

9. PARTICLE MEASUREMENT METHODS

The original December 1998 study plan included an extensive listing of the potential measurement techniques that were under consideration for use in CRPAQS. During the study planning stage in 1998 and 1999, instruments were evaluated and, in some cases, tested in the field, and choices were made for inclusion in the study. This section indicates the choices that were made and the rationale behind them. More detailed information about the measurements themselves and the details as they were used in CRPAQS (e.g., configurations, calibration methods, precisions) are available in the CRPAQS measurement reports.

9.1 Satellite Site Measurement Methods

As planned from the beginning, Airmetrics Minivol samplers were used for particle sampling at the satellite sites. These units ran at a nominal flowrate of 5 L/min and were mounted approximately 3 meters above the ground on metal cradles that were attached to aluminum poles or to power poles. Although the Minivol sampler operates from a battery, the units in CRPAQS were plugged into a constant trickle charge, since either line power or solar power was available at every site. Thus, the batteries did not need to be switched out for charging elsewhere, and there was no danger of missing a sampling period due to a dead battery.

Most Minivol samplers operated with a 2.5 μm size-cut inlet, although, as described previously, some were outfitted with 10 μm inlets, especially in some of the dustier areas. Three different filter packs were used:

- Teflon/citric acid, for quantification of gravimetric mass, elements, and ammonia
- Quartz/NaCl, for quantification of ions, carbon, and citric acid
- Teflon-impregnated glass fiber, for quantification of organic compounds (all filters sampled throughout the year at each site were combined for a single annual-average analysis)

The original December 1998 study plan called for the evaluation of several integrating nephelometers and laser diode photometers. Following a series of field and laboratory evaluations in late 1998 and early 1999, the choice for measuring light scattering in the CRPAQS satellite network was the Radiance Research Model 903 (RR903) integrating nephelometer (Richards, et al., 2001 a and b). The RR903 was selected in preference to the laser diode instruments because the response of integrating nephelometers is well-characterized; the instrument is self-calibrating, has sufficient sensitivity and accuracy, and is well-designed for field use; and the purchase price was within the CRPAQS budget (the RR903 is considerably cheaper than most commercially-available integrating nephelometers). The main reasons for not using a laser diode instrument are that detailed characterizations of their responses to varying particle sizes and indices of refraction were not available, independent calibration or audit in the field requires an aerosol sample of known properties, and the ratio of the response of the laser diode instruments to the response

of integrating nephelometers varied by more than a factor of two in comparison tests, apparently due in part to temperature dependent drift of the laser photometer baseline.

At very high relative humidity (RH) and in fog or clouds, it is desirable to heat the nephelometer sample airflow to prevent the accumulation of water on optical and electrical components, which can cause invalid data. In addition, at high RH, light scattering by a given aerosol sample can change by a factor of two or more with changes in the RH that are too small to measure reliably. Therefore, it is not possible to obtain useful estimates of PM concentrations from light scattering measurements made at very high RH. All RR903s used in CRPAQS were equipped with a smart heater, so the sample air in the nephelometer scattering chamber was at ambient temperature when the RH was less than 65%, and the maximum was limited to 73%. Over an 8% RH range beginning at the 65% threshold, the heating increased approximately linearly from zero to full power as the RH increased. The gradual onset of heating with increasing RH prevents the system from oscillating.

9.2 Anchor Site Measurement Methods

A number of high time resolution (one-hour or less) measurements of particle mass and chemical composition were deployed at the CRPAQS anchor sites, some in the annual program and others in the winter program. At the time of the December 1998 study plan, some of these methods were still under development, and testing was pending. This section summarizes the decisions that were made regarding the anchor site instruments that were discussed in the December 1998 study plan.

PM_{2.5} and PM₁₀ Continuous Mass Measurements: Several continuous mass measurement methods were considered and tested during the January 1999 Bakersfield instrument comparison. Prominent among these were the commercially available Rupprecht and Patashnick (R&P) Model 1400A Tapered Element Oscillating Microbalance (TEOM) and the Met One Model 1020 Beta Attenuation Mass (BAM) Monitor. The Met One BAM was selected for CRPAQS, for two principal reasons: 1) The TEOM uses a heated element for mass collection and analysis, and semi-volatile material can be lost from the TEOM (Allen, et al., 1997). This loss of material is especially important for semi-volatile organic compounds and for ammonium nitrate, a major component of the fine mass in the wintertime in the San Joaquin Valley. 2) The BAM is used extensively in other monitoring networks, including those operated by the ARB and local Districts, so inclusion of continuous mass data from other networks into the CRPAQS data analysis would be straightforward.

PM_{2.5} elemental carbon aethalometer: The aethalometer quantifies elemental or black (BC) carbon by light absorption. This is a major indicator of urban emissions. It was the main instrument in CRPAQS for tracking the surface concentrations of primary urban emissions on middle-, neighborhood, urban, and regional scales. Two versions of the aethalometer, both available from Thermo Andersen, were used in CRPAQS. Model RTAA 800 VIS measures light absorption at one wavelength, 880 nm. Model RTAA1000 utilizes seven wavelength channels, from 350 to 950 nm, which allows one to distinguish among fresh and aged emissions.

Thermal combustion carbon analyzer: The Ambient Carbon Particulate Monitor (ACPM, R&P Series 5400) (Rupprecht et al., 1995) was used for the continuous (i.e., 1-hour averaged) measurement of organic and elemental carbon. Organic carbon is defined as that which volatilizes at 250°C and elemental carbon as the remaining amount that volatilizes at 750°C. This is an operational definition that corresponds to organic carbon fractions reported by the commonly applied Thermal Optical Reflectance (Chow et al., 1993) method, but it is necessarily equivalent to the organic and elemental carbon fractions that are commonly reported.

Flash volatilization nitrate analyzer: The R&P Model 8400N Ambient Particulate Nitrate Monitor was selected for use in CRPAQS. This method uses an integrated collection and vaporization cell whereby particles are collected by a humidified impaction process, and analyzed in place by flash vaporization followed by a conventional NO_x analyzer. A prototype instrument was tested in Bakersfield in the January 1999 comparison test. Commercially produced units were available from R&P by the time they were installed in the CRPAQS network.

Flash volatilization sulfur analyzer: The R&P Model 8400S Ambient Particulate Sulfate Monitor was used in CRPAQS. This instrument is similar to the flash volatilization nitrate analyzer, but it uses a sulfur detector in place of a NO_x detector.

Chemiluminescence ammonia analyzer: Chemiluminescent ammonia analyzers convert ammonia to NO_x by thermal oxidation using a catalytic technique at high temperature. This type of continuous ammonia monitor has been used mostly in source emission testing rather than ambient monitoring in the past. A Thermo Environmental Instruments (TEI) Model 17C Chemiluminescence Ammonia Analyzer was tested during the January 1999 Bakersfield experiment. These tests revealed that this instrument lacked sufficient response time, precision, and detection limit to meet the needs of CRPAQS. Thus, continuous gaseous ammonia measurements were not made during CRPAQS. Ammonia was quantified using a time-integrated denuder difference technique during the 2000-2001 winter intensive period, as described below.

Nitric acid analyzer: Atmospheric nitric acid (HNO₃) concentrations were measured continuously via ozone chemiluminescence using a TEI Model 42CTL NO analyzer. In this technique, NO_y is measured, as NO, following conversion on a hot (350 C) molybdenum catalyst. NO_y minus HNO₃ (referred to as NO_y*) is measured by placing a potassium chloride (KCl) denuder upstream of a second molybdenum converter. The instrument cycles between the NO_y and NO_y* channels and HNO₃ is calculated by difference.

Sulfur Dioxide Analyzer: The TEI Model 43C-TL Trace Level SO₂ Analyzer was used at the Bakersfield-California Avenue site to detect the influence of emissions from oil production in the area. This pulsed fluorescence monitor can detect sulfur dioxide to 0.1 ppb levels and is appropriate for detecting the arrival of nearby sulfur emitters.

Single Particle Mass Spectrometer: Atmospheric Time of Flight Mass Spectrometers (ATOFMS) from UC Riverside were tested in the January 1999 Bakersfield intercomparison and were deployed at the Angiola and Fresno-first Street sites during the

2000-2001 winter intensive. These devices measure the size and chemical composition of individual particles.

Filter and Denuder Aerosol Measurements: Airmetrics-DRI sequential filter samplers (SFS) and sequential gas samplers (SGS) were used to measure time-integrated particulate and gas concentrations over sampling periods ranging from 3 to 24 hours. The SFS and SGS design has been used in many field studies for over 20 years, so its design is rugged and well-proven. SFS units equipped with PM_{2.5} size-selective inlets were used in CRPAQS to measure mass and elements with a Teflon/citric acid filter pack, and ions and carbon with a quartz/NaCl filter pack. The SFS unit were paired with SGS units equipped either with a quartz/citric acid filter pack and citric acid denuder or with a quartz/NaCl filter pack and ammonia denuder. The pairs of SFS and SGS samplers were designed to quantify ammonia and nitric acid, respectively, by denuder difference.