



Field evaluation of a modified DataRAM MIE scattering monitor for real-time PM_{2.5} mass concentration measurements

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Received 24 January 2000; received in revised form 10 April 2000; accepted 13 April 2000

Abstract

In this paper, we investigated the feasibility of using a modified DataRAM nephelometer (RAM-1, MIE Inc., Billerica, MA) as a continuous PM_{2.5} monitor to measure concentrations of ambient and concentrated aerosols in real time. The DataRAM operated with a diffusion dryer tube in its inlet in order to reduce the relative humidity of the sampled air to less than 50%. A total of 39 field tests were conducted in which the average dry DataRAM concentration was compared to the gravimetrically determined mass concentration, corrected for nitrate losses. Tests were conducted over one calendar year (from January to December 1999) in order to capture maximum seasonal variations in the levels of relative humidity, PM size distribution and chemical composition in the Los Angeles Basin.

Our experimental results indicated that the aerosol mass median diameter (MMD) is the single, most important parameter in affecting the response of the DataRAM. As the MMD increases from 0.3 to 1.1 μm, the DataRAM-to-MOUDI ratio increases from approximately 0.7 to about 1.6. The DataRAM-to-MOUDI ratio subsequently decreases to about 1.0, as the MMD further increases to 1.5 μm. For MMD values in the range of 0.4–0.7 μm (i.e., the MMD size range that is most commonly associated with urban aerosols), the DataRAM and gravimetrically measured mass concentrations (corrected for nitrate losses) agree within ± 20%. Based only on ambient data, the average DataRAM-to-gravimetric concentration ratio was 0.93 (± 0.17), whereas the average DataRAM-to-gravimetric concentration ratio for concentrated PM_{2.5} aerosols was 1.23 (± 0.20). Our field evaluation also indicated that the effect of particle chemical composition on the DataRAM-to-gravimetric concentration ratio is much less important than that of particle size distribution. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: DataRAM; Nephelometer; Particle concentrator; Diffusion dryer; PM_{2.5} direct measurement

1. Introduction

Current US federal air quality standards for protection of human health are based on non-aqueous mass concentrations of particulate matter (PM). The US

Environmental Protection Agency (US EPA) has recently promulgated a new National Ambient Air Quality Standard (NAAQS) for fine particulate matter (PM_{2.5}; particulate matter smaller than 2.5 μm in aerodynamic diameter). This new standard is in addition to the preexisting standard for PM₁₀ (including particles having aerodynamic diameters from 2.5 to 10 μm). For both standards, the Federal Reference Method (FRM) is based on the gravimetric analysis of particle filters collected over a period of 24 h. Gravimetric analysis has

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been selected because most of the particle data used for the epidemiological studies investigating associations between mortality and morbidity outcomes and ambient particle exposures are based on particle mass concentrations (Dockery et al., 1993; Vedal, 1997). Nevertheless, the values of key atmospheric metrics influencing ambient particle concentration and size distribution, such as the emission strengths of particle sources, temperature, relative humidity, wind direction and speed and mixing height, fluctuate in time scales that are substantially shorter than 12–24 h. Individual activity patterns also vary in time periods considerably shorter than 24 h. The need for developing monitors that measure particle concentration in shorter time intervals (on the order of 1–2 h, or less) is therefore of paramount importance to environmental health, as it leads to substantial improvements in exposure assessment to ambient particulates.

The correlation between particle mass concentration and light extinction due to particle scattering has been used as the principle for “in situ” monitoring of particle mass concentrations by instruments known as photometers or nephelometers (Waggoner and Weiss, 1980; Thomas and Gebhart, 1994; White et al., 1994; Brauer, 1995). In general, this correlation depends on particle size, chemical composition and hygroscopicity (Scheff and Wadden, 1979; Lewis, 1981). For example, in studies conducted in the southwestern US, White et al. (1994) showed that nephelometers reported less than half of the actual scattering by coarse particles. When this under-response was corrected for, the coarse particles were found to be responsible for approximately 25–35% of the total particle scattering. Other than comparing the contributions of coarse and fine particles to the overall light scattering, however, this study did not provide any information on how differences in particle size distribution and chemical composition might affect the relationship between particle mass concentration and light extinction.

Waggoner and Weiss (1980) compared the relationship between light scattering and particle mass concentrations in five different western US sites, affected by different particle sources (i.e., urban, industrial, rural or residential) and with a sharp contrast in relative humidity. Similar responses (expressed as the ratio of fine particle mass concentration to light scattering extinction coefficient) were found for two different nephelometers used in each location. The authors attributed this agreement to similarities in the average aerosol size distribution in each location. However, no size distribution data were produced to support this hypothesis. Thomas and Gebhart (1994) evaluated the relationship between gravimetrically determined aerosol mass concentration and light scattering as a function of particle size using exclusively laboratory-generated aerosols. The very limited field data of that study showed a fairly linear relationship between photometry and gravimetry, as long as ambient relative humidity is below 60% and the aerosol

size distribution based on mass is dominated by particles comparable to the wavelength of the light scattered by the particles. The authors concluded, however, that in the presence of coarser size fractions and higher relative humidities, additional information would be required in order to establish a correlation between photometer signals and mass concentrations of atmospheric aerosols.

The objective of the study presented in this paper was to evaluate the usefulness of a modified photometer (DataRAM nephelometer; RAM-1, MIE Inc., Billerica, MA) for providing real-time mass concentration measurement and to assess the effect of particle size and chemical composition on the relationship between the response of the photometer and the actual aerosol mass concentration. The DataRAM monitor is an integrated nephelometer and measures continuously the amount of light (with a wavelength, $\lambda = 880$ nm) scattered by particles drawn through a sensing zone at a flow rate of 21 min^{-1} . The amount of light scattered is converted to particle concentration readings. The instrument's performance is based on the well-established light scattering theory (Kerker, 1969).

In this paper, we present results from a field evaluation of this instrument conducted in Southern California over the period of one year. The DataRAM was used with a diffusion dryer in its inlet in order to exclude the contribution of the aqueous component of $\text{PM}_{2.5}$ to the overall mass concentration measured by the instrument. In their nominal configuration, light scattering photometers sample $\text{PM}_{2.5}$ at ambient RH (thereby including their aqueous component), or have used heated inlets (which would cause excessive volatilization of labile PM constituents). The performance of this modified nephelometer was compared to the actual $\text{PM}_{2.5}$ concentration (i.e., including the concentration of volatile species, such as ammonium nitrate) and the effect of physico-chemical PM characteristics, such as chemical composition and particle size distribution, on the DataRAM-to-gravimetric mass concentration was investigated. In addition to ambient measurements, the DataRAM was used to measure in real time the mass concentrations of concentrated $\text{PM}_{2.5}$ aerosols inside a whole-body exposure chamber during human exposure studies to real-life particulate pollutants in Southern California.

2. Methods

2.1. Field study setup

The experimental setup that was used to evaluate the performance of the DataRAM monitor is described in detail by Gong et al. (2000). The DataRAM was used to measure real-time $\text{PM}_{2.5}$ mass concentrations for ambient and concentrated aerosols in the Environmental Health Service's movable exposure laboratory based at Rancho Los Amigos National Rehabilitation Center

(RLANRC) in the central portion of the South Coast Air Basin. Concentrated aerosols were obtained by means of a two-stage ambient fine particle concentrator, described by Sioutas et al. (1995a, 1997a). In this system, ambient aerosols are drawn first through a Model TE-6001 size selective inlet (SSI) (Tisch Environmental Inc, Cleveland, OH), similar to those used in high-volume air samplers for routine monitoring, which excludes particles above 2.5 μm in aerodynamic diameter. The ambient aerosol is then drawn through a stainless-steel transition piece into the first stage of the concentrator, which consists of five slit-nozzle virtual impactors in parallel. Of the 10001 min^{-1} flow entering each slit, the minor flow of 2001 min^{-1} , enriched in particles by approximately a factor of 3, passes through another transition piece to the second stage, while the major flow of 8001 min^{-1} is discarded. The second stage consists of a single slit-nozzle virtual impactor identical to those of the first stage. The particle-enriched minor flow from the second stage is drawn through a dilution stage, if desirable, and then through a whole-body human exposure chamber, at a rate of 200–2501 min^{-1} under a slightly negative pressure (0.98 atm), while the major flow is discarded. The exposure atmosphere exits the chamber through multiple ports above and behind the subject's head.

Time-integrated $\text{PM}_{2.5}$ sampling was conducted using multi-stage micro-orifice uniform deposit impactors (MOUDI, MSP Corp., Minneapolis), described in detail by Marple et al. (1991), and Harvard honeycomb denuder samplers (HDS), described by Koutrakis et al. (1993), to determine total mass with size distribution, nitrate, and sulfate. MOUDI and HDS sampling ports were located in the front wall of the chamber 10 cm and 30 cm, respectively, from the perimeter of the concentrated particle inlet. Teflon filters of all samplers were pre- and post-weighed using an MT5 Microbalance (Mettler Toledo Inc, Highstown, NJ) after 24 h equilibration at 21–24°C and 40–50% relative humidity (RH). Teflon and coated glass fiber filters were subsequently extracted with 10 ml of ultra-pure water, sonicated for 30 min, and analyzed by ion chromatography to determine particulate sulfate and nitrate. Teflon filters were wetted with 200 μl of ethanol prior to extraction.

Elemental and organic carbon (EC/OC) concentrations of ambient and concentrated aerosols were measured by placing a 4.7-cm-diameter quartz filter (Pallflex Corp., Putnam, CT) upstream of the first stage of the concentrator (i.e., immediately downstream of the $\text{PM}_{2.5}$ inlet), and another 4.7-cm-diameter quartz filter in the minor flow of the second stage of the concentrator. The EC/OC concentrations were determined by thermo-analysis, which is described in detail by Fung (1990).

Temperature and relative humidity were measured every 15 min by a thermohygrometer HI-9161F (Hanna Instruments, Italy). The sampling time for each charac-

terization study varied from 4 to 7 h, depending on the time required to collect enough mass at the prevailing ambient concentrations. Before each experiment, the DataRAM was calibrated following standard calibration procedures recommended by the manufacturer. These include zeroing of the instrument (i.e., testing with particle-free air) and span checking (i.e., a secondary calibration which is performed using a built-in optical scattering/diffusing element). The instrument is calibrated by the manufacturer using SAE Fine (ISO Fine) dust with mass median diameter (MMD) of 3 μm (GSD = 2.5), density of 2.6 g cm^{-3} and refractive index of 1.54. The internal calibration ensures that before each test started, the calibration factor was 100%. This factor could be adjusted to account for differences between the calibration dust used by the manufacturer and ambient aerosol.

The study period involved 66 characterization studies from 17 November 1998 to 20 December 1999 in our site at south central Los Angeles. Of the 66 tests, 27 were conducted using the DataRAM in its conventional form, whereas in 39 field tests, a diffusion dryer (described below) was placed at the inlet of the instrument. Ambient temperature ranged from 13 to 29°C, relative humidity ranged from 22 to 87% and ambient $\text{PM}_{2.5}$ levels varied from 6.7 to 114.0 $\mu\text{g m}^{-3}$, whereas concentrated $\text{PM}_{2.5}$ levels varied from 180.5 to 340 $\mu\text{g m}^{-3}$.

2.2. Comparisons between DataRAM and gravimetrically determined $\text{PM}_{2.5}$ concentrations

The concentration readings of any nephelometer increase with RH, primarily due to the increase in the average particle size associated with the condensational growth of hygroscopic PM components (McMurry et al., 1996; Sloane, 1984). The effect of particle growth on light scattering has been studied by Sloane (1984) and Lowenthal et al. (1995) by modeling particle growth as follows:

$$\frac{D^3}{D_0^3} = 1 + \frac{\text{RH}}{1 - \text{RH}} E \rho_p f, \quad (1)$$

where D and D_0 are the wet and dry particle diameters, respectively, E is the soluble fraction of the dry PM mass, ρ_p is the dry particle density and f is a composite function, defined by Sloane (1984) as follows:

$$f = \langle i \rangle \langle \varepsilon \rangle \frac{M_w}{M_s}, \quad (2)$$

where $\langle i \rangle$ is the van't Hoff factor, ε is the dissolved (or soluble) fraction of the aerosol mass, M_w is the molecular weight of water and M_s is the average molecular weight of the dissolved aerosol constituents. Sloane and Wolff (1985) and Lowenthal et al. (1995) developed empirical models, based on actual field data, to predict f as a function of RH.

The first part of the field evaluation of the DataRAM consisted of 27 field tests in which the instrument was used in its conventional configuration (i.e., without any means of removing particle-bound water) to monitor continuously either ambient or concentrated air. The time-integrated DataRAM readings were compared to the gravimetrically determined mass concentrations with the MOUDI corrected for losses of ammonium nitrate. The corrected (or actual) $PM_{2.5}$ mass concentration measured by the MOUDI is determined as follows:

$$PM_{true} = PM_{MOUDI} + AN_{HDS} - AN_{MOUDI}, \quad (3)$$

where PM_{MOUDI} is the total mass concentration determined by adding the net mass gain in all of the MOUDI stages, AN_{MOUDI} is the total particulate nitrate concentration measured by the MOUDI and AN_{HDS} is the total nitrate concentration determined by the collocated HDS, sampling in parallel to the MOUDI. The above equation assumes that ammonium nitrate losses in the MOUDI account for the majority of losses of labile PM species. We acknowledge that losses of organic compounds from the MOUDI substrates may also lead to an underestimation of the total mass concentration. However, previous theoretical predictions (Zhang and McMurry, 1987) and experimental studies employing impactors operating under a similar or higher pressure drop to that of the MOUDI (Sioutas et al., 1997b; Hering et al., 1997) have shown that evaporative losses from impactors are considerably lower than from filters. We, therefore, assumed that organic compound losses from the MOUDI were not significant enough to affect the interpretation of the comparisons between the DataRAM and MOUDI concentrations.

The scope of this first test series was to illustrate the effect of relative humidity on the response of the DataRAM and thus to establish the rationale for its modification, which is described in the following section.

2.3. Modification of the DataRAM

Because RH appeared to be an important source of artifact in DataRAM readings (as it will be discussed in Section 3), a diffusion drying tube was attached to the DataRAM sampling line, after which its averaged concentration readings more closely approached gravimetric (MOUDI) measurements. The diffusion drying tube consists of a cylindrical stainless-steel screen, 1.2 cm in diameter and 12 cm in length, surrounded by a bed of desiccant, contained in a plastic jacket. Three different materials were tested as the desiccant used to dry the sampled particles: (1) Drierite: anhydrous calcium sulfate ($CaSO_4$) with 3% cobalt chloride ($CoCl_2$) as indicator, 8 mesh (W.A. Hammond Drierite Company LTD., Xenia, OH); (2) desiccant: 99.6% SiO_2 as 100% indicating coat, 6–8 mesh (EM Industries, Inc., Gibbstown, NY);

and (3) silica gel: 100% plain SiO_2 , 6–12 mesh (Eagle Chemical CO., INC., Mobile, AL). The experimental characterization of these materials, which is described in greater detail by Kim et al. (2000), identified silica gel as the optimum desiccant, both in terms of vapor removal efficiency and capacity. The experiments of Kim et al. (2000) showed that, operating at 21 min^{-1} , this diffusion dryer configuration removes approximately 70% of the incoming water vapor and without any loss in its vapor removal efficiency for up to 7 h of operation. Even though most of our experiments lasted for 4–5 h, after each use, adsorbed water was driven off the desiccant by baking overnight at $40\text{--}50^\circ\text{C}$. Thus, each test started with fresh supply of silica gel in order to ensure that the aerosol drawn through the DataRAM was completely dry.

A total of 39 field tests were conducted in which the average dry DataRAM concentration was compared to the gravimetrically determined mass concentration, corrected for nitrate losses. Tests were conducted over one calendar year (from January to December 1999) in order to capture maximum seasonal variations in the levels of relative humidity, temperature as well as in size distribution and chemical compositions of PM in the Los Angeles Basin.

3. Results and discussion

The relationship between the DataRAM/MOUDI concentration ratio and relative humidity is illustrated by the data in Fig. 1. DataRAM and MOUDI gravimetric measurements agree very well (i.e., ratios are close to 1) for relative humidities lower than approximately 50%, but the DataRAM-to-gravimetric concentration ratio increases exponentially at higher RH values. In addition to

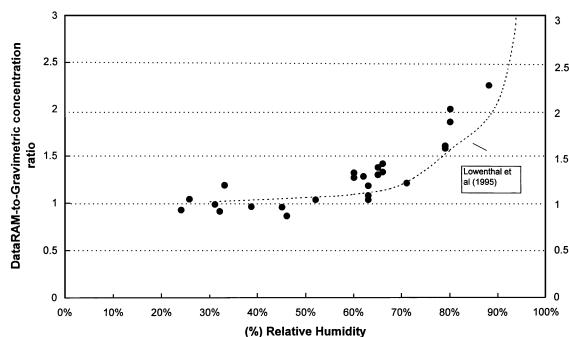


Fig. 1. Plot of the DataRAM-to-gravimetric mass concentrations (corrected for nitrate loss) as a function of relative humidity (RH). The solid line represents modeled particle volume growth predicted by Lowenthal et al. (1995) assuming that the water-soluble PM fraction is 0.53.

Table 1

Average chemical composition of PM_{2.5} at Downey (south central Los Angeles) during the period January–December 1999. Characteristics of major PM chemical species relevant to light scattering are from Sloane and Wolff (1985)

PM species	Elemental carbon	Organic carbon	Ammonium nitrate	Ammonium sulfate
Average (\pm S.D.)	0.059	0.46	0.24	0.16
Mass fraction	(\pm 0.022)	(\pm 0.19)	(\pm 0.13)	(\pm 0.09)
Range	0.03–0.12	0.15–0.81	0.09–0.57	0.05–0.39
Refractive index	1.96–0.66i	1.55	1.47	1.55
Density (g cm ⁻³)	2.0	1.40	1.77	1.73

the data, the expression derived by Lowenthal et al. (1995) to model particle volume growth (Eq. (1)) is also plotted in Fig. 1. The soluble fraction of the dry PM mass, E , was assumed to be 0.53. This was based on the average PM chemical composition in south central Los Angeles during the 12 months of this study, which is summarized in Table 1. In determining the relative mass fractions of the different PM_{2.5} species, all of nitrate was assumed to be ammonium nitrate (hence nitrate concentrations were multiplied by 1.29) and all of PM sulfate was assumed to be associated with ammonium sulfate (hence sulfate concentrations were multiplied by 1.38). Furthermore, the concentrations of OC have been multiplied by 1.4 (i.e., assuming the compound is consisting of CH₂ groups), similar to the approach followed in other studies in the Los Angeles Basin (Hering et al., 1997; Kleeman et al., 1999).

Approximately 92% of the total PM_{2.5} mass could be attributed to these four species and roughly 53.5 (\pm 10.7)% of the total mass consisted of soluble compounds. Here we have implicitly assumed that, along with ammonium nitrate and ammonium sulfate, about 25% of the total organic carbon is soluble (a similar assumption is made by Lowenthal et al. (1995) and by Kleeman et al. (1999)). As the results of Fig. 1 indicate, the modeled particle growth predicted by Lowenthal et al. (1995) for $E = 0.53$ fits very well the actual field data.

In Fig. 2, DataRAM mass concentration readings are plotted against total MOUDI mass concentrations, uncorrected as well as corrected for nitrate loss. The results shown in Fig. 2 indicate that the DataRAM and MOUDI mass concentrations are highly correlated ($R^2 = 0.80$ and 0.88 for nitrate-corrected and uncorrected concentrations, respectively). Paired t -test comparisons between the total nitrate-corrected and uncorrected MOUDI concentrations and the time-averaged DataRAM concentrations were conducted, for ambient and concentrated air. The results of this comparison, along with the correlation coefficients and p -values are shown in Table 2. The results shown Fig. 2 and in Table 2 indicate that the DataRAM concentrations

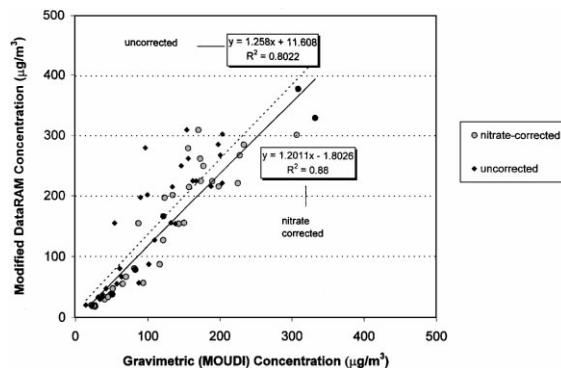


Fig. 2. Plot of DataRAM vs. nitrate-corrected gravimetric PM mass concentrations.

are generally higher than those determined with the MOUDI, with the average DataRAM-to-MOUDI concentration values being $1.18 (\pm 0.05)$ and $1.36 (\pm 0.10)$ for nitrate-corrected and uncorrected mass concentrations. Furthermore, the p -values of the paired comparison between the total PM_{2.5} MOUDI and DataRAM indicate that the difference between the two samplers is statistically significant. The substantial difference between the nitrate-corrected and uncorrected concentrations is obviously due to the significant contributions of volatile ammonium nitrate to the overall PM_{2.5} in Los Angeles (e.g., by about 24%). DataRAM and uncorrected gravimetric concentrations may be in closer agreement in other settings, in which such labile species may account for a smaller fraction of the ambient particulate mass.

Mass concentration measurements with the DataRAM are based on light scattering, and they should therefore be dependent on particle size and chemical composition (McMurry et al., 1996; Sloane, 1984). The DataRAM-to-MOUDI mass concentration ratio was subsequently regressed over the following parameters: (a) the concentrations of ammonium nitrate, sulfate as well as elemental and organic carbon (EC and OC) and (b) the mass fractions of PM_{2.5} in the following size ranges: 0–0.1, 0.1–0.5, 0.5–1.0, and 1.0–3.2 μm , respectively.

Table 2

Pairwise comparison between the PM_{2.5} mass concentrations determined by means of the DataRAM and the MOUDI

	DataRAM	Nitrate-corrected MOUDI	Uncorrected MOUDI
Mean ($\mu\text{g m}^{-3}$)	150.5	126.8	109.8
Standard deviation ($\mu\text{g m}^{-3}$)	31.7	26.7	28.9
Observations	39	39	39
Pearson correlation ^a		0.93	0.90
<i>t</i> -statistic ^a		3.14	4.89
$p(T \leq t)$ two-tail ^a		0.035	0.00004

^aCorrelation coefficient, *t*-statistic and *p*-values correspond to pairwise comparisons between nitrate-corrected MOUDI and DataRAM concentrations and between uncorrected MOUDI and DataRAM concentrations.

Table 3

Correlations between the elemental carbon, organic carbon, ammonium nitrate and ammonium sulfate concentrations

	Elemental carbon (EC)	Organic carbon (OC)	Ammonium nitrate (NH ₄ NO ₃)	Ammonium sulfate ((NH ₄) ₂ SO ₄)
EC	1			
OC	0.72	1		
NH ₄ NO ₃	0.26	0.31	1	
(NH ₄) ₂ SO ₄	−0.31	−0.29	−0.38	1

Table 4

Summary of multiple regression: DataRAM/gravimetric ratio as a function of mass fractions of three major PM_{2.5} chemical species

Species fraction	Coefficient	Standard error	<i>p</i> -value	Multiple <i>R</i>
Intercept	0.28	0.38	0.47	
<i>F</i> (OC) ^a	0.24	0.42	0.57	0.52
<i>F</i> (nitrate) ^a	1.89	1.23	0.11	
<i>F</i> (sulfate) ^a	2.1	1.47	0.13	

^aThe concentrations of nitrate and sulfate are multiplied by conversion factors of 1.29 and 1.38, respectively. The OC concentrations were multiplied by a factor of 1.4.

3.1. Dependence on the chemical species: field data

The effect of PM chemical composition on the DataRAM-to-gravimetric concentration ratio sensitivity was investigated. Ammonium nitrate and sulfate as well as elemental and organic carbon are the most common PM_{2.5} constituents in almost any urban location within the US (Finlayson-Pitts and Pitts, 1986; Lawson, 1990; Wilson, 1995; Mauderly et al., 1998). The relative fractions of each of these species may vary from location to location, but the sum of their concentrations accounts for the majority of ambient PM_{2.5} concentrations. Consequently, the conclusions from the following analysis are generalizable to other locations. Correlations between the elemental carbon, organic carbon, ammonium nitrate and ammonium sulfate concentrations are summarized in Table 3. With the exception of the expectedly strong

association between the elemental and organic carbon concentrations, the concentrations of ammonium nitrate, sulfate and organic carbon are weakly associated (i.e., the correlation coefficients range from −0.38 to 0.26), thus these parameters can be assumed to be independent. We thus conducted multiple regression analysis, with the DataRAM-to-gravimetric ratio as dependent variable and the fractions of organic carbon, nitrate, and sulfate as independent variables. Elemental carbon was excluded from the analysis because of its high correlation with organic carbon and because of its low (i.e., less than 10%) contribution to the overall mass concentration. The results of multiple regression, shown in Table 4, clearly indicate that PM chemical composition does not affect significantly the response of the DataRAM. The particle extinction coefficient (a measure of particle light scattering) depends on the particle refractive index and density.

Table 1 shows the refractive index and density of the four $PM_{2.5}$ species investigated in this study. With the exception of elemental carbon (which constitutes a small fraction of $PM_{2.5}$ by mass, as the majority of carbonaceous materials in general are associated with organic carbon), the values of refractive indices and densities are quite similar for OC, ammonium nitrate and ammonium sulfate. The similarity between the refractive indices and densities of the main $PM_{2.5}$ constituents therefore explains the lack of a significant correlation between the DataRAM-to-gravimetric concentration ratio and the fraction of these species. This finding further implies that the relative difference between the DataRAM and gravimetric mass concentration measurements can only be attributed to particle size, as it will be discussed in the following section.

3.2. Dependence on the size distribution

The concentration readings of the DataRAM nephelometer are based on the aerosol extinction coefficient, which, for a specific particle size, is given by the following equation (Kerker, 1969):

$$\sigma_e = \frac{3C_m Q_e}{2\rho_p d_p}, \quad (4)$$

where σ_e is the extinction coefficient, C_m is the particle mass concentration, ρ_p is the particle density, d_p is the particle diameter, and Q_e is the particle extinction efficiency, which depends non-monotonically on particle size. The above equation implies that it is necessary to estimate the average particle density, ρ_p , in order to determine C_m . The non-aqueous components of ambient particles smaller than $2.5\mu\text{m}$ consist primarily of ammonium sulfate ($\rho_p = 1.8\text{g cm}^{-3}$), ammonium nitrate ($\rho_p = 1.7\text{g cm}^{-3}$), elemental carbon ($\rho_p = 2\text{g cm}^{-3}$) and organic compounds ($\rho_p = 1.4\text{g cm}^{-3}$). Hence the density of a dry $PM_{2.5}$ aerosol should be in the range $1.4\text{--}1.8\text{g cm}^{-3}$. Assuming an average particle density of 1.55g cm^{-3} may over- or underestimate mass concentration measurements by no more than $\pm 12\%$.

Variations in particle size, however, may introduce considerable errors in predicting the response of a nephelometer. For refractive indices in the range of 1.4–1.6 (i.e., those of the most common $PM_{2.5}$ components), Q_e increases from about 0 (for ultrafine particles) to a maximum value of about 4 at a particle size that corresponds to approximately 1.25 times the wavelength of the incident light. DataRAM uses a light source with wavelength of $0.88\mu\text{m}$, hence a maximum scattering should be observed at about $1.1\mu\text{m}$ particles. The values of the particle extinction coefficient, Q_e , decrease quite sharply at either higher or smaller particle sizes.

Previous studies in Southern California (Hering et al., 1997; John et al., 1990) have indicated that the accumula-

tion mode may consist of two sub-modes, one peaking around $0.3\text{--}0.4\mu\text{m}$ and the other around $0.6\text{--}0.7\mu\text{m}$. The first mode is created by gas-to-particle conversion, and is referred to as “condensation mode”, whereas the second mode results from growth of hygroscopic sulfate and nitrates as well as from liquid-phase reactions that occur in fog or cloud droplets, and is known as “droplet mode”. As part of our investigation, we examined how the partitioning of ambient $PM_{2.5}$ aerosols within these modes affects the response of the DataRAM. Accordingly, particle mass concentrations in each field test were grouped in the following four aerodynamic size ranges: (a) $0\text{--}0.1\mu\text{m}$ (ultrafine particles); (b) $0.1\text{--}0.5\mu\text{m}$ (condensation mode particles); (c) $0.5\text{--}1.0\mu\text{m}$ (droplet mode particles); and (d) $1\text{--}3\mu\text{m}$ (intermediate mode particles, i.e., particles between the accumulation and coarse modes).

It should be noted that ambient and concentrated particle size distributions obtained by means of the MOUDI correspond to aerosols at ambient relative humidity conditions, but without the aqueous PM component (which has presumably volatilized during filter equilibration). In theory, the size distribution of the aerosol sampled by the DataRAM may be different than that measured by the MOUDI, as the relative humidity downstream of the DataRAM’s diffusion dryer has been considerably reduced from its ambient level. The disparity between the relative humidities of the MOUDI and DataRAM aerosols, however, is not expected to have an appreciable effect on the overall size distributions sampled by the two instruments, as roughly 50% of the aerosols by mass is associated with non-hygroscopic compounds such as elemental and organic carbon. Eqs. (1) and (2) make it possible to calculate the relative growth in particle diameter due to condensation of water vapor. Assuming a soluble $PM_{2.5}$ fraction of about 0.5 (a realistic assumption given our data), and a maximum RH value of about 85%, particles will grow on the average to a size that is about 15% larger than their original size (particle volume, however, will grow by 55%). This particle size growth is considerably smaller than the size classification resolution of the MOUDI, in which particles are grouped in size intervals of which the upper and lower cutpoints differ by a factor of 2, thus it is not expected to affect interpretations of the relationship between the DataRAM-to-gravimetric concentration ratio and particle size.

Figs. 3a–d show the relationship between the fraction of $PM_{2.5}$ mass associated with each of the PM size sub-modes and the response of the DataRAM (expressed in terms of the DataRAM-to-MOUDI concentration ratio). The DataRAM-to-MOUDI concentration ratio decreases quite sharply as the mass fraction of ultrafine particles increases, due to the weak light scattering associated with particles of that size range. An important implication of these results is that the DataRAM will substantially underestimate PM levels in environments

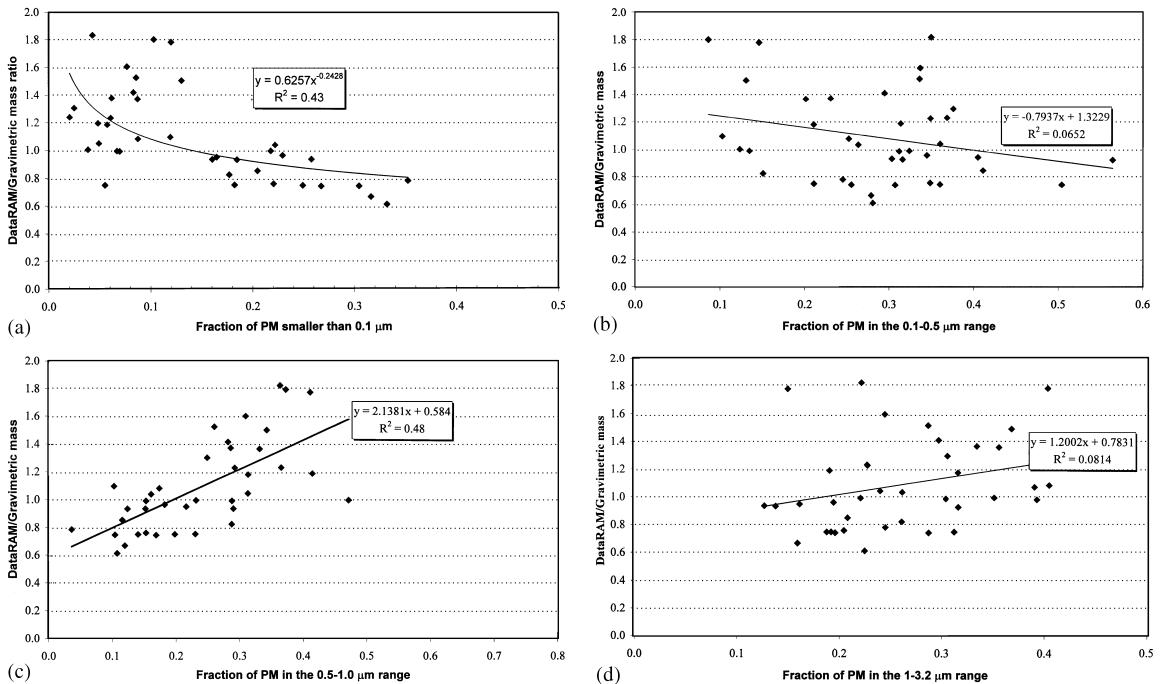


Fig. 3. (a) Ratio of DataRAM to nitrate-corrected gravimetric mass concentration vs. fraction of PM mass below $0.1 \mu\text{m}$. (b) Ratio of DataRAM to nitrate-corrected gravimetric mass concentration vs. fraction of PM mass between 0.1 and $0.5 \mu\text{m}$. (c) Ratio of DataRAM to nitrate-corrected gravimetric mass concentration vs. fraction of PM mass between 0.5 and $1.0 \mu\text{m}$. (d) Ratio of DataRAM to nitrate-corrected gravimetric mass concentration vs. fraction of PM mass between 1 and $3.2 \mu\text{m}$.

where the fraction of ultrafine particles (by mass) is significant. Examples of these environments include areas in the vicinity of freeways and indoor environments during the wintertime (Pedersen et al., 1999; Venkataraman and Friedlander, 1994; Sioutas et al., 1999).

The fraction of particles in the condensation mode range ($0.1\text{--}0.5 \mu\text{m}$) does not appear to affect the DataRAM-to-MOUDI concentration ratio, as indicated by the very low correlation coefficient in Fig. 3b. However, the fraction of $\text{PM}_{2.5}$ particles in the droplet mode ($0.5\text{--}1.0 \mu\text{m}$) range, affects significantly the response of the DataRAM, as indicated by the data plotted in Fig. 3c. The DataRAM-to-MOUDI ratio increases exponentially with increasing fraction of particles in the $0.5\text{--}1.0 \mu\text{m}$ size range, as a direct consequence of the Mie scattering theory. $0.5\text{--}1.0 \mu\text{m}$ particles represent the most sensitive particle range in terms of light scattering and if a high percentage (i.e., 35% or higher) of the ambient aerosol mass is associated with this size fraction, the DataRAM will tend to overestimate the aerosol concentration by a minimum of 30–40%. Finally, the DataRAM-to-MOUDI ratio is virtually independent of the PM mass fraction in the $1\text{--}3.2 \mu\text{m}$ range, as indicated in Fig. 3d.

Fig. 4 shows a plot of the DataRAM-to-MOUDI concentration ratio as a function of the aerosol MMD. As in our previous analysis, the MOUDI mass concen-

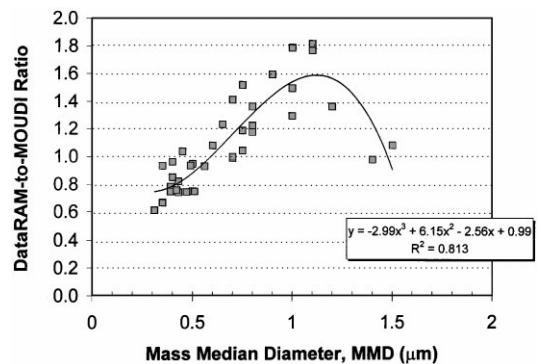


Fig. 4. DataRAM-to-gravimetric concentration (corrected for nitrate loss) ratio as a function of aerosol mass median diameter (MMD).

trations are corrected to account for nitrate lost during sampling. MMD values ranged from 0.3 to $1.5 \mu\text{m}$. The experimental data follow the classic trend predicted by the Mie scattering theory. As the MMD increases from 0.3 to $1.1 \mu\text{m}$, the DataRAM-to-MOUDI ratio increases from approximately 0.7 to about 1.6 . The DataRAM-to-MOUDI ratio subsequently decreases to about 1.0 , as the MMD increases from 1 to $1.5 \mu\text{m}$.

A best fit curve ($R^2 = 0.81$) was applied to the experimental data in order to obtain an analytical expression relating the DataRAM-to-gravimetric concentration ratio and the aerosol MMD. The following expression was obtained:

$$\frac{\text{DataRAM}}{\text{Mass Conc.}} = 0.99 - 3(\text{MMD})^3 + 6.1(\text{MMD})^2 - 2.56(\text{MMD}). \quad (5)$$

Both the results of Fig. 4 as well as Eq. (5) indicate that, for MMD values in the range of 0.4–0.7 μm (i.e., the MMD size range that is most commonly associated with urban aerosols), mass concentrations measured by the DataRAM and gravimetrically (corrected for nitrate losses) agree to within $\pm 20\%$. It should be noted that MMD values higher than 0.7 μm were almost exclusively associated with concentrated aerosols, due to the somewhat higher concentration enrichment of the “coarser” (i.e., 0.7–2 μm) particles of the accumulation mode (Sioutas et al., 1997a). Particle concentration by means of virtual impaction utilizes particle inertia, hence larger particles within the accumulation mode are concentrated more efficiently compared to smaller particles, comparable to the cutpoint of the virtual impactors (i.e., 0.2 μm). Based only on ambient data, the average DataRAM-to-gravimetric concentration ratio was 0.93 (± 0.17), whereas the average DataRAM-to-gravimetric concentration ratio for concentrated aerosols was 1.23 (± 0.20). These results suggest that, at least for ambient aerosols, the modified DataRAM readings were very close to the actual $\text{PM}_{2.5}$ mass concentrations.

4. Summary and conclusions

In this paper, we investigated the feasibility of using a modified DataRAM nephelometer (RAM-1, MIE Inc., Billerica, MA) to measure continuously $\text{PM}_{2.5}$ concentrations of ambient and concentrated aerosols in real time. A diffusion dryer was placed in the inlet of the DataRAM in order to reduce the relative humidity of the sampled air to less than 50%. A total of 39 field tests were conducted in which the average dry DataRAM concentration was compared to the gravimetrically determined mass concentration, corrected for nitrate losses. Tests were conducted over one calendar year (from January to December 1999) in order to capture maximum seasonal variations in the levels of relative humidity, temperature as well as in size distribution and chemical compositions of PM in the Los Angeles Basin.

Our experimental results indicated that the aerosol MMD is the single, most important parameter in affecting the response of the DataRAM. As the MMD increases from 0.3 to 1.1 μm , the DataRAM-to-MOUDI

ratio increases from approximately 0.7 to about 1.6. The DataRAM-to-MOUDI ratio subsequently decreases to about 1.0, as the MMD further increases to 1.5 μm . For MMD values in the range of 0.4–0.7 μm (i.e., the MMD size range that is most commonly associated with urban aerosols), the DataRAM and gravimetrically measured mass concentrations (corrected for nitrate losses) agree to within $\pm 20\%$. Based only on ambient data, the average DataRAM-to-gravimetric concentration ratio was 0.93 (± 0.17), whereas the average DataRAM-to-gravimetric concentration ratio for concentrated aerosols was 1.23 (± 0.20). Finally, our results indicated that the effect of particle chemical composition on the DataRAM-to-gravimetric concentration ratio is much less important than particle size distribution.

Acknowledgements

This work was supported in part by the Southern California Particle Center and Supersite (SCPCS), funded by the US EPA under the STAR program, the California Air Resources Board and the Health Effects Institute under contracts No. 98-1B and 99-2. Although the research described in this article has been funded in part by the United States Environmental Protection Agency through Grant # R827352-01-0 to USC, it has not been subjected to the Agency's required peer and policy review and therefore does not necessarily reflect the views of the Agency and no official endorsement should be inferred.

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