

APPENDIX A
MEASUREMENT METHODS

A. MEASUREMENT APPROACH

Field monitoring includes continuous measurements over several months and intensive studies that are performed on a forecast basis during selected periods when episodes are most likely to occur. The continuous measurements are made in order to assess the representativeness of the intensive study days, to provide information on the meteorology and air quality conditions on days leading up to the episodes, and to assess the meteorological regimes and transport patterns which lead to ozone episodes. The intensive study components are designed to provide a detailed aerometric database which, along with the emission estimates and continuous monitoring data, can be used to improve our understanding of the causes of pollutant episodes in the study region and to provide data for input to the models and for model evaluation. This section describes the options for continuous and intensive air quality and meteorological measurements (surface and aloft) to be made during CCOS.

A.1 Surface Meteorology

The types of surface meteorological measurements needed for this study include measurements of wind speed, wind direction, and temperature. Measurements of humidity, pressure, visibility, solar radiation, and ultraviolet radiation are also available at some sites. Within the study area (modeling domain), these measurements are provided by several existing networks of sites operated by several organizations including:

- Surface Airways Observations sites from the National Weather Service (NWS), operating in conjunction with the Federal Aviation Administration
- California Irrigation Management Information System sites from the California Department of Agriculture
- Remote Automated Weather Station sites from the Bureau of Land Management, California Department of Forestry, National Park Service, and U.S. Forest Service
- APCD/AQMD Aerometric Monitoring Station sites from the Bay Area AQMD, Kern County APCD, San Joaquin Valley Unified Control District, Santa Barbara APCD, Ventura County APCD, Mojave Desert AQMD, and California Air Resources Board
- Military installations
- Private companies
- Public organizations such as universities

A.1.1 Surface Wind Speed and Direction

Wind speeds are measured with anemometers at 10 m above ground to minimize the effects of nearby structures and vegetation. Anemometers, both cup and propeller type, work on the principal that the rate of rotation about a vertical or horizontal shaft is proportional to the speed of the air flow past the sensor. Anemometers used for scientific monitoring should have a

quick response to changes in wind speed as well as a low threshold for rotation for conditions of very light winds. Acceptable precision levels for anemometers are ± 0.5 m/s for most air quality studies (e.g., Thullier et al., 1993).

Wind direction measurements are made with wind vanes that orient themselves with the direction of the wind. High quality bearings are used for sensitivity and direction is resolved with an internal potentiometer that has a reference location of zero which must be physically aligned with true north when in position on the tower. The position of true north is determined with a sensitive compass or solar reference and the north position of the wind vane is then aligned in this direction. Care must be taken in the alignment procedure or in subsequent resolution of the wind direction vectors to account for the magnetic declination at the observation site.

Averaging can be done over intervals of a few points to the entire data record. The interval must be chosen with respect to the phenomena being observed. As shorter averaging intervals are chosen, periodic motion may be revealed when the period is significantly greater than the averaging period. The averaging process attenuates small-scale fluctuations due to turbulence. The averaging interval must contain sufficient data points to constitute a reasonable average, eliminating the small scale turbulent fluctuations and instrument derived errors such as response sensitivity and anemometer run-up and run-down. Five minutes is a reasonable compromise between the need to acquire a statistically valid number of samples and the nature of phenomena such as wind gusts and dispersion.

The time average of horizontal wind direction standard deviation (σ_θ) can be calculated as from one second observations over a period of 5 minutes or less (Greeley and Iversen, 1985). This minimizes the influence of the wind flow which may be non-stationary in both speed and direction over longer averaging periods.

Table A.1-1 provides specifications for CCOS/CRPAQS wind sensors. Instruments meeting these specifications were used in the Southern California Ozone Study (SCOS97-NARSTO) (Fujita et al., 1997) and the Northern Front Range Air Quality Study (NFRAQS) (Chow et al., 1998). SCOS97 performance audits were satisfactory with ± 0.25 m/s for wind speeds between 0 and 5 m/s, and $\pm 5\%$ for wind speeds greater than 5 m/s. The NFRAQS intercomparison of meteorological sensors concluded that from collocated instruments were comparable to each other at the 95% confidence level when sampling the same environment. NFRAQS and SCOS97 also demonstrated a high level of instrument functionality, with few episodes of missing data at any of the seven monitoring sites.

A.1.2 Surface Relative Humidity

Humidity indicates the amount of water vapor in the air. The most common reference for this property of the air is the relative humidity (RH), the ratio of the amount of water vapor actually in the air to the amount the air could hold at a given temperature and pressure, that is, the ratio of the actual to the saturated vapor pressure.

Accurate measurements at high RH (>85%) is important to atmospheric transformations and to visibility reduction. An accuracy of 2-3% RH is needed to adequately estimate aerosol properties. A 2-3% accuracy for RH over the 90-100% RH is attainable by several RH sensors (e.g. Vaisala, Rotronics) and corresponds to $\pm 0.5^{\circ}\text{C}$ when expressed as dewpoint temperature. Motor-aspirated radiation shields ensure adequate ventilation and exposure rates (U.S. EPA, 1989).

A.1.3 Surface Temperature

Equivalent resistance temperature detectors (RTD (e.g., Vaisala, Rotronics, Climatronics, Campbell Scientific, etc.) are used at the meteorological sites. Motor-aspirated radiation shields ensure adequate ventilation and exposure rates, according to U.S. EPA quality assurance requirements (U.S. EPA, 1989). The accuracy ($\sim 0.15\text{-}0.5^{\circ}\text{C}$) and functional precision (0.1°C) of these sensors are sufficiently good and they can be used to infer lapse rates and thus stability (e.g., estimates of ΔT) when several sensors are used on a tower. Temperature sensors are normally located at 5 m above ground level. Table 10.1-1 presents specifications for the Vaisala and Campbell Scientific (CV) temperature ($^{\circ}\text{C}$) and relative humidity (%) sensors

A.1.4 Surface Pressure

Pressure is routinely measured by the National Weather Service in terms of altimeter setting or sea level pressure. The altimeter setting is the pressure value to which an aircraft altimeter scale is set so it will indicate the altitude above mean-sea-level of the aircraft on the ground at the location the pressure value was determined. The sea level pressure is the atmospheric pressure at mean sea level. It is either measured directly or obtained by the empirical reduction of station pressure to sea level. When the earth's surface is above sea level, it is assumed that the atmosphere extends to sea level below the station and that the properties of the fictitious air column are related to conditions observed at the station.

A.1.5 Solar Radiation

Solar radiation sensors are operated at several existing ARB sites throughout the region. The measurements employ a solar pyranometer that collects direct solar beam and diffuse sky radiation passing through a horizontal beam.

A.2 Upper-Air Wind Speed, Wind Direction, and Temperature

The types of upper-air meteorological measurements needed include wind speed, wind direction, temperature, and mixing height. Measurements of humidity are also useful where they are available at some sites. A comprehensive discussion of the accuracy and methodology of upper air measurements is provided in the SJVAQS/AUSPEX Meteorological Field Measurement Program report (Thuillier, 1994).

A.2.1 Radar Wind Profilers

Radar wind profilers (RWPs) provide continuous remote measurements of wind speed and direction to altitudes of ~ 3 km AGL. The profilers emit short pulses of generally 915 MHz

electromagnetic radiation which scatter off inhomogeneities in the index of refraction of an air mass. By emitting energy directionally in three orthogonal components, the received scattered radiation provides estimates of wind speed and direction. Because of the finite length of the emitted pulse train, vertical resolution is limited to approximately 100 m. Echoes received during the detector downtime cannot be processed and this raises the threshold height to approximately 100 m above ground level. The typical five-degree beam width also limits the resolution of wind direction in a height dependent manner. There are general trade-offs between maximum range and vertical resolution and between averaging time and accuracy.

Radar wind profiler data are generally reported as 15-minute up to hourly averaged data and are representative of a three-dimensional cell. Because wind vectors may vary significantly over the course of an hour, the near-instantaneous radiosonde measurements may not compare well with radar wind profiler measurements on a case-by-case basis. However, if radiosondes and wind profilers are deployed in areas with similar winds, the statistical distribution of winds may be expected to be reasonably similar. The RWP is highly sensitive to stray electromagnetic signals and stationary or solid objects in the beam paths or their side lobes. Thus, it should be sited away from large objects such as buildings and trees and away from frequent overflights by aircraft.

A.2.2 Radio-Acoustic Sounding Systems (RASS)

Temperature aloft up to 500-700 m can be characterized using a RASS. The RASS essentially uses collocated radio wave and acoustic sources such that radio waves are scattered off the acoustic wavefronts. The propagation velocity of the acoustic wave fronts is then measured, which can be related to the (virtual) temperature of the air. This effort could install one radar profiler with RASS at critical locations along major transport paths, such as mountain passes or the coastal shoreline, for example, near Cajon and Banning Passes and along the downwind shorelines in San Diego and Santa Barbara. There is considerably less accuracy in the RASS temperature profiles compared to the those obtainable from tethered sonde measurements, particularly in areas of complex terrain where radar side lobes may present a problem. However, the RASS temperature data may be compared to QA radiosonde or tethered sonde temperature data because the virtual temperature can also be calculated from the sonde measurements of ambient temperature, dew point or relative humidity, and pressure. A favorable comparison under representative conditions would increase confidence in the RASS data at these sites.

A.2.3 Acoustic Sounders (Sodars)

The sodar uses an observational process that is similar to the RWP except that the sodar uses pulses of acoustic instead of electromagnetic energy. The sodar then detects returned acoustic energy scattered from turbulent density fluctuation (instead of index of refraction fluctuations). It provides hourly averaged wind speed and direction up to a 500-600 m maximum range with a threshold height of approximately 50-60 m. The sodar can operate routinely with little or no on-site care, but compared to radiosondes it does not measure humidity, and the equipment is expensive. The sodar is highly sensitive to extraneous sources of sound. Thus, it should be sited away from substantial and continuous noise sources such as heavily traveled roads. The sodar acoustic emissions are audible and may disturb nearby residents, which can be

a siting disadvantage compared with the RWP. With the lower vertical range, sodars should be deployed in areas of lower expected mixing heights, such as in marine layers.

A.2.4 Radiosondes

Upper-air wind speed, wind direction, and temperature can be collected by in-situ systems or by remote sensing instruments. The most commonly used in-situ systems rely on a balloon-borne sensor (radiosonde), carried aloft by a freely ascending weather balloon to measure atmospheric pressure, temperature, and moisture (relative humidity or wet bulb temperature). These thermodynamic variables are used to compute the altitude of the balloon. Wind speed and direction aloft are determined by measuring the position of the balloon as it ascends. The position data can be obtained by tracking the balloon from a fixed ground station using radio direction finding techniques (RDF) or optical tracking, or they can be obtained using one of the radio navigation (NAVAID) networks, such as loran or Global Positioning System (GPS). By measuring the position of the balloon with respect to time and altitude, horizontal wind vectors can be computed that represent the layer-averaged wind speed and wind direction for successive layers. Balloons can also measure relative humidity, which is not detected by proven remote sensing methods.

The vertical resolution of the wind data is typically 50-200 m (depending on altitude and the type of sounding system used), and the range is from about 100 m above ground level (AGL) to altitudes as high as 10,000 m altitude or higher. Radiosondes provide wind data that are averaged over short vertical distances and are thus nearly instantaneous measurements at a particular location. Although the radiosonde directly measures temperature and humidity during the short balloon flight, it is only a "snapshot" at each level of the atmosphere. As the radiosonde rises, it is transported downwind, so measurements are not made above a fixed location, as within a wind profiler, for example.

For air pollution studies such as this, balloon sounding systems can provide relatively complete profiles of winds, temperature, and moisture in the boundary layer and lower troposphere. Balloon soundings usually can be made two to eight times per day on selected sampling days within reasonable budget constraints, but they are not cost-effective for long-term monitoring.

A.2.5 Tethered Balloons

Tethered balloons employ an instrument package, called a tethersonde, which provides in situ measurements of wind speed and direction, temperature, dew point, and pressure. The package is deployed on a blimp-shaped helium balloon that is tied by light cord to a mechanical winch system. The altitude range is usually limited to less than 1 km; wind speeds over 10 meters per second may cause loss of the balloon. The tethersonde transmits the information back to a ground station, with values taken every few seconds corresponding to one value every 2-3 meters apart for average ascent and descent speeds. The accuracy of the measurements compares to that of any surface station, since the sonde package is akin to a miniature surface station carried aloft by the balloon. Advantages of the tethersonde include much better vertical resolution with no threshold height compared to the RWP or sodar. Once the system is set up

and manned, soundings can be taken through the surface layer as often as every 15 minutes. However, disadvantages of the tethered sonde include site setup/breakdown time, the need for continual manning during operations, and the difficulty in obtaining FAA permits to operate within 8 km of any airport.

A.2.6 Sonic Anemometers

Sonic anemometers deployed at surface sites would provide estimates of turbulent fluxes for the modeling effort. The variations in sound propagation over a short (30 cm) path are typically sampled at 10 Hz, providing an estimate of turbulent fluctuations over that path. One-dimensional sonic anemometers measure vertical turbulent flux, while three-dimensional sonic anemometers include turbulent fluxes in the two horizontal dimensions. These data provide boundary layer characterization, representative of the type of terrain over which the measurement is taken. Urban effects could be better incorporated in the mesoscale model. The measurement could provide better dispersion estimates for models run in the data assimilation mode, and provide real-world measurements against which model estimates of turbulent flux are compared.

A.3 Routine Surface Air Quality

The California Air Resources Board and local air pollution control districts operate a network of sampling sites that measure ambient pollutant levels. This network consists of three types of surface air quality monitoring stations. The National Air Monitoring Stations (NAMS) were established to ensure a long term national network for urban area-oriented ambient monitoring and to provide a systematic, consistent database for air quality comparisons and trend analysis. The State and Local Air Monitoring Stations (SLAMS) allow state and local governments to develop networks tailored to their immediate monitoring needs. Special purpose monitors (SPM) fulfill very specific or short-term monitoring goals. SPMs are typically used as source-oriented monitors rather than monitors which reflect the overall urban air quality. Data from all three types are submitted by state and local agencies to EPA's Aerometric Information Retrieval System (AIRS), which serves as the national repository for air quality, meteorological and emissions data.

Under Title I, Section 182, of the 1990 Amendments to the Federal Clean Air Act, the EPA proposed a rule to revise the current ambient air quality surveillance regulations. The rule requires implementing a national network of enhanced ambient air monitoring stations (Federal Register, 1993). States with areas classified as serious, severe, or extreme for ozone nonattainment are required to establish photochemical assessment monitoring stations (PAMS) as part of their State Implementation Plan (SIP). In the CCOS area, PAMS are required in Sacramento, Fresno and Bakerfield metropolitan areas. Each station measures speciated hydrocarbons and carbonyl compounds, ozone, oxides of nitrogen, and surface meteorological data. Additionally, each area must monitor upper air meteorology at one representative site. The program was phased in over a five-year schedule, beginning in 1994, at a rate of at least one station per area per year. Intended applications for the PAMS database include ozone and precursor trends, emission inventory reconciliation and verification, population exposure analyses, photochemical modeling support, and control strategy evaluation.

There are 185 active monitoring stations in northern and central California. Table A.1-2 contains a list of the monitoring sites and the air quality parameters measured at each site. Of the active sites, 130 measure ozone and 76 measure NO_x. Carbon monoxide and total hydrocarbons are measured at 57 and 14 sites, respectively. Data from these sites are routinely acquired and archived by the ARB and Districts. The following is a brief description of the measurement methods that are commonly used at routine air quality monitoring stations.

A.3.1 Ozone

Ozone is continuously measured either by ultraviolet absorption photometry or by gas-phase ethylene-ozone chemiluminescence. In the ultraviolet analyzer, a mercury vapor lamp is used to produce ultraviolet radiation at 254 nm which is absorbed by the ozone in the air sample. The ozone signal is determined by the difference between ambient air containing ozone and ambient air with the ozone removed or scrubbed. The ultraviolet analyzer is calibrated by comparison with an ozone photometer which is certified as a transfer standard. The transfer standard is certified against absolute ozone photometers located at the California Air Resources Board test and laboratory facilities. The minimum detectable level of UV monitors is about 2-5 ppbv. Accuracies and precisions are on the order of 10-15 percent or 2-5 ppbv, whichever is larger. Interferences with the UV measurement method include any gas or fine particle that absorbs or scatters light at 254 nm. Gaseous inorganic compounds normally found in the atmosphere, including NO₂ and SO₂, do not interfere, and particles are largely removed by a pre-filter. The most likely interferent is gaseous hydrocarbon compounds that are strong absorbers at 254 nm and are either partially or completely absorbed onto the scrubber. Examples are aromatic compounds, such as benzene and substituted benzenes. Interferences from hydrocarbons can account for a positive bias in the UV measurement for ozone of up to 40 ppb based on the concentration of the interferences occurring during peak ozone periods (Leston and Ollison, 1992). Kleindienst *et al.* (1993) observed about a 3 percent interference with ozone measurements under hydrocarbon loadings typical of ambient smoggy conditions. Water vapor may also interfere with the UV method when water vapor concentrations are high and variable. These interferences appear to be due to the condensation of water vapor on imperfect absorption cell windows.

The ozone/ethylene chemiluminescence method (ECL) is a Federal Reference Method for measuring ozone in ambient air (EPA, 1971). The ECL method is based on the reaction of ozone with ethylene, which produces formaldehyde in an electrically excited state and, on transition to the ground state, emits light in the visible range. This reaction is rapid and specific to ozone and takes place in a chamber coupled to a sensitive photomultiplier tube. Under controlled conditions, the signal produced by the ozone-ethylene reaction is proportional to the ozone concentration in the reaction chamber and with proper calibration it is proportional to ambient ozone concentrations. The chemiluminescence analyzer is calibrated in the same manner as the ultraviolet analyzers. The minimum detection level of commercial ECL monitors is about 2-5 ppbv. Accuracies and precisions are on the order of 10-15 percent or 2-5 ppbv, whichever is larger. The only major interference for measuring ozone by the ECL method is water vapor. The positive interference ranges from 3-12 percent. However, this interference can be adjusted for by calibrating the ECL monitors at humidities expected during peak ozone periods. In practice, this is rarely done.

The Air Pollution Control Districts measure ambient ozone concentrations with instruments made by several different manufacturers. All analyzers employ the UV photometric technique to determine ozone concentration. All analyzers have been designated as EPA Equivalent Methods. The following analyzers are deployed in the networks:

Thermo Environmental Inc., model 49
Dasibi Environmental, model 1003
Advanced Pollution Instrumentation, Inc., model 400

A.3.2 Nitrogen Oxides

Nitric oxide (NO) is continuously measured by the chemiluminescence nitric oxide-ozone method (OCM). This method is based on the gas-phase chemical reaction of NO with ozone. In this method an ambient air is mixed with a high concentration of ozone so that any NO in the air sample will react and thereby produce light. The light intensity is measured with a photomultiplier and converted into an electronic signal which is proportional to the NO concentration. To measure NO_x concentrations, the sum of NO and NO₂ (nitrogen dioxide), the air sample is first reduced to NO, either by a heated catalyst (molybdenum or gold in the presence of CO) or chemically using FeSO₄, adding to the NO already present in the sample, then into the reaction chamber for measurement as described above. The NO₂ concentration is derived by subtracting the NO concentration measurement from the NO_x concentration measurements.

Standard sensitivity instruments have detection limits of about 0.5 to 3 ppb (60 sec averaging times) and are suitable for air quality monitoring in urban and suburban areas. Thermo Environmental Instruments, Inc. (TEI) Model 42C and Monitor Labs 8440 and 8840 are examples of this type of instrument. These and similar instruments from Columbia Scientific and Bendix have been used widely by federal, state, and local agencies for routine monitoring of NO and NO₂ (actually NO_x minus NO plus other interfering nitrogen oxides). Trace level instruments, such as the TEI Model 42C-TL have detection limits of about 50 ppt (120 sec averaging times) and are better suited in rural and background sites, and onboard instrumented aircrafts.

The reduction of NO₂ to NO by these methods is not specific and a number of other nitrogen-containing species are reduced to NO that can interfere with the measurement of NO₂ (e.g., HNO₃, PAN, N₂O₅, HONO, and NO₃). Therefore the thermal catalytic method is used to measure NO, and then NO plus other nitrogen oxides as a group. If the group is not well defined, it is referred commonly as NO_x, since the species included in the group depend on factors such as inlet and line losses and environmental factors. HNO₃ is most prone to line losses. Placing the converter as close to the sample inlet as possible minimizes these losses. Chemiluminescence analyzers that are configured in this manner are commonly known as NO_y analyzers. NO_y, or reactive nitrogen oxides, consists of a variety of species, the most abundant of which are NO, NO₂, PAN and HNO₃. TEI Model 42CY is configured with dual converters, which allows estimates of HNO₃ by difference between the signals with and without an in-line nylon filter or NaCl impregnated fiber denuder.

A.3.3 Photochemical Assessment Monitoring Stations (PAMS) Program

A maximum of five PAMS sites are required in affected nonattainment areas, depending on the population of the Metropolitan Statistical Area/Consolidated Metropolitan Statistical Area (MSA/CMSA) or nonattainment area, whichever is larger. PAMS networks are based on selection of an array of site locations relative to ozone precursor source areas and predominant wind directions associated with high ozone events. Specific monitoring objectives associated with each of these sites result in four distinct site types.

Type 1 sites are established to characterize upwind background and transported ozone and its precursor concentrations entering the area and to identify those areas which are subjected to overwhelming transport. Type 1 sites are located in the predominant morning upwind direction from the local area of maximum precursor emissions during the ozone season. Typically, Type 1 sites will be located near the edge of the photochemical grid model domain in the predominant upwind direction from the city limits or fringe of the urbanized area.

Type 2 sites are established to monitor the magnitude and type of precursor emissions in the area where maximum precursor emissions are expected. These sites also are suited for the monitoring of urban air toxic pollutants. Type 2 sites are located immediately downwind of the area of maximum precursor emissions and are typically placed near the downwind boundary of the central business district. Additionally, a second Type 2 site may be required depending on the size of the area, and will be placed in the second-most predominant morning wind direction.

Type 3 sites are intended to monitor maximum ozone concentrations occurring downwind from the area of maximum precursor emissions. Typically, Type 3 sites will be located 10 to 30 miles downwind from the fringe of the urban area.

Type 4 sites are established to characterize the extreme downwind transported ozone and its precursor concentrations exiting the area and identify those areas that are potentially contributing to overwhelming transport in other areas. Type 4 sites are located in the predominant afternoon downwind direction, as determined for the Type 3 site, from the local area of maximum precursor emissions during the ozone season. Typically, Type 4 sites are located near the downwind edge of the photochemical grid model domain.

The current status of the implementation of PAMS by local air pollution control districts in central California is outlined in Table A.1-3. PAMS precursor monitoring is conducted annually in California during the peak ozone season (July, August and September) according to the schedule shown in Table A.1-3. Eleven PAMS sites will be in operation during summer 2000 (four in Sacramento County, four in Fresno County, and three in Kern County). The table includes minimum network requirements that are specified in the EPA rule and the alternative network specifications submitted to EPA by ARB on behalf of the affected districts in the state. The California Alternative Plan was deemed by EPA to satisfy the PAMS monitoring objectives and has been approved for use by districts in California.

EPA methods TO-14 and TO-11 are specified by the EPA for sampling and analysis of speciated hydrocarbons and carbonyl compounds, respectively (EPA, 1991). Table A.1-

4contains the minimum list of targeted hydrocarbon species. For carbonyl compounds, state and local agencies are currently required to report only formaldehyde, acetaldehyde and acetone. The ARB and districts laboratories may be able to quantify and report several C₃ to C₇ carbonyl compounds that appear in the HPLC chromatograms. 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. 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 (0-3 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.

Total nonmethane hydrocarbon (NMHC) concentrations are also measured by analysis of the canister samples by preconcentration direct injection flame ionization detection (PDFID). 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 air is burned in a hydrogen flame creating a quantity of ions from the hydrogen molecules in the air sample. The ions conduct a small electrical current which is measured by an electrometer, which in turn produces an electronic signal proportional to the number of ions collected. Thus, the total hydrocarbon data are reported as parts per billion carbon (ppbC). Total nonmethane hydrocarbon (NMHC) concentrations are monitored at some PAMS sites by automated-Preconcentration Direct Injection Flame Ionization Detection (PDFID) (e.g., Xontech 850).

A.4 Supplemental Measurements of Ozone

Supplemental air quality measurements are needed during intensive operational periods (IOPs) in order to examine the three-dimensional distribution of ozone in the study area and to quantify some of the important species, other than those routinely monitored, which participate in ozone photochemistry.

A.4.1 Ozonesondes

In addition to atmospheric pressure, temperature, and moisture (relative humidity or wet bulb temperature), balloon-borne radiosondes can be equipped with instrumentation to measure the vertical distributions of ozone mixing ratios. Ozonesondes have lower quantifiable limit of less than 15 ppb with precision of ± 5 ppb or $\pm 10\%$.

Ozonesondes provide ozone data that are averaged over short vertical distances and are thus nearly instantaneous measurements at a particular location. The data are only "snapshots" at each level of the atmosphere. As the radiosonde rises, it can be transported downwind, so measurements are not made above a fixed location. The typical response time of the instrument

(> 80% of step change in 1 minute) may affect accuracy during ascent through sharp gradients in ozone mixing ratios. Balloon soundings usually can be made two to eight times per day on selected sampling days within reasonable budget constraints, but they are not cost-effective for long-term monitoring. Use of ozonesondes are most cost-effective when coupled to existing radiosonde releases.

A.4.2 Ozone Aloft — Lidar Measurements

In the more than 30 years since the invention of the laser, the evolution of lidar (light detection and ranging) technology has led to great advances in atmospheric remote sensing (Measures, 1984). A particular form of lidar, the Differential Absorption Lidar (DIAL) has made it possible to measure the concentration distributions of many tropospheric trace gases and pollutants (Rothe *et al.*, 1974a; Measures, 1984; Grant *et al.*, 1992).

A basic lidar system consists of a transmitter and a receiver located next to each other. The transmitter, typically a pulsed laser, sends a short pulse of collimated light into the atmosphere. A small part of this light pulse is scattered back into the receiver by atmospheric particles and gas molecules. Light scattered at a distance r will arrive at the receiver after a round trip time $t = 2r/c$, where c is the speed of light. The lidar return signal S as a function of distance r is described by the lidar equation (Measures, 1984).

$$S(r, \lambda) = A(r, \lambda) C(\lambda) \frac{\beta(r, \lambda)}{r^2} \exp\left[-2 \int_0^r \sigma(x, \lambda) dx\right] ,$$

where A is the overlap integral between the transmitted laser beam and the field of view of the telescope, C is the system constant, β is the backscattering coefficient, σ is the volume extinction coefficient, and λ is the wavelength of the laser. While the overlap integral A can be determined from measurements in a homogeneous atmosphere, the system constant C is generally unknown and for each measured signal $S(r, \lambda)$ there are two atmospheric parameters $\beta(r, \lambda)$ and $\sigma(r, \lambda)$ one would like to determine. The lidar equation is therefore under-determined and cannot be solved without additional assumptions or data. To obtain at least semi-quantitative information about the range-resolved atmospheric extinction, one generally assumes an empirical relationship between the backscattering coefficient $\beta(r, \lambda)$ and the extinction coefficient $\sigma(r, \lambda)$ (Gibson, 1994), together with an estimate of a boundary condition for the extinction coefficient within the measurement range (Fernald *et al.*, 1972; Klett, 1981). The mathematical technique used for this semi-quantitative analysis is based on Hitschfeld's work for the analysis of radar data (Hitschfeld and Bordan, 1954) and is often referred to as Klett inversion (Klett, 1981).

Differential absorption lidar (DIAL) is a multi-wavelength lidar that uses the wavelength-dependent absorption of atmospheric constituents to measure their range resolved concentration (Measures, 1984). For this purpose, the extinction coefficient σ at a distance r and wavelength λ_i may be written as

$$\sigma(r, \lambda_i) = \sigma_i(r) + \alpha_i n(r) ,$$

where σ_i is the extinction coefficient due to scattering at λ_i , α_i denotes the absorption coefficient at λ_i , and n is the concentration of the absorbing gas. If the lidar equation is applied at two different wavelengths λ_i and λ_j with substantially different absorption coefficients, the concentration n at range r can be calculated from the ratio of the lidar signals at the two wavelengths as

$$n(r) = \frac{1}{2\Delta\alpha_{ij}} \frac{d}{dr} \left[\ln \frac{S_j(r)}{S_i(r)} \right] - \frac{\Delta\sigma_{ij}(r)}{\Delta\alpha_{ij}} + \frac{1}{2\Delta\alpha_{ij}} \frac{d}{dr} \left[\ln \frac{\beta_i(r)}{\beta_j(r)} \right] + \frac{1}{2\Delta\alpha_{ij}} \frac{d}{dr} \left[\ln \frac{A_i(r)}{A_j(r)} \right],$$

where $\alpha_{i,j} = \alpha_i - \alpha_j$ and $\sigma_{i,j} = \sigma_i - \sigma_j$. The laser line (wavelength) with the larger (smaller) absorption coefficient is referred to as “on-line” (“off-line”). The first term in this equation is the main term, while the others are correction terms; the second term and the third term, respectively, are corrections for differential aerosol extinction [$E_{i,j}$] and backscatter [$B_{i,j}$] between the two wavelengths, whereas the fourth term is a correction for the incomplete overlap [$O_{i,j}$]. The extinction correction vanishes ($[E_{i,j}] = 0$) if the extinction due to scattering is identical for λ_i and λ_j , the backscatter correction vanishes ($[B_{i,j}] = 0$) if the ratio of the backscattering coefficients for λ_i and λ_j is independent of distance, and the overlap correction vanishes ($[O_{i,j}] = 0$) if the ratio of the overlap integrals for λ_i and λ_j is independent of distance. In contrast to extinction and backscattering corrections, the overlap correction is a pure system parameter, independent of atmospheric conditions, requiring only an initial system calibration.

Several criteria pollutants (i.e., ozone (O_3) (Molina and Molina, 1986), sulfur dioxide (SO_2) (Manatt and Lane, 1993), and nitrogen dioxide (NO_2) (Davidson *et al.*, 1988)) have absorption features in the middle ultraviolet (shown in Figure A.1-1) where an absence of disturbing interference from other atmospheric gases, large backscattering cross-sections for both particles and gases, low solar background, and the commercial availability of both tunable and fixed frequency lasers as radiation sources make the development of appropriate active remote sensors feasible.

In particular, SO_2 and NO_2 have enough fine structure in their spectra so that their concentration can be measured with DIAL utilizing two closely (≈ 1 nm) spaced wavelengths (Rothe *et al.*, 1974b; Browell, 1982; Galle *et al.*, 1988). In this case differential extinction and backscattering corrections are negligible and the systematic errors of the DIAL measurement become independent of aerosol loading. However, to utilize the spectral fine structure efficiently, tunable lasers have to be used.

In contrast, the O_3 absorption spectrum is quite smooth, necessitating a wider spacing between the two wavelengths, on the order of 20 nm. Therefore, differential extinction and backscattering corrections become important. While the extinction correction is generally negative (i.e., the measured concentration is too high without correction) and on the order of a few ppb, the backscattering correction can become much larger in regions with large gradients of aerosol concentration. For small aerosol loading the backscattering is dominated by Rayleigh scattering with its λ^{-4} wavelength dependence, while for large aerosol loading particle scattering with its approximately λ^{-1} wavelength dependence contributes most of the backscattering. Therefore, a rapid change with distance r from polluted to clear air, as encompassed for example

in inversion layers, requires a positive backscattering correction, while the opposite change requires a negative correction. In the case of thin aerosol layers this can lead to a dispersion shape of the required correction or of the uncorrected, measured ozone concentration.

To calculate the backscattering correction one needs range resolved data for the aerosol backscatter coefficient at both DIAL wavelength. Generally, one can guess the wavelength dependence of the backscattering coefficient (Charlson, 1972) and may try to obtain the backscattering coefficient at the “off” wavelength from a lidar inversion (Klett, 1981). However, even this task is quite difficult in the near ultraviolet, especially in the lower troposphere (Kovalev and Moosmüller, 1994).

Ozone DIAL measurements can also be influenced by the simultaneous optical absorption by SO₂ and to a far lesser degree by NO₂. Generally this effect becomes only problematic in power plant plumes and can be minimized by proper selection of laser wavelengths (Moosmüller *et al.*, 1994).

While DIAL systems have been used for the remote measurement of atmospheric pollutants for more than two decades (Rothe *et al.*, 1974a), their hardware, use, and data analysis procedures have not become routine. They still require close attention, skilled personnel and considerable resources. Of particular importance are well designed, implemented, and tested hardware and data analysis algorithms. Especially the interdependence between hardware and data analysis algorithms has to be stressed. Generally, their performance evolves, and hopefully improves, together in an iterative fashion. The successful use of these systems is highly dependent on skilled, experienced, and dedicated operators and developers, which are often identical.

It should be noted that range, precision, spatial, and temporal resolution of DIAL measurements are closely related and fair comparisons between different systems can only be made if all of these parameters are given. Lower and upper range limits are of different importance for zenith looking ground based systems and nadir looking airborne systems. For ground based systems the lower range limit is of particular importance as it is identical to the height above ground at which measurements start for a zenith looking operation. For airborne systems, the flight altitude can generally be chosen so that the upper range limit approximates the height above ground.

The precision of the DIAL measurements is generally best around the distance from the system where complete overlap between laser beams and field of view of the telescope is obtained. With increasing distance from the system the signal level and consequently the signal-to-noise ratio and precision of the DIAL measurement deteriorate. For ground based systems this trend is frequently reduced by decreasing the range resolution with increasing distance. This is a sensible approach, as the scale of atmospheric structure generally increases with increasing altitude. However, for airborne, downlooking lidar systems the opposite is true — the finer scale atmospheric structure is generally encountered towards the far end of their measurement range, close to the ground where the measurement precision is the lowest. In addition, these systems are moving, with a typical averaging time of 15 s corresponding to about 1 km of horizontal movement. If atmospheric structure smaller than the distance covered in the averaging time (e.g.,

1 km) is encountered, the data averaging becomes rather problematic. Both these problems can make measurements close to the ground difficult for airborne, downlooking lidar systems.

Aerosol extinction and backscattering corrections have not been implemented in the routine data analysis for any of the following systems. Its inclusion would be a worthy goal for the analysis of CCOS data.

Ground-Based Ozone Profiling Atmospheric Lidar (OPAL)

The Atmospheric Lidar Division of NOAA's Environmental Technology Laboratory in Boulder has developed a transportable ozone and aerosol lidar specifically for the measurement of ozone in the boundary layer and the lower free troposphere. This lidar has been employed in several field experiments:

- July 1993, Intercomparison Experiment in Davis, CA, sponsored by ARB (Zhao *et al.*, 1994)
- September 1993, LAFRS Experiment in Claremont, CA, sponsored by ARB (Zhao *et al.*, 1994)
- August, 1995, Ozone Transport Experiment in Victorville, CA, sponsored by ARB
- October–November 1995, Table Mountain Vertical Ozone Transport and Intercomparison Experiment in Boulder, CO, sponsored by NOAA.
- June–August 1997, Southern California Ozone Study (SCOS97-NARSTO) (Fujita *et al.*, 1998)
- Summer 1999, Southern Oxidants Study (SOS99) in Nashville and in Atlanta.

OPAL is based on a solid state laser, the Nd:YAG laser with a fundamental wavelength of 1064 nm and a pulse repetition rate of up to 10 Hz. The third harmonic of this wavelength (i.e., 355 nm) with an operating pulse energy of 7–10 mJ is used for aerosol profiling with a range of about 9 km. The fourth harmonic of the fundamental (i.e., 266 nm) with an operating pulse energy of 20–30 mJ is used as “on-line” for the ozone measurement. The “off-line” for the ozone measurement is generated by Raman shifting the second harmonic (i.e., 532 nm) by the vibrational frequency of the deuterium molecule (i.e., 2987 cm^{-1}) to 632.5 nm, and subsequent sum-frequency mixing of 532 nm and 632.5 nm, yielding an “off-line” at 289 nm. This process takes place in a specially designed Raman cell, yielding a pulse energy of 1–2 mJ. This process utilizes the laser energy better than the more direct Raman shifting of the fourth harmonics (Ancellet *et al.*, 1989; Zhao *et al.*, 1994), while yielding the same wavelength.

The receiver section utilizes an 8”-diameter telescope to collect the backscattered light. Dichroic beamsplitters separate the light from the different laser lines for the detection by photomultiplier tubes. The signals are digitized by 12 bit A/D converters for the subsequent analysis.

Ozone measurements can be obtained for a range of up to 3 km under moderate to high surface ozone concentrations (< 150 ppb) while, for extremely high concentrations, a range of 2 km can still be achieved. Aerosol profiles for a maximum range of about 10 km can be obtained with a range resolution of 15 m. The lower range limit is very good (≈ 50 m) due to the use of an innovative technique for the compression of the lidar dynamic range (Zhao et al., 1992). Using the 266/289 nm wavelengths pair, averaging 600-1200 pulses (5-10 min at 2 Hz or 1-2 min at 10 Hz), the retrieval of ozone concentrations has a range resolution from a few tens of meters in the lower boundary layer to 150-200 m at about 3 km. Range resolution decreases with height because the signal-to-noise ratio decreases with distance.

The measurement direction of the lidar system can be scanned in one dimension from 30° to 150° yielding a two dimensional ozone measurement. The vertical scanning capability provides a valuable internal system check, frequent calibration, and was desired for both monitoring and modeling studies. This system is being modified to add a new wavelength at 299 nm, to provide a longer maximum range of ozone measurements in a thick boundary layer. The modified system will be deployed in the SOS99 experiment in Nashville and in Atlanta this summer.

Cost Estimate: Cost estimate for NOAA's ground based ozone lidar (OPAL):

1 month deployment including 150 hours of operation \$230k

Aircraft Ozone Lidar

The Atmospheric Lidar Division of NOAA's Environmental Technology Laboratory in Boulder is operating an airborne, downlooking UV-DIAL, which was originally developed by EPA's Environmental Monitoring Systems Laboratory – Las Vegas. This system is capable of measuring range resolved ozone concentrations and aerosol, nadir looking from its airborne platform to near the ground level. It has been tested and employed in several field experiments:

- July 1991, Initial Ground Tests at the Lake Mead National Recreation Area, Nevada (Moosmüller *et al.*, 1992)
- May 1992, Initial Airborne Tests in Southeastern Michigan (Moosmüller *et al.*, 1993; McElroy *et al.*, 1994; Moosmüller *et al.*, 1994)
- July–August 1993, COAST Study in Southeastern Texas (McElroy *et al.*, 1994; Moosmüller, 1994)
- June–July 1995, Southern Oxidant Study in Tennessee
- October–November 1995, Table Mountain Vertical Ozone Transport and Intercomparison Experiment in Boulder, CO, Ground Based Operation.

This system is based on a KrF excimer laser, which generates 700 mJ, 20 ns-long pulses at 248 nm with a maximum pulse repetition rate of 20 Hz. Raman cells produce transmitted laser beams at frequencies shifted from the KrF fundamental by integral multiples of the vibrational

frequencies of hydrogen (4160 cm^{-1}) and deuterium (2987 cm^{-1}). The pulse power of the five utilized laser lines ranges from 5–12 mJ.

The receiver section consists of a 20"-diameter downlooking telescope for collection of the backscattered light and a spectrograph/detector system for the simultaneous detection of five individual laser lines (i.e., 276.9 nm, 291.6 nm, 312.9 nm, 319.4 nm, and 359.4 nm). Normally the 276.9 nm and 312.9 nm wavelengths are used as on- and off- lines for the ozone analysis. The 359.4 nm line is well suited for the measurement of aerosol profiles. The PMT signals are digitized by 12 bit A/D converters with a spatial resolution of 30 m. The resulting data together with the OMA spectra are stored on magnetic tape and simultaneously displayed on a monitor in real time to allow for optimization and control of the system operation.

The current measurement range for ozone is from about 0.8 km to 2.5–3 km, with the lower limit corresponding to the complete overlap of laser beams with the field of view of the telescope. The lower limit might be reduced somewhat in the future by applying the overlap correction in the data analysis and/or different alignment of the hardware. Generally, the DIAL data are analyzed for ozone concentrations down to about 90–150 m above ground.

Cost Estimate: Cost estimate for NOAA's airborne ozone lidar including preliminary on-site data processing. Final data processing is included as separate item:

1 month deployment and 80 flight hours	\$300k
Additional week including additional 20 flight hours	\$ 70k
Final data processing, approximately	\$150k

Possible Scheduling Conflicts: The airborne system is currently scheduled to participate in the SOS 2000 experiment (Houston) from August 15 through September 15, 2000.

A.5 Supplemental Measurements of Oxidized Nitrogen Species

Accurate measurements of NO and NO₂ in the atmosphere are of considerable importance because of the role of these compounds in the production of ozone and other photochemically derived air pollutants, such as peroxyacetyl nitrate (PAN), the nitrate radical (NO₃), and nitric acid (HNO₃). Proper evaluation and exercise of photochemical models require low detection limits (<1 ppbv) and interference-free measurements of these species. Routine monitoring techniques for measurement of NO and NO₂ and other oxides of nitrogen do not meet these requirements, thus, the photochemical models are unable to reproduce the measured atmospheric concentrations of these species accurately. Recent improvements in routine monitors and the development of ultrasensitive and specific methods for measuring the nitrogen oxide species of interest (e.g., NO, NO₂, NO_x, NO_y, HONO, HNO₃, NO₃, and PAN) provide more accurate and reliable input data for photochemical models. Most of these methods were evaluated recently by Solomon (1995) during the SJVAQS/AUSPEX/SARMAP air quality study. Measurement of oxidized nitrogen species during CCOS will be made primarily by the commercially available

instruments described below. Redundant measurements by alternative spectroscopic method such as a tunable diode laser absorption spectroscopy (TDLAS) or differential optical absorption spectroscopy (DOAS) would be desirable if sufficient funds are available.

A.5.1 NO₂ and PAN by Gas Chromatography with Luminol Chemiluminescence Detection

The Luminol NO₂ analyzer operates on the principle that gaseous NO₂ undergoes a surface reaction with a specially formulated solution containing water, luminol, sodium sulfate, sodium hydroxide, and alcohol (“Luminol II” solution). The luminol is oxidized and the product chemiluminesces in the 425 nm region. The luminol solution is presented to the air stream on a wick which is replenished with solution from a reservoir. The solution is introduced at the top of the wick and removed to a waste container by a two channel peristaltic pump. A 250 ml reservoir holds sufficient solution for about 3 days of operation. The light emitted by the chemiluminescence reaction is detected by a photomultiplier tube, amplified and output to a chart recorder and data logger. The signal is very sensitive, with a detection limit of 5 pptv if zeroed every 30 minutes or 50 ppt if zeroed daily.

Although luminol can produce chemiluminescence with other oxidants, these reactions usually require the presence of metal ion catalyst. Use of deionized water in the solution formulation prevents chemiluminescence from other oxidizers such as hydrogen peroxide. Only O₃ and PAN were found to produce luminescence, and addition of other substances to the solution, such as sodium sulfite, make the response to O₃ negligible for NO₂ mixing ratios above 1 ppbv. The interference by PAN is a constant fraction of the PAN mixing ratio, although the fraction may depend on the formulation, batch, and age of the luminol solution.

The LCM method has been adapted to measure PAN as well as NO₂. The Unisearch/Scintrex Model LPA-4 is the only commercial instrument for measuring PAN in the atmosphere. In this method, PAN is separated from NO₂ and other organonitrates by gas chromatography, thermally reduced to NO₂, and measured using the same luminol detector described above for the luminol chemiluminescence measurement of NO₂. The more reactive oxides of nitrogen, such as HNO₃, HONO, NO₃, and other reactive interfering species such as ozone are retained on the column. NO, while passing through the GC column, is not detected by the luminol detector. One major advantage of this method is that the instrument can be calibrated in the field with NO₂ rather than the thermally unstable PAN, which is required for the GC/electron capture detector method.

As a further modification to the LPA-4, the LNC-3 converter/sequencer can be used to enable the measurement of NO_x as well as NO_y. The NO_y converter in the model LNC-3M converter/sequencer consists of a hot stainless steel tube operated at 400 °C. At this temperature, two otherwise difficult to measure NO_y species, namely HNO₃ and isopropyl nitrate, have been shown to convert at efficiencies approaching 100 percent. The resulting NO_x (NO + NO₂) is then measured by using a CrO₃ converter upstream of the LMA3 Luminol NO₂ analyzer. The cycle time between species is one minute each for NO₂, NO_x and NO_y, and five minutes for PAN. Detection limit for PAN is 30 ppt and 50 ppt for the other nitrogen species. NO and NO_z (NO_y - NO_x) are obtained from the difference. NO_z minus PAN yields an upper estimate for nitric acid. Because of the cycle time the modified LPA-4 cannot be used on-board an aircraft.

A TEI 42S which has been modified to measure NO_y is now commonly used by contractors that perform airborne air quality measurements because of its high sensitivity and fast response (see Section 5.4 for additional details).

A.5.2 NO_2 and HNO_3 by Tunable Diode Laser Absorption Spectroscopy

The TDLAS method takes advantage of the high monochromaticity and rapid tunability of a Pb salt diode laser to measure absorptions from single rotational-vibrational lines in the middle infrared spectrum of a molecule. Almost all gases absorb radiation in this spectral region. However, since many gases absorb in this region, very high spectral resolution is required to prevent interferences from other gases in the sampled air. The atmospheric sample is pumped rapidly at the reduced pressure through a White cell, which also provides the long optical path lengths required to achieve the desired detection limits. The tunable diode laser is a small Pb crystal with variable amounts of Sn, Se, Te or S. The wavelength region at which the laser emits radiation is governed by the proportions of the three elements in the crystal. Techniques of measuring NO , NO_2 and HNO_3 by TDLAS has been described by Hasties (1983) and Mackay (1993) and measuring H_2O_2 and HCHO by MacKay (1994).

The precision of the measurements is experimentally found to be better than ± 1 percent. The accuracy depends on the ability to accurately measure the various flows and on the ability to determine the mixing ratio of the calibration standard. The computed accuracy for H_2O_2 , HCHO and HNO_3 is ± 15 percent (MacKay, 1994).

A.5.3 NO_2 , HONO, and NO_3 Radical by Differential Optical Absorption Spectroscopy (DOAS)

In this method, in situ atmospheric concentrations are determined by measuring the absorption of the species of interest in the ultraviolet/visible wavelength region. The DOAS is based on measuring the difference between the absorbance at a wavelength where the species of interest has a distinct peak, and another wavelength on either side of the peak. High sensitivities are obtained by combining the detector with a long-pathlength, multiple-reflectance system to yield optical pathlengths up to 10 km. Concentrations are determined from the pathlength and from absorption coefficients. Therefore, this is an absolute, highly specific, and nearly interference-free measurement that can be considered as a reference method.

The DOAS has been used to measure several pollutants in the atmosphere, including NO_2 , HONO, NO_3 , HCHO , SO_2 , O_3 and OH. Several species can be monitored simultaneously. Detection limits as low as about 1 ppbv for NO_2 , 0.020 ppbv for NO_3 , 3.3 ppbv for HCHO , and 0.6 ppbv for HONO have been reported for pathlengths of 0.5 to 8 km (Finlayson-Pitts and Pitts, 1986; Plane, 1989; Winer and Biermann, 1989; Plane and Nien, 1991).

A.5.4 Automated Particle Nitrate Monitor

The Aerosol Dynamics Inc. (ADI) automated particle nitrate monitor (Aerosol Dynamics Inc., Berkeley, CA) is a new method being developed to provide automated, high-time-resolution measurements of fine particle nitrate concentration. The ADI Automated Particle Nitrate

monitor uses an integrated collection and vaporization cell whereby particles are collected by a humidified impaction process, and analyzed in place by flash vaporization. The measurements for the Northern Front Range Air Quality Study (NFRAQS) in the Denver area represent the first deployment of the system (Chow et al., 1998). Fine particle nitrate concentrations were measured at the Brighton site with five measurements per hour during a three-to-four day pollution episode between 01/16/97 and 01/20/97. During the winter 1997 field campaign, the system operated over two, one-week periods yielding concentrations of fine particle nitrate with five determinations per hour. The automated particle nitrate monitor captured the time variability in fine particle nitrate concentrations with a time resolution of 12 minutes and a precision of approximately $0.5 \mu\text{g}/\text{m}^3$. The absolute accuracy of the nitrate concentrations, as indicated through comparison with nitric-acid-denuded particulate nitrate measurements on filter packs, showed agreement within $\pm 0.6 \mu\text{g}/\text{m}^3$ for most measurement periods, but exhibited a discrepancy of a factor of two for the highest nitrate concentration measurement periods. The reason for this difference is not known, and additional data is needed to qualify the accuracy and precision of the method.

The approach for continuous nitrate measurements is similar to the manual method used for more than 20 years to measure the size distribution of sulfate aerosols (Hering and Friedlander, 1982). The difference is that the particle collection and analysis has been combined into a single cell, allowing the system to be automated. Particles are humidified, and collected onto a metal strip by means of impaction. The humidification essentially eliminates the rebound of particles from the collection surface without the use of grease (Winkler, 1974; Stein et al., 1994). Interference from vapors such as nitric acid is minimized by using a nitric acid denuder upstream of the humidifier. At the end of the 10-minute particle sampling period, the valving is switched to stop particle collection and to pass a nitrogen carrier gas through the cell and into a gas analyzer. The deposited particles were analyzed for nitrate by flash-vaporization in a nitrogen carrier gas, with quantitation of the evolved gases by a chemiluminescent analyzer operated in NO_x mode (Yamamoto and Kousaka, 1992). The flow system is configured such that there are no valves on the aerosol sampling line. Details of the method are given by Hering (1997).

Field calibration and validation procedures include on-line checks of particle collection efficiency, calibration of analysis step with aqueous standards applied directly to the collection substrate, and determination of blanks by measurements of filtered, ambient air. Particle collection efficiencies were checked by means of an optical particle counter which operated between the collection cell and the pump. The analysis step of the monitor was calibrated by application of aqueous standards of sodium nitrate and ammonium nitrate applied directly to the metal collection substrate. To ensure that the system did not respond to ammonium ion, standards of ammonium sulfate were also applied. These calibrations were done in the field at the beginning and end of each intensive sampling period. Field blanks were determined by placing a Teflon-membrane filter at the inlet of the system, collecting for the 10-minute sampling period, and then analyzing the strip exactly as done for a normal sample.

The data are reduced based on the response of the system to aqueous nitrate standards which were applied at four concentration levels, corresponding to deposits of 0, 40, 80 and 160 ng of nitrate. Standards data from the beginning and end of the sampling episode are combined

to generate a calibration curve in the form of “ $y=ax^n$ ”. This method forces the least squares regression line to pass through the zero-nanogram level response. For the Denver data set the regression is nearly linear, with $r=0.92$. Additionally, the data are corrected for field blank based on the average reading obtained when sampling through a Teflon-membrane filter. The field blank corresponded to approximately $0.84 \mu\text{g}/\text{m}^3$ of fine-particle nitrate. This value is approximately 10 times higher than the analysis blank, presumably due to interference from a gaseous constituent. The data are corrected for 9% particle losses in the inlet, measured in the laboratory using monodisperse aerosol. These losses were observed to be independent of particle size in the range from 0.1 to $0.8 \mu\text{m}$.

Level 1A data validation included a review of all logged system parameters and daily log sheets, and an inspection of time series display of the reduced data. System parameters that are automatically logged by the data acquisition system include temperature and relative humidity of the sample collection, and capacitor voltage prior to each vaporization step. Parameters recorded manually on the daily log sheets include flow and pressure meter readings such as the purge gas rotameter readings and the differential pressure at the inlet of the NO_x analyzer. The reduced data are displayed as a time series to inspect for possible outliers. Potential level II validation checks include comparison to dried particle light scattering using a nephelometer, and comparisons to filter nitrate acquired on a quartz-fiber/sodium-chloride-impregnated cellulose-fiber filter pack in a PM_{2.5} sequential filter sampler equipped with an upstream nitric acid denuder.

A.6 In-Situ Instrumented Aircrafts

Instrumented aircraft will be used to measure the three-dimensional distribution of ozone, ozone precursors and meteorological variables. The aircraft will provide information at the boundaries of the modeling domain and will document the vertical gradients, the mixed layer depth, and nature of the polluted layers aloft. In addition to the NOAA lidar aircraft, there are five aircraft that are available to CCOS during the summer of 2000. The University of California, Davis single-engine Cessna 182 can be used to provide initial condition in the central portion of the modeling domain and provide data to determine the presence of pollutant transport between the Bay Area/Sacramento region to the upper Sacramento Valley, the San Joaquin Valley and the Sierra Nevada. It can also provide data to validate the ground-based lidar measurements by NOAA. UCD may have a second, similarly equipped aircraft that can be used to extend coverage towards the southern end of the San Joaquin Valley or up to the northern end of the Sacramento Valley. The Sonoma Technology twin-engine Piper Aztec can provide boundary and initial conditions in the western (over-water) and northern portion of the study domain. It can also provide data to characterize ozone and NO_y fluxes through the passes along the coastal range. An overview of the UCD and STI instrumentation complete with data quality objectives, i.e., accuracy is given in Table A.6-1 and A.6.2, respectively.

The NOAA Long-EZ N3R is a research aircraft measures turbulent exchange of momentum, energy and trace gases, such as CO₂, H₂O, and O₃, in flights as close as 10 m to the surface. The Best Aircraft Turbulence (BAT) probe measures mean and turbulent wind parameters with fidelity. Many remote sensing and in situ instruments are available. The nominal sensor suite includes the BAT probe, an infrared H₂O and CO₂ gas analyzer, a net radiometer,

upward and downward PAR (photosynthetically active radiation) radiometers, and sensors for dew point, and surface temperature. Other sensors can be carried including lasers, laser arrays, Ka-band radar, visible light cameras, and a multi-band radiometer.

The NOAA twin otter is an advance atmospheric research platform. It is specially suited for measuring eddy fluxes and concentration gradients through the mixed layer. It offers unique capabilities to explore the rates of exchange of atmospheric properties through the lower atmosphere, and especially between the atmosphere and the surface. The aircraft measures air temperature, dew point, pressure, 3-D winds, and radiation variables. Atmospheric chemistry sampling uses a flow-through air inlet system for measuring NO, NO_x, NO_y, SO₂, O₃, CO and reactive hydrocarbons.

A.7 Supplemental Measurements of Volatile Organic Compounds

A.7.1 Collection and Analysis of Hydrocarbons and Oxygenated Species

Canister Sampling

Stainless steel SUMMA™-polished canisters of 6-L capacity are customarily employed for volatile hydrocarbon (C₂-C₁₂) collection. These canister samples are to be analyzed for speciated hydrocarbons by a method consistent with EPA Method TO-14, as well as for CO, CO₂, methane, and oxygenated species. Prior to sampling, the canisters are to be cleaned by repeated evacuation and pressurization with humidified zero air, and certified as described in the EPA document "Technical Assistance Document for Sampling and Analysis of Ozone Precursors" (October 1991, EPA/600-8-91/215).

The sampling procedure should essentially follow the pressurized sampling method described by EPA Methods TO-12 and TO-14 and the EPA document "Technical Assistance Document for Sampling and Analysis of Ozone Precursors" (October 1991, EPA/600-8-91/215). A stainless steel Viton pump draws in ambient air from the sampling manifold to fill and pressurize the sample canisters. A flow control device maintains a constant flow into the canisters over the desired sample period. This flow rate is preset to fill the canisters to about 1 atm above ambient pressure at the end of the sampling period (as described by EPA Method TO-14). For automatic operation, the timer starts and stops the pump at the appropriate time. The timer also opens the solenoid valve when the pump starts and closes it when the pump stops. The use of the solenoid manifold valves permits the automatic selection of preloaded canisters. The multiple-event sampling systems, allowing unattended collection of up to six canister samples are recommended for this study.

After sampling, an identification tag should be attached to each canister with the canister serial number, sample number, and sampling location, date, and time recorded on this tag. In addition a field sampling form and chain-of-custody form should be filled out giving all pertinent information on the collection of the sample.

GC/FID Analysis

Gas chromatography with flame ionization detector is the established technique for monitoring volatile hydrocarbons, ozone precursors, in ambient air. An air sample is taken from the canister and passed through the sample concentration system. This system usually consists of a freeze-out loop, made from chromatographic-grade stainless steel tubing packed with 60/80 mesh deactivated glass beads, and a 10-port sampling valve. First, the sample is transferred from the canister through the loop immersed in liquid oxygen to the volume transfer measurement apparatus. The C₂ and heavier hydrocarbons are cryogenically trapped inside the loop when air is transferred to an evacuated flask of known volume. From the difference in pressure inside the flask, the volume of the air sample can be calculated, based on the ideal gas law. When a sufficient volume of the air sample has been transferred from the canister to the concentration system, the 10-port valve is switched to position 2, the liquid oxygen is replaced with boiling water, and the contents of the trap are injected into a chromatographic column where separation of the C₂-C₁₂ hydrocarbons takes place. No Perma-Pure permeable membrane or other moisture-removal device should be used prior to concentration, since the use of such drying devices results in the loss of certain volatile organic compounds of interest (all polar compounds and some olefins and aromatics). It can also introduce contaminants into the system and it lowers the total NMHC by 10-20% (Sagebiel and Zielinska, 1994).

The chromatographic column used for the C₂-C₁₂ hydrocarbon analysis is usually a 60 m long DB-1 fused silica capillary column (or equivalent) with a 0.32 mm inside diameter and 1 μm phase thickness. However, the DB-1 column does not provide complete separation of the light C₂ and some important C₄ hydrocarbons. Therefore, a separate analysis of the canister sample is recommended to obtain accurate concentrations for ethane, ethylene, acetylene, 1-butene, and isobutylene. The chromatographic column used for this analysis is usually GS-Alumina PLOT fused silica capillary column (or equivalent) with an internal diameter of 0.53 mm and a length of 30 m. A separate gas chromatograph or two-dimensional (2D) chromatography could be used for this analysis.

The GC/FID response is calibrated in ppbC, using primary calibration standards traceable to the National Institute of Standards and Technology (NIST) Standard Reference Materials (SRM). The NIST SRM 1805 (254 ppb of benzene in nitrogen) is used for calibrating the analytical system for C₂-C₁₂ hydrocarbon analysis, whereas 1 ppm propane in a nitrogen standard (Scott Specialty Gases), periodically traced to SRM 1805, is used for calibrating the light hydrocarbon analytical system. Based on the uniform carbon response of the FID to hydrocarbons, the response factors determined from these calibration standards are used to convert area counts into concentration units (ppbC) for every peak in the chromatogram.

Identification of individual compounds in an air sample is usually based on the comparison of linear retention indices (RI) with those RI values of authentic standard compounds, as well as with the RI values obtained by other laboratories performing the same type of analysis using the same chromatographic conditions. Appendix A-1 lists target species, together with other pertinent information. Note that all PAMS target compounds listed in the EPA document "Technical

Assistance Document for Sampling and Analysis of Ozone Precursors" (October 1991, EPA/600-8-91/215) are also on this list.

The gas chromatographs should be connected to a data acquisition system. The software performs data acquisition, peak integration and identification, hardcopy output, post-run calculations, calibrations, peak re-integration, and user program interfacing. Typically, over 85% of total detectable C₂-C₁₂ hydrocarbon mass is identified and quantified. The detection limit for hydrocarbon VOC is approximately 0.1 ppbC for each compound.

Methane (CH₄), carbon monoxide (CO), and carbon dioxide (CO₂) are to be measured from the canister samples using GC/FID. Since the FID does not respond to CO and CO₂, these species are to be converted to methane by a methanator, positioned after the GC column, but ahead of the FID. The minimum detection limit for both CO and CH₄ should be < 20 ppbv, whereas for CO₂ < 3 ppmv. The precision of measurements should be generally better than 10%.

Methyl t-butyl ether should be quantified from canister samples, using the method of analysis for C₃-C₁₂ hydrocarbons. The individual response factor should be determined for MTBE and its concentration reported in ppbC.

A.7.2 Carbonyl Compounds

Formaldehyde and other volatile carbonyl compounds are to be collected, utilizing solid adsorbent cartridges coated with 2,4-dinitrophenylhydrazine (DNPH) reagents, by the method consistent with the EPA document "Technical Assistance Document for Sampling and Analysis of Ozone Precursors" (October 1991, EPA/600-8-91/215). The method is based on the specific reaction of organic carbonyl compounds with DNPH deposited on silica gel or C₁₈ bonded SepPak cartridges in the presence of an acid to form stable derivatives, hydrazones, which are subsequently analyzed by high performance liquid chromatography (HPLC).

A carbonyl sampling system consists of a diaphragm pump capable of maintaining air flow through the cartridges of 500 - 1500 ml/min, flowmeter, six-port solenoid manifold allowing unattended collection of up to six carbonyl samples, needle valves for flow rate regulation, and check valves to protect cartridges from outside air when air is not being sampled through a given cartridge. For automatic operation, the timer starts and stops the pump at the appropriate time. The timer also opens the six-port solenoid valve when the pump starts and closes it when the pump stops. A charcoal filter is attached to the pump outlet in order to remove traces of acetonitrile from DNPH cartridges.

Carbonyl compounds collected in the cartridges (as hydrazones) are eluted with HPLC grade acetonitrile and analyzed by HPLC with UV detection at 360 nm. A reverse phase HPLC column is used. Identifications are made based on matching the HPLC retention times with those of authentic standards. A three-level calibration curve (plus blank) is constructed for each quantified hydrazone. C1-C7 carbonyl compounds are recommended for quantification as follows: formaldehyde, acetaldehyde, acetone, acrolein, propionaldehyde, crotonaldehyde, methyl ethyl ketone, methacrolein, butyraldehyde, benzaldehyde, valeraldehyde, tolualdehyde, and hexanaldehyde.

A.7.3 C8-C20 Hydrocarbons by Tenax Sampling and Analysis by GC/FID or GC/MS

Volatile hydrocarbons in the range of C₈-C₂₀, are usually collected using Tenax solid adsorbent. The Tenax sampling unit draws two parallel streams of air allowing for the collection of duplicate samples, with the pump downstream of the Tenax. The flow rates are controlled by a flow controller or are measured before and after each run using a calibrated mass flow meter and the mean value is used to calculate volumes of air sampled. Prior to use, the Tenax solid adsorbent is cleaned by Soxhlet extraction with hexane/acetone mixture, packed into Pyrex glass tubes and thermally conditioned for four hours by heating at 300 °C under nitrogen purge. Approximately 10% of the precleaned Tenax cartridges are tested by GC/FID for purity prior to sampling. After sampling, the Tenax cartridges are capped tightly using clean Swagelok caps (brass) with graphite/vespel ferrules, and placed in metal containers with activated charcoal on the bottom.

Tenax samples are usually analyzed by the thermal desorption-cryogenic preconcentration method, followed by quantification by high resolution gas chromatography with flame ionization detection (GC/FID) or mass spectrometric detection (GC/MSD) of individual hydrocarbons. In some cases, analysis may also include identification by Fourier transform infrared/mass spectrometric detection (GC/IRD/MSD). A 60 m (0.32 mm i.d., 0.25 mm film thickness) DB-1 capillary column (or equivalent) is usually used. For analytical system calibration, a set of standard Tenax cartridges is prepared by spiking the cartridges with a methanol solution of standard SVHC, prepared from high-purity commercially available C₉-C₂₀ aliphatic and aromatic hydrocarbons. For the GC/FID system, the calibration is based on the uniform response of FID detector to carbon atoms. The FID response factor per one nanomole of carbon is determined experimentally, using n-dodecane and 1,3,5-trimethylbenzene deposited on Tenax cartridges. Three different concentrations (plus one blank) are used to construct calibration curves. The response factor per one nanomole of carbon for each compound used for calibration is averaged to give one uniform response factor for all hydrocarbons (both aliphatic and aromatic). For GC/MS, calibration is based on the response factors of authentic standards. In addition, Tenax cartridges spiked with paraffinic and aromatic hydrocarbons are periodically analyzed by GC/FID or GC/MS to verify quantitative recovery of these hydrocarbons from the cartridges.

A.7.4 Continuous Formaldehyde by Fluorescent Detection of Dihydropyridine Derivative

Formaldehyde is measured by an instrument that continuously measures the fluorescent, dihydropyridine derivative formed by the reaction of formaldehyde with 1,3-cyclohexanedione (CHD) and ammonium ion (Dong and Dasgupta, 1994; Fan and Dasgupta, 1994). The present instrument from AnalTech (Lubbock, TX) is a fully automated measurement system. The instrument is designed to operate continuously or more typically, alternate between a sample gas and zero air. The instrument is also configured to measure aqueous HCHO.

The product with CHD is substantially more sensitive and is used in the present instrument. The reaction with CHD proceeds at a rate that is first order in CHD concentration and first order in ammonium ion concentration. When a dilute formaldehyde solution is mixed with an equal volume of a reagent containing 10 mg% CHD and 1.3 M CH₃COONH₄ at pH 4.9

and heated to 95°C, the reaction is completed in under 3 min. The excitation and emission maximum of the fluorescent product are broadly centered at 395 and 465 nm, respectively.

For gas-phase formaldehyde measurements, the system is configured as a gas phase flow injection analyzer in which the gaseous analyte is continuously transferred to an aqueous stream by a Nafion membrane based diffusion scrubber (DS) and the resulting aqueous stream is continuously analyzed by the liquid phase analysis system.

A.7.5 Automated GC/MS System

A continuous gas chromatography – mass spectrometry (GC/MS) system with an initial sample preconcentration is proposed for the analysis of VOC in ambient air during Central California Ozone Study (CCOS). This system would allow for measurement of hydrocarbons, oxygenated hydrocarbons, halogenated compounds, and other volatile organic compound concentrations with a temporal resolution of approximately 1-hour. GC/MS system would allow for identification and quantification of much broader classes of organic compound as compared with GC/FID system.

Preconcentration System. The analysis of VOC at levels found in ambient air requires an initial sample preconcentration to reach the detection limit on the order of 0.1 – 0.2 ppbv. Commercially available automatic preconcentration systems are usually based on combination of multisorbent traps, such as XonTech Model 930 organic vapor concentrator or Model 940 cryofocusing trap. The multisorbent traps usually contain a combination of Tenax, Carbotrap and Carbosieve S-III solid adsorbents in various amount and proportions. These sorbents are relatively strong and they may introduce some artifact when more reactive organic compounds are required to be quantified.

As an alternative, the automatic preconcentration trap could be custom build, utilizing cryofocusing loops filled with very weak, inert adsorbent, such as glass beads. Such systems are being currently developed by the University of Miami (Rod Zika, personal communication), NCAR (Eric Apel, personal communication) and NOAA (Paul Goldan).

GC/MS Systems. Commercially available GC/MS system could be used for this project. A new Hewlett Packard GC/MSD system offers enhanced sensitivity over older HP5970 MSD. An ion trap Varian Saturn GC/MS is an alternative to a conventional quadrupole MS and offers very good sensitivity; 0.1 – 0.2 ppbv detection limit is a standard for most of the analytes.

To obtain data for C2 hydrocarbons without using excessive amount of liquid N2, a dual capillary column (2-D) chromatography is proposed. A PLOT type column (such as Al2O3 or GasPro GSC) would allow for separation of light C2-C4 hydrocarbons, whereas narrow bore DB-1 or equivalent capillary column assures separation of higher boiling organic compounds. Additional FID detector could be used in parallel with MS detector for the quantification of light (C2-C4) hydrocarbons.

A.8 Photolysis Frequencies and Rates

As discussed in Section 2.5.1, the formation of photochemical air pollution depends on the photolysis of NO₂, O₃, HONO, HCHO, aldehydes and ketones and other compounds. The two most important photolysis rates are those for NO₂ and ozone. The rate of ozone formation is controlled through the photolysis of NO₂.



The magnitude of ozone concentrations is related to the NO₂ photolysis frequency, J, and NO₂ to NO concentration ratio.

$$[\text{O}_3] = J [\text{NO}_2] / k [\text{NO}] \quad (2)$$

The photolysis of O₃ to make excited oxygen atoms, O¹D, produces ozone by making HO radicals that react with VOC to make HO₂ and organic peroxy radicals.



A compound's photolysis frequency, J, is determined by the product of the spherically integrated photon flux (actinic flux), I(λ), the compound's absorption cross sections, σ(λ), and its quantum yields, φ(λ), all integrated over the range of available wavelengths.

$$J = \int I(\lambda) \times \sigma(\lambda) \times \phi(\lambda) d\lambda \quad (5)$$

The quantity J should be considered a frequency because its dimension is time⁻¹. Photolysis rates are the product of the photolysis frequency and the photolysis species concentration.

Although photolysis frequencies are often a major cause of differences between modeling studies they are usually not accurately measured in field studies. Photolysis frequencies are often calculated for assumed sky conditions or they are estimated from Epply and UV radiometer measurements. These procedures may yield photolysis frequencies that are uncertain by as much as 30 to 40% (Madronich, 1987).

Chemical actinometers where the photolysis frequencies are measured directly provide the most accurate J values in principle. However, chemical actinometers are expensive and difficult to use under field conditions. The use of spectrally resolving radiometers to measure actinic flux and the calculation of photolysis frequencies from Equation (5) is more practical. An advantage of using spectral radiometer data is that any photolysis frequency may be calculated from this data in the future. A significant disadvantage of spectral radiometers is their relatively high cost.

Radiometers have been developed that mimic the response of O₃ and NO₂ to photolysis. If calibrated against chemical actinometers these radiometers provide a relatively inexpensive way of measuring the photolysis frequencies of O₃ and NO₂. The measured photolysis frequencies for O₃ and NO₂ should be used to provide an important constraint on the application of photochemical air quality models to modeling the CCOS measurements.

**Table A.1-1
Meteorological Sensor Specifications**

Sensor	Accuracy	Range	Response Time	Sensitivity	Stability	Error
AIR db Pr	±0.7 mb	600-1100 mb	ms-range	.01 mb		
CS207 T	±0.4 °C	-33 - +48°C				<0.1 °C linear error
CS207 RH	± 5 %	0 - 100 %				<±3.0 %
CS500 T	±0.4 ±0.6	-40 - +60 °C				
CS500 RH	±2% @ 0-90% ±3% @ 90-100%	0 - 100 %			±1%/yr	
Li-Cor 200SA Solar	Within 95-98% of Eppley standard	.15-3.0 μm	10 μs	80 μA per 1000 Wm ⁻²	<±2%/yr	Abs error: ±5% of Eppley
REBS Net Rad		.25-60 μm	30 s			
RM Young Speed	±.25 m/s, ws: 0-5 m/s ±5%, ws >5 m/s	0-60 m/s 100 m/s (peak gust)		0.9 m/s		
RM Young Direction	±5 Deg	0-355 Deg electrical		1 m/s @ 10° displ.		
Vaisala T	±0.4 °C	-35 - +50 °C				
Vaisala RH	±2% @ 0-90% ±3% @ 90-100%	0 - 100 %	15 s		1%/yr	

Table A.1-2 (continued)
Air Quality Monitoring Site in Northern and Central California

Site ID	Air Basin	City	Site Address	Land Use	Location Type	EL_MSL	Parameters Measured									
							CO	NMHC	Carb	HC	NO2	O3	PM10			
RMD	SFBA	Richmond	1065 7th St.	Industrial	Suburban	6										
CCD	SFBA	Concord	2975 Treat Blvd	Residential	Suburban	26	1				1	1	1	1		
OKA	SFBA	Oakland	822 Alice St.	Commercial	Urban / Center City	7	1									
SFE	SFBA	San Francisco	939 Ellis St.	Commercial	Urban / Center City	38	1									
SFA	SFBA	San Francisco	10 Arkansas St.	Industrial	Urban / Center City	5	1				1	1	1	1		
SEH	SFBA	San Leandro	Hospital-15400 Foothill Blvd	Residential	Suburban	36										
LVF	SFBA	Livermore	2614 Old 1st St.	Commercial	Urban / Center City	146	1				1	1	1	2		
HLM	SFBA	Hayward	3466 La Mesa Dr.	Residential	Rural	287										
FCW	SFBA	Fremont	40733 Chapel Way.	Residential	Suburban	18	1				1	1	1	1		
RED	SFBA	Redwood City	897 Barron Ave.	Industrial	Suburban	5	1				1	1	1	1		
SJD	SFBA	San Jose	935 Piedmont Road	Residential	Rural	0										
MVC	SFBA	Mountain View	160 Cuesta Dr.	Residential	Suburban	24										
SJ4	SFBA	San Jose	1206 N 4th St	Residential	Urban / Center City	24	2				1	1	1	3		
SJK	SFBA	San Jose	Hlth Cir-2220 Moorpark Ave	Residential	Suburban	360										
SJT	SFBA	San Jose	528 Tully Rd.	Industrial	Suburban	38										
LGS	SFBA	Los Gatos	306 University Ave.	Residential	Urban / Center City	183										
SMM	SFBA	San Martin	13030 Murphy Ave.	Residential	Rural	87										
GRY	SFBA	Gilroy	9th & Princeville	Residential	Suburban	55										
SOW	SJV	Stockton	8778 Briattle Place Stockton-Wagner Holt	Residential	Suburban	7										
SOC	SJV	Stockton	4310 Claremont	Commercial	Suburban	13	1									
SOH	SJV	Stockton	Hazleton-Hd	Residential	Urban / Center City	13	1				1	1	1	3		
SOM	SJV	Stockton	13521 E. Mariposa	Not Available	Not Available	17										
TPP	SJV	Tracy	24371 Patterson Pass Road	Agricultural	Rural	31										
MIS	SJV	Modesto	1100 I St	Other Unknown Reside	Urban / Center City	27										
	SJV	Modesto	814 14th St-Modesto Rover	Commercial	Urban / Center City		1				1	1	1			
M14	SJV	Modesto	814 14th St.	Commercial	Urban / Center City	27	1				1	1	1	2		
TSM	SJV	Turlock	900 S Minaret Street	Residential	Suburban	56	1				1	1	1	1		
MRA	SJV	Merced	385 S. Coffee Avenue	Agricultural	Rural	86										
FNP	SJV	Shaver Lake	North Perimeter Road	Forest	Rural	0										
M29	SJV	Madera	Rd. 29 1/2 No. Of Ave 8	Agricultural	Rural	0					1	1	1	1		
FSS	SJV	Fresno	Sierra Skypark#2-Blythe & Chmmt	Residential	Suburban	98	1									
CLO	SJV	Clovis	908 N Villa Ave	Residential	Urban / Center City	86	1	1	1	1	1	1	1	1		
FIS	SJV	Fresno	1145 Fisher Street	Commercial	Urban / Center City	90	1									
FSF	SJV	Fresno	3425 N First St	Residential	Suburban	96	1	1	1	1	1	1	1	3		
FSD	SJV	Fresno	4706 E. Drummond St.	Commercial	Suburban	162	1									
PLR	SJV	Parlier	9240 S. Riverbend	Not Available	Not Available	166					1	1	1	1		
SLK	SJV	Sequoia Nat Park	Lower Kaweah-Sequoia NP	Forest	Rural	1890										
LMK	SJV		Lookout Point-Mineral King Road	Forest	Rural	0										

Table A.1-2 (continued)
Air Quality Monitoring Site in Northern and Central California

Site ID	Air Basin	City	Site Address	Land Use	Location Type	EL_MSL	Parameters Measured								
							CO	NMHC	Carb	HC	NO2	O3	PM10		
VCS	SJV	Visalia	310 N Church St	Commercial	Urban / Center City	92	1						1	1	3
HIR	SJV	Hanford	807 South Irwin Street	Residential	Suburban	99								1	1
COP	SJV	Corcoran	1520 Patterson Ave.	Residential	Suburban	0									2
COV	SJV	Corcoran	Van Dorsten Ave.	Not Available	Not Available	61									3
SHA	SJV	Shafter	548 Walker Street	Commercial	Suburban	126		1		1	1	1			
OLD	SJV	Oildale	3311 Manor St.	Industrial	Suburban	180								1	1
BGS	SJV	Bakersfield	1128 Golden State Highway	Commercial	Urban / Center City	123		1	1	1	1	1	1	1	1
BKA	SJV	Bakersfield	5558 California Ave	Mobile	Urban / Center City	120	1				1	1	1	1	5
EDS	SJV	Edison	Johnson Farm	Agricultural	Rural	128					1	1	1	1	
ARV	SJV	Arvin	20401 Bear Mtn Blvd	Agricultural	Rural	145		1		1	1	1	1	1	
TAC	SJV	Taft	College-29 Emmons Park Dr.	Commercial	Suburban	292									3
MCS	SJV	Maricopa	School-755 Stanislaus St.	Residential	Suburban	289								1	
MLK	GBV	Mono Lake	Simus Res-Hwy 167	Not Available	Rural	1948									1
LEE	GBV	Lee Vining	Sms-Hwy 395	Not Available	Not Available	2071									1
MAG	GBV	Mammoth Lakes	Gateway Hc.	Commercial	Urban / Center City	2396	1							1	1
LPE	GBV	Lone Pine	501 E. Locust St.	Residential	Suburban	1128									2
DVL	GBV	Death Valley	Death Valley NP	Desert	Rural	125								1	
KCG	GBV	Keeler	190 Cerro Gordo Road	Residential	Rural	1097									4
OLW	GBV	Olancho	131 Walker Creek Rd.	Desert	Rural	1100									2
COS	GBV	Coso Junction	Rest Area On Hwy 395	Not Available	Not Available	1010									2
CJN	GBV	Coso Junction	10 Mi E Of Coso Junction	Desert	Rural	1315									1
SVD	NCC	Scotts Valley	4859 Scotts Valley Dr #E	Commercial	Rural	122								1	
DVP	NCC	Davenport	Fire Dept.	Residential	Rural	0	1							1	1
SCQ	NCC	Santa Cruz	2544 Soquel Avenue	Commercial	Suburban	78								1	1
WAA	NCC	Watsonville	444 Airport Blvd	Commercial	Suburban	67								1	1
HST	NCC	Hollister	1979 Fairview Rd.	Residential	Rural	126								1	1
MLS	NCC	Moss Landing	7539 Sandholt Road	Commercial	Rural	10									1
SL2	NCC	Salinas	Ii-1270 Natividad Rd	Residential	Suburban	13	1							1	1
MON	NCC	Monterey	24580 Silver Cloud Ct.	Commercial	Rural	0								1	
CMV	NCC	Carmel Valley	35 Ford Rd-Tularcito Sch	Residential	Suburban	131								1	1
PIN	NCC	Pinnacles National Mon	Ne Entrance	Forest	Rural	335								1	
KCM	NCC	King City	750 Metz Road	Industrial	Rural	116								1	1
PRF	SCC	Paso Robles	235 Santa Fe Avenue	Residential	Suburban	100								1	1
ATL	SCC	Atascadero	6005 Lewis Avenue	Commercial	Suburban	262								1	2
MBP	SCC	Morro Bay	Morro Bay Blvd & Kern Ave	Commercial	Urban / Center City	18								1	1
SLM	SCC	San Luis Obispo	1160 Marsh St.	Commercial	Urban / Center City	66	1							1	1
GCL	SCC	Grover City	9 Le Sage Dr.	Residential	Suburban	4								1	1
ARR	SCC	Arroyo Grande	000 Ralcoo Way	Commercial	Rural	300									1

Table A.1-3
PAMS Sites in the CCOS Area

Site	Type of Site	Measurement Method	
		Hydrocarbons	Carbonyl Compounds
Sacramento			
Elk Grove-Bruceville	PAMS - 1	Canister/GC-FID ^a	
Sacramento-Airport Rd.	PAMS - 2	Canister/GC-FID ^a	
Sacramento-Del Paso	PAMS - 2A	Canister/GC-FID ^a	DNPH/HPLC ^b
Folsom-50 Natoma Street	PAMS - 3	Canister/GC-FID ^a	
Fresno			
Madera	PAMS - 3/1	Canister/GC-FID ^a	
Clovis Villa	PAMS - 2	Canister/GC-FID ^a	DNPH/HPLC ^b
Fresno-1st Street	PAMS - 2	Canister/GC-FID ^a	
Parlier	PAMS - 3	Canister/GC-FID ^a	
Bakersfield			
Bakersfield-Golden State Highway	PAMS - 2	Canister/GC-FID ^a	DNPH/HPLC ^b
Arvin	PAMS - 3	Canister/GC-FID ^a	
Shafter	PAMS - 2	Canister/GC-FID ^a	DNPH/HPLC ^b
Ventura			
Emma Wood Beach	PAMS - 1	Canister/GC-FID ^a	
El Rio	PAMS - 2	Canister/GC-FID ^a	DNPH/HPLC ^b
Simi Valley	PAMS - 3	Canister/GC-FID ^a	

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 - Canisters collected every third day (four 3-hr samples beginning at 0000, 0600, 1300, and 1700, PDT).

Analyzed for PAMS species and total by PDFID.

b - DNPH cartridge samples collected every third day (four 3-hr samples beginning at 0000, 0600, 1300, and 1700, PDT).

Table A.1-4
PAMS Target Species

1	Ethylene	29	2,3-Dimethylpentane
2	Acetylene	30	3-Methylhexane
3	Ethane	31	2,2,4-Trimethylpentane
4	Propene	32	n-Heptane
5	Propane	33	Methylcyclohexane
6	Isobutane	34	2,3,4-Trimethylpentane
7	1-Butene	35	Toluene
8	n-Butane	36	2-Methylheptane
9	trans-2-Butene	37	3-Methylheptane
10	cis-2-Butene	38	n-Octane
11	Isopentane	39	Ethylbenzene
12	1-Pentene	40	m&p-Xylene
13	n-Pentane	41	Styrene
14	Isoprene	42	o-Xylene
15	trans-2-Pentene	43	n-Nonane
16	cis-2-Pentene	44	Isopropylbenzene
17	2,2-Dimethylbutane	45	n-Propylbenzene
18	Cyclopentane	46	1-ethyl 3-methylbenzene
19	2,3-Dimethylbutane	47	1-ethyl 4-methylbenzene
20	2-Methylpentane	48	1,3,5-Trimethylbenzene
21	3-Methylpentane	49	1-ethyl 2-methylbenzene
22	2-Methyl-1-Pentene	50	1,2,4-Trimethylbenzene
23	n-Hexane	51	n-decane
24	Methylcyclopentane	52	1,2,3-Trimethylbenzene
25	2,4-Dimethylpentane	53	m-diethylbenzene
26	Benzene	54	p-diethylbenzene
27	Cyclohexane	55	n-undecane
28	2-Methylhexane		Total NMOC

Table A.6-1
UCD Instrumentation

Parameter Measured	Technique	Manufacturer	Time Response	Measurement Range	Accuracy
Pressure (Altitude)	Capacitive	Setra	1 s - 3 s	-30 m - 3700 m	± 0.3 mB ± 3 m
Temperature	Platinum RTD	Omega	1 s - 3 s	-20°C - 50°C	± 0.2 °C
Relative Humidity	Capacitive	Qualimetrics	1 s - 3 s	10% - 98%	$\pm 3\%$
Air Speed	Thermal Anemometer	T.S.I.	1 s - 3 s	15 m/s - 75 m/s	± 0.4 m/s
Heading	Electronic Compass	Precision Navigation	1 s - 3 s	0° - 359°	± 2 °
Position	GPS	Garmin	10 s	Lat. - Long.	± 15 m
Particle Concentration	Optical Counter	Climet	10 s	2 channels: $d > 0.3 \mu\text{m}$ & $d > 3 \mu\text{m}$	$\pm 2\%$
NO, NO ₂ Concentration	O ₃ Titration Chemilumin.	Monitor Labs.	10 s - 15 s	0 ppmv - 20 ppmv	± 0.5 ppbv
Ozone Concentration	UV Absorption	Dasibi 1008	10 s - 15 s	0 ppbv - 999 ppbv	± 3 ppbv

Table A.6-2
STI Instrumentation

Parameter Measured	Technique	Manufacturer	Time Response	Measurement Range(s)	Accuracy ^a (Full Range)
NO/NO _y Concentration	Chemilumin.	Thermo Env. Model 42S	< 20 s	50 ppb, 100 ppb, 200 ppb	± 10%
Ozone Concentration	Chemilumin.	Monitor Labs. 8410E	12 s	200 ppb, 500 ppb	± 10%
b _{scat}	Integrating Nephelometer	MRI 1560 Series	1 s	100 Mm ⁻¹ , 1000 Mm ⁻¹	± 10%
Dew Point	Cooled Mirror	Cambridge Systems 137-C	0.5 s/°C	-50°C - 50°C	± 10%
Altitude	Altitude Encoder	II-Morrow	1 s	0 m - 5000 m	± 10%
Altitude (backup)	Pressure Transducer	Validyne P24	< 1 s	0 m - 5000 m	± 10%
Temperature	Bead Thermistor/ Vortex Housing	YSI/MRI	5 s	-30°C - 50°C	± 10%
Temperature (backup)	Platinum Resistance	Rosemont 102 AV/AF	1 s	-50°C - 50°C	± 10%
Position	GPS	II-Morrow	< 1 s	Lat. - Long.	± 50 m
Data Logger (includes time)	Dual Floppy Acquisition	STI 486 System	1 s	± 9.99 VDC	± 10%
NO/NO _w ^b	Chemilumin.	Thermo Env. Model 42S	< 20 s	50 ppb, 100 ppb, 200 ppb	± 10%
SO ₂ ^b	Pulsed Fluorescence	Thermo Env. Model 43S	15 s	1 ppb, 5ppb, 50 ppb, 200 ppb	± 10%
CO ^b	Gas Filter Correlation	Thermo Env. Model 48S	< 20 s	1 ppm, 2 ppm, 5 ppm, 10 ppm	± 10%

^a For values between 10% and 90% of full scale

^b Without modifying the aircraft for additional power, only one of these three instruments can be operated.

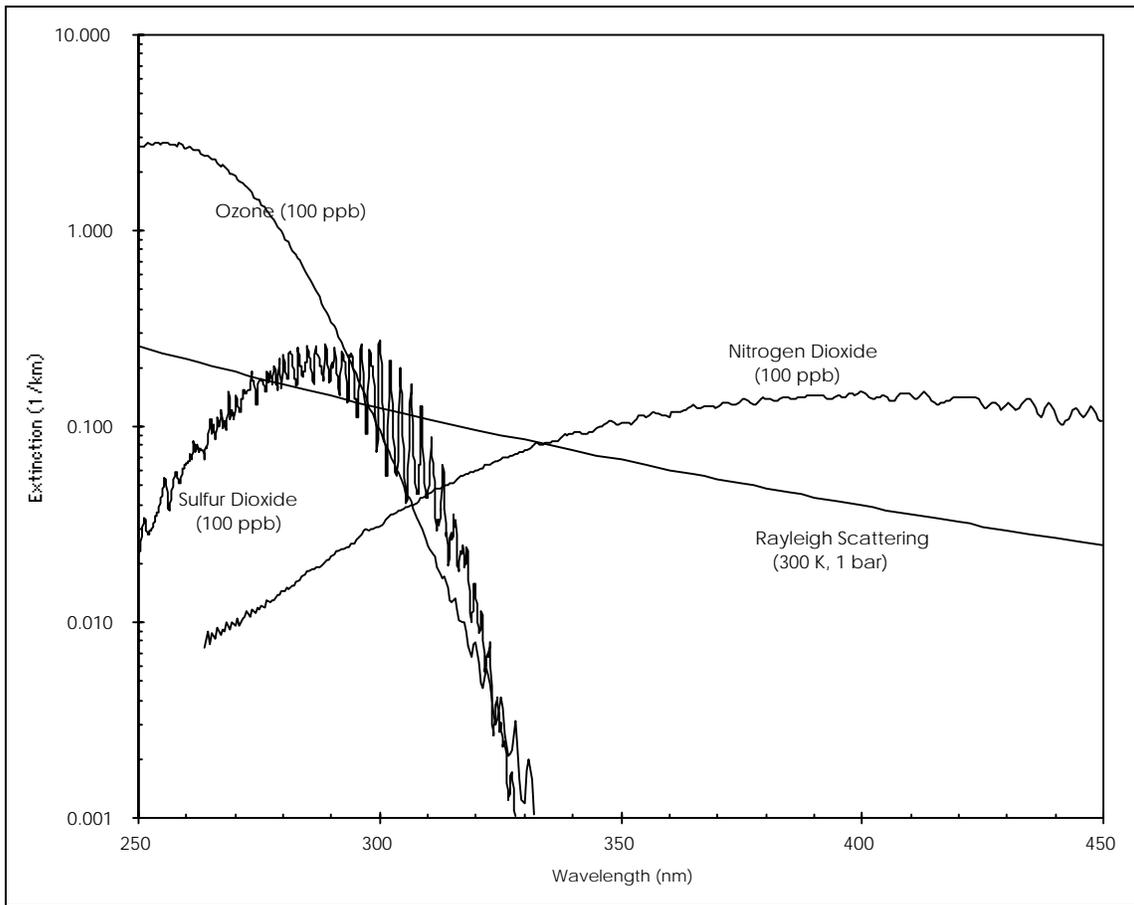


Figure A.1-1. Ultraviolet Absorption Spectra of Ozone, Sulfur Dioxide, and Nitrogen Dioxide.

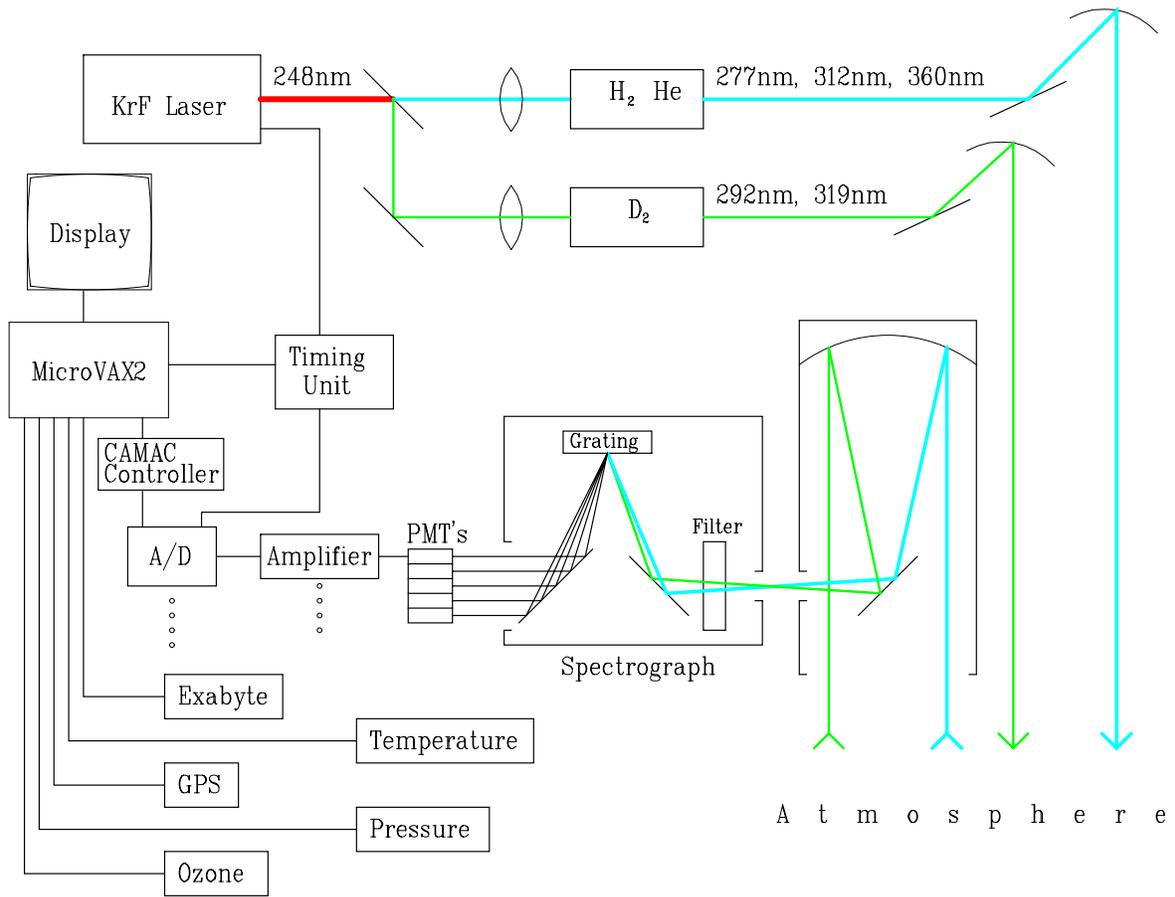


Figure A.1-2. Schematic diagram of NOAA's airborne ozone lidar.