

Physical and Chemical Characterization of Atmospheric Ultrafine Particles in the Los Angeles Area

LARA S. HUGHES AND GLEN R. CASS*
*Environmental Engineering Science Department MC 138-78,
 California Institute of Technology, Pasadena, California 91125*

JEC GONE, MICHAEL AMES, AND
 ILHAN OLMEZ

*Nuclear Reactor Laboratory, Massachusetts Institute of
 Technology, Cambridge, Massachusetts 02139*

Atmospheric ultrafine particles (diameter $< 0.1 \mu\text{m}$) are under study by inhalation toxicologists to determine whether they pose a threat to public health, yet, little is known about the chemical composition of ultrafine particles in the atmosphere of cities. In the present work, the number concentration, size distribution, and chemical composition of atmospheric ultrafine particles is determined under wintertime conditions in Pasadena, CA, near Los Angeles. These experiments are conducted using a scanning differential mobility analyzer, laser optical counter, and two micro-orifice impactors. Samples are analyzed to create a material balance on the chemical composition of the ultrafine particles. The number concentration of ultrafine particles in the size range $0.017 < d_p < 0.1 \mu\text{m}$, analyzed over 24-h periods, is found to be consistently in the range $1.3 \times 10^4 \pm 8.9 \times 10^3$ particles cm^{-3} air. Ultrafine particle mass concentrations are in the range $0.80\text{--}1.58 \mu\text{g m}^{-3}$. Organic compounds are the largest contributors to the ultrafine particle mass concentration. A small amount of sulfate is present in these particles, at concentrations too low to tell whether it exists as unneutralized sulfuric acid. Iron is the most prominent transition metal found in the ultrafine particles. These data may assist the health effects research community in constructing realistic animal or human exposure studies involving ultrafine particles.

Introduction

Recent epidemiological studies that have examined air pollutant concentrations in relation to health statistics conclude that elevated fine particulate matter concentrations ($d_p \leq 2.5 \mu\text{m}$) are associated with increased mortality and morbidity (1, 2). Effects are reported at total particulate matter concentrations below $100 \mu\text{g m}^{-3}$; in some cases there is no easily discerned threshold concentration below which the adverse effects of particulate matter exposure are seen to vanish. The particulate concentrations reported to be associated with adverse effects in epidemiological studies are much lower than those observed to cause health effects in laboratory toxicology studies, and toxicologists historically have not been able to demonstrate the mechanisms by which such low fine particulate matter concentrations might cause

serious health damage (3). Motivated by this paradox, there is particular interest in examining those aspects of airborne particulate matter that might be capable of producing injury while at the same time not contributing greatly to measured airborne particle mass concentrations.

Certain toxicological investigations suggest that atmospheric ultrafine particles may be responsible for some of the adverse effects observed due to exposure to atmospheric particulate matter concentrations. For the purposes of the present discussion, ultrafine particles will be defined in accordance with current practice in the community of toxicologists as those particles which are smaller than about $0.1 \mu\text{m}$ in diameter. Many thousand particles of that size may be present within each cubic centimeter of outdoor air while at the same time accounting for a negligibly small fraction of the airborne particle mass concentration. Several current hypotheses about the possible mechanisms for damage to the respiratory system due to ultrafine particles give clues as to the particle chemical properties that might be important. Oberdorster et al. (4–6) have proposed that ultrafine particles even at small mass concentrations may have serious negative health effects because of their high number concentration and ability to penetrate into the interstitial space of the lungs; it is possible that the sheer number of such particles can overwhelm the alveolar macrophages, whose job it is to clear the lungs of inhaled substances. In this case, the distinction between solid particles such as carbon black versus nearly neutralized soluble particulate components such as ammonium sulfate aerosol might be expected to be important, because if the ultrafine particles were soluble, they could be cleared without requiring the intervention of particle-scavenging macrophages. Ironically, it is also conceivable that when subjected to a high ultrafine particle number concentration, “overload” may occur, in which the alveolar macrophages themselves cause injury to the lungs by releasing excessive quantities of oxygen radicals, proteases, and certain proteins (4). Alternatively, others have suggested that ultrafine particles coated with unneutralized strong acids may, upon deposition, cause tissue damage due to their acidity (7–9). In that case, a finding that ultrafine particles were largely made of sulfuric acid would be an interesting result. In addition, acids or catalytic metals on the surfaces of irritant particles can be more efficiently transferred to the lungs by ultrafines than by an equal mass of larger particles. This is both because of the larger surface area-to-mass ratio inherent in the smaller particles and because the ultrafines have a higher deposition efficiency in the alveolar region. Finally, investigators have suggested that trace metals distributed widely throughout the lung on ultrafine particles could catalyze the formation of oxidants within the lung which in turn produce tissue damage (10, 11). In this case, a finding that ultrafine particles contained catalytically active species such as Fe, Mn, V, or Ni from metallurgical fumes or fuel combustion or Pt, Pd, and Rh from motor vehicle catalytic converters, or Lanthanide series catalysts (e.g., Ce) could be significant.

If these distinctions attributed to ultrafine particles turn out to be physiologically important, they may help to explain the difference between epidemiological findings inferred from exposure to real ambient particles versus those laboratory toxicology studies that in the past have been based largely on synthetic, pure-substance, lab-generated aerosols consisting of smaller number concentrations of circa $0.5 \mu\text{m}$ diameter (fine, but not ultrafine) particles. The few inhalation

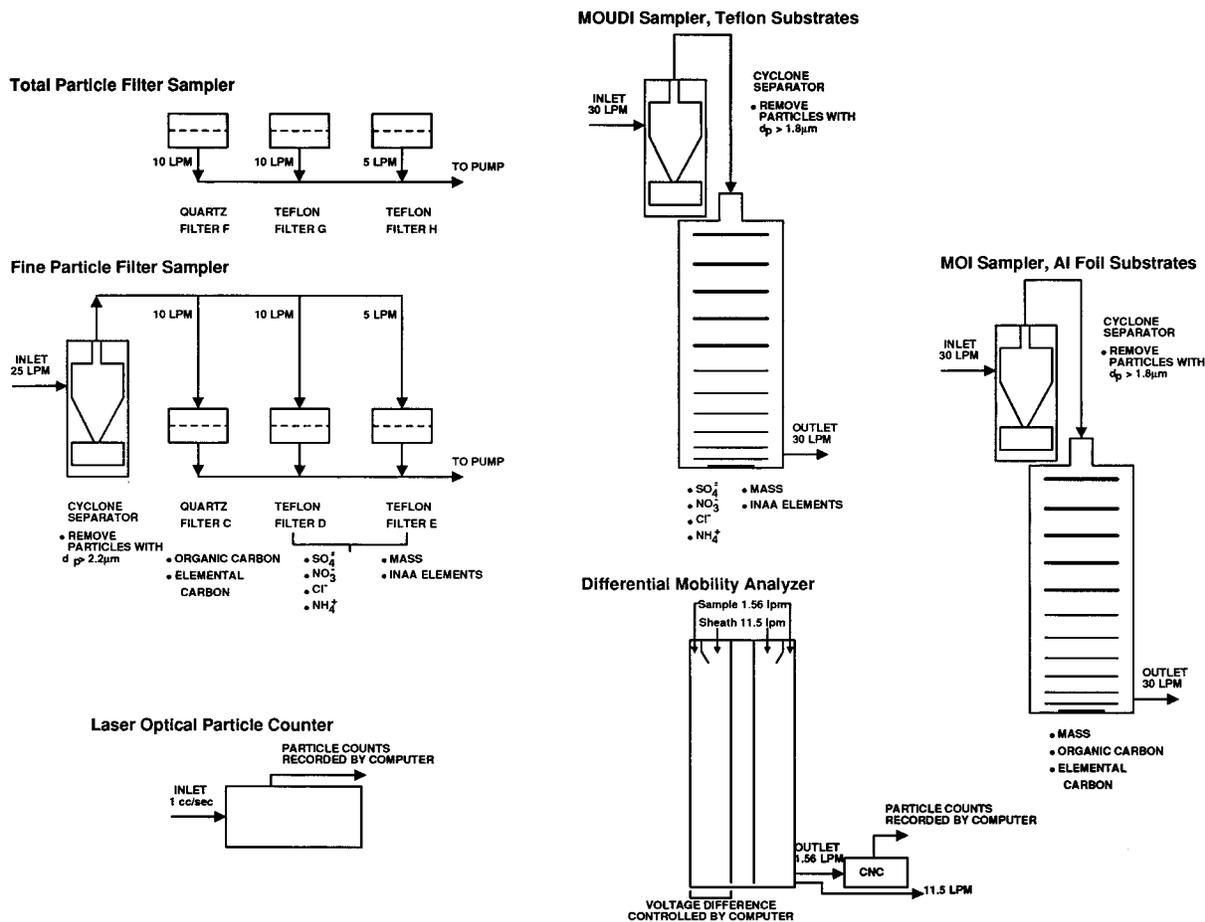


FIGURE 1. Schematic diagram of equipment used to measure fine and ultrafine particle size distribution and chemical composition.

experiments that have been conducted to date using ultrafine particles have been conducted with model Teflon and TiO_2 aerosols (4–6, 12). In order to construct future experiments that represent ambient atmospheric ultrafine particles as accurately as possible, it is first necessary to know the chemical composition of actual atmospheric ultrafine particles.

Though ultrafine particle number concentrations may be large, ultrafine mass concentrations are so small that they are in no way constrained by current air quality standards. Over the past decade, national ambient air quality standards in the United States for particles smaller than $10 \mu\text{m}$ in diameter (PM10) required that ambient particle mass in that size range not exceed $150 \mu\text{g m}^{-3}$ over 24-h periods, nor average more than $50 \mu\text{g m}^{-3}$ on an annual basis. Recently adopted new national ambient air quality standards for fine particles smaller than $2.5 \mu\text{m}$ in diameter limit fine particle concentrations such that they should not exceed $65 \mu\text{g m}^{-3}$ over 24-h periods or $15 \mu\text{g m}^{-3}$ as an annual average. The ultrafine particles studied here constitute only a small fraction of the new fine particle mass concentration limit. For that reason, emission control strategies designed to attain the new fine particle standards will not necessarily have to reduce ultrafine particle concentrations in order to meet the required mass concentration limits. Ultrafine particles are emitted from certain sources, particularly combustion sources (13, 14). Controls applied to combustion sources for the purposes of meeting fine particle standards directed mainly at control of somewhat larger accumulation mode particles may or may not have the indirect effect of lowering ultrafine particle concentrations as well. While control equipment applied to stationary combustion sources (e.g., electrostatic precipitators, bag houses) may more effectively reduce ultrafine

particle emissions than is the case for accumulation mode fine particles (15), design changes applied to other combustors to reduce particle mass emissions may not have a similar effect. That a reduction in ultrafine particles is by no means assured is indicated by recent examination of particles emitted from a newer (1991) diesel engine in which ultrafine particle emissions increased relative to 1988 engines even as particle mass emission rates were decreased (16, 17). This could occur if the newer engine causes incomplete burnout of soot particles, causing particle agglomerates to disintegrate into many smaller particles in a manner somewhat analogous to the production of many small particles from the combustion of a single coal particle (see Figure 6.13 of ref 15). Ultrafine particle emissions measurements must be made on a larger number of engines before the observations to date can be generalized.

Little work has been done to simultaneously measure both the number distribution and chemical composition of atmospheric ultrafine particles in an urban environment. Number counts for particles in this size range were obtained as early as the 1930s using Aitken's condensation nucleus counter. Detailed size distribution measurements for ultrafine particles were later acquired using electrical mobility analyzers. For example, the 1969 Pasadena Smog Aerosol Project (18, 19) made use of such an instrument, an automated Whitby Aerosol Analyzer (WAA) (20) to measure the particle number distribution over the particle diameter range $0.0075\text{--}0.6 \mu\text{m}$; two Lundgren impactors (21) were also used in that project to measure particle mass concentration and chemical composition, but the size range over which those impactors operate did not extend to the very small sizes needed to specifically examine the chemical composition of the ultrafines.

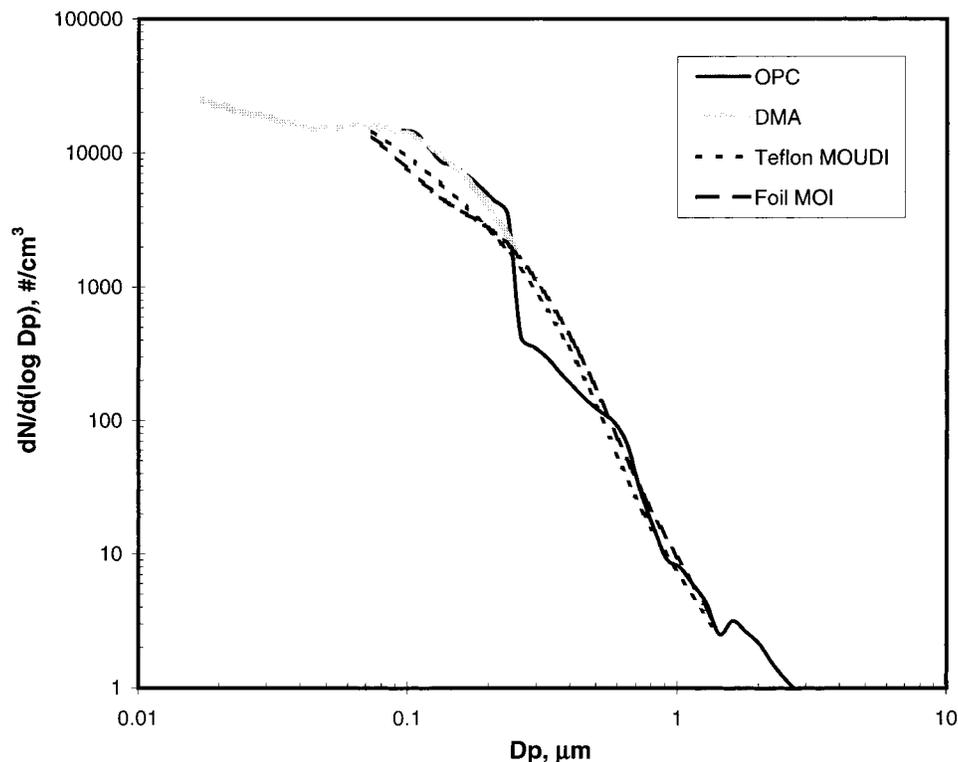


FIGURE 2. Atmospheric particle number distribution as a function of particle size averaged over the 24-h period of January 23, 1996, at Pasadena, CA. Results from all four instruments used in these experiments show degree of agreement between measurement methods.

More recently, cascade impactors have been developed which can collect particles within the ultrafine size range, allowing chemical analysis as well as mass distribution measurement to take place more readily. The low pressure impactor (LPI) designed by Hering (size range 0.05–4.0 μm) (22) was used to collect fine and ultrafine particles in the desert at Zilnez Mesa, AZ, followed by analysis for sulfur compounds by flash volatilization/flame photometric detection and elemental analysis by PIXE (23). The aim of those measurements was to determine the light scattering coefficient of various-sized particles. During the 1987 Southern California Air Quality Study (SCAQS), a variety of impactors were deployed simultaneously to measure a broader range of aerosol chemical components. Berner impactors (size range 0.075–16 μm) (24) were used for inorganic ions analysis (25); Micro-Orifice Uniform Deposit Impactors (MOUDIs), size range 0.056–18 μm , were used for organic carbon and elemental carbon particle size distributions (26, 27); and a Davis Rotating drum Unit Monitoring (DRUM) sampler (size range 0.069–8.54 μm) (28) was deployed to obtain elemental composition data by PIXE analysis (28). The impactor data from the SCAQS study are presented separately for the various chemical components measured, and for that reason, an overall picture of ultrafine aerosol composition is difficult to glean.

Other chemical analyses of size-segregated atmospheric aerosol samples include the work of Dodd et al. (29), who measured the concentrations of 44 elements in rural air using a prototype horizontally configured micro-orifice impactor (30) with a particle diameter size range of 0.083–1.03 μm and an 8-stage MOUDI (size range 0.092–4.9 μm). Measurements made at the Grand Canyon as part of the 1990 Navajo Generating Station Visibility Study (31, 32) included size-segregated samples collected with three simultaneously operated MOUDIs, for the ultimate purpose of studying the hygroscopicity of ambient particles in the desert southwestern U.S. These samples were analyzed for elemental and organic carbon concentrations, for trace elements by PIXE, and for SO_4^{2-} and NO_3^- by ion chromatography.

TABLE 1. Airborne Ultrafine Particle Number Concentration over the Size Range $0.017 < d_p < 0.1 \mu\text{m}$ Averaged over 24-h Periods at Pasadena, CA, January–February, 1996

date	number concentration cm^{-3} air
1/23/96	1.4×10^4
1/29/96	7.1×10^3
2/4/96	9.0×10^3
2/10/96	2.9×10^4
2/17/96	8.7×10^3

The aim of the present paper is to describe a measurement program designed to systematically measure both the number distribution and chemical composition of the ultrafine particles present in polluted urban air. In order to collect comprehensive data on number counts, size, and composition, particle counters and several impactors running at the same time are needed, in effect the simultaneous application of all of the individual techniques noted above. Accordingly, these experiments were conducted using a high-resolution scanning differential mobility analyzer and condensation nucleus counter (DMA/CNC), a laser optical counter (OPC), and a pair of identical impactors (Micro-Orifice Uniform Deposit Impactors, abbreviated MOUDI when rotated and MOI when not rotated). Samples were analyzed to create a material balance on the chemical composition of the ultrafine particles. Comparisons will be made to the composition and mass concentration of the entire fine particle complex ($d_p < 2 \mu\text{m}$) in order to explore the extent to which the properties of ultrafine particles can or cannot be judged from more widely available fine particle filter data.

Experimental Section

Size distribution measurements and sampling of fine and ultrafine ambient particles were carried out over the course of one winter month in January/February, 1996. Measurements were made at 6-day intervals from a rooftop in

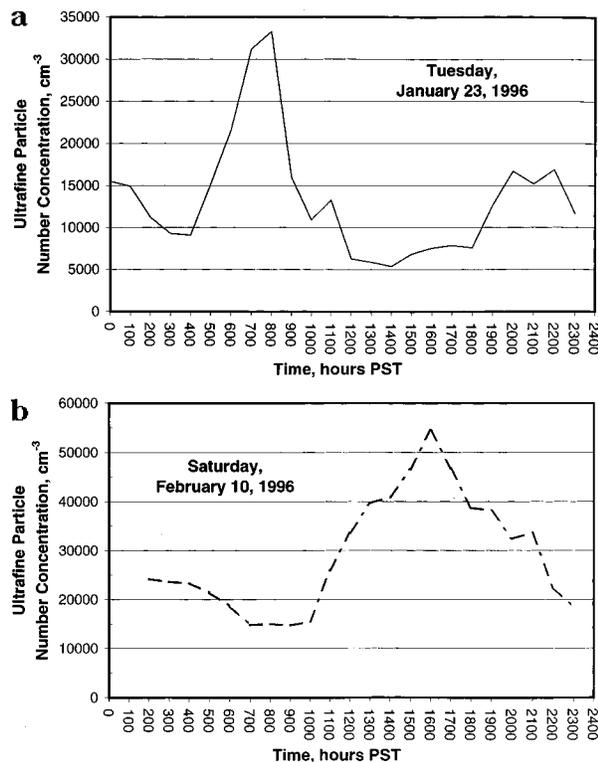


FIGURE 3. Time series of 24-h average ultrafine particle ($0.017 < d_p < 0.1 \mu\text{m}$) number concentrations, as measured by the DMA/CNC combination showing (a) Tuesday, January 23, 1996, with high concentrations near midnight and at the time of the morning traffic peak, and (b) Saturday, February 10, 1996, a day with early morning fog.

Pasadena, CA, and all instruments were operated continuously for a 24-h period during each sampling event. Two cascade impactors, a differential mobility analyzer/CNC combination, a laser optical particle counter, and a filter-based fine particle sampler were all operated simultaneously and used to obtain several different measurements of particle number distribution, mass concentration, and chemical composition. A schematic diagram of the equipment used is presented in Figure 1.

A differential mobility analyzer (DMA, TSI Inc., model 3071) was used in conjunction with a condensation nucleus counter (CNC, TSI Inc., model 3760) to measure particle number concentrations in 175 size intervals over the size range $0.017 < d_p < 0.250 \mu\text{m}$. The ultrafine particle size range, $d_p < 0.1 \mu\text{m}$, was examined in 120 measured size intervals. Both instruments were interfaced with a personal computer which operated the DMA as a scanning electrical mobility spectrometer (33) and enabled the acquisition of particle number distributions over the complete range of sizes every 90 s during each 24-h period studied.

A laser optical particle counter (OPC, Particle Measuring Systems, model ASASP-X) was used to corroborate the size distribution data from the DMA/CNC combination over the size range where the two instruments overlap and to extend size distribution measurements to larger particle sizes. This instrument recorded particle number distributions in 31 channels over the size range $0.090 < d_p < 3.0 \mu\text{m}$ every 4–10 s. Two 10-stage Micro-Orifice Uniform Deposit Impactors (MOUDI, MSP Corp., model 100) (34) were simultaneously operated to measure 24-h average fine particulate mass and chemical composition as a function of particle size. A Teflon-coated cyclone separator was placed ahead of the inlet of each impactor in order to capture coarse particles ($d_p > 1.8 \mu\text{m}$) that might otherwise enter the impactor and distort the

mass distribution measurements by bouncing from their appropriate collection stages. The fine and ultrafine particles reported here were collected on stages 5–10 of the impactors over the size range $0.056\text{--}1.8 \mu\text{m}$ particle diameter; the upper stages of the impactor also were loaded with impaction substrates, but were not analyzed chemically. An afterfilter downstream of the impaction stages collected particles smaller than $0.056 \mu\text{m}$ diameter. One impactor was equipped with aluminum foil substrates (MSP Corp.) and a quartz fiber afterfilter (Pallflex, 2500 QAO), while the other impactor was operated with Teflon filter substrates (Teflo, Gelman Science, $1.0 \mu\text{m}$ pore size) and a Teflon afterfilter (Zefluor, Gelman Science, $1.0 \mu\text{m}$ pore size). Since one key objective of this experiment was to measure the size distribution of fine organic aerosols and since the fine aerosol in Los Angeles generally has a sticky liquid film, no grease or oil was used on the substrates in order to avoid organic contamination. The impactor containing the foil substrates was operated as a micro-orifice impactor (MOI) and was not rotated during operation so that lubricant was not necessary to that system; a uniformly deposited sample was not needed for elemental and organic carbon analysis.

In addition to the above instruments, 24-h samples of total (no size separation) and fine ($d_p < 2.2 \mu\text{m}$) airborne particulate matter were collected using a filter-based system. Total particulate matter was collected on one open-faced quartz fiber filter (Pallflex, 2500 QAO) and on two parallel Teflon filters (Gelman Sciences, Teflo, $2.0 \mu\text{m}$ pore size) at the flow rates shown in Figure 1. For fine particle samples, ambient air was passed through a glass inlet line to a Teflon-coated cyclone separator (35) at a nominal flow rate of 25 Lpm before particle collection on another set of one quartz (Pallflex, 2500 QAO) and two Teflon (Gelman Sciences, Teflo, $2.0 \mu\text{m}$ pore size) filters, also as shown in Figure 1. The air flow rate through each filter was measured with a rotameter before and after each 24-h sampling period. While these filter samples did not offer the size-specific information available from the impaction substrate samples, they served as an important check on the entire quantity of fine particle material in the atmosphere. These samples have the advantage of a greater available mass, thereby facilitating chemical analysis procedures.

Mass concentration determinations were made on all foil and Teflon substrates and Teflon afterfilters, by repeated weighing before and after use on a Mettler model M-55-A mechanical microbalance maintained in a temperature- and humidity-controlled environment ($21.8 \pm 0.2 \text{ }^\circ\text{C}$, $38 \pm 3\%$ RH). Foil substrates were precleaned by baking for 40–50 h at $550 \text{ }^\circ\text{C}$, and all quartz fiber filters were precleaned by baking for at least 10 h at $550 \text{ }^\circ\text{C}$. All impactor substrates and filters were cut in half before chemical analysis to allow the use of several different chemical analysis methods. The samples collected on aluminum foil and quartz fiber filter material were analyzed for elemental and organic carbon using the thermal-optical carbon analysis method of Huntzicker et al. (36) as modified by Cary (37). Samples collected on Teflon substrates underwent analysis by ion chromatography (Dionex Corp, Model 2020i) for the anions NO_3^- , SO_4^{2-} , and Cl^- (38), analysis by an indophenol colorimetric procedure for NH_4^+ (39) using an Alpkem rapid flow analyzer (Model RFA-300), as well as neutron activation analysis for trace elements detection (40). Only the bottom six stages ($0.056 \leq d_p \leq 1.8 \mu\text{m}$) and afterfilter of the micro-orifice impactors were analyzed chemically; the ultrafine particles of special interest here were collected on the substrate of the last impaction stage ($0.056 \leq d_p \leq 0.097 \mu\text{m}$) and on the afterfilter ($d_p \leq 0.056 \mu\text{m}$).

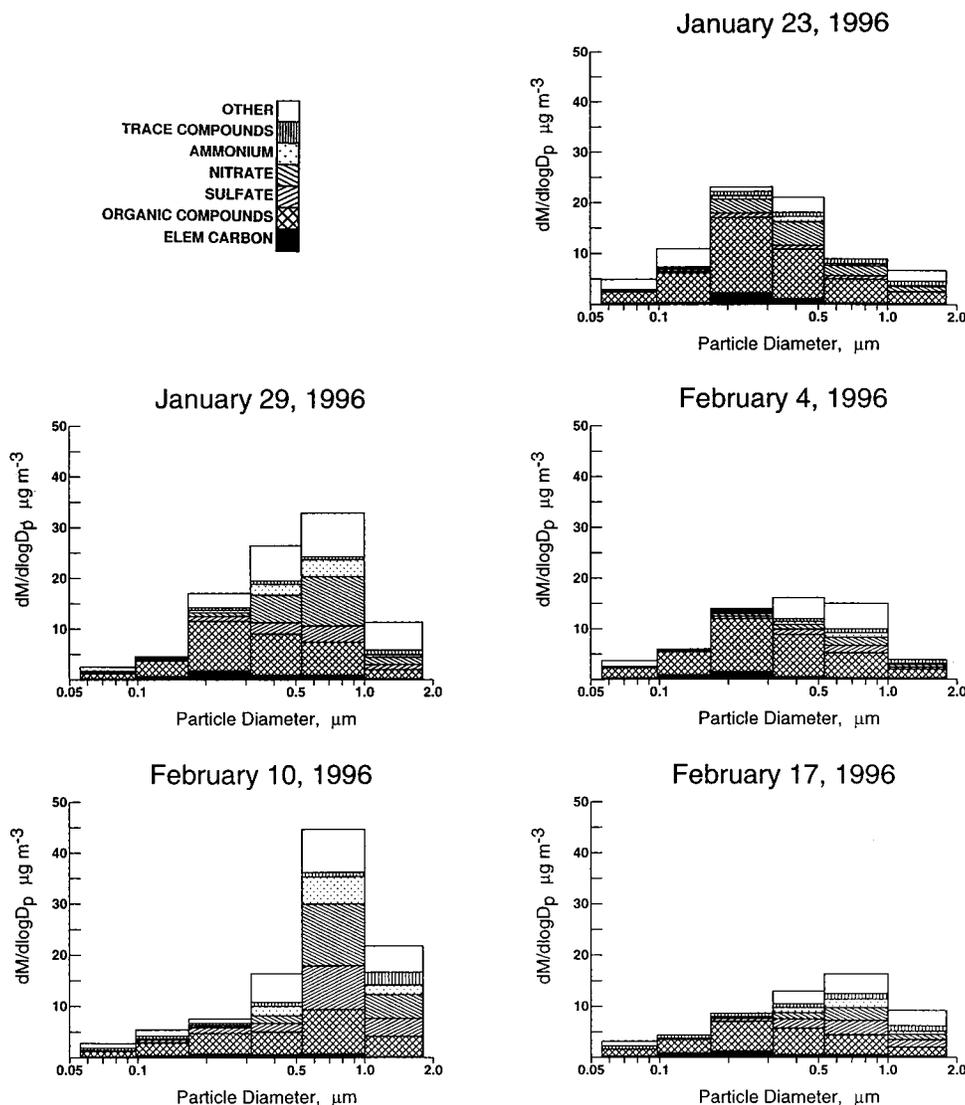


FIGURE 4. The mass distribution of the chemical composition of wintertime fine and ultrafine particles measured at Pasadena, CA. Distributions are 24-h averages for the dates shown. The most abundant trace elements other than Na and Mg are shown at the molecular weight of their common oxides.

Results

An example of the number distribution of airborne fine and ultrafine particles as measured by each of the instruments used in this study is illustrated in Figure 2. Impactor mass concentrations measured gravimetrically are converted to equivalent number concentrations using an assumed particle density of 1.7 g cm^{-3} . The data from the four instruments used generally coincide over the size range from $0.09 \mu\text{m}$ to just above $1 \mu\text{m}$ diameter where the DMA, the OPC and both impactors overlap in whole or in part. The OPC signal terminates below $0.09 \mu\text{m}$ diameter, the quartz fiber afterfilter that is loaded into the impactor used for carbon analysis is not suited to gravimetric determination of mass concentration, and in the case of the Teflon MOUDI afterfilter, there is no well-defined size at which to plot a point on the number distribution curve. Therefore, the particle number distribution shown in the ultrafine particle size range below $0.056 \mu\text{m}$ particle diameter depends largely on the data from the differential mobility analyzer/CNC combination. Table 1 shows the number concentration of atmospheric ultrafine particles in winter months in Pasadena, CA, obtained by integrating the aerosol size distributions such as the one shown in Figure 2 over the size range $0.017\text{--}0.1 \mu\text{m}$ particle diameter. Twenty-four hour average ultrafine particle num-

ber concentrations fall in the range $1.3 \times 10^4 \pm 8.9 \times 10^3$ particles/ cm^3 air. To put this in perspective, at a tidal volume of 1.2 L/breath and a respiration rate of about 10 breaths/min, a person breathing such urban air would take on the order of 2×10^{11} ultrafine particles/day into their respiratory tract. Taking into account the deposition efficiency as a function of the size distribution of the particles (41, 42), approximately 10^{11} ultrafine particles in the size range $0.017\text{--}0.1 \mu\text{m}$ diameter will deposit daily in the respiratory tract of such a person.

Ultrafine particle number concentration exposure can vary as a function of time of day. Figure 3 illustrates two examples of the daily time series of hourly average ultrafine particle number concentrations for particles in the size range 0.017 to $0.1 \mu\text{m}$ particle diameter. Figure 3a shows the time series data at Pasadena for Tuesday, January 23, 1996. There is a pronounced peak in ultrafine particle number concentration that day that occurs during the time of the morning rush hour traffic peak and higher than average values during the period around midnight, which is often a time with low mixing depths and low wind speeds in the Los Angeles area. In contrast, Figure 3b presents the time series data for Saturday, February 10, 1996, showing concentrations close to the long-term average value over the whole study during

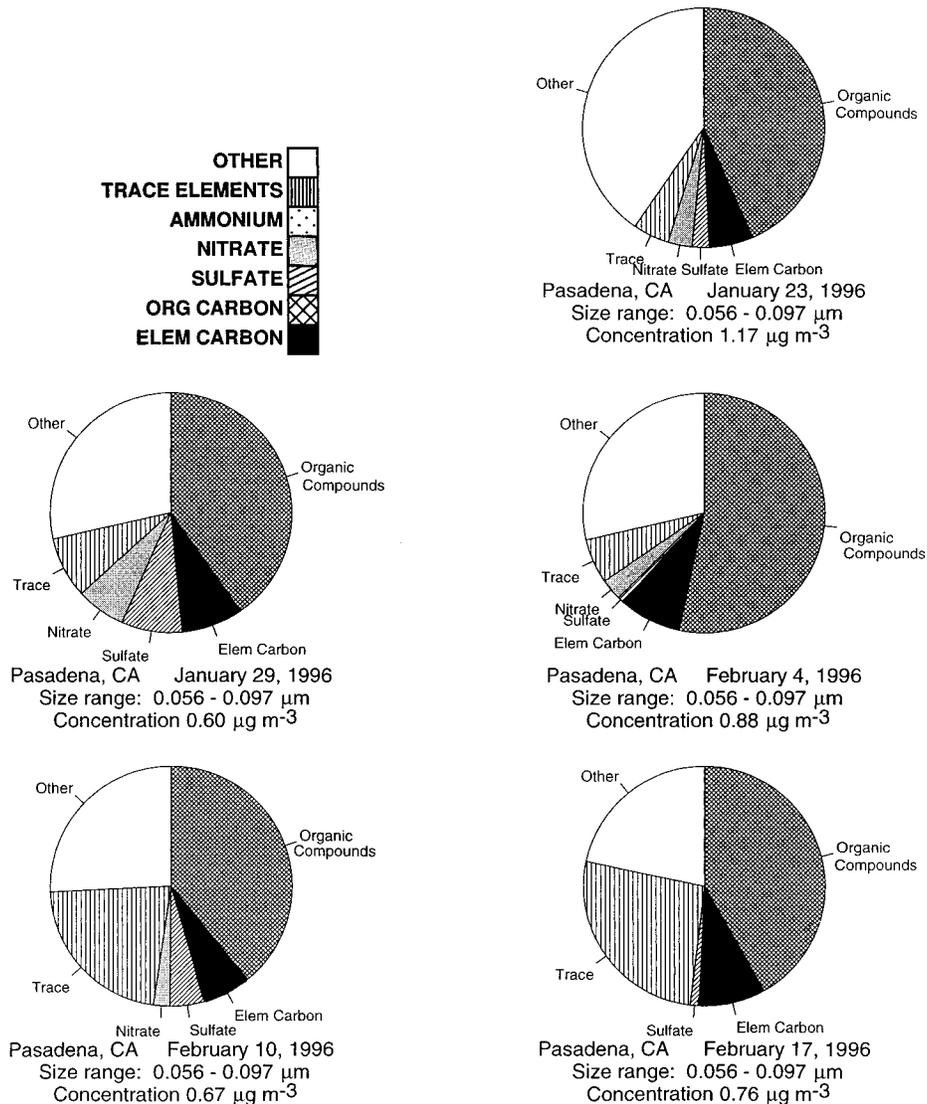


FIGURE 5. The chemical composition of wintertime ultrafine particles of size $0.056 < d_p < 0.097 \mu\text{m}$ measured at Pasadena, CA. The most abundant trace elements other than Na and Mg are shown at the molecular weight of their common oxides.

the early hours of that day, followed by a peak in ultrafine particle concentrations late in the day. The early morning hours of February 10 were accompanied by fog with droplets large enough to create a persistent downward flux of fog drops settling under the influence of gravity. The fog drops may have scavenged some of the ultrafine particles that otherwise would have been present during the early morning hours. Data presented later in this paper (Figure 4) that describe the size distribution of the chemical composition of the fine and ultrafine particles on February 10 show an enrichment in sulfates in particles having diameters from 0.5 to $1.0 \mu\text{m}$, which is symptomatic of sulfate production in fog drops in the Los Angeles area (43, 14, 44). Whether or not the afternoon peak in ultrafine particles on February 10 is in any way related to fog processing is unknown. The remaining days studied show diurnal patterns more like Figure 3a than Figure 3b, but with generally lower ultrafine particle counts during the morning traffic peak.

While ultrafine particle number concentrations are very large, the particle mass concentration contributed by ultrafines is small by comparison to those air quality standards that have been established to protect public health from damage due to airborne particles. Table 2 shows that the mass concentration of ultrafine particles in the size range $0.056\text{--}0.097 \mu\text{m}$ aerodynamic diameter ranges from 0.6–

TABLE 2. Airborne Ultrafine and Fine Particle Mass Concentrations Averaged over 24-h Periods at Pasadena, CA, January–February, 1996

date	fine particle mass conc, ^a $\mu\text{g m}^{-3}$ $d_p < 1.8 \mu\text{m}$	ultrafine particle mass conc, ^a $\mu\text{g m}^{-3}$ $0.056 < d_p < 0.097 \mu\text{m}$	ultrafine particle mass conc, ^b $\mu\text{g m}^{-3}$ $0.017 < d_p < 0.056$
1/23/96	21.49	1.17	0.36
1/29/96	25.52	0.60	0.20
2/4/96	14.86	0.88	0.24
2/10/96	24.89	0.67	0.91
2/17/96	14.02	0.76	0.20

^a Obtained gravimetrically from impactor substrates. ^b Obtained by integration of differential mobility analyzer/CNC data and using an assumed particle density of 1.7 g cm^{-3} .

$1.17 \mu\text{g m}^{-3}$. The value for the mass concentration of extremely small particles measured on the Teflon impactor afterfilters is an uncertain estimate of the true mass concentration because the impactor afterfilter used to collect those samples could be subject to positive or negative artifacts due to gaseous pollutant adsorption or semi-volatile particle

TABLE 3. Elemental Content of Ultrafine Particles Compared to Fine Particles Measured over 24-h Periods at Pasadena, CA, January–February, 1996

element	fine particle mass from filter sampler mean conc (range), ng m ⁻³ <i>d_p</i> < 2.2 μm	fine particle mass from sum of impactor stages and afterfilter mean conc (range), ng m ⁻³ <i>d_p</i> < 1.8 μm	ultrafine particle mass from final impactor stage plus afterfilter mean conc (range), ng m ⁻³ <i>d_p</i> < 0.097 μm
Groups I and II			
Na	226.7 (84.3–420.0)	190.2 (64.9–416.1)	27.0 (0.75–34.8)
K	243.4 (40.5–441.5)	240.6 (166.9–278.0)	<i>b</i>
Cs	0.083 (0.041–0.13)	0.18 (0.15–0.24)	0.016 (0.0081–0.028)
Ba	22.4 (6.5–45.7)	12.0 (8.4–15.6)	1.04 (2.8) ^a
Transition Metals			
Sc	0.022 (0.0016–0.068)	0.015 (0.010–0.022)	0.0046 (0.0081) ^a
Ti	46.7 (13.4–110.0)	46.7 (34.2–64.1)	7.65 (4.07–10.2)
V	5.46 (1.72–11.8)	5.27 (1.37–12.3)	0.059 (0.14) ^a
Cr	25.0 (0.18–78.7)	19.9 (2.46–61.2)	7.32 (26.2) ^a
Mn	7.89 (2.10–17.4)	4.79 (2.42–6.94)	0.74 (2.43) ^a
Fe	382.4 (115.8–790.0)	285.8 (132.6–470.2)	67.5 (148.3) ^a
Zn	44.2 (7.01–120.0)	24.9 (7.70–57.7)	3.68 (6.56) ^a
Mo	1.33 (3.15) ^a	0.40 (0.068–0.59)	0.072 (0.19) ^a
Cd	0.72 (0.061–1.44)	0.26 (0.093–0.44)	0.061 (0.12) ^a
Au	0.0031 (0.0016–0.0067)	0.00050 (0.0014) ^a	<i>b</i>
Hg	0.036 (0.016–0.068)	0.049 (0.026–0.071)	0.0052 (0.00014–0.012)
Lanthanides			
La	0.36 (0.20–0.43)	0.36 (0.17–0.68)	0.11 (0.00082–0.51)
Ce	0.37 (0.12–0.70)	0.43 (0.081–0.99)	0.19 (0.82) ^a
Sm	0.013 (0.0050–0.031)	0.023 (0.0047–0.080)	0.015 (0.00030–0.073)
Eu	0.077 (0.039–0.19)	0.076 (0.058–0.12)	0.013 (0.023) ^a
Yb	0.015 (0.028) ^a	0.014 (0.0040–0.031)	0.0028 (0.0059) ^a
Lu	0.0014 (0.0025) ^a	0.0029 (0.0014–0.0060)	0.00038 (0.0013) ^a
Actinides			
Th	0.059 (0.13) ^a	0.042 (0.016–0.085)	0.0065 (0.018) ^a
U	0.019 (0.052) ^a	0.035 (0.055) ^a	0.0057 (0.019) ^a

^a Sample with lowest concentration is below detection limit; only high end of range is shown. ^b All samples are below detection limit.

evaporation (45). An alternate estimate of the mass concentration of particles smaller than 0.056 μm diameter can be obtained by integrating the size distribution measured by the differential mobility analyzer/CNC combination (DMA in Figure 1) over the size range 0.017–0.056 μm. At an assumed particle density of 1.7 g cm⁻³, the mass concentration of these very small particles would total 0.20–0.91 μg m⁻³ over the days studied, as shown in Table 2. Combining the data in the two columns farthest to the right in Table 2 on a daily basis, the mass concentration of ultrafine particles of size 0.017–0.097 μm was in the range 0.80–1.58 μg m⁻³ over 24-h averaging times.

To provide data that are relevant to the hypotheses outlined in the Introduction about the possible relationship between ultrafine particle chemical composition and health, the impactor samples taken here were subjected to extensive chemical analysis as described earlier. Size distributions of the chemical composition of the entire fine particle portion of the atmospheric aerosol during these experiments are shown in Figure 4. In constructing that figure, as well as Figure 5, organic compound mass concentrations are estimated as 1.4 times the organic carbon measured, to account for H, O, S, and N present in organic compounds (46), and the most abundant trace elements other than Na and Mg are shown at the equivalent mass concentration of their common oxides. The “other” category refers to the apparent particle mass concentration determined gravimetrically that cannot be assigned to identified chemical components. It is possible that this unidentified mass includes additional organic compound mass, which would be the case if the ultrafine organics consist largely of oxygenated organics with a mass-to-organic carbon ratio of greater than 1.4 (at present the actual compounds present are not known). As expected,

the fine particle mass concentration is dominated by particles larger than 0.1 μm diameter. Nitrates and sulfates are commonly found in particles larger than 0.2–0.3 μm diameter, with the highest concentrations of these water soluble inorganic ionic species present in particles larger than 0.5 μm diameter. In contrast, particles 0.1 < *d_p* < 0.3 μm are largely carbonaceous, and particles in the ultrafine range *d_p* < 0.1 μm are found to consist of 46–62% elemental carbon plus organic compounds.

Figure 5 shows pie charts which display the chemical composition of the ultrafine particles collected on impactor stage 10 (diameter range 0.056–0.097 μm). As in Figure 4, the apparent particle mass concentration that cannot be assigned to identified chemical components is labeled as “other” material. Typically, when constructing material balances on aerosol chemical composition, unidentified components constitute 0–35% of the fine particle mass (23, 47–51). Here, the unidentified material in the ultrafine particle size range amounted to 23–40%; the slightly larger discrepancy is expected due to the very small amounts of material available for analysis. Organic compounds are the largest contributors to these wintertime ultrafine particles followed by black elemental carbon particles. The organic carbon (OC) and elemental carbon (EC) in ultrafine particles collected on the last stage of the impactors at Pasadena during the January–February 1996 experiments can be compared to the OC and EC collected on the lowest stages of the impactor samples reported by McMurry (26) during the 1987 Southern California Air Quality Study. The data described in this paper show an average concentration of 0.26 μg m⁻³ OC and 0.06 μg m⁻³ EC between 0.056 and 0.097 μm particle diameter at Pasadena, CA, in the winter of 1996. The SCAQS data show an average concentration of 0.35 μg m⁻³ OC and

0.10 $\mu\text{g m}^{-3}$ EC between 0.046 and 0.086 μm particle diameter at Claremont, CA in the summer of 1987; an average of 0.11 $\mu\text{g m}^{-3}$ OC and 0.00 $\mu\text{g m}^{-3}$ EC between 0.036 and 0.072 μm particle diameter at Rubidoux, CA in the summer of 1987; an average of 0.48 $\mu\text{g m}^{-3}$ OC and 0.18 $\mu\text{g m}^{-3}$ EC between 0.034 and 0.062 μm particle diameter at Long Beach, CA, in the fall of 1987; and an average of 0.51 $\mu\text{g m}^{-3}$ OC and 0.25 $\mu\text{g m}^{-3}$ EC between 0.036 and 0.072 μm particle diameter at Los Angeles, CA in the fall of 1987.

The sulfate content of the ultrafine particles measured during these wintertime Los Angeles area experiments is very low, averaging $3.4 \pm 3.0\%$ of the ultrafine particulate matter collected on impactor stage 10 (i.e., typically less than 10 ng m^{-3} as sulfur). This eliminates the possibility that the ultrafine particles are mostly sulfuric acid at the place and time studied. An ion balance on these ultrafine particles shows that SO_4^{2-} exceeds NH_4^+ , leaving open the possibility that some unneutralized sulfuric acid is present; the measurements are inconclusive, however, since the mass in the ultrafine sizes is small enough that even if NH_4^+ was present in quantities necessary to balance SO_4^{2-} , it would still be below the detection limits of the NH_4^+ analysis procedure. By comparison, ultrafine sulfur concentrations reported for the 1987 SCAQS experiments by (28) using DRUM impactors show higher concentrations, generally above 100 ng m^{-3} as sulfur (exact comparison is not possible due to differences in the size cuts used by the micro-orifice versus DRUM impactors).

The potentially catalytic transition element content of the ultrafine particles (both impactor stage 10 samples and afterfilter samples) is described in Table 3. The most abundant catalytic trace metal present is iron, which is one of the metals shown by Dreher et al. (11) to be capable of catalyzing the production of oxidative damage in pulmonary systems. Pt, Pd, and Rh are not detected by the neutron activation analysis performed here; therefore, the contribution of noble metal emissions from motor vehicle catalytic converters cannot be estimated. Lanthanide series elements that also are used as catalysts are present in the ultrafine particle data set shown in Table 3. Cerium concentrations in ultrafine particles averaged 0.19 ng m^{-3} , for example.

Acknowledgments

This work was supported by the Center for Air Quality Analysis at Caltech. Thanks are due to Drs. Kent Hoekman and Steve Ziman of Chevron for assistance with this research. Aerosol carbon analyses were performed by Bob Cary at Sunset Labs, Forest Grove, OR.

Literature Cited

- Dockery, D. W.; Pope, C. A.; Xu, X.; Spengler, J. D.; Ware, J. H.; Fay, M. E.; Ferris, B. G.; Speizer, F. E. *N. Engl. J. Med.* **1993**, *329*, 1753–1759.
- Pope, C. A.; Dockery, D. W.; Schwartz, J. *Inhalation Toxicol.* **1995**, *7*, 1–18.
- Schlesinger, R. B. *Inhalation Toxicol.* **1995**, *7*, 99–109.
- Oberdorster, G.; Ferin, J.; Gelein, R.; Soderholm, S. C.; Finkelstein, J. *Environ. Health Perspect.* **1992**, *97*, 193–199.
- Oberdorster, G.; Ferin, J.; Lehnert, B. E. *Environ. Health Perspect.* **1994**, *102*, 173–179.
- Oberdorster, G.; Gelein, R. M.; Ferin, J.; Weiss, B. *Inhalation Toxicol.* **1995**, *7*, 111–124.
- Chen, L. C.; Peoples, S. M.; Amdur, M. O. *Am. Ind. Hyg. Assoc. J.* **1991**, *52*, 187–191.
- Schlesinger, R. B. *Environ. Health Perspect.* **1989**, *79*, 121–126.
- Lippman, M.; Schlesinger, R. B.; Leikauf, G.; Spektor, D.; Albert, R. E. *Ann. Occupational Hyg.* **1982**, *26*, 677–690.
- Ghio, A. J.; Stonehuerner, J.; Pritchard, R. J.; Piantadosi, C. A.; Quigley, D. R.; Dreher, K. L.; Costa, D. L. *Inhalation Toxicol.* **1996**, *8*, 479–494.
- Dreher, K. L.; Jaskot, R. H.; Lehmann, J. R.; Richards, J. H.; McGee, J. K.; Ghio, A. J.; Costa, D. L. *J. Toxicol. Environ. Health* **1997**, *50*, 285–305.
- Oberdorster, G. *Particulate Sci. Technol.* **1996**, *14*, 135–151.
- Hildemann, L. M.; Markowski, G. R.; Jones, M. C.; Cass, G. R. *Aerosol Sci. Technol.* **1991**, *14*, 138–152.
- Eldering, A.; Cass, G. R. *J. Geophys. Res. A* **1996**, *101*, 19343–19369.
- Flagan, R. C.; Seinfeld, J. H. *Fundamentals of Air Pollution Engineering*; Prentice-Hall: Inc.: Englewood Cliffs, NJ, 1988.
- Bagley, S. T.; Baumgard, K. J.; Gratz, L. D.; Johnson, J. H.; Leddy, D. G. *Characterization of fuel and aftertreatment device effects on diesel emissions*, Technical Report 76, Health Effects Institute: Cambridge, MA, 1996.
- Baumgard, K. J.; Johnson, J. H. *The effect of fuel and engine design on diesel exhaust particle size distributions*; SAE Technical Paper Series 960131, Society of Automotive Engineers: Warrendale, PA, 1996.
- Whitby, K. T.; Liu, B. J.; Husar, R. B.; Barsic, N. J. *J. Colloid Interface Sci.* **1972**, *39*, 136–176.
- Whitby, K. T.; Husar, R. B.; Liu, B. Y. H. *J. Colloid Interface Sci.* **1972**, *39*, 177–204.
- Whitby, K. T.; Clark, W. E. *Tellus* **1966**, *18*, 573–586.
- Lundgren, D. A. *J. Air Pollut. Control Assoc.* **1967**, *17*, 225–228.
- Hering, S. V.; Flagan, R. C.; Friedlander, S. K. *Environ. Sci. Technol.* **1978**, *12*, 667–673.
- Quimette, J. R.; Flagan, R. C. *Atmos. Environ.* **1982**, *16*, 2405–2419.
- Wang, H. C.; John, W. *Aerosol Sci. Technol.* **1988**, *8*, 157–172.
- Wall, S. M.; John, W.; Ondo, J. L. *Atmos. Environ.* **1988**, *22*, 1649–1656.
- McMurry, P. H. *Organic and elemental carbon size distribution of Los Angeles aerosol measurements during SCAQS: Final report to California Air Resources Board*; Technical Report A732-075, University of Minnesota, 1989.
- McMurry, P. H.; Zhang, X. Q. *Aerosol Sci. Technol.* **1989**, *10*, 430–437.
- Cahill, T. H.; Matsumura, R. F.; Surovick, M.; Unger, C.; Wilkenson, K. *Size-time-compositional analysis of aerosols during SCAQS: Final report to California Air Resources Board*; Technical Report A732-074, University of California-Davis, 1990.
- Dodd, J. A.; Ondov, J. M.; Tuel, G.; Dzabay, T. G.; Stevens, K. R. *Environ. Sci. Technol.* **1991**, *25*, 890–903.
- Kuhlmeier, G. A.; Liu, B. Y. H.; Marple, V. A. *Am. Ind. Hyg. Assoc. J.* **1981**, *42*, 790–795.
- Zhang, X. Q.; McMurry, P. H.; Hering, S. V.; Casuccio, G. S. *Atmos. Environ.* **1993**, *27A*, 1593–1607.
- Pitchford, M. L.; McMurry, P. H. *Atmos. Environ.* **1994**, *28*, 827–839.
- Wang, S. C.; Flagan, R. C. *Aerosol Sci. Technol.* **1990**, *13*, 230–240.
- Marple, V. A.; Rubow, K. L.; Behm, S. M. *Aerosol Sci. Technol.* **1991**, *14*, 434–446.
- John, W.; Reischl, G. J. *Air Pollut. Control Assoc.* **1980**, *30*, 872–876.
- Huntzicker, J. J.; Johnson, R. L.; Shah, J. J.; Cary, R. A. In *Particulate Carbon, Atmospheric Life Cycle*; Wolff, G. T.; Klimisch, R. L., Eds.; Plenum: New York, 1982.
- Birch, M. E.; Cary, R. A. *Aerosol Sci. Technol.* **1996**, *25*, 221–241.
- Mulik, J.; Puckett, R.; Willims, D.; Sawicki, E. *Anal. Lett.* **1976**, *9*, 653–663.
- Bolleter, W. T.; Bushman, C. T.; Tidwell, P. W. *Anal. Chem.* **1961**, *33*, 592–594.
- Olmez, I. In *Methods of Air Sampling and Analysis, 3rd ed.*; J. P. Lodge, J., Ed.; Lewis Publishers: Inc.: Chelsea, MI, 1989.
- Task Group on Lung Dynamics. *Health Phys.* **1966**, *12*, 173–207.
- Phalen, R. F.; Cuddihy, R. G.; Fisher, G. L.; Moss, O. R.; Schlessing, R. B.; Swift, D. L.; Yeh, H. C. *Radiat. Prot. Dosim.* **1991**, *38*, 179–184.
- Meng, Z. Y.; Seinfeld, J. H. *Aerosol Sci. Technol.* **1994**, *20*, 253–265.
- Kleeman, M. J.; Cass, G. R.; Eldering, A. J. *Geophys. Res. A* **1997**, *102*, 21355–21372.
- McDow, S. R.; Huntzicker, J. J. *Atmos. Environ.* **1990**, *24A*, 2563–2571.
- Grosjean, D.; Friedlander, S. K. *J. Air Pollut. Control Assoc.* **1975**, *25*, 1038–1044.
- Mazurek, M.; Masonjones, M. C.; Masonjones, H. D.; Salmon, L. G.; Cass, G. R.; Hallock, K. A.; Leach, M. J. *Geophys. Res.* **1997**, *102*, 3779–3793.

- (48) Chow, J. C.; Watson, J. G.; Fujita, E. M.; Lu, Z.; Lawson, D. R.; Ashbaugh, L. L. *Atmos. Environ.* **1994**, *28*, 2061–2080.
- (49) Chow, J. C.; Watson, J. G.; Lu, Z.; Lowenthal, D. H.; Frazier, C. A.; Solomon, P. A.; Thuillier, R. H.; Magliano, K. *Atmos. Environ.* **1996**, *30*, 2079–2112.
- (50) Salmon, L. G.; Christoforou, C. S.; Cass, G. R. *Environ. Sci. Technol.* **1994**, *28*, 805–811.
- (51) Salmon, L. G.; Cass, G. R.; Kozlowski, R.; Hedja, A.; Spiker, E. C.; Bates, A. L. *Environ. Sci. Technol.* **1996**, *30*, 872–880.

Received for review March 26, 1997. Revised manuscript received December 18, 1997. Accepted January 6, 1998.

ES970280R