	4.0	3.4	3.4
pa234m	1.40	1.50	1.4	1.2	2.0	2.0	2.0	2.9	2.1
tolue	18.31	18.69	17.9	17.2	19.7	20.1	14.0	19.2	20.5
hep2me	1.45	1.44	0.9	2.3	1.6	1.7	4.0	1.6	1.6
hep3me	1.50	1.36	1.3	2.1	1.8	1.8		2.8	
n_oct	1.87	1.96	1.6	2.3	2.6	2.5	3.0	1.9	2.9

Appendix A.1 - SCOS97-NARSTO Hydrocarbon Measurement Comparison Data

Mnemonic	SCAQMD lab	SCAQMD Auto-GC	SDAPCD	VCAPCD	ARB	ARB	AAC	BAAQMD	BRC
etbz	2.44	2.47	2.7	2.1	3.1	3.2	4.0	3.1	3.4
mp_xyl	7.49	7.68	7.0	7.3	10.5	11.2	8.0	9.9	11.0
styr		0.64	1.8	1.0			5.0	1.2	
o_xyl	2.50	2.67	2.7	2.8	4.7	4.2	2.0	4.4	4.5
n_non	1.00	1.24	1.3	1.0	1.6	1.4		1.0	1.2
iprbz		0.37							
n_prbz		1.48			1.0	1.0	4.0	1.0	1.3
m_etol	1.77	3.29	2.6	1.9	2.8	2.8	4.0	1.6	2.0
p_etol	1.13	1.49	0.7	1.0	1.7	1.3		0.9	4.0
bz135m	0.87	0.90	4.2	1.0	1.6	1.5	3.0	0.8	2.0
o_etol		0.76	1.5		1.4	1.6	3.0	5.0	1.6
bz124m	2.59	3.56	2.4	3.1	5.7	6.7	7.0		5.2
n_dec	2.28	4.00	3.0	2.4	2.1	1.8	2.0	7.0	2.3
bz123m		1.06		1.0	1.5	1.2	4.0	0.7	
detbz1		1.03						5.4	
detbz2		0.34					2.0	6.7	
n_unde	1.38	1.87	1.2	1.1	3.0	1.1	2.0	1.6	
<u>Other ID</u>									
budi13								0.6	0.8
butyn									
b1e3me								1.5	
b1e2m									0.5
b2e2m								0.5	0.4
cpente					1.3	1.4		0.4	
p1e4me									
p1e3me									
hex1e								0.7	
c6ole1									
t3hexe									
c3hexe									
t2hexe									
p2e2me									
c2hexe									
p2e3mc									
p2e3mt									
p2e3me									
pen22m									
bu223m									
cpene1									
pen33m									
hexe4m									
hep1e								0.7	
cyhexe									
c7ole1									
cpa13m					1.1	1.2			
pa3et									
c7ole2									
t3hepe									
h2e2me								0.4	
c8ole1									
c8ole2									
c8ole3									
p1e244								0.3	0.8
c8pa1									
hex25m					1.1			0.4	1.5

Appendix A.1 - SCOS97-NARSTO Hydrocarbon Measurement Comparison Data

Mnemonic	SCAQMD lab	SCAQMD Auto-GC	SDAPCD	VCAPCD	ARB	ARB	AAC	BAAQMD	BRC
hex24m									1.3
c8pa2									
hx23dm								0.6	1.0
hep4me								1.8	
c8pa3									
hex3et					4.3	5.4			2.0
hex225									
oct1e									
chx11m									
hex235									
hep24d								2.9	
hep44d									
hep26d									
hep25d								0.7	
hep33d									
c9ole1									
c9ole2									
c9ole3									
oct2me									
oct4me									
oct3me								1.0	
c9par1									
none1									
c9par2									
c9par3									
c9ole4									
c9par4									
ipcyhx									
a_pine									
oct26d								0.7	
c10ol1									
oct36m									
c10p_a									
b_pine									
c10ar1									1.5
i_bubz									
s_bubz								4.1	
c10ol2									
c10p_c									
limon									
indan									
indene									
c10ar2									
n_bubz								1.8	
detbz3								5.2	
c10ar3									
bzdme									
c10ar4									
iptol									
c10ar5									
c10ar6									
c11p_a									
bz1245									
bz1235									
c11p_b									

Appendix A.1 - SCOS97-NARSTO Hydrocarbon Measurement Comparison Data

Mnemonic	SCAQMD lab	SCAQMD Auto-GC	SDAPCD	VCAPCD	ARB	ARB	AAC	BAAQMD	BRC
ind_2m									
ind_1m									
c11ar1									
c11ar3									
naphth									
n_dode								1.0	
<u>Oxygenated</u>									
metoh									
ethoh									
mtbe								16.0	10.0
aceto								13.2	
acetal								10.1	
pral2m									
bual									
buone									
pental									
pe2one									
hexal									
heptal									
octal									
nonal									
bzalde									
<u>Subtotals</u>									
par	120.53	126.11	158.0	127.7	152.5	149.6	142.0	157.4	156.8
ole	19.40	20.95	27.0	74.1	35.5	36.8	27.0	40.7	38.0
aro	41.98	51.04	48.1	44.2	59.2	60.3	65.0	79.7	61.5
C2par	8.17	7.56	2.9	2.9	16.7	16.6	6.0	15.5	16.3
C2ole	16.38	12.30	20.2	52.3	24.2	24.1	18.0	18.1	24.8
C3par	12.74	12.38	12.1	13.6	19.7	19.6	13.0	16.6	19.7
C3ole	2.34	2.65	2.5	3.3	5.4	5.2	3.0	4.4	5.0
C4par	10.26	10.71	10.1	12.1	14.7	14.8	11.0	12.5	14.3
C4ole	0.00	1.53	3.5	18.5	4.6	5.1	0.0	8.2	5.9
C5par	33.74	35.72	67.4	36.2	35.2	36.1	32.0	35.8	36.6
C5ole	0.68	4.40	0.8	0.0	1.3	2.4	6.0	7.0	2.3
C6par	25.60	25.83	33.6	28.4	30.3	30.3	46.0	33.1	31.2
C6ole	0.00	0.07	0.0	0.0	0.0	0.0	0.0	1.9	0.0
C6aro	4.88	4.61	4.6	5.8	5.5	5.5	5.0	7.2	6.0
C7par	15.27	16.60	17.2	17.3	15.0	14.9	15.0	12.9	18.5
C7ole	0.00	0.00	0.0	0.0	0.0	0.0	0.0	1.1	0.0
C7aro	18.31	18.69	17.9	17.2	19.7	20.1	14.0	19.2	20.5
C8par	8.64	8.76	8.3	10.4	12.6	11.3	11.0	14.4	15.1
C8ole	0.00	0.00	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C8aro	12.43	13.46	14.2	13.2	18.3	18.6	19.0	18.6	18.9
C9par	2.45	2.68	2.2	3.3	3.2	3.1	4.0	8.0	2.8
C9ole	0.00	0.00	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C9aro	6.36	12.91	11.4	8.0	15.7	16.1	25.0	10.0	16.1
C10par	2.28	4.00	3.0	2.4	2.1	1.8	2.0	7.0	2.3
C10ole	0.00	0.00	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C10aro	0.00	1.37	0.0	0.0	0.0	0.0	2.0	24.7	0.0
C11par	1.38	1.87	1.2	1.1	3.0	1.1	2.0	1.6	0.0

Sampling an

Appendix A.1 - SCOS97-NARSTO Hydrocarbon Measurement Comparison Data

Mnemonic	BRC	DRI	DRI	DRI	DRI	EPA	Mantech	SCAQMD- lab	SCAQMD- Aut
<u>Sample</u>									
Site	LA	LA	LA						
Date	970610	970610	970610	970610	970610	970610	970610	970610	970610
Start	810	810	810	810	810	810	810	810	810
Dur	240	240	240	240	240	240	240	240	240
Can ID	SJV-94	79054	79054	79025	79025	MTC32		54326	54326
Flag	d		r	d	d,r				
<u>Total</u>									
PAMS	248.1	260.62	260.44	260.63	257.13	285.63	190.0	258.1	276.5
other id	8.4	30.99	30.85	29.24	28.86	105.30			
unid	62.9	21.20	21.31	20.20	21.43	172.72		99.3	171.9
tnmhc	319.4	322.14	321.40	315.01	315.24	563.65		357.4	448.4
idoxy	10.5	29.92	32.05	22.28	23.43	29.53	112.2		
<u>PAMS</u>									
ethene	11.7	11.73	11.79	12.11	11.67	9.40		13.6	12.7
acetyl	12.7	16.91	16.84	17.08	17.02	13.38		8.4	4.9
ethane	16.1	17.38	16.49	17.68	16.83	22.57		17.6	17.0
prope	4.6	4.69	5.05	5.00	4.82	5.31		6.0	6.3
n_prop	19.4	19.68	20.03	19.93	19.37	20.88		20.6	21.2
i_buta	5.5	5.74	5.94	5.69	5.68	5.63	5.4	5.7	6.1
lbut1e		0.85	0.82	0.80	0.76	8.60	7.7		1.5
libute	4.2	3.45	3.36	3.43	3.33				
beabyl									
n_buta	8.9	9.45	9.45	9.40	9.24	9.47	6.6	9.4	9.9
t2bute	0.6	0.38	0.33	0.44	0.38		0.4		0.5
c2bute	0.3	0.27	0.27	0.25	0.29	0.45	0.4		0.6
ipenta	23.3	23.91	23.60	23.98	23.67	23.08	30.3	25.1	31.0
pente1	0.2	0.26	0.29	0.25	0.24	0.65	0.9	0.7	3.4
n_pent	11.4	10.89	10.81	10.76	10.82	11.91	11.4	11.8	11.5
i_pren	0.2	0.31	0.47	0.43	0.33	0.36	0.8		0.6
t2pene	0.3	0.37	0.25	0.30	0.26	0.32			0.5
c2pene	0.2	0.19	0.31	0.21	0.23	0.19			0.3
bu22dm	1.9	2.08	1.98	2.16	2.15	5.78	1.7	1.4	1.8
cpenta	1.8	1.43	1.37	1.47	1.46	1.41		2.3	1.6
bu23dm	2.6	2.66	2.54	2.59	2.63	2.18		2.7	3.7
pena2m	7.6	8.59	8.68	8.71	8.66	8.96	5.9	8.2	8.5
pena3m	5.0	4.95	4.96	4.99	5.09	5.03	4.0	5.0	5.0
p1e2me		0.24	0.13	0.18	0.18	5.44			0.5
n_hex	5.3	4.77	4.59	4.65	4.66	4.57	5.5	4.8	4.8
mcpyna	5.5	5.56	5.45	5.42	5.47	5.74	5.5	5.4	5.5
pen24m	2.1	2.03	1.99	2.00	1.99	2.05	1.7	2.0	2.1
benze	6.0	5.94	5.83	5.67	5.71	6.17	8.0	6.9	6.1
cyhexa	2.8	2.83	3.03	3.03	3.00	3.05	2.8	3.0	2.8
hexa2m	3.2	3.11	3.22	3.04	3.02	4.50	2.9	2.9	3.1
pen23m	3.4	3.47	3.38	3.43	3.42	3.21	3.4	3.5	3.5
hexa3m	3.5	3.84	4.04	3.72	3.68	3.39		6.0	3.7
pa224m	6.3	6.35	6.32	6.38	6.24	6.40	4.8	5.8	5.4
n_hept	2.7	2.52	2.75	2.74	2.75	2.82	3.1	2.6	2.8
mecyhx	3.3	3.80	3.76	3.66	3.72	3.04	3.1	3.4	4.4
pa234m	2.1	2.12	2.10	2.15	2.11	2.41	1.7	2.1	2.4
tolue	20.6	20.98	21.08	21.03	20.91	21.35	21.1	22.1	23.1
hep2me	1.6	1.78	1.80	1.78	1.76	1.66	2.0	1.9	3.5
hep3me		1.55	1.84	1.62	1.56	1.81	1.6	2.0	1.9
n_oct	3.0	2.07	1.96	2.10	2.15	3.20	2.2	2.1	2.4

Appendix A.1 - SCOS97-NARSTO Hydrocarbon Measurement Comparison Data

Mnemonic	BRC	DRI	DRI	DRI	DRI	EPA	Mantech	SCAQMD- lab	SCAQMD- Aut
etbz	3.3	3.16	3.14	3.15	3.12	3.65	3.1	3.2	3.3
mp_xyl	11.0	10.99	10.90	10.86	10.75	7.74	12.0	13.3	12.2
styr		1.29	1.27	1.45	1.38	4.93		0.7	0.8
o_xyl	4.5	4.08	4.14	4.11	4.04	4.44	4.7	4.3	4.4
n_non	1.2	1.17	1.16	1.20	1.19	1.32	1.4	1.1	1.3
iprbz		0.44	0.45	0.41	0.41				0.3
n_prbz	1.3	0.97	0.97	0.93	0.92	1.00	1.3	1.0	1.8
m_etol	2.1	2.95	2.94	2.93	2.84	4.53	4.2	3.7	4.6
p_etol	3.7	1.44	1.43	1.42	1.38	1.65	1.3	1.8	2.5
bz135m	2.1	2.16	2.53	1.85	1.93	2.75	2.0	1.8	1.8
o_etol	1.7	1.07	1.06	1.04	1.03	1.40	1.4	1.0	1.4
bz124m	5.5	6.52	6.33	6.16	6.04	8.29	5.9	5.5	6.3
n_dec	1.8	1.55	1.43	1.41	1.34	2.01	1.9	1.4	3.3
bz123m		1.44	1.40	1.28	1.31	2.21	1.4	1.5	1.9
detbz1		0.20	0.25	0.16	0.16				1.6
detbz2		0.96	1.03	0.91	0.93	1.83	2.6	1.4	0.8
n_unde		1.10	1.11	1.10	1.10	1.51	2.3	1.5	2.0
Other ID									
budi13	0.8	1.35	1.20	1.25	1.21	1.20			
butyn						0.14			
b1e3me	0.2	0.16	0.17	0.16	0.18	0.19			
b1e2m	0.4	0.51	0.46	0.46	0.43	0.46			
b2e2m	0.4	0.47	0.44	0.43	0.51	0.32			
cpente		0.19	0.21	0.34	0.19	0.11			
p1e4me						2.12			
p1e3me						0.48			
hex1e		0.34	0.21	0.26	0.15	0.52			
c6ole1						0.32			
t3hexe		0.07	0.06		0.06	0.53			
c3hexe		0.07	0.07						
t2hexe		0.38	0.19	0.14	0.14	0.22			
p2e2me		0.06	0.05	0.05	0.08	0.10			
c2hexe		0.12	0.14	0.05	0.20	0.41			
p2e3mc		0.07	0.07	0.05	0.07	2.85			
p2e3mt		0.53	0.55	0.45	0.43	0.89			
p2e3me									
pen22m						0.77			
bu223m						0.67			
cpene1						0.96			
pen33m		0.38	0.39	0.27	0.26				
hexe4m						0.10			
hep1e									
cyhexe		0.47	0.51	0.45	0.43	2.98			
c7ole1		0.11	0.12	0.15	0.12	1.12			
cpa13m		1.23	1.22	1.20	1.17				
pa3et		1.53	1.51	1.48	1.49	1.50			
c7ole2						0.24			
t3hepe		0.15	0.13	0.12	0.12				
h2e2me									
c8ole1						1.80			
c8ole2						0.18			
c8ole3		0.15	0.22	0.10	0.10	0.18			
p1e244	0.8					2.56			
c8pa1		0.07	0.13	0.12	0.11	0.40			
hex25m	1.5	0.84	0.88	0.90	0.80	0.85			

Appendix A.1 - SCOS97-NARSTO Hydrocarbon Measurement Comparison Data

Mnemonic	BRC	DRI	DRI	DRI	DRI	EPA	Mantech	SCAQMD- lab	SCAQMD- Aut
hex24m	1.3	1.99	1.94	2.00	1.96	1.96			
c8pa2		0.76	0.63	0.56	0.63	0.94			
hx23dm	1.0	0.76	0.87	0.85	0.86	1.30			
hep4me		0.91	0.82	0.59	0.63	2.29			
c8pa3		0.33	0.29	0.35	0.37	0.28			
hex3et	2.0								
hex225		0.36	0.32	0.36	0.37	1.36			
oct1e		1.24	1.21	1.29	1.29	0.65			
chx11m									
hex235						2.06			
hep24d						0.65			
hep44d		0.34	0.34	0.34	0.34	2.97			
hep26d		0.40	0.43	0.43	0.48	0.50			
hep25d		1.35	1.37	1.40	1.26	1.76			
hep33d		0.53	0.50	0.52	0.52				
c9ole1		0.19	0.19	0.19	0.15	0.53			
c9ole2						0.22			
c9ole3		0.87	0.85	0.82	0.82	1.35			
oct2me		1.06	1.01	1.00	1.03				
oct4me						3.39			
oct3me		0.83	0.81	0.81	0.81	1.02			
c9par1		0.09	0.09	0.09	0.08	2.73			
none1		0.34	0.32	0.34	0.34	0.74			
c9par2		0.16	0.16	0.19	0.16	0.54			
c9par3		0.15	0.16	0.15	0.16	0.32			
c9ole4		0.12	0.10	0.09	0.12	1.74			
c9par4						0.66			
ipcyhx						1.29			
a_pine		0.28	0.30	0.40	0.34	0.44			
oct26d						3.16			
c10ol1						5.71			
oct36m		0.52	0.53	0.49	0.49	1.24			
c10p_a		0.47	0.48	0.48	0.48	4.37			
b_pine						0.95			
c10ar1						0.79			
i_bubz		0.68	0.75	0.67	0.52	0.28			
s_bubz		0.20	0.16	0.07	0.09	0.22			
c10ol2		0.37	0.38	0.27	0.28	30.16			
c10p_c		0.42	0.41	0.37	0.40	0.64			
limon		0.52	0.47	0.41	0.34	0.92			
indan		0.65	0.64	0.53	0.41				
indene		0.49	0.48	0.39	0.29				
c10ar2		0.77	0.79	0.73	0.68				
n_bubz									
detbz3		0.17	0.18	0.15	0.15				
c10ar3									
bzdme									
c10ar4		0.29	0.46	0.28	0.39				
iprtol		0.54	0.54	0.54	0.53				
c10ar5		0.23	0.23	0.23	0.22				
c10ar6			0.17	0.19	0.20				
c11p_a									
bz1245		0.34	0.37	0.34	0.35				
bz1235		0.37	0.38	0.36	0.37				
c11p_b									

Appendix A.1 - SCOS97-NARSTO Hydrocarbon Measurement Comparison Data

Mnemonic	BRC	DRI	DRI	DRI	DRI	EPA	Mantech	SCAQMD- lab	SCAQMD- Aut
ind_2m									
ind_1m									
c11ar1									
c11ar3									
naphth		1.08	1.24	0.99	1.10				
n_dode		0.57	0.55	0.55	0.60				
Oxygenated									
metoh									
ethoh						0.89	23.7		
mtbe	10.5	13.70	13.75	12.55	12.15	12.79	10.7		
aceto		8.67	9.48	4.16	5.19	16.74	25.7		
acetal									
pral2m		0.28	0.33	0.25	0.30				
bual		0.71	0.96	0.45	0.61		29.4		
buone		2.26	2.45	1.38	1.61		3.8		
pental							7.5		
pe2one							2.3		
hexal		1.00	0.92	0.75	0.69		7.0		
heptal							4.7		
octal		1.18	1.23	1.07	0.89		6.5		
nonal		1.70	2.17	0.55	0.71		14.6		
bzalde		0.42	0.76	1.12	1.28				
Subtotals									
par	155.1	169.56	168.82	169.55	167.40	199.76	111.1	161.4	172.0
ole	36.8	49.27	49.01	49.14	47.90	103.33	10.2	28.7	31.7
aro	61.8	69.26	70.02	67.91	67.46	73.23	68.7	68.0	72.8
C2par	16.1	17.38	16.49	17.68	16.83	22.57		17.6	17.0
C2ole	24.4	28.64	28.63	29.19	28.69	22.78		22.0	17.6
C3par	19.4	19.68	20.03	19.93	19.37	20.88		20.6	21.2
C3ole	4.6	4.69	5.05	5.00	4.82	5.31		6.0	6.3
C4par	14.4	15.19	15.39	15.09	14.92	15.10	12.0	15.1	16.1
C4ole	5.9	6.30	5.98	6.17	5.97	10.39	8.6	0.0	2.6
C5par	36.5	36.23	35.78	36.21	35.95	36.40	41.7	39.1	44.1
C5ole	1.9	2.46	2.60	2.58	2.37	2.60	1.7	0.7	4.7
C6par	30.7	31.44	31.23	31.55	31.66	35.31	25.3	30.6	32.0
C6ole	0.0	2.35	1.98	1.63	1.74	15.22	0.0	0.0	0.5
C6aro	6.0	5.94	5.83	5.67	5.71	6.17	8.0	6.9	6.1
C7par	18.2	20.38	20.75	20.06	20.01	20.45	14.2	20.4	19.5
C7ole	0.0	0.26	0.25	0.27	0.24	1.46	0.0	0.0	0.0
C7aro	20.6	20.98	21.08	21.03	20.91	21.35	21.1	22.1	23.1
C8par	15.2	18.37	18.47	18.51	18.28	21.05	10.3	12.1	12.1
C8ole	0.0	1.39	1.43	1.39	1.39	2.81	0.0	0.0	0.0
C8aro	18.8	19.52	19.45	19.57	19.29	20.76	19.7	21.4	20.7
C9par	2.8	7.77	7.66	7.53	7.46	20.11	3.4	3.1	4.8
C9ole	0.0	2.01	1.94	1.83	1.72	4.58	0.0	0.0	0.0
C9aro	16.4	16.99	17.11	16.02	15.86	21.83	17.4	16.3	20.6
C10par	1.8	2.02	1.91	1.89	1.82	6.38	1.9	1.4	3.3
C10ole	0.0	1.17	1.15	1.08	0.96	38.18	0.0	0.0	0.0
C10aro	0.0	5.83	6.55	5.62	5.69	3.12	2.6	1.4	2.3
C11par	0.0	1.10	1.11	1.10	1.10	1.51	2.3	1.5	2.0

Sampling an

Appendix A.1 - SCOS97-NARSTO Hydrocarbon Measurement Comparison Data

Mnemonic	SDAPCD	VCAPCD	BRC	Mantech	SDAPCD	EPA	VCAPCD	DRI	DRI
<u>Sample</u>									
Site	LA	LA	SM	SM	SM	SM	SM	SM	SM
Date	970610	970610	970610	970610	970610	970610	970610	970610	970610
Start	810	810	1630	1630	1630	1630	1630	1630	1630
Dur	240	240	70	70	70	70	70	70	70
Can ID	AMB-082		SJV-23		AMB-084	MTL19		X106	X106
Flag									r
<u>Total</u>									
PAMS	264.2	329.4	24.8	28.9	90.5	80.7	51.5	33.27	33.53
other id			0.8			126.3		14.54	14.67
unid	60.8		28.7		76.1	174.6		5.97	4.66
tnmhc	324.8		54.8		166.5	381.6		51.77	52.47
idoxy			0.0	120.2	0.0	22.6		12.06	16.07
<u>PAMS</u>									
ethene	12.6	19.3	0.9		1.1	2.1	2.0	1.06	0.95
acetyl	11.4	59.8	1.6		1.3	2.4	27.2	2.29	2.18
ethane	6.1		3.2		1.3	10.5		4.01	3.69
prope	5.2	9.7	0.3		0.8	1.3		0.52	0.41
n_prop	19.8	27.2	1.0		1.4	1.2		1.29	1.21
i_buta	5.6	5.5	0.5			0.5		0.56	0.45
lbutle	5.0	14.0		3.8	1.3		3.2	0.17	0.12
libute			0.5			4.6		0.43	0.40
beabyl									
n_buta	9.1	12.8	1.0	1.5	1.0	1.0	1.2	1.54	1.10
t2bute						0.2			
c2bute						0.2			
ipenta	41.0	27.2	2.1		63.7	2.0	2.4	2.04	2.13
pente1		1.2		0.6		0.2		0.05	0.04
n_pent	12.5	12.5	1.1		1.1	1.0	1.0	0.94	0.96
i_pren									
t2pene						0.2		0.07	0.11
c2pene						0.1		0.05	0.05
bu22dm	1.9	2.2	0.3			15.9		0.39	0.23
cpenta	1.5	1.5	0.2			0.2		0.16	0.14
bu23dm	2.5	3.5	0.3			0.3	1.9	0.32	0.25
pena2m	17.5	8.7	0.9		2.8	0.7	1.1	0.88	1.01
pena3m	4.9	5.2	0.5			0.7		0.71	0.63
p1e2me						4.7			
n_hex	4.6	5.0	0.5	0.9		0.5		0.35	0.43
mcypna	5.4	6.0	0.6	0.7		0.8	1.4	0.62	0.58
pen24m	1.9	2.6	0.3			0.3	1.1	0.19	0.22
benze	5.7	6.6	0.7	3.5	0.9	1.0	1.0	0.78	0.64
cyhexa	2.7	3.1	0.3			0.4		0.27	0.32
hexa2m	2.9	3.2	0.4			0.5		0.35	0.32
pen23m	3.4	3.6	0.4			0.5		0.36	0.37
hexa3m	4.0	3.5	0.4		1.1	0.6	1.1	0.78	0.77
pa224m	5.2	6.0	0.7			1.0		0.61	0.65
n_hept	2.5	2.9	0.3	0.7		0.7		0.23	0.29
mecyhx	3.3	3.8				0.5		0.25	0.27
pa234m	2.0	1.3	0.3			0.8		0.23	0.24
tolue	20.5	20.9	2.3	4.8	2.1	2.9	2.2	2.06	2.01
hep2me	1.1	2.0						0.22	0.24
hep3me	1.9	1.3				0.5		0.15	0.17
n_oct	1.7	3.0	0.4			3.7		0.32	0.23

Appendix A.1 - SCOS97-NARSTO Hydrocarbon Measurement Comparison Data

Mnemonic	SDAPCD	VCAPCD	BRC	Mantech	SDAPCD	EPA	VCAPCD	DRI	DRI
etbz	3.1	3.0	0.5			0.5		0.35	0.35
mp_xyl	11.0	10.9	1.6	2.3	1.4	1.1	2.3	1.30	1.32
styr	1.2	4.7			1.1	0.1		1.14	1.17
o_xyl	4.1	4.8	0.7	1.1		0.8		0.57	0.53
n_non	1.1	1.3				0.2		0.14	0.12
iprbz								0.06	0.07
n_prbz	1.0	1.2				0.7		0.18	0.16
m_etol	3.8	3.0		1.7	1.2	1.2		0.41	0.41
p_etol	1.2	1.3				0.4		0.22	0.23
bz135m	1.1	1.6		0.9	2.2			1.28	2.74
o_etol	1.8	1.3				0.5		0.20	0.20
bz124m	4.6	6.0		1.9	0.7	1.8	1.0	1.23	1.38
n_dec	2.5	1.2			2.0	1.1		0.13	0.13
bz123m	0.9	1.6				1.0	1.4	0.21	0.20
detbz1								0.03	0.04
detbz2		1.1		2.8		6.4		0.37	0.47
n_unde	1.4	1.3		1.8	2.0	0.7		0.20	0.20
Other ID									
budi13								0.55	0.60
butyn						0.3			
b1e3me									
b1e2m						0.1		0.07	0.07
b2e2m						0.2		0.20	0.14
cpente						0.1			
p1e4me									
p1e3me						0.4			
hex1e						0.5		0.03	0.07
c6ole1						0.4			
t3hexe						0.2			
c3hexe									
t2hexe						0.2		0.07	0.06
p2e2me									
c2hexe						0.3		0.04	0.02
p2e3mc						6.6			
p2e3mt						0.4		0.17	0.20
p2e3me									
pen22m						1.2			
bu223m									
cpene1						2.3			
pen33m						0.4		0.09	0.11
hexe4m						0.1			
hep1e									
cyhexe						6.4		0.04	0.04
c7ole1						0.1		0.08	0.08
cpa13m								0.12	0.12
pa3et						0.3		0.16	0.15
c7ole2						0.3			
t3hepe									
h2e2me									
c8ole1						5.5			
c8ole2						0.2			
c8ole3						0.2			
p1e244			0.8			1.1			
c8pa1								0.16	0.07
hex25m						0.3		0.09	0.09

Appendix A.1 - SCOS97-NARSTO Hydrocarbon Measurement Comparison Data

Mnemonic	SDAPCD	VCAPCD	BRC	Mantech	SDAPCD	EPA	VCAPCD	DRI	DRI
hex24m						0.3		0.24	0.23
c8pa2						0.6		0.13	0.09
hx23dm						1.1		0.11	0.10
hep4me						3.1			
c8pa3						0.1		0.04	0.09
hex3et									
hex225						0.3		0.05	0.09
oct1e						0.5		0.11	0.14
chx11m								0.07	0.05
hex235						0.6			
hep24d						0.1			
hep44d						0.9			
hep26d						0.4			
hep25d						0.8		0.14	0.10
hep33d						0.5			
c9ole1						0.7			
c9ole2						0.3			
c9ole3						1.1		0.06	0.07
oct2me								0.06	0.09
oct4me						1.0			
oct3me						0.5		0.13	0.11
c9par1						3.7			
none1						0.1			
c9par2						0.7			
c9par3						0.2			
c9ole4						5.5			
c9par4						0.3			
ipcyhx						1.6			
a_pine						0.5		0.23	0.21
oct26d						3.6			
c10ol1						8.6			
oct36m						2.1			
c10p_a						3.3			
b_pine						9.4			
c10ar1						0.5			
i_bubz								0.03	0.07
s_bubz						0.2			
c10ol2						43.8		0.09	0.03
c10p_c						0.6			
limon						0.7		10.39	10.32
indan									
indene									
c10ar2								0.08	0.19
n_bubz									
detbz3									
c10ar3									
bzdme									
c10ar4								0.05	0.06
iprtol								0.09	0.09
c10ar5								0.05	0.04
c10ar6									
c11p_a									
bz1245								0.06	0.06
bz1235								0.08	0.07
c11p_b									

Appendix A.1 - SCOS97-NARSTO Hydrocarbon Measurement Comparison Data

Mnemonic	SDAPCD	VCAPCD	BRC	Mantech	SDAPCD	EPA	VCAPCD	DRI	DRI
ind_2m									
ind_1m									
c11ar1									
c11ar3									
naphth								0.25	0.45
n_dode								0.13	0.10
Oxygenated									
metoh									
ethoh				8.0		1.4			
mtbe						1.6		1.70	1.75
aceto				21.7		21.0		3.14	4.21
acetal									
pral2m								0.13	0.09
bual				17.8				0.25	0.58
buone				3.9				0.37	0.39
pental				15.0					
pe2one				3.1					
hexal				12.0				1.27	1.30
heptal				8.2					
octal				13.8				2.48	2.72
nonal				24.8				2.64	4.62
bzalde								0.08	0.41
Subtotals									
par	170.0	157.4	15.7	5.6	76.4	66.7	11.2	19.70	18.73
ole	34.2	104.0	3.3	4.4	4.5	111.5	32.4	16.77	16.31
aro	60.0	68.0	5.8	18.9	9.6	19.0	7.9	11.08	12.95
C2par	6.1	0.0	3.2		1.3	10.5	0.0	4.01	3.69
C2ole	24.0	79.1	2.5		2.4	4.6	29.2	3.35	3.13
C3par	19.8	27.2	1.0		1.4	1.2	0.0	1.29	1.21
C3ole	5.2	9.7	0.3		0.8	1.3	0.0	0.52	0.41
C4par	14.7	18.3	1.5	1.5	1.0	1.5	1.2	2.10	1.55
C4ole	5.0	14.0	0.5	3.8	1.3	5.3	3.2	1.15	1.12
C5par	55.0	41.2	3.4	0.0	64.8	3.1	3.4	3.14	3.23
C5ole	0.0	1.2	0.0	0.6	0.0	0.8	0.0	0.44	0.41
C6par	39.5	33.7	3.4	1.6	2.8	19.2	4.4	3.54	3.45
C6ole	0.0	0.0	0.0	0.0	0.0	22.0	0.0	0.35	0.39
C6aro	5.7	6.6	0.7	3.5	0.9	1.0	1.0	0.78	0.64
C7par	18.0	19.6	1.8	0.7	1.1	4.6	2.2	2.37	2.47
C7ole	0.0	0.0	0.0	0.0	0.0	0.5	0.0	0.08	0.08
C7aro	20.5	20.9	2.3	4.8	2.1	2.9	2.2	2.06	2.01
C8par	10.8	11.6	1.4	0.0	0.0	8.6	0.0	2.31	2.16
C8ole	0.0	0.0	0.0	0.0	0.0	6.3	0.0	0.11	0.14
C8aro	19.4	23.4	2.8	3.4	2.5	2.5	2.3	3.36	3.37
C9par	2.2	3.3	0.0	0.0	0.0	13.0	0.0	0.61	0.64
C9ole	0.0	0.0	0.0	0.0	0.0	7.7	0.0	0.06	0.07
C9aro	14.4	16.0	0.0	4.4	4.1	5.6	2.4	3.79	5.39
C10par	2.5	1.2	0.0	0.0	2.0	4.3	0.0	0.13	0.13
C10ole	0.0	0.0	0.0	0.0	0.0	63.0	0.0	10.71	10.56
C10aro	0.0	1.1	0.0	2.8	0.0	7.1	0.0	1.09	1.54
C11par	1.4	1.3	0.0	1.8	2.0	0.7	0.0	0.20	0.20

Sampling an

Appendix A2

Methodology for Determining Carbonyl Compounds in Ambient Air

Section 5.0

Methodology for Determining Carbonyl Compounds in Ambient Air

Determination of ambient concentrations of carbonyl compounds is a requirement of 40 CFR Part 58, ' Subpart E, enhanced O₃ network monitoring programs. Carbonyl compounds have been shown to contribute to the formation of photochemical O₃. Formaldehyde, acetaldehyde, and acetone are specifically required target compounds for PAMS; however, other carbonyl compounds may be added to the target list consistent with individual program objectives. The methodology used to accomplish carbonyl compounds monitoring is Compendium Method TO-1 1A.' Method TO-1 1A, presented in Appendix D, provides sensitive and accurate measurements of carbonyl compounds and involves sample collection and analysis procedures. In this method, a cartridge(s) containing a solid sorbent is used to capture the target compounds. Information on solid sorbents used is presented in Section 4.4 of Method TO-11A. Ozone has been identified as an interferent in the measurement of carbonyl compounds when using Method TO-1 1A. To eliminate this interference, removal or scrubbing of O₃ from the sample air stream is mandatory. Section 5.1 presents information on O₃ scrubbers. Sample analysis is accomplished using high performance liquid chromatography (HPLC) with ultraviolet/visible detection.

Under 40 CFR Part 58, ' Subpart E, States are required to obtain 3-hour and 24-hour integrated measurements of carbonyl compounds at specified collection frequencies based on individual enhanced O₃ monitoring site type requirements. The sample collection frequencies range from one 24-hour sample every sixth day to eight 3-hour samples every day. Specific sample collection frequencies and minimum network monitoring requirements for carbonyl compounds are presented in Table 5-1. (Note: This section is intended to be independent of other sections. Figures, tables, and text from other sections are repeated as required.) The sample collection frequencies necessitate the use of an automated multiple-event sample collection approach. Section 5.2 presents information on multiple-event sample collection systems, including a generic equipment description and operating procedure and recommended specifications applicable to evaluation and procurement.

Table 5-1 - PAMS Minimum Monitoring Network Requirements

Population of MSA/CMSA ¹	Required Site Type	Minimum VOC's Sampling Frequency ²	Minimum Carbonyl Compounds Sampling Frequency ²
Less than 500,000	(1)	A or C	-
	(2)	A or C	D or F
500,000 to 1,000,000	(1)	A or C	E
	(2)	B	-
	(3)	A or C	-
1,000,000 to 2,000,000	(1)	A or C	E
	(2)	B	-
	(2)	B	-
	(3)	A or C	-
	(3)	A or C	-
More than 2,000,000	(1)	A or C	E
	(2)	B	E
	(2)	B	-
	(3)	A or C	-
	(3)	A or C	-
	(4)	A or C	-

¹Whichever area is larger.

²Frequency Requirements Are As Follows:

A Eight 3-hour samples every third day and one additional 24-hour sample every sixth day during the monitoring period.

B Eight 3-hour samples every day during the monitoring period and one additional 24-hour sample every sixth day year-round.

C Eight 3-hour samples on the 5 peak O3 days plus each previous day, eight 3-hour samples every sixth day and one additional 24-hour sample every sixth day during the monitoring period.

D Eight 3-hour samples every third day during the monitoring period.

E Eight 3-hour samples on the 5 peak O3 days plus each previous day and eight 3-hour samples every sixth day during the monitoring period.

F Eight 3-hour samples on the 5 peak O3 days plus each previous day, eight 3-hour samples every sixth day and one additional 24-hour sample every sixth day during the monitoring period.

Table 5-1 PAMS Minimum Monitoring Network Requirements (Continued)

The minimum sampling frequency requirements for speciated VOC monitoring are prescribed in 40 CFR Part 58, Subpart E, Appendix D - Network Design for State and Local Air Monitoring Stations (SLAMS) National Air Monitoring Stations (NAMS), and Photochemical Assessment Monitoring Stations (PAMS). Section 4.3 - Monitoring Period requires, at a minimum, that o₃ precursor monitoring be conducted annually throughout the months of June, July, and August when peak o₃ values are expected. Section 4.4 - Minimum Monitoring Network Requirements specifies the minimum required number and type of monitoring sites and sampling frequency requirements based on the population of the affected MSA/CMSA or non-attainment area, whichever is larger. The minimum speciated VOC sampling frequency requirements are summarized by site type below:

- Site Type I - Eight 3 -hour samples every third day and one additional 24-hour sample every sixth day during the monitoring period; or eight 3-hour samples on the 5 peak o₃ days plus each previous day and eight 3-hour samples and one 24-hour sample every sixth day, during the monitoring period.
- Site Type 2 - (population less than 500,000) - Same as Site Type 1.
- Site Type 2 - (population greater than 500,000) - Eight 3-hour samples every day during monitoring period and one additional 24-hour sample every sixth day year around.
- Site Type 3 - (population greater than 500,000) - Same as Site Type 1.
- Site Type 4 - (population more than 2,000,000) - Same as Site Type I

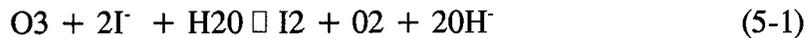
Samples collected should represent a time-integrated average for the required sampling period. It is important to understand that the 3-hour sample integration period is a maximum requirement in the sense that samples can be collected more frequently at shorter sampling intervals (i.e., three 1 -hour periods) but not less frequently for longer sampling intervals.

5.1 Ozone Scrubbers

The EPA has determined through laboratory tests that O₃ present in ambient air interferes with the measurement of carbonyl compounds when using Method TO- 11 A. Ozone can interfere with carbonyl analyses in three ways:

- The ozone reacts with the 2,4-dinitrophenylhydrazine (DNPH) on the cartridge, making the DNPH unavailable for derivatizing carbonyl compounds;
- The ozone also degrades the carbonyl derivatives formed on the cartridge during sampling; and
- If the analytical separation is insufficient, the DNPH degradation products can coelute with target carbonyl derivatives.

The extent of interference depends on the temporal variations of both the ozone and the carbonyl compounds and the duration of sampling. Carbonyl compound losses have been estimated to be as great as 48% on days when the ambient O₃ concentration reaches 120 ppbv. Eliminating this measurement interference problem by removing or scrubbing O₃ from the sample air stream prior to collection of the carbonyl compounds is a mandatory facet of carbonyl compounds sample collection for enhanced O₃ monitoring programs. Two types of O₃ scrubbers, the Denuder O₃ scrubber and the Cartridge O₃ scrubber, have been developed. Both the Denuder and Cartridge O₃ scrubbers use potassium iodide (KI) as the scrubbing agent. Scrubbing is based on the reaction of O₃ with KI, specifically:



where:

O₃ ozone (ambient)

H₂O water (ambient)

I⁻ the iodide ion from potassium iodide forming molecular iodine (I₂), oxygen (O₂), and the hydroxide ion (OH⁻)

Both O₃ scrubber designs effectively remove O₃ at sample collection flow rates up to 1 L/minute and have sufficient scrubbing capacity to meet the needs of carbonyl compounds measurement for enhanced O₃ monitoring programs.

This section presents details of the two types of O₃ scrubber equipment and recommended procedures for their use.

5.1.1 Denuder Ozone Scrubber

The Denuder O₃ Scrubber is a copper tube coated internally with a saturated solution

of KI. The tube is coiled and housed in a temperature-controlled chamber that is heated to, and maintained at, 66C during sample collection. Heating prevents condensation from occurring in the tube during sampling. The scrubber is connected to the inlet of the sample collection system. Sample air is extracted from a sample probe and distribution- manifold (see Section 5.2.3) and pulled through the scrubber by an oilless vacuum pump. Ozone in the sample air is converted (i.e., scrubbed) by the chemical reaction previously described in Section 5. 1.

The Denuder O₃ Scrubber is reusable. The copper tube should be recoated with a saturated solution of KI after each six months of use. The Denuder O₃ Scrubber prepared as described in TO- 11 A has been found to effectively remove ozone from the air strewn for up to 100,000 ppb-hours. Thus, the scrubber will last for six months of 24-hour sampling on every sixth day when sampling air with an average ozone concentration of 120 ppbv. To recoat the denuder, fill the copper tube with a saturated solution of KI in water. Allow the solution to remain in contact with the tube for a few minutes. Then, drain the tube. Dry the tube by blowing a stream of clean air or nitrogen through the tube for about one hour.

An alternative to using a KI coated copper tube is to use a modified Dasibi ozone scrubber device. Replace the manganese dioxide coated screens with 15 KI coated copper or stainless steel screens assembled in a cartridge holder. Wash the screens in pure water in a sonic bath. Dry the screens. Then, coat the screens by dipping them into a saturated KI solution in water. Air dry the KI coated screens. This procedure deposits about 4 mmoles or about 700 mg of KI over a sandwich of 15 two-inch diameter screens. Assemble the coated screens in the Dasibi encasement with a fiberglass filter at each end. Close and seal the encasement including the O-rings with the screws. Based on this removal capacity, this scrubber will last approximately 300 days when sampling air with an average ozone concentration of 120 ppbv at a rate of 1 L/min.

5.1.1.1 Denuder Ozone Scrubber Equipment

Figure 5-1 presents a cross-sectional view of the Denuder O₃ Scrubber. The scrubber is comprised of the following components:

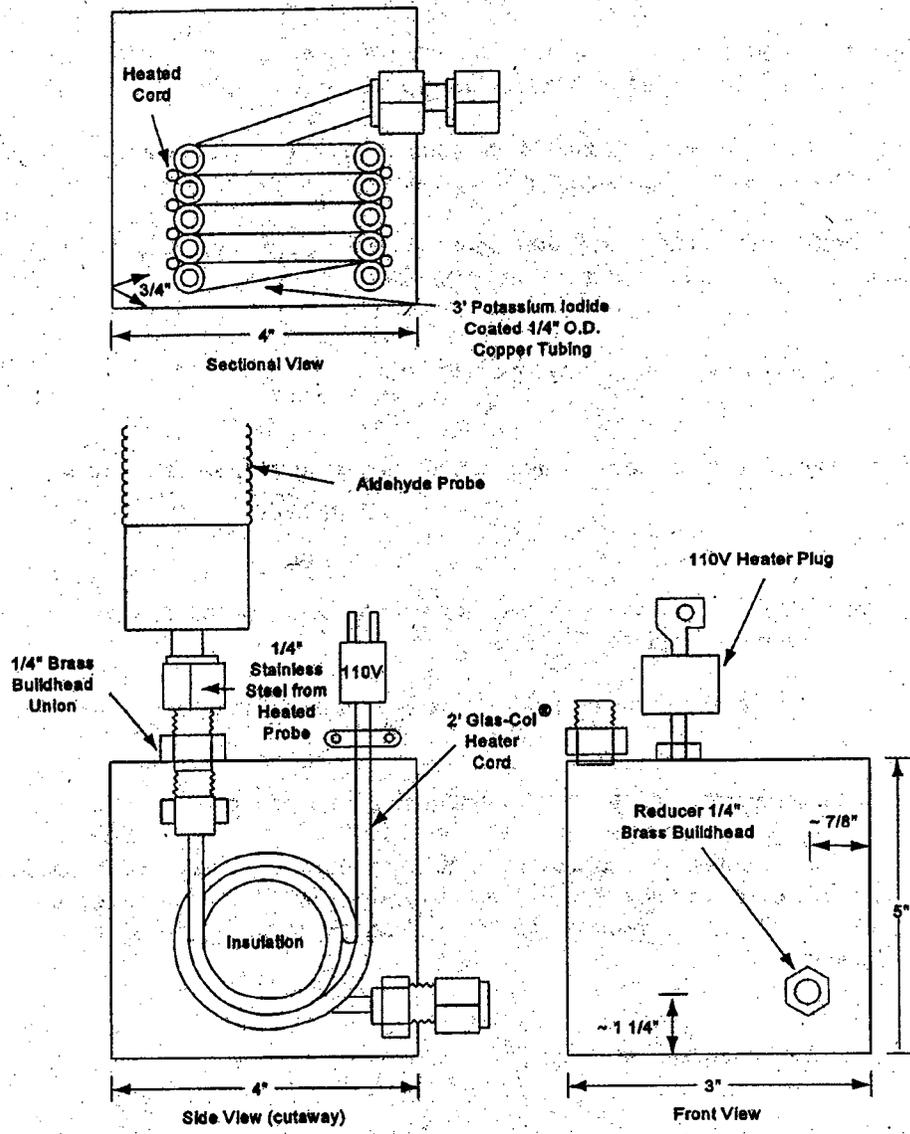
Copper tubing - A 3 foot length of 1/4-inch O.D. copper tubing, coiled into a spiral approximately 2 inches in diameter. Used as the body of the O₃ scrubber.

Potassium iodide - The inside surface of the copper coil is coated with a saturated solution of ACS Reagent Grade KI. Used to provide the O₃ scrubbing mechanism.

Cord heater - A 2 foot long cord heater, rated at approximately 80 watts, wrapped around the outside of the copper coil. Used to provide heat to prevent condensation of water or organic compounds from occurring within the coil.

Thermocouple - A Chromel-Alumel (Type K) thermocouple located between the surface of the copper coil and the cord heater. Used to provide accurate temperature measurement for temperature control.

Temperature controller - A Type K active temperature controller. Used to maintain the O3 scrubber at 66'C as referenced by the Type K thermocouple.



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Figure 5-1. Cross-Sectional View of the Denuder O3 Scrubber

Fittings - Bulkhead unions attached to the entrance and exit of the copper coil. Used to allow connection to other components of the sampling system.

Chassis box - Conveniently sized aluminum enclosure. Used to contain the fittings, coated copper tube, heater, and thermocouple.

5.1.1.2 Denuder Ozone Scrubber Operational Procedure

Recommended procedural steps for operation of the Denuder O₃ Scrubber are as follows:

- (1) Connect the inlet of the Denuder O₃ scrubber to the sample probe and distribution manifold (see Figure 5-1).
- (2) Connect the outlet of the Denuder O₃ scrubber to the sample collection system inlet.
- (3) Set the temperature controller to maintain the scrubber at 66 °C.
- (4) Conduct sampling in accordance with the recommended procedures for operating multiple-event sample collection systems as described in Section 5.2.2 and/or Method TO- 11 A sampling procedures as described in Section 5.11 (see Appendix D).

5.1.2 Cartridge Ozone Scrubber

The Cartridge O₃ Scrubber is a standard Sep-Pak[®] Plus cartridge (i.e., identical in size and shape to the precoated DNPH Silica Sep-Pak[®] cartridge) filled with approximately 1 gram of ACS Reagent Grade KI. The scrubber is positioned at the inlet of the sample collection system. Sample air is extracted from the sample probe and distribution manifold (see Figure 5-1) and pulled through the O₃ scrubber by an oilless vacuum pump. Ozone in the sample air is converted (i.e., scrubbed) by the chemical reaction previously described in Section 5. 1.

The Cartridge O₃ Scrubber is commercially available (i.e., Waters Corporation) and- is disposable. The theoretical removal capacity of the scrubber, based on 100% consumption of KI, is 200 Mg Of O₃. Based on experience in the field, the cartridge O₃ scrubber should be replaced every three weeks.

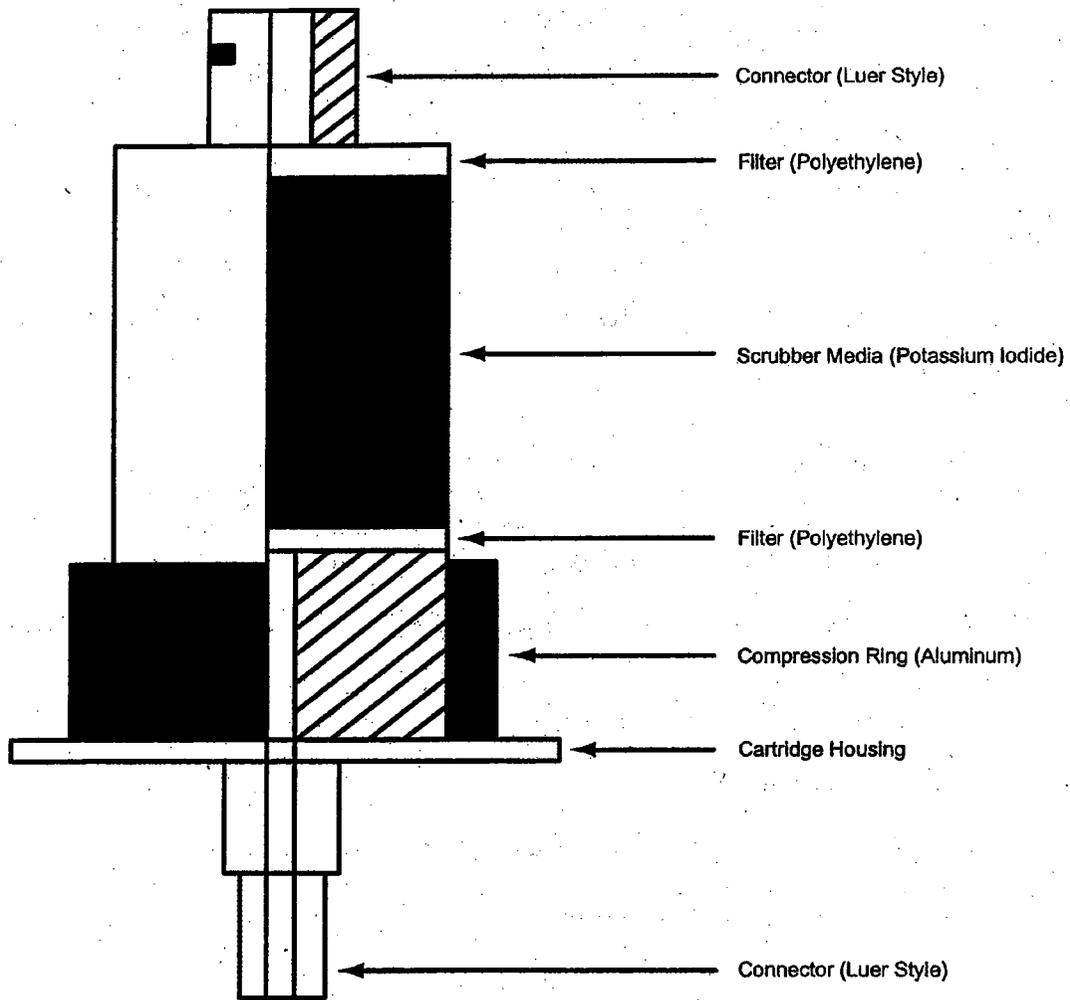
5.1.2.1 Cartridge Ozone Scrubber Equipment

Figure 5-2 presents a cross-sectional view of the Cartridge O₃ Scrubber. The scrubber is comprised of the following components:

Cartridge housing - A two-part plastic vessel with an O.D. of approximately 2 inches and an overall length of approximately 1-5/8 inches. One of the parts has a female Luer style connector that serves as the scrubber inlet. The other part has a male Luer style connector that serves as the scrubber outlet. Used to contain the scrubber media.

Potassium iodide - The scrubber medium is granular ACS Reagent Grade KI. Used to provide the ozone scrubbing mechanism.

Inlet and outlet filters - Polyethylene fritted filters located inside the cartridge housing at the inlet and outlet ends. Used to retain the scrubber media inside the cartridge housing during sampling.



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Figure 5-2. Cross-Section View of the Cartridge O3 Scrubber

Compression ring - An aluminum ring sized to fit around the outside of the two cartridge housing parts and seal them through compression. Used to provide a secure leak-free seal between the two cartridge housing parts.

5.1.2.2 Cartridge Ozone Scrubber Operational Procedure

Recommended procedural steps for operation of the Cartridge O3 Scrubber are as follows:

1. Connect the inlet of the Cartridge O3 scrubber to the sample probe and distribution manifold (see Section 2.4. 1. 1).
2. Connect the outlet of the Cartridge O3 scrubber to the sample collection system inlet.
3. Ensure that a leak-free connection is obtained.
4. Conduct sampling in accordance with the recommended procedures for operating multiple-event sample collection systems as described in Section 5.2.2 and/or Method TO- 11 A sampling procedures as described in Section 5. 10 of Method TO-1 IA (See Appendix D). **Note: Heating of the cartridge ozone scrubbers to 35C may be advisable under certain circumstances to prevent condensation of water.**

5.2 Multiple-event Sample Collection Systems

The use of solid sorbent cartridge sample collection systems to satisfy the sample collection frequencies specified in Table 5-1 necessitates the use of multiple-event sample collection systems. Multiple-event collection systems should be capable of unattended operation in order to allow for multiple sample collection in a practical, non-labor intensive manner. Multiple-event sampling systems are manufactured commercially or can be custom manufactured by the user for a specific application. Several multiple-event sampling systems are commercially available.

The following sections generally describe multiple-event sampling equipment, procedures, and specifications. Also, recommended system specifications applicable to the evaluation and procurement of multiple-event sampling systems are presented.

5.2.1 Multiple-event Collection System Equipment

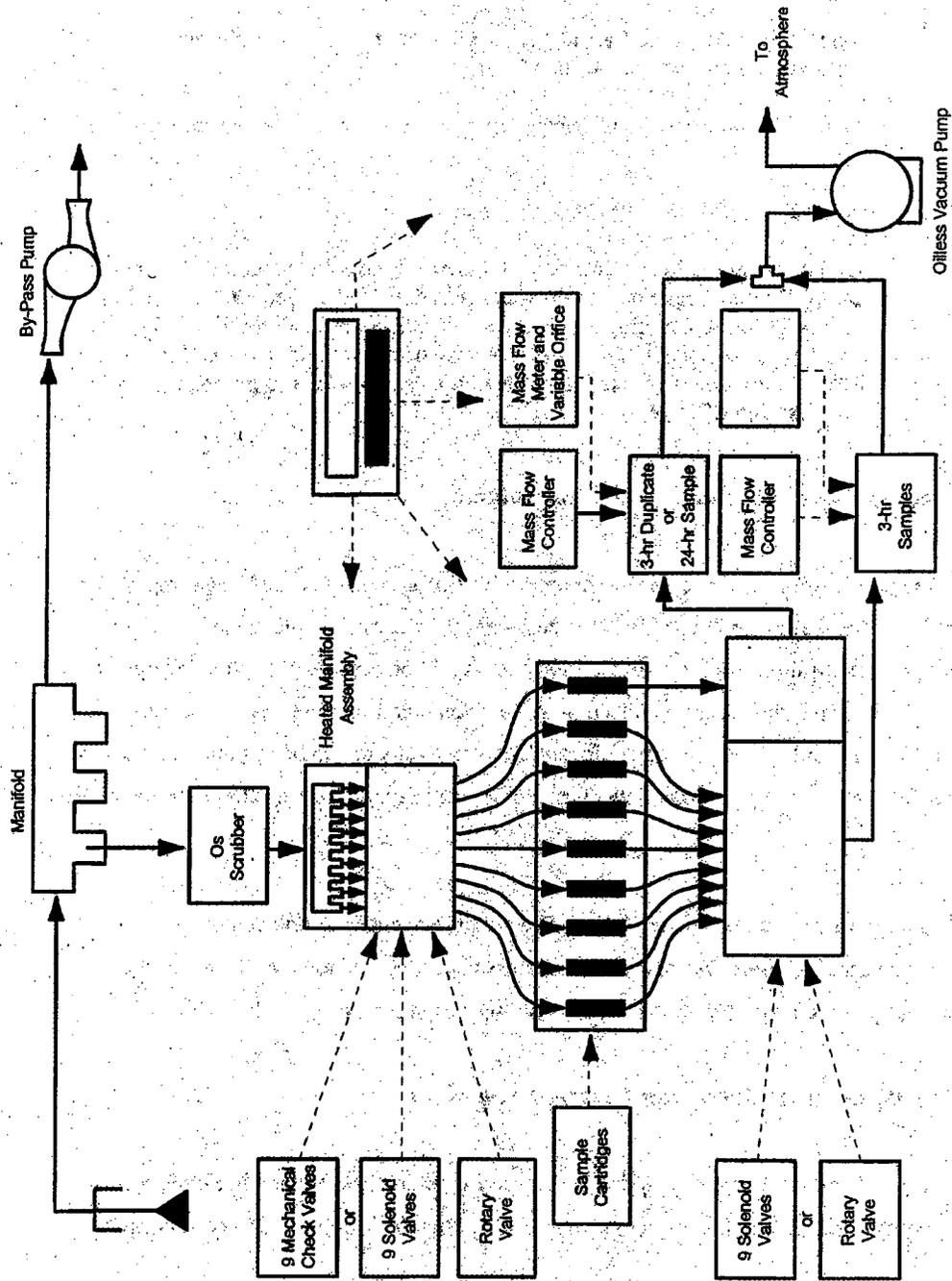
A typical multiple-event sampling system configuration is presented in Figure 5-3.: The multiple-event cartridge sampling system is comprised of the following primary components:

Inlet probe and manifold assembly - Constructed of glass (see Figure 5-1) or stainless steel. Used as a conduit to extract sample air from the atmosphere at the required sampling height and distribute it for collection.

By--pass pump - A single- or double-headed diaphragm pump, or a caged rotary

blower. Used to continuously draw sample air through the inlet probe and manifold assembly at a rate in excess of the sampling system total uptake. All excess sample air is exhausted back to the atmosphere.

Sample pump - An oilless vacuum pump, capable of achieving an inlet pressure of -25 inches Hg continually. Used to extract sample air from the manifold assembly and pull it through the sample cartridges during collection.



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Figure 5-3. Schematic of a Typical Multiple-Event Carbonyl Cartridge Sampling System

Sample inlet line - Chromatographic-grade stainless steel tubing. Used to connect the sampler to the manifold assembly. This line should be kept as short as possible.

Ozone scrubber - A Denuder or Cartridge type of O₃ scrubber. Used to remove ambient O₃ from the sample air stream prior to exposure to the sample cartridge.

Sample cartridges - A plastic housing containing silica gel or C 18 solid sorbent (see Section 4.4 of Method TO-11A in Appendix D) coated with DNPH. Used to contain the collected sample for transportation and analysis.

Adjustable orifice and mass flow meter assembly, or electronic mass flow controller - An indicating flow control device(s). Used to maintain a constant flow rate ($\pm 10\%$) over a specific sampling period under conditions of changing temperature (20-40C) and humidity (0- 100% relative).

Microprocessor - An event control and data acquisition device. Used to allow unattended operation (i.e., activation and deactivation of each sampling event) of the collection system, and to record sampling event specific process data (i.e., start and end times, elapsed times, collection flow rates, etc.).

Check valves, solenoid valves, or a multi-port rotary valve - Eight stainless steel check valves, eight solenoid valves with electric-pulse-operated or low temperature coils, stainless steel bodies, and Viton[®] plunger seats and o-rings, or 1 multi-port stainless steel body rotary valve with Viton[®] o-rings. Used to provide access to or isolation of the inlet side of the sample cartridges.

Solenoid valves or a multi-port rotary valve - Eight solenoid valves with electric-pulse-operated or low temperature coils, stainless steel bodies, and Viton plunger seat and o-rings, or 1 multi-port stainless steel body rotary valve with Viton[®] o-rings. Used to provide access to or isolation of the outlet side of the sample cartridges.

Tubing and fittings (Stainless steel or Teflon[®]) - Hardware for isolation and interconnection of components. Used to complete system interconnections. All stainless steel tubing in contact with the sample prior to analysis should be chromatographic grade stainless steel and all fittings should be 316 grade stainless steel. Note that if the manifold is heated, stainless steel tubing should be used because of the potential of off-gassing of the tubing.

Note: Elapsed-time indicators installed in-line with sample pumps can provide backup documentation that all samples ran for 180 minutes and can indicate that a malfunction occurred with the programmable timers or that power was interrupted.

5.2.2 Multiple-event Sampling Procedures

Samples are collected on individual solid sorbent sample cartridges using a single pump and one or more flow control devices. An oil-less vacuum pump draws ambient air from the sampling probe and manifold assembly through the sample cartridge at a constant flow rate during each specific sampling event.

A flow control device(s) is used to maintain a constant sample flow rate through each sample cartridge over each specific sampling period. The flow rate used is a function of the desired total volume of ambient air sampled and the specified sampling period. The flow rate is calculated as follows:

$$F = \frac{V \times 1000}{T \times 60} \quad (5-2)$$

where:

- F flow rate (milliliters/minute)
- V desired total volume of ambient air sampled (liters)
- 1000 milliliters in a liter
- T sample period (hours)
- 60 minutes in an hour

For example, if the desired total volume of ambient air to be sampled is 168 L over each individual 3-hour cartridge collection episode, the flow rate specific to each cartridge collection episode is calculated as follows:

$$F = \frac{168 \times 1000}{3 \times 60} = 933 \text{ milliliters/minute} \quad (5-3)$$

During operation, the microprocessor control device is programmed to activate and deactivate the components of the sample collection system, consistent with the beginning and end of each individual sample collection period.

Cartridge sampling systems can collect sample from a shared sample probe and manifold assembly as described in Section-5.2.3 or from a dedicated stainless steel sample probe, manifold assembly, and by-pass pump. If a dedicated probe, manifold assembly, and by-pass pump are used, a separate timer device should be incorporated to start the by-pass pump several hours prior to the first sampling event of a multiple-event collection period to flush and condition the probe and manifold assembly components.

The connecting lines between the manifold assembly and the sampling system should be kept as short as possible to minimize the system residence time.

The flow rate through each sample cartridge should remain relatively constant over the entire collection period of each sampling event. Each adjustable orifice and mass flow meter assembly, or mass flow controller, used as a flow control device should be calibrated against a primary flow measurement standard (i.e., a bubble flow meter, etc.). Calibrations should include multiple points of comparison (i.e., indicated flow versus measured flow), across the entire range of the flow control device at increments reflecting 10% of the range. Calibration curves are generated from these comparisons and are used to set actual desired flow rates based on the flow rates indicated by the flow control devices. Calibration of the flow control devices should be repeated periodically according to program specific QA/QC schedules as developed by the user.

Generic steps for operating a typical multiple-event sample collection system are as follows:

1. Set the sampling system to the desired sample collection flow rate(s) (i.e., referencing the corresponding calibration curve(s) and considering the desired total volume of ambient air to be sampled and the sampling period for each sampling event).
2. Program the microprocessor event control system to start and stop sample collection consistent with program specific collection frequency requirements.
3. Attach all sample cartridges to the sampling system.
4. Record the start and end time of each collection event and the corresponding flow rate onto the sampling field data sheet and calculate an average flow rate. The microprocessor event control and data acquisition system should automatically store these data for each collection event. The final total volume of ambient air sampled should be close to the desired total volume.
5. Remove each sample cartridge (i.e., one at a time), cap both ends, and attach an identifier to each (i.e., again, one at a time to avoid mislabeling). Sample event number, sample type, location, collection date, should be recorded on the field data sheet.
6. Place cartridges in tightly enclosed transport containers and transport the samples and corresponding information to the central laboratory for preparation and analysis.

5.2.3 Sample Probe and Manifold

A sample probe and manifold assembly should be used to provide a representative air sample for collection and subsequent analysis. Sample probe and manifold assemblies are commercially available or can be custom fabricated.

The sample probe is constructed of glass that is approximately 1 inch in outside diameter (O.D.). The inlet of the sample probe is configured with an inverted funnel, approximately 4 inches O.D. The sample manifold is constructed of glass, approximately 1 and 1/2 inches O.D. The manifold has ports used for sample

distribution. The number of ports located on the manifold must be equal to or greater than the total number of monitoring systems that sample will be delivered to. The port nearest to the inlet of the manifold should be reserved for VOC sampling; the second port or any other port may be used for carbonyl sampling.

Teflon[®] bushings are used to connect sample lines to the manifold. Because the manifold and ports are constructed of glass, care must be taken to not place excessive stress on the assembly to avoid breakage. For VOC sampling, the sample lines should be constructed of 1/8 inch O.D. stainless steel tubing. The 1/8 inch tubing is flexible and will accommodate the flow rates typically associated with VOC sample collection. The sample lines should be kept as short as possible to reduce sample transfer time. For carbonyl sampling, the sample lines should be constructed of 1/4 inch O.D. stainless steel tubing; the scrubber and the carbonyl sample cartridge holder assembly should be positioned as close to the manifold as possible.

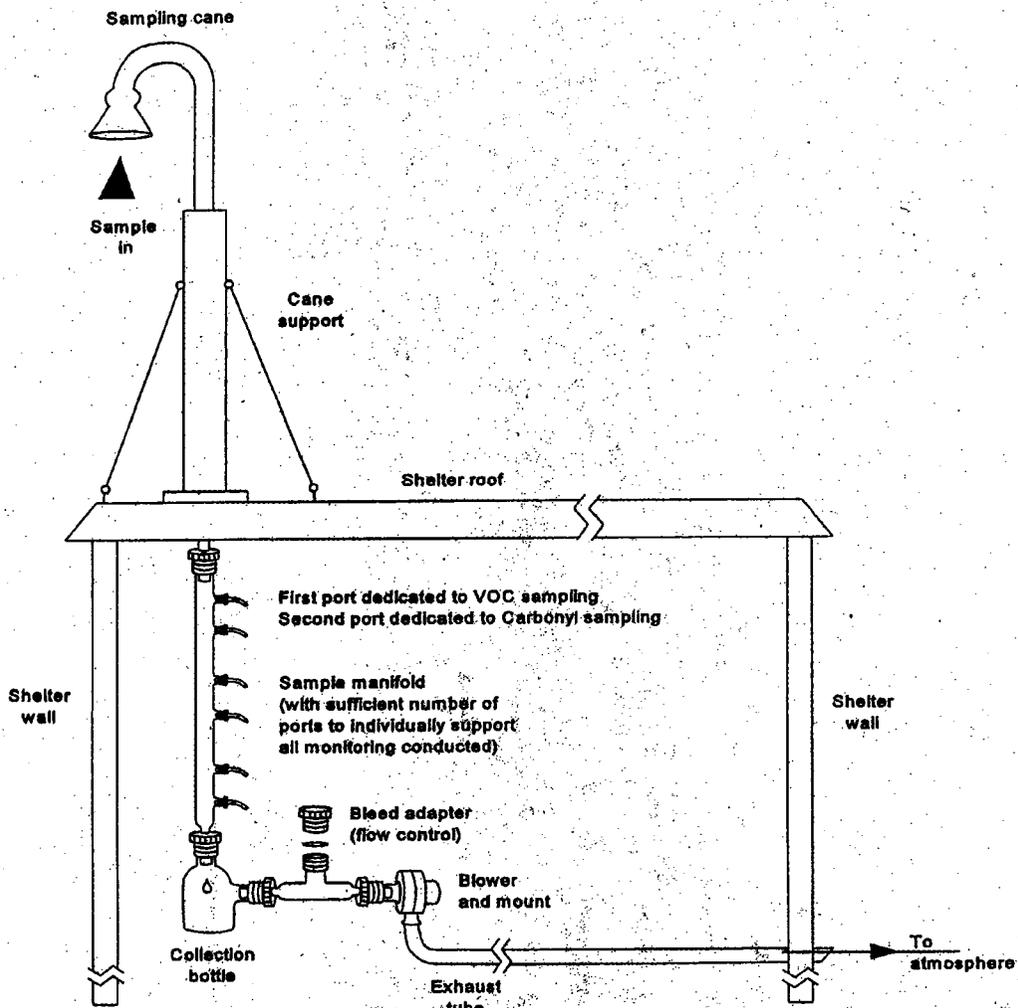
A blower and bleed adapter are located at the exit end of the sample manifold. The blower is used to pull sample air through the probe and manifold and the bleed adapter is used to control the rate at which the sample air is pulled through the manifold. An excess of sample air is pulled through the sample probe and manifold to prevent back diffusion of room air into the manifold and to ensure that the sample air is representative of outside ambient air. Sample air flow through the sample probe and manifold should be at least two times greater than the total air flow being removed for collection and analysis by all systems on the manifold.

The vertical placement of the sample probe and inlet funnel should be at a height of 3 to 15 meters above ground level. Because the O₃ monitoring requirements involve multiple- pollutant measurements, this range serves as a practical compromise for probe position. In addition, the probe inlet should be positioned more than 1 meter, both vertically and horizontally, away from the housing structure. The probe inlet should be positioned away from nearby obstructions such as a forest canopy or building. The vertical distance between the probe inlet and any obstacle should be a least two times the height difference between the obstacle and the probe inlet. Unrestricted air flow across the probe inlet should occur within an arc of at least 270 degrees. The predominant and second most predominant wind direction must be included in this arc. If the probe inlet is positioned on the side of a building, a 180 degree clearance is required- More specific details of Probe positioning are presented in the “Enhanced Ozone Monitoring Network Design and Siting Criteria Guideline Document.”³ The glass probe should be reinforced or supported along the straight vertical axis of the assembly. Typically this support is provided by routing the probe shaft through a rigid section of metal or plastic tubing that is secured to the housing structure.

The manifold can be positioned in either a horizontal or vertical configuration. Figure 5-4 presents the manifold assembly in the vertical configuration. Figure 5-5 presents the

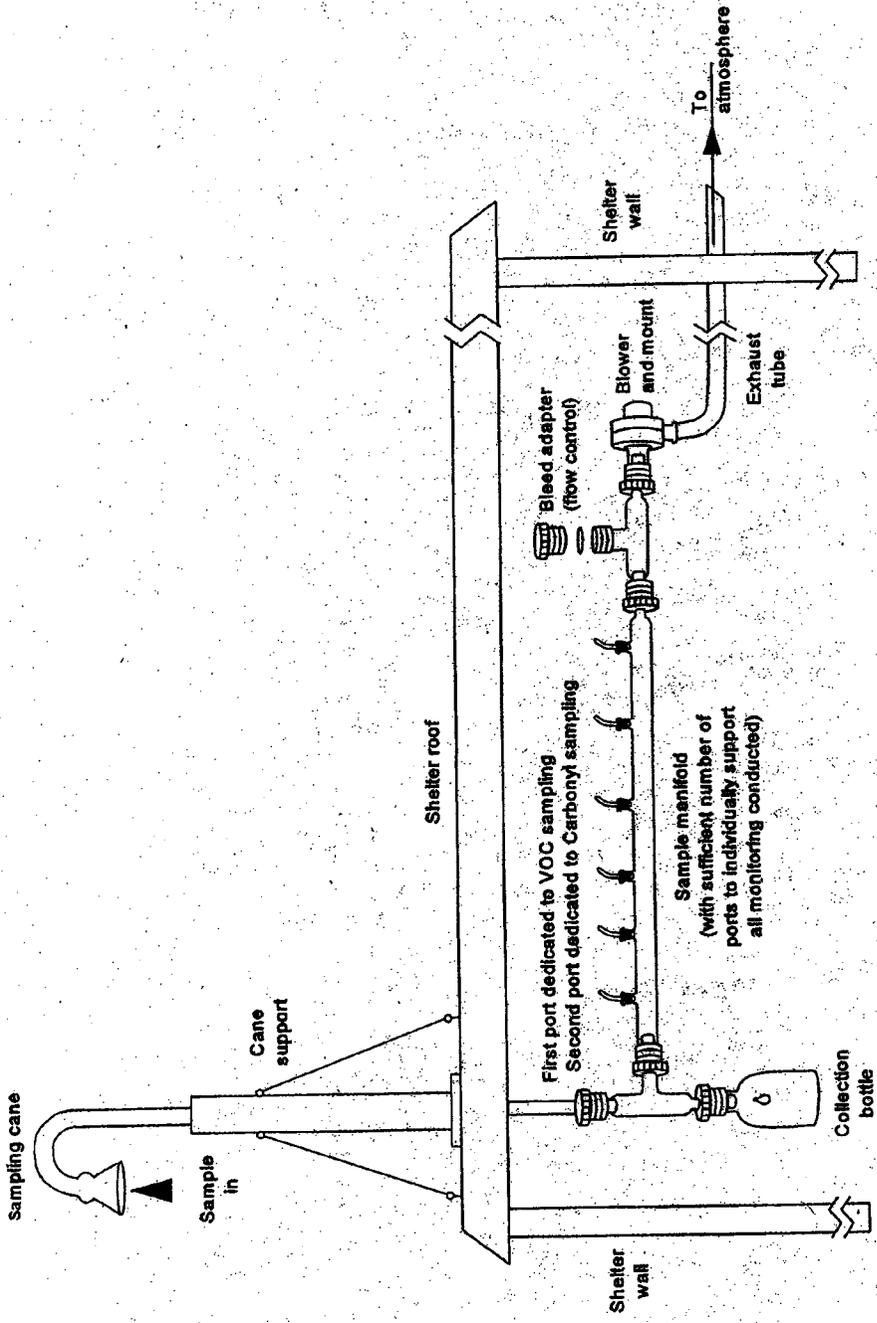
manifold assembly in the horizontal configuration. If the horizontal configuration is used, sample ports must point upward so that material that may be present in the manifold will not be transferred into the sample lines.

With continuous use the sample probe and manifold can accumulate deposits of particulate material and other potential contaminants. The sample probe and manifold should be cleaned to remove these materials. The recommended frequency for cleaning is quarterly. To clean the assembly, disconnect the sample lines and blower from the manifold. The sample lines and blower are not cleaned. For safety, electric power to the blower should be terminated until the cleaning process is completed. Disassemble the individual components by disconnecting the probe, manifold, and coupling devices from each other. The individual components should then be cleaned using heated high purity distilled water and a long handled bottle-brush. The components should then be rinsed with the distilled water and allowed to dry completely before reassembling. If required, mild glass cleaner or detergent can be used to clean particularly dirty components. However, care should be taken to select cleaners and detergents that are advertised to have low organic compound content and the number of rinses performed could be increased to ensure that all residues are removed.



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Figure 5-4. Vertical Configuration



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Figure 5-5. Horizontal Configuration

5.2.4 Multiple-event System Specifications

The use of sample cartridges to practically address the sampling frequency and schedule for carbonyl compounds specified in Table 5-1 requires the use of multiple-event cartridge sampling systems. The use of a single-event system to collect eight back-to-back 3-hour cartridge samples would require that an operator be physically present on site to manually complete the activities associated with the start and stop of each sampling event.

To ensure that a multiple-event sample collection system will meet the user's program needs, system specifications and other pertinent general considerations should be presented to, and addressed by, the candidate vendor(s) prior to procurement. Primary system specifications are presented below. However, additional system specifications and considerations may be added at the discretion of the user.

- An in-depth, detailed manual covering all aspects of the sample collection system (i.e., operation, maintenance, etc.) must be provided by the vendor.
- The overall size of the sampling system should be kept as compact as possible. The sampling systems are usually installed into existing sampling site shelters where many other parameters (i.e., criteria pollutants concentrations, meteorological conditions, etc.) are also measured. Each of the other parameters requires separate instrumentation and consequently the shelters can become very crowded.
- The sample collection system should meet all applicable electrical and safety codes, operate on standard 110 Vac power, and incorporate a main power fuse or circuit breaker. Specific potential electrical hazards and/or other safety considerations should be detailed in a supplied user's manual.
- The overall configuration, and components comprising that configuration, should allow for simple operation, maintenance, and service of the sample collection system. Materials used in the construction of components of the sample collection system should exhibit nonbiasing characteristics. The components themselves should generally conform to the descriptions presented in Section 5.2. 1. All surfaces that come in direct contact with sampled air should be constructed of glass, stainless steel, or Viton[®].
- To avoid cross-contamination, the sample collection system must have provisions to isolate the inlet and outlet of each sample cartridge when that cartridge is not collecting sample.
- The sampling system must incorporate or provide for removal of O₃, consistent with the O₃ scrubber designs detailed in Section 5. 1.
- Ideally, the sampling system should be able to accommodate the most intensive sample collection event frequency presented in Figure 5-6 on an automated unattended basis, and simultaneously accommodate a duplicate collection for one of

the 3-hour sampling events as recommended for quality control purposes. These requirements mean that the sampling system should have the capability to collect the following during any given 24-hour period:

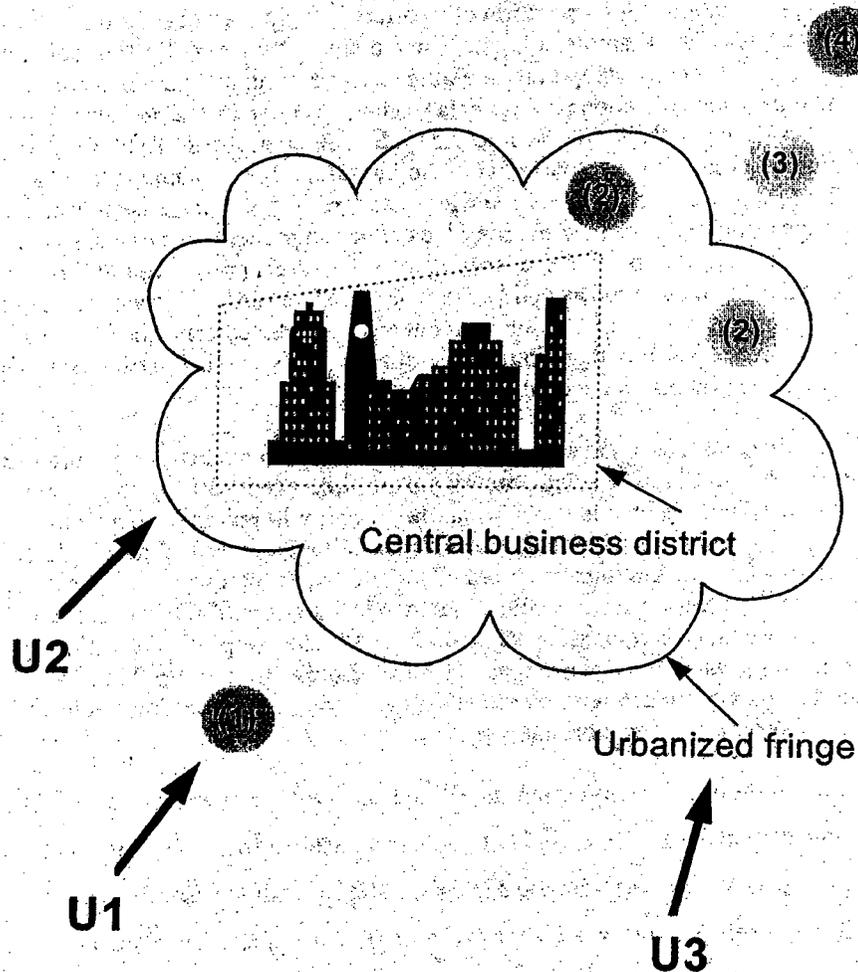
- Eight 3-hour cartridge samples;
- One 3-hour duplicate cartridge sample, collected concurrently with one of the eight 3-hour cartridge samples; and
- One 24-hour cartridge sample, collected concurrently with the eight 3-hour cartridge samples, but not concurrent with a duplicate 3-hour cartridge sample.

It is imperative that the sample collection system have the collection capabilities detailed above. If not, a second sampling system would be required to address the 24-hour sample collection, and consequently more overall labor and space would be needed to fully address the network monitoring requirements.

The ability of the sampling system to perform sample collections as presented above would require the operator to visit the site only twice during the 24-hour period being characterized; once to install sample cartridges prior to sampling and once to remove sample cartridges containing the collected samples. Each 24-hour period is scheduled to begin at 12:00 A.M. (i.e., midnight) and end at 11:59 P.M. of the day being characterized. The sampling system must be able to automatically address these periods (i.e., must be able to start and stop at the specified times without requiring an operator to go to the site and manually actuate the system).

- The sampling system should incorporate a microprocessor event control and data acquisition device. At a minimum this microprocessor should be able to be programmed to control the start and stop times of every collection event within a given 24-hour sampling duration. The microprocessor should also be able to simultaneously collect and store all the sample collection process data pertaining to each sampling event as follows:

Isolated Area Network Design



Note:

U1 and U2 represent the first and second most predominant high ozone day morning wind direction.
U3 represents the high ozone day afternoon wind direction.

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(1), (2), (3), and (4) are different types of PAMS sites. (See Table 5-1).

Figure 5-6. Isolated Area Network Design

- Start and stop times for each sample collection; and
- Beginning and ending collection flow rates for each cartridge collection.

The microprocessor should incorporate a battery backup system to address power failure situations. Incorporation of a battery backup system should result in fewer invalidated sample collections and a higher sample collection completion rate. The battery backup system would ensure that all programmed control activities and collection process data would be retained for a predetermined interval should standard power to the system be interrupted. Retaining the programmed control activities would allow sampling to resume automatically at the next programmed event time when standard power is once again established to the sampling system. Retaining the collection process data obtained for samples collected prior to the termination of standard power would allow these samples to be qualified as valid or invalid based on sampling start and stop times and initial and flow- rates. Although not absolutely necessary, the incorporation of a miniature printer that would allow for a report style listing of all sample collection process data would be advantageous.

Expedient and responsive vendor support should be a mandatory requirement and primary consideration when procuring a multiple-event cartridge sampling system. The user should specify that the vendor will maintain an adequate supply of replacement parts and a staff of qualified service technicians to ensure that the absolute minimum number of sample collection events are missed should a sample collection system failure occur. The user should specify that the vendor guarantee that parts/components be delivered to the sampling site within two working days of order placement. The user should also specify that a sample collection system delivered to the vendor for repair be serviced and returned to the user within seven working days.

The manufacturer of a carbonyl sampling devices note and experience at some of the PAMS sites indicate that the carbonyl sampler should not be located inside a shelter but outside to alleviate the possibility of off-gassing from the shelter interfering with the samples. The sampling methodology itself does not specify the location of the sampler. The wisdom of locating the carbonyl. sampler outside rather than inside a shelter would depend upon the composition of the shelter and the security of the sampler if it is located in an outside area.

5.3 Process Blanks

To ensure data quality and obtain quantitative carbonyl compound concentrations, the collection of blanks is necessary. For the purposes of PAMS, there are three types of blanks used to ensure data quality: certification blanks, field blanks, and trip blanks. The guidance given here should be considered a minimum and users are encouraged to build upon this guidance as necessary.

- **Certification blanks** consist of a minimum of three laboratory blank cartridges that are eluted with acetonitrile and analyzed to verify the acceptability of a specific cartridge lot from a commercial vendor. Certification blanks are analyzed for each specific lot used for sampling. The mean mass plus 3 standard deviations ($\bar{x} + 3s$) for the group of three laboratory blanks is used to assess acceptability.
- **Field blanks** are blank cartridges which are sent to the field, connected to the sampling system and treated identically to the samples except that no air is drawn through the cartridge. Field blanks are used to assess the background carbonyl levels for cartridges used during the ambient sample collection process.
- **Trip blanks** are blank cartridges of the same lot that are sent to the field, stored, and returned to the laboratory with the sample cartridges. Trip blanks are optional and may be used to resolve contamination problems determined from the field blanks. Trip blanks can be used to determine whether the contamination occurred during the sampling process or during the shipping and storage process.

5.3.1 Blank Criteria

The acceptance criteria for blanks are discussed below. The criteria for certification are considered conservative; most certification blank results will be well below these criteria. If the mean mass plus 3 standard deviations ($\bar{x} \pm 3s$) for the group of three laboratory blanks meets the criteria, then no further certification or laboratory blanks are required for a particular lot. If large differences are observed for the 3 laboratory blank samples, additional laboratory blanks should be analyzed to obtain values for the mean and standard deviation. For the certification blanks to be acceptable, the following criteria should be met:

- Formaldehyde: $< 0.15 \text{ } \bar{\mu}\text{g/cartridge}^*$
- Acetaldehyde: $< 0.10 \text{ } \bar{\mu}\text{g/cartridge}$
- Acetone: $< 0.30 \text{ } \bar{\mu}\text{g/cartridge}$
- Other aldehydes or ketones, concentration (per individual component): $< 0.10 \text{ } \bar{\mu}\text{g /cartridge}$.

*The equivalent formaldehyde concentration in ppbv as taken from Table 3 in EPA Compendium Method TO-11 A (see Appendix D) is 0.679 ppbv for a 180 L sample volume.

Using good techniques and collection systems (not mixing lots or vendors), field blanks should consistently be at levels that are less than 2 times the average measured laboratory blank value for a specific lot. The laboratory blank is a cartridge blank used for lot certification that has never been shipped to the field. If field blanks do not meet these criteria, corrective action is required. Sites that are unable to achieve these levels for field blanks must determine the source of contamination. An assessment of the air in the sampling shelter may also provide useful information in the determination of sources for field blank and sample contamination.

As a minimum, a sampling system blank sample should be collected at least on an annual basis before initiation of sampling. Collection of a pre- and post-sampling blank is strongly recommended to aid in the qualification of data. If the sampler is subjected to only a single blank audit, a failure to meet QA/QC limits will leave open the question of whether the previous year's data should be flagged or not. It is possible for a sampler to become contaminated (or appear to become contaminated) during the down season, in which case there would be no reason to invalidate the data from the previous year. Pre- and post-season audits remove the ambiguity. Collect a sampler blank using carbonyl-free air when possible. Generate carbonyl free air by purging air through acidic DNPH solution in a bubbling device or DNPH- coated cartridge. Alternatively, measure the carbonyl content of the air using a DNPH-coated cartridge and subtract the carbonyl content in the air from that in the sampler blank. Before collecting the sampler blank, flush the system using the same procedures as used for collecting a sample.

5.3.2 Frequency of Collection

At least one field blank, or the square root of the field sample size, whichever is larger, should be collected and analyzed with each sample lot collected at the site. The square root of the sample size is used to result in more field blanks for a smaller sample size and fewer field blanks for a larger sample size. For example, if 100 field samples will be taken at the site, then 10 field blank samples (the square root of 100) are collected and analyzed. If multiple lots are used, ensure that each lot has the necessary number of associated field blanks. Certification blanks are not included in the number of field blanks. Certification blanks are analyzed in addition to field blanks to verify acceptability of a specific cartridge lot from the vendor. At a minimum, three laboratory blanks from each lot are used for certification. Table 5-2 gives an example collection schedule for a field samples from a single lot.

Table 5-2. Example Schedule for the Collection of Blanks

Field Sample Size	Lab Blanks for Lot Certification	Field Blanks (square root of the sample size)
50	3	7
100	3	10
200	3	16

Since field blank samples may not be collected on every sampling day, the issue of maintaining consistency in the overall data treatment using blank subtraction is a challenge. For PAMS blank subtraction must be performed using the average field blank mass obtained for each field sample lot. Using the information in Table 5-2 as an example, for a sample size of 100, the average mass for the 10 field blank samples is

subtracted from each of the 100 samples. Again, it is important that cartridge lot be tracked and the appropriate number of field blanks be collected and subtracted from the samples for each lot used.

5.4 Breakthrough Analysis

Method TO- 11 A requires the use of a back-up cartridge during the first sampling event. If less than 10% of the analyte is collected on the back-up cartridge, then back-up cartridges are only required for 10% of the field samples. If more than 10% of the analyte is collected on the back-up cartridge, then use back-up cartridges for all sampling events. Breakthrough is more likely to occur when sampling at high flow rates, and when sampling very dry or very humid air, sampling air containing high levels of oxides, and when sampling air containing high levels of carbonyl compounds. Perform breakthrough analyses on the 24-hour sample or on the last 3-hour sample. Be careful in determining the flow rate because two cartridges installed may create a higher pressure drop, decreasing the sampling rate. If breakthrough occurs, reduce the breakthrough by replacing the ozone scrubber more frequently, sampling at a lower flow rates using larger capacity cartridges, or heating the cartridges slightly to prevent moisture condensation when sampling very humid air.

5.5 Collection of Collocated Samples

A collocated sample is collected from one manifold by two independent sampling during the same sampling period. Collect collocated samples as indicated in Table 5-2. Compare the collocated samples in replicate. The replicate analyses should agree to within $\pm 10\%$. Means of the replicate analyses for the collocated samples should agree to within $\pm 20\%$. If the collocated samples do not agree to within $\pm 20\%$ and the replicate analyses are within $\pm 10\%$, check the samples to ensure that they are truly collocated and check the sample flow rates to ensure that the sampler is working correctly. Also verify that the sampler is not leaking by conducting a leak check as described in Section 10.2 of TO-11A (see Appendix D).

5.6 Quality Assurance and Quality Control

General quality assurance and quality control requirements are provided in Section 13.6 of TO-11A (see Appendix D). Each laboratory should develop SOPs for the sampling and analysis of carbonyls and should develop criteria for sampling and analysis that are specific to each laboratory. Table 5-3 provides the quality assurance and quality control procedures consistent with Method TO-11A.

5.7 General Cartridge Handling Guidelines

Unintentional exposure of the DNPH cartridges and eluted samples to aldehyde and ketone sources can result in contamination of the samples, creating a positive bias in the collected data. Various aldehydes and ketones are ubiquitous in the environment. For example, biological processes can produce formaldehyde, acetone, and acetaldehyde on peoples' skin and in peoples' breath. Wear polyethylene gloves at all times when handling the DNPH cartridges during sampling collection and analysis. In addition, laboratory air often holds high concentrations of acetone (and sometimes formaldehyde). Measure background levels of carbonyls in the laboratory air using a DNPH cartridge and sample pump. If high background levels are present, handle the cartridges in a nitrogen-purged glove box or under a purge of carbonyl free air. Labeling inks, adhesives, and packing containers are all additional sources of contamination. Avoid packing cartridges in old newspapers, writing directly on the cartridges with ink, or placing adhesive labels directly on the cartridges. Additionally, DNPH is light sensitive. Always protect the cartridges from direct sunlight.

Parameter	Frequency	Limits	Corrective Action
Flow calibration	Each sampling event, pre- and post-checks	±10%	Mark sample as suspect
Mass flow meter calibration factor	Every quarter	1.0 ± 0.1	Repair mass flow meter
Leak check	Each sampling event, pre- and post-checks	No air flow	Check for leaks
Sampler blank	Pre- and post-seasons	> MDL	Clean sampler, qualify data if required
Collocated samples	10% of field samples	±20%	Mark sample as suspect
Back-up cartridges	10% of field samples	≤10% of total on back-up cartridge	Use back-up cartridges for all samples
Trip blanks	10% of field samples	<0.15 µg formaldehyde/cartridge	Blank correct data
Field blanks	10% of field samples	<0.15 µg formaldehyde/cartridge	Blank correct data
Spiked cartridges	10% of field samples	80 to 120% recovery	Flag data
Multi-point calibration	Every 6 months	≥0.999	Recalibrate
Continuing calibration standard	Every analytical run	±10%	Recalibrate
Method detection limits	Annually or after each instrument change	<0.1 ppbv for 180 L sample volume	Modify instrument as needed
Replicate injections	10% of samples	±10%	Reanalyze samples
Performance evaluation sample	Before and after samples	±15%	Reanalyze samples

Table 5-3. Quality Assurance and Quality Control Criteria

5.8 References

1. U.S. Environmental Protection Agency. Code of Federal Regulations. Title 40, Part 58. Ambient Air Quality Surveillance, Final Rule Federal Register, Vol. 58, No. 28, February 12, 1993.
2. Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air. Compendium Method TO-11A. Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High Performance Liquid Chromatography (HPLC). EPA-625/R-96/010b. Cincinnati, OH: U.S. Environmental Protection Agency, 1997.
3. Grassick, D. and R. Jongleux. Enhanced Ozone Monitoring Network-Design and Siting Criteria Guideline Document. Contract No. 68-D0-0125. Research Triangle Park, NC: U.S. Environmental Protection Agency, 1991.

Appendix B

**DRI 12-Port Manifold Canister Sampling System
Operator Instructions**

DRI 12-Port Manifold Canister Sampling System
Operator Instructions
Revised August 20, 1996

1.0 CONTACT

Questions or comments regarding the manifold canister sampling system should be addressed to Larry Sheetz of the Desert Research Institute (e-mail larrys@sage.dri.edu, 702/677-3199).

2.0 GENERAL DESCRIPTIONDESCRIPTION

The manifold canister sampler is designed to collect up to twelve 6-liter canister samples simultaneously at a maximum flow rate of approximately 1.6 liters/min. A stainless steel Viton pump draws in ambient air from a 316 stainless steel 12-port manifold to fill and pressurize the canisters. A flow control device maintains a constant flow into the canisters over the desired sampling period. The sampling system is shipped in two pieces, which are both contained in one shipping box. The sampler is contained in a white 2'x2'x2' box. This box also contains the manifold assembly, which is packed in an aluminum box, and a plastic bag containing all necessary fittings and tools. The twelve 1/8-inch stainless steel sampling lines that are used to connect the canisters to the sampling manifold are contained in a separate brown cardboard box.

3.0 QUALITY ASSURANCE STATEMENTASSURANCE STATEMENT

Prior to shipment of the manifold sampler, the 12-port manifold, fittings and stainless steel sampling lines are cleaned with deionized water and baked at 170°C for 24 hours. The canister sampling system is cleaned prior to field sampling by purging them with humidified zero air for 48 hours, followed by purging with dry UHP zero air for 1 hour. The canister sampling system is certified clean by the GC/FID analysis of humidified zero air collected through the sampling system. The system is considered clean if the concentration of any individual targeted compound is less than 0.2 ppbv and total NMOC concentration is less than 20 ppbC. In addition, a challenge sample, consisting of a blend of organic compounds of known concentration in clean humidified zero air, is collected through the sampling system and analyzed by the GC/FID method. The sampling system is considered non-biasing if recoveries of each of the challenge compounds is in the range of 80-120% (EPA document EPA/600-8-91/215). The 12-port manifold sampler is also pressure tested for possible leaks.

4.0 PREPARATION FOR SAMPLINGFOR SAMPLING

1. Before departing for the field, ensure that all sampling components that are described in section 2 are accounted for. Verify that all canisters are properly labeled and have at least -25 psi vacuum. Take appropriate number of blank field data sheets.

5.0 SAMPLER SETUPSETUP

2. Remove aluminum case and plastic bag from white sampling box.

3. Remove the 12-port sampling manifold from the aluminum case and place on the right edge of the white sampling box using the thumb screws to fasten in place (note photograph). The thumb screws can be left loose at this point to allow the manifold to slide until ¼-inch tubings are installed.
4. Remove the longer of the two ¼-inch tubing (marked with purple tape on one end) from the aluminum case. Use the 9/16-inch wrench (contained in the plastic bag) to remove the cap from the pump in the sampling box, and attach the end of the ¼-inch tubing with the purple tape. Connect the opposite end of the tube to the T-fitting on the 12-port sampling manifold (the connection pointing to the back of the sampler).
5. Remove the remaining ¼-inch tubing (marked with gray tape on one end) from the aluminum case. Remove the cap from the port marked canister on the sampler assembly, and attach the end of the ¼-inch tubing with the gray tape. Connect the opposite end of the tube to the 3-way T-fitting on the 12-port sampling (the connection pointing to the front of the sampler).
6. Tighten thumb screws on the sampling manifold after aligning the ¼-inch tubing. Attach the sampling line to filter holder. Adjust alignment of the filter holder before tightening.
7. Remove the 110-v power cord from plastic bag and plug cord into the power socket located in the right rear of the sample
8. Plug power cord into wall power source. Sampling fan and timer clock should come on.
9. Remove cap from sample exhaust (located above timer).

6.0 ATTACHING CANISTERS TO THE 12-PORT SAMPLING MANIFOLD.

ATTACHING CANISTERS TO THE 12-PORT SAMPLING MANIFOLD

1. Place up to twelve cans in four rows of three as shown in the photograph.
2. After placing cans in position, remove 1/8-inch stainless steel canister sampling lines from cardboard box. Note that the shortest lines are marked lines 1 through 3. These numbers correspond to the position on the 12-port sampling manifold. Remove aluminum foil from both ends of the sampling line and connect the lines to the sampling manifold and canisters starting with the canisters closest to the sampler. Remove caps on the 12-port sampling manifold as each sampling line is installed. Check that caps on all unused ports are tightly fasten.

7.0 OPERATION OF MANIFOLD SAMPLER OF MANIFOLD SAMPLER

The valve (marked with a white arrow) on the 12-port sampling manifold has two positions: atmosphere and pressure. The sampling lines are open to the atmosphere when the arrow points to the back of the sampler. To pressurize the canister, the arrow is position to point to the front of the sampler.

1. Place manifold valve in pressure position (i.e., pointing to front of sampler).
2. Open canister valves one at a time noting that each canister is under vacuum by reading the pressure gauge nearest to the front of the sampler. All canisters should have been checked for vacuum back in the laboratory prior to going out to the field. Connecting a canister that is not under vacuum can cross contaminate all other open canisters that are connected to the manifold.
3. After connecting all canisters and turn manifold valve to atmosphere position (i.e., pointing to back of sampler). All canisters will come up to zero (ambient) pressure. Check pressure gauge.
4. Turn manifold valve to pressure position (i.e., pointing to front of sampler).
5. Turn pump on by positioning the toggle switch (located front left of the timer box) to the on position (right). Pump will come on and the red and green lights on the timer will come on. Red light means that the pump is on, and the green light means that the sampling solenoid is open.
6. Leave pump on until the gauge pressure reads 15 psi. At a flow rate of 1.6 liters/min, it should take approximately 40 minutes to fill twelve canisters.
7. To terminate sampling, turn toggle switch to the off position and immediately close all canister valves. Sampling is complete.
8. Fill out the appropriate information on the field data sheets.
9. Carefully reinstall all parts, manifold and sampling tubes.

Appendix C

**Protocol for SCOS97
Performance Audits and Field Measurement Comparisons
for Carbonyl Compounds**

Revised July 3, 1997

**Protocol for SCOS97
Performance Audit and Field Comparisons
for Measurements of Carbonyl Compounds**

1.0 Purpose and Overview

1.1 Performance audits and field comparisons are being conducted for measurements carbonyl compounds as part of an external quality assessment program for the SCOS97-NARSTO. The purpose of these audits and comparisons are to document differences that may exist between measurement groups.

1.2 The audit consists the following three components.

- Review by Desert Research Institute (DRI) of standard operating procedures (SOPs) used by each measurement group. Aspects of SOPs to be reviewed by DRI include cleaning and certifying samplers, sample volume determination, type of substrate, DNPH loading and blank levels, reagent pH, breakthrough, ozone removal, sample handling and storage, extraction efficiency, analytical calibration methods and reference materials, and data processing and management.
- Performance audit involving sampling from a standard mixture of carbonyl compounds under field condition for both surface- and aircraft-based sampling (see Section 3).
- Field measurement comparisons involving collocated sampling at Azusa during a non-IOP day with anticipated ozone value of at least 0.15 ppm (see Section 4).

2.0 Participants, Communications, and Management

2.1 Coordination, Data Compilation and Analysis

Desert Research Institute (Dr. Eric Fujita, ericf@sage.dri.edu, 702/677-3311 FAX - 702/677-3157) P.O. Box 60220 (Street Address: 5625 Fox Ave.) Reno, NV 89506. Questions regarding the audit protocol should be addressed to Dr. Fujita.

California Air Resources Board (Dr. Randy Pasek, rpasek@arb.ca.gov, 916/324-8496 FAX - 916/322-4357) P.O. Box 2815, Sacramento, CA 95812-2815.

2.2 Audit Equipment

Desert Research Institute (Larry Sheetz, larrys@sage.dri.edu, office - 702/677-3199, cellular - 702/742-0986 FAX - 702/677-3157) P.O. Box 60220 (Street Address: 5625 Fox Ave.) Reno, NV 89506. Address questions regarding the gas standard dilution and delivery systems to Larry Sheetz.

2.3 Preparation and Analysis of Carbonyl Standard

Desert Research Institute (Dr. Barbara Zielinska, barbz@sage.dri.edu, 702/677-3198 FAX - 702/677-3157) P.O. Box 60220 (Street Address: 5625 Fox Ave.) Reno, NV 89506.

2.4 Participating Laboratories

July 3, 1997

- A. San Diego Air Pollution Control District (Mahmood Hossain, mhossain@sdapcd.co.san-diego.ca.us, 619/694-3358 Fax 619/694-2730) 9150 Chesapeake Dr. San Diego, CA 92123-1026.
- B. South Coast Air Quality Management District (Steve Barbosa, sbarbosa@aqmd.gov, 909/396-2171, Fax 909/396-2175) 21865 E. Copley Dr. Diamond Bar, CA 91765-4182.
- C. Ventura County Air Pollution Control District (Doug Tubbs, doug@vcmtss.mhs.compuserve.com, 805/662-6950, FAX 805/645-1444) 669 County Square Drive, Ventura, CA 93003.
- D. Atmospheric Analytical Consultants (AAC) (Dr. Sucha Parmar, sparmar@aol.com 805/650-1642, Fax 805/650-1644) 4572 Telephone Road Suite 920, Ventura, CA 93003.
- E. Atmospheric Assessment Associates (AtmAA) (Dr. Kochy Fung, 818/223-3277; Fax - 818/223-8250) 23917 Craftsman Rd. Calabasas, CA 91302
- F. Desert Research Institute (Dr. Barbara Zielinska, barbz@sage.dri.edu, 702/677-3198 FAX - 702/677-3157) P.O. Box 60220 (Street Address: 5625 Fox Ave.) Reno, NV 89506.
- G. University of California, Davis (Dr. Judith Charles, mjcharles@ucdavis.edu, 916/752-8757, fax 916/752) University of California, Davis, Davis, Ca 95616.

3. Performance Audits with a Standard Mixture

- 3.1 The carbonyl performance audit consists of sampling under field conditions with addition of a standard mixture of carbonyl compounds from a 6-liter stainless steel canister to an ambient sample. DRI will supply the standard mixture and a dilution system. Appendix A provides operating instructions for the DRI gas standard dilution and delivery system. The main supply of the standard mixture will be maintained at the Desert Research Institute in a 33-liter canister. DRI will analyze samples from the main supply at the beginning, midpoint, and conclusion of the audit. DRI will also analyze the contents of the 6-liter transfer canisters twice, once prior to sending the mixture to the audited laboratory and a second time upon its return.
- 3.2 Measurement Group A, B, C, D, E, and G, listed in Section 2.4, are expected to participate. Although the same laboratory is performing the chemical analyses for Groups C and D, the use of different samplers require the collection of separate samples by each group.
- 3.3 Each group will collect two replicate samples from the transfer canister according to their normal sampling protocol with the following restrictions. The standard audit protocol will consist of a 3-hour ambient sample using two DNPH cartridges in series (same as a breakthrough experiment) at a nominal flow rate of 1 liter of ambient air per minute. Contact DRI if you wish to use any other sampling interval or flow rate. The standard mixture is added at a nominal flow rate of 5 milliliters per minute in between the two cartridges. If an ozone scrubber is normally used in sampling, the scrubber should be place

- upstream of the sample cartridge and downstream of the gas addition. The front cartridge serves to scrub ambient carbonyl compounds and ozone. Data should be reported for both sample and scrubber cartridges. The loadings on the scrubber cartridge will be used to characterize the incoming ambient. A third cartridge should be placed downstream of the sample cartridge to quantify any breakthrough that may occur (leave out if pressure drop becomes a problem).
- 3.4 Each group will collect two samples from the standard canister according to each group's SOP. A minimum of two field blanks will be collected during the audit. During the audit, cartridge end-caps for the blank cartridges will be removed and left off for the time required to place new cartridges in the sampler (typically a few minutes). After this brief exposure the blank cartridges will be sealed again with the end-caps (check that plugs are tight), and placed inside the sampler until the sample cartridges are removed from the sampler and placed in coolers for transport to the laboratory.
 - 3.5 In addition to the samples collected in accordance with Section 3.4, SDAPCD and AtmAA will also collect one sample from a Tedlar bag (used for aircraft sampling) by first filling the bag with the standard mixture diluted with scrubbed ambient air (using a DNPH cartridge as in section 3.3) or zero air (also with inline scrubber). Transfer a sample from the bag to the cartridge in accordance with procedures used in SCOS. Analyze both scrubber and sample cartridges.
 - 3.6 Because there is only one dilution system, it is essential that all groups be prepared to conduct the audit expeditiously when it is their turn. Each group should return the gas dilution system and 6-liter canister (with a minimum pressure of 10 psig) to DRI within five working days after receipt of the equipment. A new supply of the standard mixture will be sent to the next laboratory. Approximate schedule for delivery of audit samples is as follows: SCAQMD (July 9); SDAPCD (July 17-18); VCAPCD (July 29 – August 1); AAC (week of August 11); AtmAA (week of August 25); and UCD (week of September 8).
 - 3.7 Each analytical laboratory will process and analyze all samples for this audit within five working days after sample collection. Each laboratory will perform two replicate measurements for each of the two samples in order to determine analytical precision.
 - 3.8 Each laboratory will report their data to Dr. Randy Pasek in hardcopy and electronic form (either ASCII, database, or spreadsheet) within one month of receipt of the audit sample. The submittal will include: mass of individual carbonyl compounds per sample (values reported as the carbonyl compounds rather than the hydrazones), sampling times (min), flow rate for addition of the standard gas mixture (ml/min), ambient sampling rate (lpm). The data from each of the audited laboratories will be forwarded to Dr. Eric Fujita once DRI's data for the initial and final standard concentrations are sent to ARB.
 - 3.9 A copy of the database and the draft report of the findings and conclusions of the comparison study will be sent to all participants within two weeks after receipt of all data. Corrections by participants to originally submitted data must be accompanied by sufficient documentation of the reasons.

4. Field Measurement Comparisons.

- 4.1 The collocated ambient sampling examines variations among measurement groups in reported values of carbonyl compounds under actual field conditions when ozone levels are comparable to those encountered during SCOS97 Intensive Operational Periods. One of the main objectives of the collocated sampling is to compare values obtained for samples collected by DNPH-impregnated silica gel cartridges with KI denuder versus DNPH-impregnated C₁₈ cartridges without an ozone scrubber. The comparison will also examine amounts of breakthrough by collecting duplicate cartridges in series, and levels and variability of field blanks.
- 4.2 Laboratories A, B, C, D, E, and F, listed in Section 2.4, are expected to participate in the field measurement comparison.
- 4.3 The inter-laboratory comparisons will consist of collocated samplings at the Azusa monitoring station through a common sampling manifold that is provided at the site. SCAQMD will confirm that flow through the manifold exceeds the combined flows drawn through all sampling ports. Collocated sampling will be conducted during the second half of July or early August on two consecutive non-IOPs days with anticipated ozone values of at least 0.15 ppm.
- 4.4 Because all PAMS groups do not have spare samplers, samples will be collected during a two-day period in between scheduled PAMS sampling days. ARB will request a waiver from EPA to skip a PAMS sampling day on behalf of those groups that will need to use a sampler that is currently deployed at a PAMS site. In order to allow sufficient time to for setup and return trip, samples will be collected during the afternoon of the first day and the morning of the second day. Four 3-hour samples will be collected in all with the following schedule: first day – 1300 to 1600 and 1700 to 2000; second day – 0600 to 0900 and 0900 to 1200. All times in PDT.
- 4.5 Forecast prepared by the SCOS forecasting team will be considered in scheduling the collocated sampling. The possible sampling period based on the restrictions described in section 4.4 are: July 22-25, July 28 – August 1, August 6-8 and August 12-15. Randy Pasek will monitor the daily forecast and projections to determine a possible go decision for collocated sampling. Eric Fujita will notify participants by e-mail or fax of the probability of sampling two days in advance. Final decision will be made by 2:00 p.m. prior to the first sampling day. Sampling will continue uninterrupted as planned once sampling is initiated.
- 4.6 A duplicate sample will be collected during the 0900-1200 sampling period of the second day by groups that have the ability to collect parallel samples.
- 4.7 A backup cartridge, placed in series with the primary sample, will be collected during the 1300 to 1600 sampling period on the first day and 0600-0900 sampling period on the second day of sampling.
- 4.8 A minimum of two field blanks will be collected during the comparison, one for each day of sampling. During each service visit, cartridge end-caps for one or more blank cartridges will be removed and left off for the time required to place new cartridges in the sampler (typically a few minutes). After this brief exposure the blank cartridges will be

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sealed again with the end-caps (check that plugs are tight), and placed inside the sampler until the next service visit (i.e., time between installation of cartridges in the sampler and removal and placement of cartridges in transport cooler).

- 4.9 Cartridges (sample, duplicate, backup, and blank) will be stored and shipped in strict accordance with each group's standard operating procedures.
- 4.10 Each analytical laboratory will process and analyze all samples for this comparison study within ten working days after receipt of the samples by the laboratory. Each laboratory will perform replicate analyses for all four samples in order to determine analytical precision.
- 4.11 Each laboratory will report their data to Dr. Randy Pasek in hardcopy and electronic form (either ASCII, dbf, excel or lotus) within four week of field sampling. The submittal will include: concentration data and associated uncertainties for individual C1 to C7 carbonyl compounds (or total C4, C5 and C6 carbonyl compounds); field data needed to calculate sample volumes including temperature and pressure if volume adjustments are made and nominal volume uncertainty; and laboratory data (mass of analyte per sample, extraction volume and correction for extraction efficiency and uncertainty if applicable, and all blank samples used in deriving the mean blank subtractions). Data will be forwarded to Dr. Eric Fujita after ARB has received DRI's data.
- 4.12 DRI will recalculate concentrations based on the field and analysis data and associated uncertainties. A copy of the database and the draft report of the findings and conclusions of the comparison study will be sent to all participants within two weeks after receipt of all data. DRI will resolve any discrepancies with concentration data reported by each group. Corrections by participants to originally submitted data must be accompanied by sufficient documentation of the reasons.

Appendix A

Operating Instructions for the DRI Gas Standard Dilution and Delivery System Performance Audits for SCOS97-NARSTO Carbonyl Measurements Revised July 3, 1997

1. Contact

Questions or comments regarding the gas standard dilution and delivery system should be addressed to Larry Sheetz of the Desert Research Institute (office - 702/677-3199, cellular - 702/742-0986, larrys@sage.dri.edu). Questions regarding the audit protocol should be addressed to Eric Fujita of the Desert Research Institute (702/677-3311, FAX - 702/677-3157, ericf@sage.dri.edu).

2. General Description

The gas standard dilution and delivery system is designed to allow the addition of standard gas mixtures from a 6-liter canister at a constant flow of up to 20 sccm (70° F and 29.92 in. Hg). It consists of a Sierra Instruments, Inc. Gas-Trak mass flow controller, model number 810C-SQR-249 (Serial No. C1261), a 6-liter stainless steel gas standard transfer canister, and a 3-way valve and tee assembly. The flow controller is preset to provide a flow of 5.0 ml per minute. Prior to shipment of the gas dilution and delivery system, the fittings and stainless steel sampling lines are cleaned with deionized water and baked at 170°C for 24 hours.

The dilution and delivery system and all accessories are self contained in a blue 1'x1'x2' fiberglass box, which is shipped in a wooden crate. A storage compartment located in the top portion of the blue box contains a plastic bag with all necessary fittings, fuses and tools, sampling log book and instruction manual.

3. Preparation and Transfer of Gas Standards

Carbonyl compounds were directly injected by microsyringe into a one-liter glass bulb. The mixture in the glass bulb was transferred into a 33-liter stainless steel canister by sweeping the contents of the bulb into the canister with humidified nitrogen gas to a pressure of 30 psi. Dry nitrogen gas was then added to the canister to bring the total canister pressure up to 80 psi. The mixture was prepared on May 19, 1997. The first sample from the standard mixture will be collected onto C₁₈ DNPH cartridges during the week of June 15.

Aliquot of the standard mixture will be withdrawn from the 33-liter canisters into 6-liter transfer canisters about ten days before the mixture is sent to an audited laboratory. After an equilibration period of one week, a sample will be collected on DNPH C₁₈ cartridges for HPLC analysis at DRI. A second sample will be collected after the standard mixture is returned to DRI.

4. Preparation for Sampling

- 4.1 Before departing for the field, ensure that all sampling components that are described in section 2 are accounted for. Verify that all cartridges are properly labeled. Take appropriate number of blank field data sheets.
- 4.2 Check the operation of your carbonyl sampler in accordance with your own standard operating procedures, and set the flow of the sampler to approximately 1 liter/min.
- 4.3 Prepare the number of blank DNPH cartridges that are specified in the audit protocol and a fresh KI denuder or scrubber, if it is part of your normal sampling procedure.

5. Gas Standard Dilution and Delivery System Setup

- 5.1 Remove the blue fiberglass box containing the dilution and delivery system from the wooden shipping crate.
- 5.2 Before opening the blue box, install the rear support by inserting the support peg into the rear of the box (see Figure 1). Unlock the latches in the front of the box, and carefully open the lid to its full open position.
- 5.3 Pull power cord from the upper portion of the box and connect the plug to a 118 V AC, 60 cycle power source (standard 110 volt outlet).
- 5.4 Remove the sampling line system from the storage compartment that is located on the upper half of the blue box. Install the ¼ inch stainless steel tubing that is connected to the 3-way valve and tee assembly to the flow controller outlet marked sample line (see Figure 2). Using the ¼ inch Teflon line provided, connect one open end of the tee to your sampling system, upstream of the KI denuder or scrubber and the sample DNPH cartridge, and the other open end of the tee to the sample inlet. Attach a second DNPH cartridge to the inlet to remove any carbonyl compounds present in the ambient air.

6. Flow Controller Measurements and Initial Purge

- 6.1 Place the valve in a position pointing to the left (open to atmosphere, labeled QA gas purge). Turn the power on and let the flow controller zero stabilize. Record five readings at ten-second intervals. Do not attempt to adjust if reading is within -0.5 and 0.5 ml/min.
- 6.2 Open the 6-liter transfer gas standard canister and record canister pressure in the logbook. The flow of standard gas will begin to purge the sample line. Allow the system to purge for at least five minutes to stabilize the flow. Record five readings at ten-second intervals. The flow should read about 5 ml/min. Allow the flow to stabilize further if the variability of the five readings exceeds ± 0.1 ml/min. (Adjustments should be made only if the indicated flow is greater than 7 or less than 3 ml/min. Adjustment can be made by turning the screw labeled local set point with the screwdriver provided in the storage compartment.

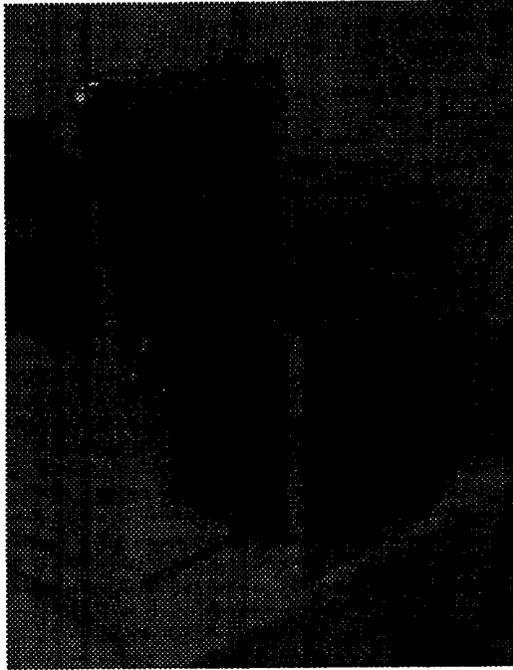


Figure 1. Install rear support before opening the gas delivery system.

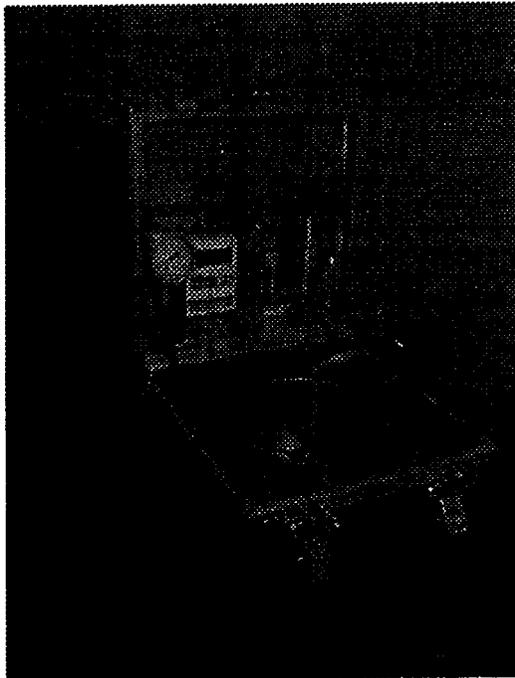


Figure 2. Standard installation.

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7. Collection of the Audit Sample

- 7.1 Turn your carbonyl sampler on and begin ambient sampling through your cartridge sampling line. Measure and record the sampler flow rate.
- 7.2 Start the flow of standard gas to the carbonyl sampling line by turning the valve to the right (labeled QA gas sampling). Continue sampling for the sampling time prescribed in the audit protocol.
- 7.3 At the end of the sampling period, turn off the flow of standard gas by turning the valve to the left (QA gas purge). Immediately record flow rate and canister pressure, and close canister (turning handle on the canister valve clockwise).
- 7.4 Turn power off and finish recording appropriate information on the field data sheets.
- 7.5 Replace all items to the storage box and lock "s" hook.
- 7.6 Push power cord in, close the box, and remove the stabilizing peg from rear of the box.
- 7.7 Replace the blue fiberglass box into the shipment crate and send the crate to the next laboratory according to the audit protocol

July 3, 1997

Figure 3. Setup for collecting carbonyl audit sample.

Appendix D

**Protocol for SCOS97-NARSTO
Field and Laboratory Comparisons
for Speciated Halogenated Hydrocarbon Measurements**

(July, 17 1997)

**Protocol for SCOS97-NARSTO
Field and Laboratory Comparisons
for Speciated Halogenated Hydrocarbon Measurements**

1.0 Purpose and Overview

- 1.1 Field and laboratory comparisons of halogenated hydrocarbon measurements are being conducted as part of an external quality assessment program for the SCOS97-NARSTO. The purpose of these audits and comparisons are to document differences that may exist between measurement groups.
- 1.2 The comparison will consist of two ambient canister samples collected by CE-CERT at Azusa during the second IOP. Canister samples will be analyzed in round-robin fashion by groups performing measurements of halogenated hydrocarbons during the SCOS97-NARSTO.

2.0 Participants

2.1 Coordination, Data Compilation and Analysis

Desert Research Institute (Dr. Eric Fujita, ericf@sage.dri.edu, 702/677-3311 Fax - 702/677-3157) P.O. Box 60220 (Street Address: 5625 Fox Ave.) Reno, NV 89506

California Air Resources Board (Dr. Randy Pasek, rpasek@arb.ca.gov, 916/324-8496 FAX - 916/322-4357) P.O. Box 2815, Sacramento, CA 95812-2815.

2.2 Collection of Ambient Comparison Samples

CE-CERT (Dennis Fitz, dfitz@helium.ucr.edu, 909/781-5781, FAX 909/781-5790) 1200 Columbia Avenue, Riverside, CA 92507.

2.3 Participating Laboratories

(1) DGA, Inc. (Dr. Daniel Grosjean, no e-mail, 805/644-0125 Fax 605/644-0142) 4526 Telephone Road, Ventura, CA 93003.

(2) Biospheric Research Corporation (Dr. Rei Rasmussen, rrasmus@ese.ogi.edu, 503/690-1077; Fax - 503/690-1669) 17010 N.W. Skyline Blvd. Portland, Oregon 97231

(3) Desert Research Institute (Dr. Barbara Zielinska, barbz@sage.dri.edu, 702/6773198; Fax - 702/677-3157) mailing address: P.O. Box 60220 Reno, NV 89506 shipping address: 5625 Fox Avenue Reno, NV 89506

(4) Desert Research Institute (David Schorran, daves@sage.dri.edu, 702/6773198; Fax - 702/677-3157) mailing address: P.O. Box 60220 Reno, NV 89506 shipping address: 5625 Fox Avenue Reno, NV 89506

(5) ManTech Environmental Technology, Inc. (Dr. Hunter Daughtrey, Hunter@epamail.epa.gov, 919/541-4540, Fax 919/541-3566) 2 Triangle Dr. Research Triangle Park, NC 27709.

3.0 Specific Objectives and Approach

- 3.1 Determine significant systematic biases greater than 20% for values greater than ten times the lower quantifiable limit (species specific) due to analytical methods and procedures.

4.0 Management and Communication Protocol

- 4.1 Dennis Fitz of CE-CERT will arrange for collection of ambient samples.
- 4.2 Randy Pasek of the ARB will receive and forward data from participants to DRI for analysis.
- 4.2 Eric Fujita of DRI will prepare a summary report for review by participants.

5.0 Documentation

Each laboratory is to submit the following documentation to Randy Pasek: 1) description of analysis methods and standard operating procedures; and 3) definition of minimum detection limits and measurement precision.

6.0 Comparison Samples

- 6.1 The two canister samples that will be used in this laboratory comparison will be those normally collected by CE-CERT during SCOS intensive operational periods at the Azusa sampling site, and analyzed by Biospheric Research Corporation for speciated hydrocarbons. BRC will also analyze the two comparison samples for halogenated hydrocarbons. These samples will then be sent to DRI (Zielinska), DRI (Schorran) and Mantech, in round-robin fashion in that order, for analysis of halogenated hydrocarbons. Continuous measurements of halogenated hydrocarbons that are made at Azusa by DGA, Inc. will also be included in the comparison.
- 6.2 The two canister samples that will be used for the comparison will be those collected during the 1300-1600 sampling period on the first and second days of the second IOP (the first IOP occurred on July 14). If data from DGA are not available for either of the two samples, the corresponding samples collected during the next IOP day will be used instead. CE-CERT will check to ensure that the canisters contain a minimum of 15 psig.
- 6.3 Each laboratory should analyze the two comparison samples within eight working days after receiving the samples. All laboratories are allowed a total sample volume of 1.0 liters for analysis (including any replicates).
- 6.4 The last group in the round-robin (Mantech) will return the two canister samples to BRC immediately upon completion of analysis.

7.0 Data Submittal and Analysis

- 7.1 Each laboratory will send hardcopies of chromatograms and a data report (species identification, retention times, and individual species concentrations in ppbv to Randy Pasek within three weeks after receiving the samples. The data should also be sent electronically in a spreadsheet or database format.
- 7.2 Corrections to originally submitted data must be accompanied by sufficient documentation of the reasons.
- 7.3 Analysis of the data by DRI will include linear regression of data for each participating laboratory versus the average values (individual values exceeding two standard deviations

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of the mean of all values will be removed from the average). Differences in species concentrations of greater than 20% (for concentrations above 0.1 ppbv) between individual laboratories versus the adjusted mean values. Chromatograms will be examined to identify possible discrepancies in species identification.

- 7.4 Results will be sent to all participants for review and comments within three weeks after all data reports have been submitted. Each of the laboratories will be identified in the report by code only (letter code selected at random) in the draft report. The final report will contain the letter code key as an appendix.

Appendix E

**Protocol for SCOS97-NARSTO
Measurement Comparison for Biogenic Hydrocarbons**

(August 5, 1997)

**Protocol for SCOS97-NARSTO
Measurement Comparison for Biogenic Hydrocarbons**

1.0 Purpose and Overview

- 1.1 Field and laboratory comparisons of biogenic hydrocarbon measurements are being conducted as part of an external quality assessment program for the SCOS97-NARSTO. The purpose of these comparisons are to document differences that may exist between measurement groups, and to compare isoprene values obtained from canister samples and solid adsorbent samples.
- 1.2 The comparison will consist of an ambient sample collected by UC, Riverside using canisters and absorbent tubes.

2.0 Participants

2.1 Data Compilation and Analysis

Desert Research Institute (Dr. Eric Fujita, ericf@sage.dri.edu, 702/677-3311 Fax - 702/677-3157) P.O. Box 60220 (Street Address: 5625 Fox Ave.) Reno, NV 89506

California Air Resources Board (Dr. Randy Pasek, rpasek@arb.ca.gov, 916/324-8496 FAX – 916/322-4357) P.O. Box 2815, Sacramento, CA 95812-2815.

2.2 Collection of Ambient Samples

University of California, Riverside Statewide Air Pollution Research Center (Dr. Janet Arey)

2.3 Participating Laboratories

(1.) University of California, Riverside (Dr. Janet Arey, arey@mail.ucr.edu, 909/787-3502; Fax 909/787-5004) Statewide Air Pollution Research Center-6, University of California, Riverside, CA 92521

(2.) Biospheric Research Corporation (Dr. Rei Rasmussen, rrasmus@ese.ogi.edu, 503/690-1077; Fax - 503/690-1669) 17010 N.W. Skyline Blvd. Portland, Oregon 97231

(3.) Desert Research Institute (Dr. Barbara Zielinska, e-mail: barbz@sage.dri.edu, 702/6773198; Fax – 702/677-3157) mailing address: P.O. Box 60220 Reno, NV 89506 shipping address: 5625 Fox Avenue Reno, NV 89506

(4.) ManTech Environmental Technology, Inc. (Dr. Hunter Daughtrey, Hunter@epamail.epa.gov, 919/541-4540, Fax 919/541-3566) 2 Triangle Dr. Research Triangle Park, NC 27709. *Analyze canister supplied by DRI.*

3.0 Specific Objectives and Approach

- 3.1 Determine significant systematic biases greater than 20% for values greater than ten times the lower quantifiable limit (species specific) due to analytical methods and procedures.

4.0 Management and Communication Protocol

- 4.1 Dr. Arey of UCR, SPRAC arranged for the collection of ambient samples.

August 5, 1997

4.2 Dr. Randy Pasek of the ARB will receive and forward data from participants to DRI for analysis.

4.2 Dr. Eric Fujita of DRI will prepare a summary report for review by participants.

5.0 Documentation

Each laboratory is to submit the following documentation to Randy Pasek: 1) description of analysis methods and standard operating procedures; and 3) definition of minimum detection limits and measurement precision.

6.0 Comparison Samples

6.1 UCR collected two canister samples along with an adsorbent tube sample on the campus of UC, Riverside during the afternoon of August 1, 1997. The two canisters, one supplied by Biospheric Research Corporation and one by Desert Research Institute, were collected simultaneously using a DRI sampler to a minimum of 15 psig. BRC and DRI will analyze their respective canisters. DRI will send their canister to Mantech after completing their analysis.

6.2 Each laboratory should analyze the comparison sample within five working days after receiving the samples.

6.3 Mantech will return the canister to DRI immediately upon completion of analysis.

7.0 Data Submittal and Analysis

7.1 Isoprene is the main compound of interest for this comparison. Although some questions exist concerning the analysis of terpenes from canisters samples, these compounds should also be reported if observed in the sample. Each laboratory will send a data report (species identification and concentrations in ppbC) to Randy Pasek within three weeks after receiving the samples.

7.2 Corrections to originally submitted data must be accompanied by sufficient documentation of the reasons.

7.3 Results will be sent to all participants for review and comments within three weeks after all data reports have been submitted.

Appendix F

Protocol for SCOS97-NARSTO Performance Audit and Collocated Instrument Intercomparison for Nitrogen Species Measurements

[Please note that due to exigencies of SCOS97-NARSTO operations, some elements of this program including the mentor program were not carried out. Due to delays in data delivery, preliminary data analysis results are unlikely to be available before October 1998.]

**Protocol for SCOS97-NARSTO
Performance Audit and Collocated Instrument Intercomparison
for Nitrogen Species Measurements**

1. Purpose and Overview

1.1 Performance and system audits of nitrogen species measurements are conducted as part of an internal quality assessment program for the SCOS97-NARSTO. In most instances, this protocol defines internal operational checks and collocated instruments intercomparison studies by participating entities as performance audits. These audits intend to assess the quality of these diverse measurements and to assure uniform data integrity and data quality throughout this network.

1.2 During SCOS97, there will be six closely related total reactive nitrogen species (NO_Y) instruments:

TECO 42CY type a (NO , NO_Y) -- 4 units (2 Aircraft)

TECO 42CY type b (NO_Y , HNO_3) -- 7 units

TECO 42+molybdenum converters (NO , NO_Y) -- 2 units

TECO 42+molybdenum converters (NO_Y , HNO_3) -- 1 unit

TECO 42S+molybdenum converters (NO_Y , HNO_3) -- 2 units

TECO 42S+molybdenum converters (NO , NO_Y) -- 2 unit (1 Aircraft)

These instruments will be operated in 200, 500, and 1000 ppbV full range; each range is specific to an instrument depending on expected total reactive nitrogen species load at that instrument site. Instruments on board airplanes and at San Nicolas Island will be in 200 ppbV range. Instruments in source and down wind areas (e.g., Azusa and Los Angeles Main stations) will be in the 1000 ppbV range. These instruments are fundamentally standard NO_X instruments with their converter placed forward at the inlet.

There will be two gas chromatography electron capture detection (GC-ECD) instruments deployed separately to measure peroxyacetylene and peroxypropionyl nitrates (PAN & PPN).

GC-ECD will be operated either continuously or at the zero day of an intensive operating period (IOP). There will be two Luminox (LPA-4) instruments deployed separately and operated continuously to measure PAN and nitrogen dioxide (NO_2).

During ozone intensive operational periods (IOP), ammonia and nitric acid will also be measured at two sites using double diffusion denuders four times a day, each lasting three hours, beginning at 7:00 am. There will be a TAMS 150 tunable diode laser absorption spectroscopy (TDLAS) instrument measuring NO_2 and nitric acid collocated with denuder measurements and TECO 42CY type b at Azusa. Limited measurements of ammonia and

nitric acid will also be done at five sites using denuder difference and stack filter sampling methods respectively.

- 1.3 The system audit consists of a review by Air Resources Board (ARB) of standard operating procedures (SOPs) used by each measurement group; performance audits will be on-site performance checks monthly by CE-CERT, and performance audits of each audit group once the network is put into routine operation.

2. Participants

2.1 Environmental Chamber Acceptance Testing & SOP

College of Engineering-Center for Environmental Research & Technology (Mr. Dennis Fitz, dfitz@helium.ucr.edu, 909/781-5781 FAX-909/781-5790) 1200 Columbia Avenue, Riverside, CA 92507.

2.2 Special Audit Gas (*n-propyl nitrate*)

Air Resources Board Monitoring & Laboratory Division (ARB MLD) (Mr. Larry Molek, lmolek@arb.ca.gov, 916/327-4889 FAX-916/327-8217) 1390 T Street, Sacramento, CA, 95812.

2.3 Operational Checks & Calibration

a. Aerovironment (Mr. David Pankratz, pankratz@aerovironment.com, 818/395-4635 FAX 818/359-9628) 222 East Huntington Drive, S200, Monrovia, CA 91016 -- Cajon Pass, Calabasas.

College of Engineering-Center for Environmental Research & Technology (Mr. Kurt Bumiller, kurt.bumiller@ucr.edu, 909/781-5796 FAX909/781-5790) 1200 Columbia Avenue, Riverside, CA 92507 -- Azusa, Banning, Chino, Diamond Bar, Los Angeles North Main, Riverside, and San Nicolas Island.

Mojave Desert Air Quality Management District (Mr. Bob Ramirez, bramirez@mdaqmd.ca.gov, 760/245-1923 FAX 760/245-2699) 15428 Civic Drive, Suite 200, Victorville, CA 92392-2383 -- Barstow.

San Diego County Air Pollution Control District (Mr. Mahmoud Hossain, mhossain@sdapcd.co.san-diego.ca.us, 619/694-3358 FAX 619/694-3858) 9150 Chesapeake Drive, San Diego, CA 92123 -- Alpine, Mount Soledad, and EOPACE western boundary airplane hangar at Montgomery Field

e. United States Marines (Dr. Norm Helgeson, nhelges@nfesc.navy.mil, 805/982-1335 FAX 805/982-1409) -- Naval Facilities Engineering Services Center, Code 421, 1100 23rd Avenue, Port Hueneme, CA 93043 -- 29 Palms.

f. Ventura County Air Pollution Control District (Mr. Dennis Mikel, 805/662-6951 FAX 805/662-6977, dennis@vcmtss.mhs.compuserve.com) 669 County Square Drive, Ventura, CA 93003 -- Simi Valley.

g. Sonoma Technology Inc. (Mr. Jerry Anderson, 707/527-9372 FAX 707/527-9398, jerry@sonomatech.com) 5510 Skylane Blvd., Suite 101, Santa Rosa, CA 95403-1083 -- northern boundary airplane hangar at Camarillo Airport.

h. University of California, Davis (Dr. John Carroll, 916/752-3245 FAX 916/752-1552, carroll@atm1.ucdavis.edu) Hoagland Hall Room 151, Department of Land, Air, and Water Resources, University of California, Davis, CA 95616 -- South Coast Air Basin airplane hangar at El Monte Airport

2.4 NO_y Species

a. Aerovironment (Mr. David Pankratz, pankratz@aerovironment.com, 818/395-4635 FAX 818/359-9628) 222 East Huntington Drive, S200, Monrovia, CA 91016 -- Cajon Pass, Calabasas (NO₂ and PAN).

b. College of Engineering-Center for Environmental Research & Technology (Mr. Kurt Bumiller, kurt.bumiller@ucr.edu, 909/781-5796 FAX 909/781-5790) 1200 Columbia Avenue, Riverside, CA 92507 -- Azusa (NO₂, PAN, PPN, NH₃, and HNO₃) and Riverside (NH₃ and HNO₃).

c. Daniel Grosjean Associates (Dr. Daniel Grosjean, 805/644-0125 FAX 805/644-0142) 4526 Telephone Road, Suite 205, Ventura, CA 93003 -- Simi Valley (PAN and PPN).

d. California Institute of Technology (Dr. Glen Cass, 818/395-6888 FAX 818/395-2940, glen@eqt.caltech.edu) Department of Chemical Engineering, California Institute of Technology, 1201 E. California Blvd, Pasadena, CA 91125 -- Azusa, Chino, Diamond Bar, Los Angeles North Main, and Riverside (NH₃ and HNO₃).

2.5 Monthly Audits

College of Engineering-Center for Environmental Research & Technology (Mr. John Collins, jcollins@cert.ucr.edu, 909/781-5793 FAX-909/781-5790) 1200 Columbia Avenue, Riverside, CA 92507.

2.6 Scheduled Audits

a. Mojave Desert Air Quality Management District (Mr. Bob Ramirez, bramirez@mdaqmd.ca.gov, 760/245-1923 FAX 760/245-)15428 Civic Drive, Suite 200, Victorville, CA 92392-2383 -- Barstow and 29 Palms.

b. San Diego County Air Pollution Control District (Mr. Mahmoud Hossain, mhossain@sdapcd.co.san-diego.ca.us, 619/694-3358 FAX 619/694-3858) 9150 Chesapeake Drive, San Diego, CA 92123 -- Alpine and Mount Soledad.

c. Ventura County Air Pollution Control District (Mr. Dennis Mikel, 805/662-6951 FAX 805/662-6977, dennis@vcmtss.mhs.compuserve.com) 669 County Square Drive, Ventura, CA 93003 -- Simi Valley.

2.7 Audit Intercomparison

Air Resources Board Monitoring & Laboratory Division (Ms. Alice Westerinen, awesteri@arb.ca.gov, 916/327- FAX-916/327-8217) 1390 T Street, Sacramento, CA, 95812.

2.8 Raw Data Review for Network Maintenance

College of Engineering-Center for Environmental Research & Technology (Mr. Kurt Bumiller, kurt.bumiller@ucr.edu, 909/781-5796 FAX-909/781-5790) 1200 Columbia Avenue, Riverside, CA 92507.

2.9 Network Mentor Program

Aeronomy Laboratory, National Oceanic and Atmospheric Administration (Mr. Eric Williams, ewilliams@al.noaa.gov, 303/497-3226 FAX 303/497-5126) R/E/AL7, 325 Broadway, Boulder, CO, 80303.

2.10 Coordination and Data Compilation

College of Engineering-Center for Environmental Research & Technology (Mr. Kurt Bumiller, kurt.bumiller@ucr.edu, 909/781-5796 FAX-909/781-5790) 1200 Columbia Avenue, Riverside, CA 92507.

2.11 Data Archive

Air Resources Board Technical Support Division (ARB TSD)(Mrs. Liz Niccum, lniccum@arb.ca.gov, 916/324-6917 FAX 916/327-8524) 2020 L Street, Sacramento, CA, 95814.

2.12 Preliminary Data Analysis

Air Resources Board (ARB RD)(Dr. Ash Lashgari, alashgar@arb.ca.gov, 916/323-1506 FAX- 916/322-4357) 2020 L Street, Sacramento, CA 95814-4219.

3. Specific Objectives and Approach

3.1 Review compliance with SOP developed by CE-CERT or identify differences between this SOP and other participants' procedures that may cause differences in the data produced by various elements of the network. This review will include examination of analytical calibration methods and reference materials, and data processing and management.

3.2 A Performance audit of TECO 42, 42CY, and 42S plus their external converters would be essentially the same as the performance audits of all NO/NO_x analyzers. The difference arises

from the fact that the NO_y configuration converts larger number of nitrogen species and the conversion of nitric acid and PAN is far more efficient. This efficiency is achieved through forward deployment of the converter. During the installation process, station operators should prepare for introduction of calibration gases at the instrument inlet just ahead of the converter on the roof of the measurement site.

- 3.3 Performance audits of NO/NO_x analyzers is conducted using the through-the-probe method as generated by instrumentation contained in the audit van. Known quantities of National Institute of Standards and Technology (NIST) traceable gases is diluted with 22 liters per minute (lpm) of pure air and is then introduced to the site analyzer through a 150 foot gas presentation line connected to the site inlet probe.

The audit standard should be an EnviroNics 9100 dilution flow metering system, an Aadco 737R pure air system to generate NO-free dilution air (zero air) and compressor capable of supplying 22 lpm system, a superbend cylinder of compressed gas containing a mixture of NO and CO (along with other gases) in NIST-traceable concentrations, a Thermo Environmental (TEI) Carbon Monoxide analyzer, model 48, two cylinders of compressed gas with known amounts of CO, and one cylinder of compressed ultrapure air.

The EnviroNics 9100 systems also contains an ozone generator and second mixing chamber for the generation of NO₂. When ozone is mixed with NO, a gas phase titration (GPT) results which oxidizes some NO to NO₂. The generated NO₂ is calculated from the change in NO. The analyzer NO₂ readings and the converter efficiency are determined from the GPT.

Before starting the audit, the TEI 48 and the dilution system is warmed up for at least two hours. The CO analyzer is first calibrated using the zero air cylinder and two CO cylinders.

The CO concentration of the gas mixture generated by the EnviroNics 9100 using the Aadco pure air and gas from the mixed gas cylinder is then measured with the TEI 48. The dilution ratio of the generated audit sample is calculated. The generated NO concentration is calculated using the dilution ratio and the cylinder concentration.

The first audit point introduces zero air to the site. The next steps consist of introducing NO to the analyzer for the response of NO and NO_x channels followed by the generation of NO₂ by GPT. A total of three NO₂ concentration for NO, NO₂, and NO_x delivered to the site analyzer will be 0.35 to 0.45 ppmV, 0.15 to 0.2 ppmV, and 0.03 to 0.08 ppmV. A final response to zero air is done at the end of the audit.

Readings are recorded from the primary data acquisition system. Sufficient time is allowed for the response to stabilize before recording any information. The measured values from the display, analog output, and data logger are compared to the audit concentration.

The dilution ratio is calculated according to the equation:

$$\text{Dilution Ratio} = \frac{\text{True CO Response (ppmV)}}{\text{Superblend Cylinder CO Concentration (ppmV)}}$$

The true concentration in ppmV will be calculated from:

True Concentration = Superblend Concentration x Dilution Ratio

The NO₂ channel response and the efficiency of the NO_x to NO converter is tested with NO₂ generated in the GPT section of the dilution system. These tests are done at 3 different NO₂ and NO_x concentrations while the NO concentration remains between 80 to 120 ppbV (if possible). NO gas with concentrations for the three points are near 500, 275, and 170 ppbV.

The responses of the NO and NO_x channels to this NO are recorded and adjusted by the linear regression equations relating instrument response to calibration concentration. Ozone is mixed with the NO to generate NO₂ concentrations near 400, 175, and 70 ppbV which are introduced to the instrument. The responses of NO and NO_x are recorded and corrected for the calibration results.

The converter efficiency, Conv Eff, is determined in the following steps:

Conv Eff = 100 [NO - Rem NO] / [NO]

NO = (Orig NO - Rem NO) / Slope NO

NO_x = (Orig NO_x - Rem NO_x) / Slope NO_x

where: Orig NO is adjusted response of NO channel before ozone is mixed,

Rem NO is adjusted response of NO channel after ozone is mixed,

Orig NO_x is adjusted response of NO_x channel before ozone is mixed,

Rem NO_x is adjusted response of NO_x channel after ozone is mixed,

An overall converter efficiency is calculated by averaging the efficiencies at the three levels.

A converter efficiency less than 96% will require an AQDA.

Although not recommended during routine operation, testing the effects of the PFA line at the end of the study may also be useful. In this approach, inlets at the end of very short sampling lines are supplied with known quantities of NO_y species and their conversion responses are compared with standard length sampling lines. This type of instrument evaluation may be part of the CE-CERT's closing audit program for NO_y instruments.

To test for the full conversion of nitric acid and PAN, n-propyl nitrate with an appropriate dilution system will be made available from CE-CERT through the monthly audit process.

Three canisters of n-propyl nitrate (NPN) will be made available through the ARB MLD to CE-CERT for evaluation and detailed adjustments to the SOP and final distribution to participants. Please note that during the NARSTO-Northeast and the Southern Oxidant Study (SOS), knowing the concentration of calibration standards of NPN has proven difficult (> ± 20%).

Finally, TECO 42S instruments have ½ to 1 ppbV sensitivity; their lower than model 42 instruments limit of detection make the interpretation of the converter efficiency test using air canisters of 1 to 2 ppbV purity difficult.

- 3.4 TECO 42CY model has been improved to include a GPT cycle every thirty seconds, to cool the photo multiplier tube significantly, to redo the sampling lines, and to include an internal

desiccant. This instrument's limits of detection may be at 50 pptV. Thus, performance audit of TECO 42CY model instrument type a is somewhat different than performance audits of model 42 and 42 S plus their external converters. Through its internal GPT cycle, the instrument in essence produces better air purity than commercially available for introduction at the inlet. This should be kept in mind when auditing these instruments following essentially the steps in 3.2. TECO 42CY type b has no NO channel and thus the conversion test has to be modified to include NPN as noted in the SOP. Introducing nitric acid through a dilution systems at three concentrations to both channels of the type b instrument is another way to insure that the nylon filter is functioning correctly and all of the nitric acid is being converted through the NO_y channel. This procedure would require the operator to physically be present on top of the site roof with a stable and known supply of nitric acid. This is difficult to manage. It is best to test conversion of nitric acid, PAN, and other NO_y species during the acceptance testing protocol and after the study in the closing audits at CE-CERT. If mid-term conversion of NO_y species is needed, CE-CERT can provide PAN and nitric acid standards and recommended procedures upon request to each entity's evaluation laboratory. Comparison of the conversion of nitric acid, PAN, and NPN will be useful in further developing instrument operations, maintenance, and quality control procedures.

- 3.5 CE-CERT will conduct closing audits in the same manner as the acceptance testing was conducted. In addition, CE-CERT may subject some instruments to testing in environmental chambers.
- 3.6 NO₂ instruments, the LPA-4 and the TAMS 150 TDLAS, have to be challenged with NO₂ produced from titration of NO with ozone as noted in 3.2. For LPA-4, the DRI document about the results from the San Joaquin Valley Air Quality Study operation of LPA-3 should be reviewed for reference. CE-CERT and Ventura County Air Pollution Control District (VCAPCD) will coordinate with AV and each other to conduct one monthly intercomparison audit at Calabasas with special focus on the LPA-4 instrument.
- 3.7 PAN instruments, the LPA-4 and the GC-ECD, have to be challenged with known concentrations of PAN generated by CE-CERT to be injected directly into or diluted in a tedlar bag and injected afterwards into the instrument inlet. For LPA-4 and GC-ECD, the DRI document about the results from the San Joaquin Valley Air Quality Study operation of LPA-3 should be reviewed for reference. 3.8 Denuders will be audited using 15 lpm flow meters through contract arrangements to be determined later.
- 3.8 TAMS 150 TDLAS will be audited using 10 lpm flow through contract arrangements to be determined later.

4. Audit Schedule

- 4.1 Mojave, San Diego, and Ventura districts and Aerovironment (AV) staff will maintain checks and calibrations as specified in the SOP and coordinate their audits with CE-CERT. These audits will be performed to permit both audit groups to check their reference standards, compare standard operating procedures, and for district staff to become familiar with the use of NPN for NO_y instrument audits.
- 4.2 ARB MLD will visit AV sites between July 21st and 25th, 1997 for a standard audit. CE-CERT audit team will coordinate with ARB MLD audit team to meet the ARB MLD audit team at the AV sites and to compare audits of the NO conversion through the NO_y instruments. CE-CERT will share standard operating procedures and experience with NPN with ARB MLD.
- 4.3 Mojave Desert Air Quality Management District (MDAQMD) audit team will coordinate with CE-CERT for monthly audits of their site and the site at the U.S. Marines facility to compare conversion of NO through the NO_y instruments and to use NPN to compare conversion of additional nitrogen compounds. CE-CERT and Mojave district audit teams will compare standard operating procedures, calibration instruments, and reference standards.
- 4.4 San Diego County Air Pollution Control District audit team is scheduled to audit their two sites July 7 to 11, 1997. CE-CERT will coordinate with San Diego district to schedule a monthly audit to coincide with this schedule at these sites to compare conversion of NO through the NO_y instruments and to use NPN to compare conversion of additional nitrogen compounds. CE-CERT and San Diego district audit teams will compare standard operating procedures, calibration instruments, and reference standards.
- 4.5 VCAPCD audit team will coordinate with CE-CERT for monthly audits of their site to compare conversion of NO through the NO_y instruments and to use NPN to compare conversion of additional nitrogen compounds. CE-CERT and Ventura district audit teams will compare standard operating procedures, calibration instruments, and reference standards. CE-CERT will provide PAN standards to audit the GC-ECD instrument at Simi Valley.
- 4.6 CE-CERT will conduct weekly and monthly audits for all other sites. Daniel Grosjean Associates will provide PAN standards to audit the GC-ECD instrument at Azusa. CE-CERT will use flow meters successfully audited by ARB MLD to audit the flow through the denuders.
- 4.7 If time and resources permit, CE-CERT and Ventura district audit teams will visit the Calabasas site together on one monthly audit of the NO_y instruments at that site to compare their audit results and to audit LPA-4 measurements of NO₂ and PAN.
- 4.8 No audits shall coincide within an IOP window.
- 4.9 All audit reports will be compiled and transmitted by email or by fax soon after the audit to CE-CERT. These will be compiled into the network audit results and retransmitted to the ARB MLD for their review and ARB TSD Data Archive for review and adjustment to the SCOS97 nitrogen species database.

- 4.10 MDAQMD, VCAPCD, AV, and CE-CERT will participate in a mentor program with Mr. Eric Williams of the National Oceanic and Atmospheric Administration (NOAA) Aeronomy Laboratory who will observe, advise, and provide a systems type of oversight for the nitrogen species network.

5. Data Qualification Statements

- 5.1 The purpose of these statements is to provide data users with information on the specifics of data quality, i.e., the measurement uncertainty described in terms of accuracy and precision for nitrogen species measurements.
- 5.2 The NARSTO-Northeast and the SOS nitrogen species network operators have used the method of addition (MOA) which has as its background the ambient air matrix, instead of zero air, to develop these accuracies and precisions. The MOA is essentially spiking an ambient air sample with known quantities of NO, NO₂, and NPN. It requires two mass flow controllers precisely managing and metering the flow to be able to calculate response factors (RF) to these spikes which are automatically introduced at the instrument inlet. The RF is defined as the change in instrument response divided by the concentration added to the ambient concentration by the MOA calibration system. Details are provided in the literature that accompanies this protocol.
- 5.3 For logistical reasons, because nitrogen species concentrations in some parts of the study area are very high and for long-term compliance with EPA regulations, many participants may not be able to institute the MOA. In the absence of response factors from MOA, NO, NO₂ and NO_Y can be used for calculation of accuracies and precisions.
- 5.4 This protocol proposes that NO, total NO_Y, and NO_Y species measurements achieve estimates of accuracy of $\pm 10\%$ (data quality objective 1). For collocated measurements, estimates of precision should also achieve $\pm 10\%$ (data quality objective 2). Data with precisions and accuracies more than $\pm 10\%$ less than $\pm 15\%$ should be cause to review the quality assurance procedures for the measurement instrument and/or have the instrument readuited, repaired, or taken out of the network for substantial work at the instrument manufacturer. Data below accuracies and precisions of $\pm 15\%$ should not be incorporated into the data archive.
- 5.5 In terms of NO and NO_Y, data accuracy is deviation from a reference value and/or is calculated by regression techniques:

Reference values are provided by analyses of known or standard reference materials. For NO and NO_Y, the 95% confidence interval can be calculated from the variability in RF or provided by the automatic method of additions (MOA) checks, performed every 6 hours for NO and every 12 hours for NO_Y, during routine operations. The MOA checks can be performed at about 20 ppbV. Statistics calculated using RF, or NO, NO₂ and NO_Y should be mathematically equivalent to those calculated using relative difference between changes in monitor response and known concentrations. NARSTO-NE and the SOS operators considered MOA results valuable because they tend to evaluate the influence of the ambient air matrix. In the NARSTO-Northeast study, they used the 95% confidence intervals of 7 day

coefficient of variation (CV) of RFs as their measures of accuracy at each site. CV is the ratio of standard deviation to the mean of a set of measurements multiplied by 100 and expressed as percent. The SCOS97-NARSTO operators would use the 95% confidence intervals of 7 day CV of NO, NO₂ and NO_Y ratios.

Regression coefficient and regression intercept for the gas-replacement multi-point calibrations conducted at the beginning and at the end of the study can also be used to estimate accuracy. In this case, the data quality objective 1 is translated to regression slopes of 1 ± 0.1 , regression intercept of ± 3 ppbV, and r^2 of greater than 0.999. The SCOS97-NARSTO operators would also use both this and the earlier methods to complete data qualification statements for NO_Y species during SCOS97-NARSTO. The ARB and the CE-CERT staff would be available if additional labor to provide these accuracies is required.

Please note that it may be difficult to know NPN concentrations to less than within 20% which may create difficulties in interpreting the outcome of the monthly NPN checks in terms of measurement accuracy.

- 5.6 In terms of NO and NO_Y, data precision is a measure of mutual agreement among individual measurements of the same specie under similar conditions. Precision can be estimated by repeated measurements with the same instrument and calibration system, and by collocated instrument intercomparison measurements.

Where there are no collocated measurements, precision for NO and NO_Y measurements can be determined by using the standard deviation of the 7 day RF for all of the routine MOA checks (20 ppbV for both NO and NO_Y) or the 7 day NO, NO₂ and NO_Y of the SCOS97-NARSTO routine checks. Most SCOS97-NARSTO participants would use the second method for estimating precisions.

During SCOS97-NARSTO, there will be the following collocated measurements:

NO channels of a standard and an NO_Y instrument at San Nicolas Island and at Barstow

TDLAS HNO₃ channel, an NO_Y instrument HNO₃ channel, and three-hour denuders at Azusa

NO_Y instrument HNO₃ channel, and three-hour denuders at Riverside

Limited sampling of HNO₃ at Azusa, at Diamond Bar, at Chino, at Los Angeles North Main, and at Riverside with an NO_Y instrument HNO₃ channel

Limited sampling of NH₃ by stack filter at Azusa and Riverside with denuders.

In this case, precisions are the 95% confidence interval of percent differences between the two or the three collocated measurements. ARB and CE-CERT staff labor would be available if additional labor is required to provide these precisions.

Please note that it may be difficult to know NPN concentrations to less than within 20% which may create difficulties in interpreting the outcome of the monthly NPN checks in terms of measurement precision.

6. Potential Quality Control Problems

6.1 Evaluating NO conversion problems include:

Accuracy of the NO standard used (15 ppmV recommended)

Protocol for determination of instrument sensitivity and background level

Short and long term stability of the detector

Correction for interferences and artifacts.

6.2 Ammonia is considered an interference in conversion of NO_y species.

6.3 Molybdenum converters must be constantly evaluated for:

Changes in conversion efficiency for each of the principle NO_y species

Interferences and artifacts

Errors in calibration

6.4 For possible resolution to these potential problems, please consult pages 5-11 of the accompanying document entitled "Recommendations for Modification of the SCION Network NO_y, RH, and CO Measurement Equipment," and when possible seek the CE-CERT staff's advice, support, and recommendation.

7. Intensive Operation Periods Summary

7.1 For this network, all districts and Aerovironment will compile anecdotal and exceptional events during an IOP-O₃ in an IOP summary to the ARB RD for compilation into the SCOS97 Data Archive soon after the closing of IOP window.

8. Network Maintenance

8.1 All districts and Aerovironment will transmit by email, via FTP, or by fax, their raw ozone, surface meteorology, and nitrogen species data to CE-CERT for network maintenance and problem detection daily or each two days. The form of this transmission is governed by each district's data security and data handling procedures. Each district will coordinate and resolve all issues regarding this transmission with CE-CERT.

9. Preliminary Data Analysis

9.1 As each district transmits quality assured ozone, surface meteorology, and nitrogen species data to the EPA AIRS system, they would also provide this data to CE-CERT and to ARB RD for preliminary analyses. Using the audit report and IOP summaries, a preliminary report analyzing these data will be transmitted to all districts 90 days after all of the data is available to ARB RD. This report will provide statistical intercomparison of collocated measurements at Azusa (TDLAS, TECO 42CY type b, and denuder for HNO₃)(denuder and stack filter for NH₃), at Riverside (denuder and stack filter for NH₃), and at Los Angeles North Main, at Chino, and at Diamond Bar (TECO 42CY type b, and denuder for HNO₃). The report will include an analysis of total NO_y vs. the sum of nitrogen species measured at Azusa, at Calabasas, and at Cajon Pass. Finally, the report will include analyses of NO_y samples from background, source, and downwind locations and their correlation with episode types, meteorology, ozone concentrations, and ratios of important age determining VOC's. All quality assured (Level Ib) data is transmitted to ARB TSD.

10. Problem Resolution

10.1 If quality control and performance audit issues arise which cannot be resolved between participants, a special session of the QA and AQ working groups will meet in a low probability IOP window to resolve them.

11. References

Williams, E.J., Baumann, K., Roberts, J.M., Bertman, S.B., Norton, R.B., and Fehsenfeld, F.C., et al., Intercomparison of NO_y Measurement Techniques, submitted to Journal of Geophysical Research, Southern Oxidant Study Special Issue, March 31, 1997.

NARSTO-Northeast Memo from Mueller & Roberts Regarding Data Qualification Statements, September 29, 1996.

Calvert, J.G., Apel, E., Williams, E., Parrish, D., Springston, S., Zika, R., Recommendations for Modification of the SCION Network NO_y, RH, and CO Measurement Equipment, September 24, 1993.

Fujita, E., Bowen, J., Green, M.C., and Moosmüller, H., 1997 Southern California Ozone Study (SCOS97) Quality Assurance Plan, Draft April 4, 1997 version.