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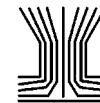
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Time-Resolved Aerosol Collector for CCSEM/EDX Single-Particle Analysis

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An automated Time-Resolved Aerosol Collector (TRAC) has been developed for sequential sampling of field-collected aerosols for laboratory-based Computer Controlled Scanning Electron Microscopy/Energy Dispersed X-ray (CCSEM/EDX) single-particle analysis. The collector is optimized for the use of grid-supported 50 nm carbon films as deposition substrates. The carbon films have low enough X-ray background to permit EDX analysis down to 0.1–0.2 μm particles, including detection of low-Z elements: C, N, and O. The TRAC provides unattended sampling onto a set of 151 individual grids, at sequential time intervals as short as 1 min. After collection, the samples are sealed and refrigerated pending analysis. The utility of the TRAC-CCSEM/EDX approach is exemplified using the aerosol samples collected during the Texas 2000 Air Quality Study (August 15–September 15, 2000). We are able to follow the time evolution in the relative contribution of non-volatile particles such as ammonium sulfate, mineral dust, sea salt, and carbonaceous in the aerosol makeup. The results show, among other things, the diurnal cycles in appearance of fine carbonaceous and ammonium sulfate particles and substantial mixing/coating of mineral particles with ammonium sulfates.

INTRODUCTION

One of the most intense areas of current research in aerosol science is the heterogeneous chemistry of airborne particles and

its impact on the atmospheric environment (e.g., Ravishankara 1997; Gard et al. 1998; Jacob 2000). Ambient aerosols are typically a diverse mix of particles having different sizes and chemical compositions, which also varies strongly with time. To understand the effect of the heterogeneous chemistry of aerosols, ideally one would need the exact chemical speciation of individual particles, size- and time-resolved.

An effective technique for such measurements is Single-Particle Mass Spectrometry (SPMS), which is the only method that provides real-time in situ analysis of sizes and compositions of individual particles (e.g., Jayne et al. 2000; Johnston and Wexler 1995; Noble and Prather 1999, 2000). Unfortunately, field deployment of these instruments is sometimes hindered by their size and power requirements. We looked for an alternative approach to SPMS that could also provide single-particle and time-resolved characterization of ambient aerosols using a device that could be easily deployed for unattended sampling from remote areas or from small moving platforms such as private planes or cars. We have adopted an approach of collecting sequential aerosol samples at very short time intervals (1–10 min) using small and simple-to-deploy field collector, subsequently returning them for laboratory-based analysis using Computer-Controlled Scanning Electron Microscopy with Energy Dispersed detection of X-rays (CCSEM/EDX).

CCSEM/EDX is one of the electron probe microanalysis (EPMA) methods in which particles are bombarded by a computer-controlled electron beam, and the resulting X-ray fluorescence is then monitored by an EDX spectrometer. CCSEM/EDX as well as other EPMA methods have been extensively used in the past to characterize the size, morphology, and elemental composition of individual particles collected in different field campaigns. Specific examples of EPMA single-particle studies can be found in a number of recent reviews (e.g., Buseck and Anderson 1998; De Bock and Van Grieken 1999; Fletcher et al. 2001). However, most of these studies focused on a precise (sometimes at the level of tenth of a percent) quantitative analysis of several thousand individual particles collected in just a few time-integrated samples. For such detailed particle speciation,

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X-ray counting times of 50–100 s per particle were typically necessary to obtain enough counting statistics with a sufficiently small peak-to-background ratio.

Our goal is somewhat different: in order to obtain the time-resolved aerosol composition data, we need to analyze thousands of particles in tens or even hundreds of sequential samples. To make CCSEM/EDX analysis an effective tool for such a task the throughput of analyzed particles must be substantially higher than most of the CCSEM/EDX researches have previously employed. For example, if N particles are analyzed in any particular sample containing 10 major particle types, the relative uncertainty in the estimation of particle-type abundance based on $N/10$ observations is about $\sqrt{N/10}$ (assuming that the particles are uniformly distributed among different types). Then a 10% relative error requires N of about 1000 particles per each analyzed sample. With X-ray counting times of 50–100 s per particle only one or two samples could be analyzed in a day. Therefore, in order to make the analysis feasible in a reasonable period of time (20–25 samples per day) the X-ray counting time must be reduced to the level of 1–5 s per particle. Obviously, this time reduction leads to a decreased accuracy of single-particle speciation, but on the other hand, allows obtaining time-resolved single-particle data. This kind of rapid CCSEM approach has been successfully used in the past (e.g., Casuccio et al. 1983; Schwoeble et al. 1988); however, particle speciation in these works was limited to elements higher than sodium ($Z > 11$) due to the use of Be window in X-ray spectrometry.

Modern X-ray detectors with ultrathin polymer windows now permit routine detection of low Z elements like C, N, and O (e.g., Huang and Turpin 1996; Ro et al. 2000, 2001a, 2001b; Osán et al. 2000). Selecting a better substrate for the CCSEM/EDX analysis can also enhance detection of the low Z elements. Several research groups have independently demonstrated that the use of grid-supported ultrathin carbon films as deposition substrates is crucial to the performance of single-particle CCSEM/EDX analysis (Gregory et al. 1998; Laskin and Cowin 2001; Seaman 2001). The carbon films of ~ 50 nm thickness give an exceptionally low background in the EDX analysis and allow superior automated analysis of particles down to 0.1–0.2 μm size, including semi-quantitative detection of low- Z elements (C, N, and O) at very short counting times (Laskin et al. 2002; Laskin and Cowin 2001).

Design and development of an aerosol collector is strongly optimized to meet the needs of the specific analysis. Whereas different research groups and companies have developed a number of time-resolved collectors optimized for sequential bulk analysis of aerosols (e.g., “DRUM Impactor” by Lundgren 1971, and Raabe et al. 1988; “Sequential Filter-Pack Sampler” by Rupprecht & Patashnick Co., Inc.; “Aerosol Streaker” by PIXE International Co., Inc.), no collector has been optimized for EDX single-particle analysis and specifically for use of grid-supported films as deposition substrates.

We have developed an automated Time-Resolved Aerosol Collector (TRAC) that deposits aerosol samples onto grid-

supported thin films unattended, with a programmable sampling time as short as one sample per minute. The TRAC was successfully deployed for one month of ground field operation during the Texas 2000 Air Quality Study (TexAQS 2000), where nearly 3000 individual samples with a time resolution of 10 min were taken and stored, covering the entire month of the field campaign.

In this work we present and discuss the design and performance of the TRAC and the utility of the TRAC-CCSEM/EDX analytical approach, featuring some preliminary data from the TexAQS 2000 experiment.

EXPERIMENTAL

Time-Resolved Aerosol Collector (TRAC)

The TRAC is a conventional one-stage jet-to-plate impactor that deposits aerosols from a single jet of particle-laden air upon an impaction plate. The aerosol samples are deposited on a traveling impaction plate (“sample tray” hereafter) with 151 thin film substrates prearranged on it. During the run, each substrate is exposed individually to the impactor nozzle for a preset time, as short as 1 min. Figure 1 shows a photograph of the TRAC. The collector is constructed from a modified six-inch Quick-Access door (MDC Vacuum Products Inc., Hayward, CA) and a flange forming a sealed chamber. The assembly is fixed vertically, and the deposition nozzle is located at the center of the chamber door (right side of the photograph). The sample tray is seen on the chamber wall. The tray is coupled magnetically to an XY stage located outside the chamber. The chamber wall and the bottom part of the tray holder are coated with a Teflon[®] film in order to reduce friction between the two sliding parts. The whole collector assembly includes deposition chamber, peristaltic pump, XY stage and controller, mass flow meter, diffusion dryer tube, and a laptop computer.

The TRAC has a deposition nozzle of 0.46 mm diameter and a nozzle-to-surface distance of 2–3 mm, and operates at flow rates of 0.8–0.9 slpm. For these conditions, the calculated (Marple et al. 1993) effective cutoff size d_{50} lies in the range of 0.36–0.38 μm . The deposition efficiency of TRAC was also evaluated experimentally using polystyrene spheres (PSL) of known size. For this purpose an optical particle counter (Lasair 1001, Particle Measuring Systems, Inc., Boulder, CO) was connected to the impactor exhaust line. Particles were generated with an atomizer followed by a diffusion dryer and then were sampled using the impactor. The number densities of the PSL spheres in the exhaust line (C_0) were measured first with the sample tray moved away from the nozzle (no deposition). Then the sample tray was moved back, exposing one of the substrates to the nozzle, and the concentration of particles leaving the impactor (C_1) was measured again by the particle counter. These measurements were repeated for each given size of the PSL spheres and the corresponding deposition efficiencies were determined as:

$$\text{Efficiency (\%)} = 100 \times (1 - C_1/C_0)$$

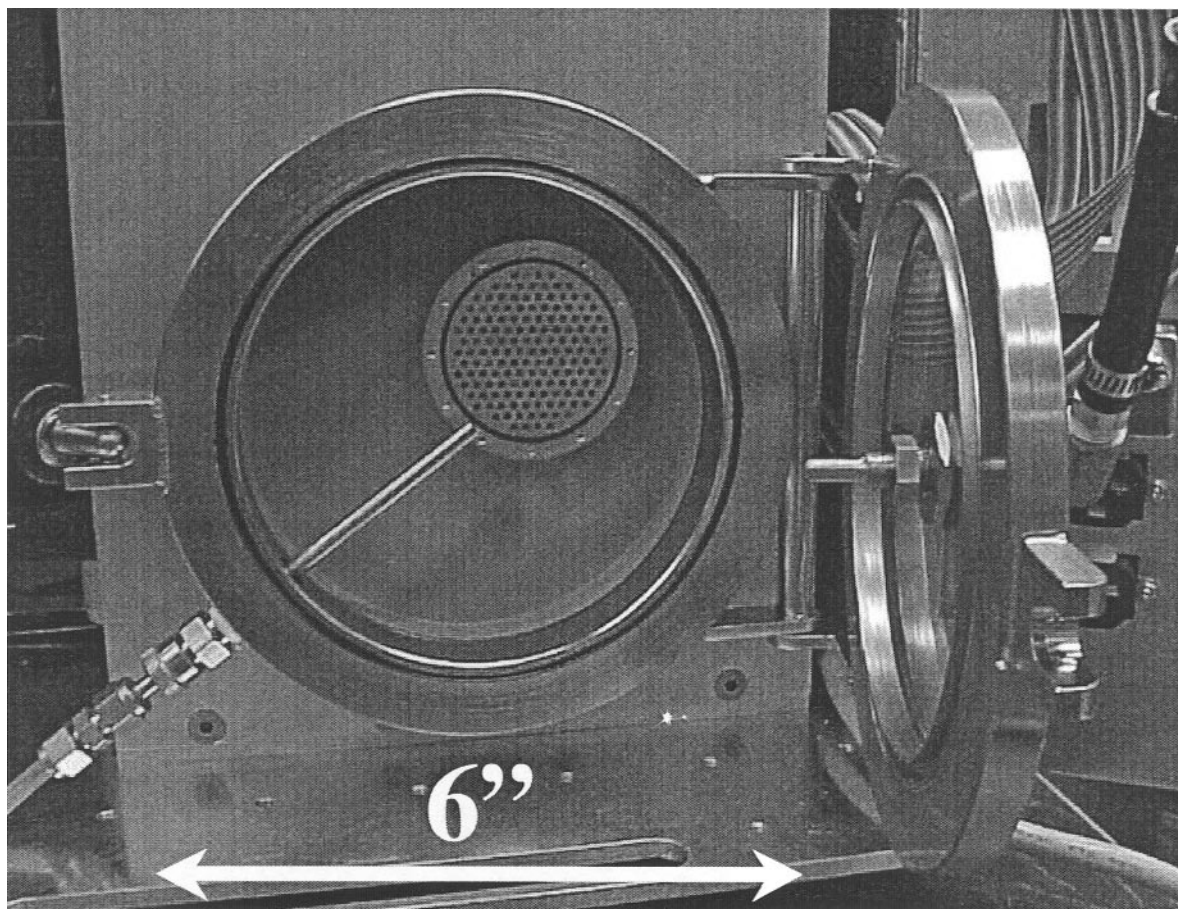


Figure 1. Time-resolved aerosol collector displayed with the chamber door open. The sample tray with substrates is seen on the chamber wall. The sample tray is magnetically coupled to the computer-controlled XY stage located behind the chamber. The deposition nozzle is located at the center of the chamber door (right side of the photograph).

The results of these tests are shown in Figure 2 together with the calculated values of d_{50} cutoff size. As can be seen, deposition efficiencies evaluated experimentally are consistent with the calculated values. A slope value, defined as a ratio between the sizes of particles collected with 16% and 84% efficiencies (d_{16}/d_{84}), is approximately 1.7 for the TRAC impactor. This value indicates a fairly sharp cutoff characteristic of the impactor (Chow and Watson 1998). The collector also deposits some of the particles down to $\sim 0.2 \mu\text{m}$ size, although very inefficiently. However, since most ambient aerosols are typically characterized by an increase in particle number densities with decrease in particle size, often plenty of $\sim 0.2 \mu\text{m}$ particles can be found by microscopic analysis.

TEM (transmission electron microscopy) grids are placed individually into the body of the sample tray, facing the impactor nozzle. The tray is sealed with a cover disk before and after an experiment and thus is ready for extended storage. During the run the sample tray follows a computer-controlled XY motion pattern and exposes each grid to the impactor nozzle for a preset dwell time.

At first glance, grid-supported carbon films look too fragile for routine use in the powerful air stream of the impactor. However, we found that when the grids were carefully and tightly fixed to the smooth featureless surface they could withstand the aerosol impact quite well. The arrangement of the TEM grids in the sample tray is schematically shown in Figure 3. The tray is made out of brass and has a number of specially milled holes with step-kind edges. Each grid is placed inside the hole, and precision cylindrical rollers plug grids tightly against the step-kind edges. The tray with installed grids is then sealed with two cover disks. In the field, the operator installs the tray in the collector chamber, removes the upper cover before collecting the samples, and places it back after the samples are collected.

Choice of the filmed grids is a trade-off between required strength of the films (small openings, thick films) and the desire to have larger film area for the superior analysis and lowest carbon and grid material X-ray background (large openings, thinner films). Two types of carbon films supported by copper 400-mesh grids were found to be a good compromise. Namely, Carbon Type-B (Ted Pella, Inc., Redding, CA) and Formvar/C

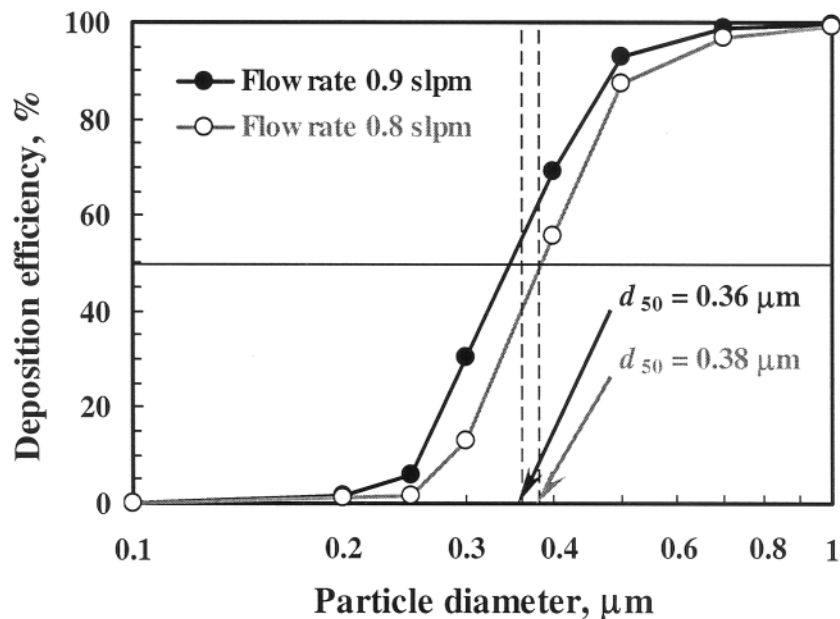


Figure 2. Deposition efficiency of the TRAC ($D_{\text{nozzle}} = 0.457$ mm) at the flow rates of 0.8 and 0.9 slpm. Dots represent experimental results and vertical dashed lines correspond to theoretical d_{50} cutoff values. Horizontal line depicts 50% deposition efficiency of the impactor.

(Electron Microscopy Sciences, Inc., Fort Washington, PA) films endure the settings presented here with only occasionally broken films in individual grid cells. Their thickness is listed as ~ 50 nm.

Field Deployment of the TRAC during TexAQ5 2000 Experiment

The TRAC was deployed for one month of aerosol sampling on the 62nd floor of the Williams Tower in Houston during

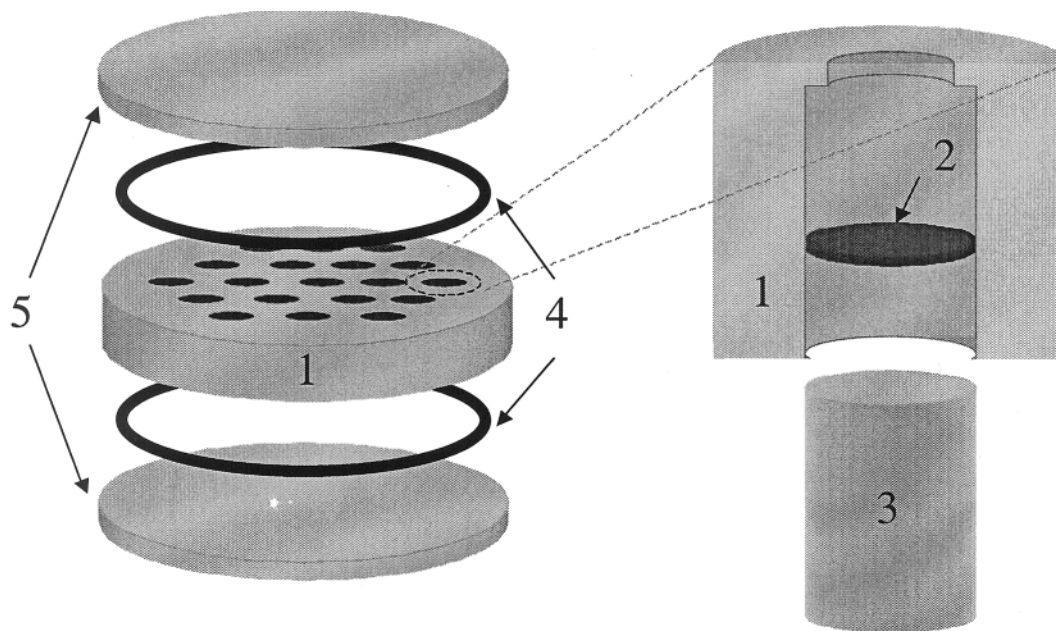


Figure 3. Schematic view of the sample tray assembly. Each TEM grid (2) is placed inside of the tray (1) in specially milled holes. Precise cylindrical rollers (3) plug grids tightly in their positions. The sample tray assembly is then sealed with two o-rings (4) and two cover disks (5).

the Texas 2000 Air Quality Study (TexAQS 2000). In that field campaign, about 250 researchers from different institutions and agencies undertook the air quality study in the State of Texas. Measurements of hazardous gaseous and particulate air pollutants were made at approximately 20 ground stations and by several research aircraft. Instruments for gas and particle monitoring from several research groups were co-located with us at the Williams Tower. Comparison with their data will be very valuable in the assessment of our data. However, in this paper, we focus our discussion only on the utility and performance of the TRAC-CCSEM/EDX approach.

The aerosol collector was deployed along with a Lasair 1001 (Particle Measuring Systems, Inc., Boulder, CO) optical particle counter (OPC). Aerosol samples were isokinetically withdrawn from the common sampling line used by different researchers. After being dried in a diffusion dryer, the aerosol flow was split between the aerosol collector and the OPC. Particle number concentrations from the OPC were averaged for each of the 10-minute sampling intervals during which individual TRAC substrates were exposed to the deposition nozzle. The OPC had size bins of 0.1–0.2 μm , 0.2–0.3 μm , 0.3–0.4 μm , 0.4–0.5 μm , 0.5–0.7 μm , 0.7–1.0 μm , 1.0–2.0 μm , and 2.0–2.5 μm . Selection of the deposition time was made upon the following considerations: the samples must be taken frequently enough to follow changes in aerosol concentration and the total number of samples taken at the field campaign must be reasonable from handling and budget perspectives.

CCSEM/EDX Single-Particle Analysis

A detailed description of our CCSEM/EDX system, its mode of operation, and use of the thin-film substrates for particle analysis was published elsewhere (Laskin and Cowin 2001) and thus will be described here only briefly. A LEO Gemini 982 digital Field Emission Gun Scanning Electron Microscope (FEG-SEM) was used in this work. The EDX spectrometer is a Pentafet 6901 spectrometer (Oxford Instruments America, Inc., Concord, MA) with a Si(Li) detector with an active area of 10 mm² and ATW2 window, which allows X-ray detection from the elements higher than beryllium ($Z > 4$). The LEO 982 microscope is equipped with DiskInspector hardware and software (Oxford Instruments America, Inc., Concord, MA) for automated particle analysis. The system automatically “tiles” the sample area with fields of view at the working magnification, the area is then automatically inspected on a field-by-field basis. In each field of view particles are recognized by an increase of the detector signal above a preselected threshold level. Imaging of particles was acquired using the mixed signal of backscattered and secondary electrons (BSE and SE). After recognizing the particles in a field of view, the program acquires an X-ray spectrum from each detected particle. In this work, a magnification of $\times 1800$ was used with the screen resolution of 1024×768 pixels, yielding a size of $0.067 \times 0.067 \mu\text{m}$ for one pixel. Features larger than 7 grouped pixels (equivalent circle diameter of 0.2 μm)

were considered as particles by the software. Spot size of the electron beam from a field emission gun is substantially smaller than the size of individual particles and for the settings presented here was conservatively measured as 8 nm. This indicates that in principle magnification as high as $\times 15000$ could be used for the instrument settings and conditions presented here. However, the choice of magnification is always a trade-off between the imaging quality and the analysis time because higher magnification requires more fields of view to be imaged. The magnification of $\times 1800$ was set as a reasonable compromise for the task of this work.

During the X-ray acquisition, the electron beam rastered continuously over the entire particle. The X-ray spectra were acquired for 5 s of live time, at a beam current of 150 pA and an accelerating voltage of 20 kV. The relative dead times of the EDX spectrometer never exceeded 25%.

For quantification of the EDX results, the DiskInspector software utilizes a simple normalization method, which does not include corrections for the effects of particle size and shape. The apparent particle composition is determined from the measured intensities of the X-ray spectral peaks relative to intensities of thick, flat standards. The software uses a filtered least-squares fitting procedure to fit experimental spectra with the set of stored X-ray “library” peaks (profiles) for each of 29 elements selected in this work: C, N, O, F, Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Sr, Sn, Sb, I, Ba, and Pb.

RESULTS AND DISCUSSION

During the TexAQS 2000 we collected and stored nearly 3000 aerosol samples for laboratory analysis. We do not plan to analyze all collected samples one by one. Our general analytical strategy is to analyze enough samples to map out the general trend of the aerosol time evolution. We use the record of the aerosol concentration data from the OPC to select the appropriate samples for preliminary analysis. After the preliminary analysis is completed, we use the obtained data to guide more detailed studies of the samples, at finer time intervals and/or with other analytical methods.

Records of the OPC data for eight individual size bins showed a marked difference between the time-resolved patterns of “finer” and “coarser” particles with a dividing size of 0.7 μm . We note that in this paper we will use the “finer” and “coarser” terms to reflect the observed particle modes. This is not to be confused with the standard U.S. Environmental Protection Agency definition of “fine” (PM_{2.5}) and “coarse” (PM₁₀) particles. Figure 4 shows a six-day (8/26/00–9/1/00) segment of the aerosol concentration data obtained from the optical counter and binned for the two modes, namely 0.2–0.7 μm particles (finer) and 0.7–2.5 μm particles (coarser). Each vertical pair of points corresponds to one aerosol sample taken onto a substrate and stored for the analysis. As can be seen from the plot, the particle concentrations in two modes follow very different time-resolved patterns. Finer particles tend to follow diurnal cycles, while coarser

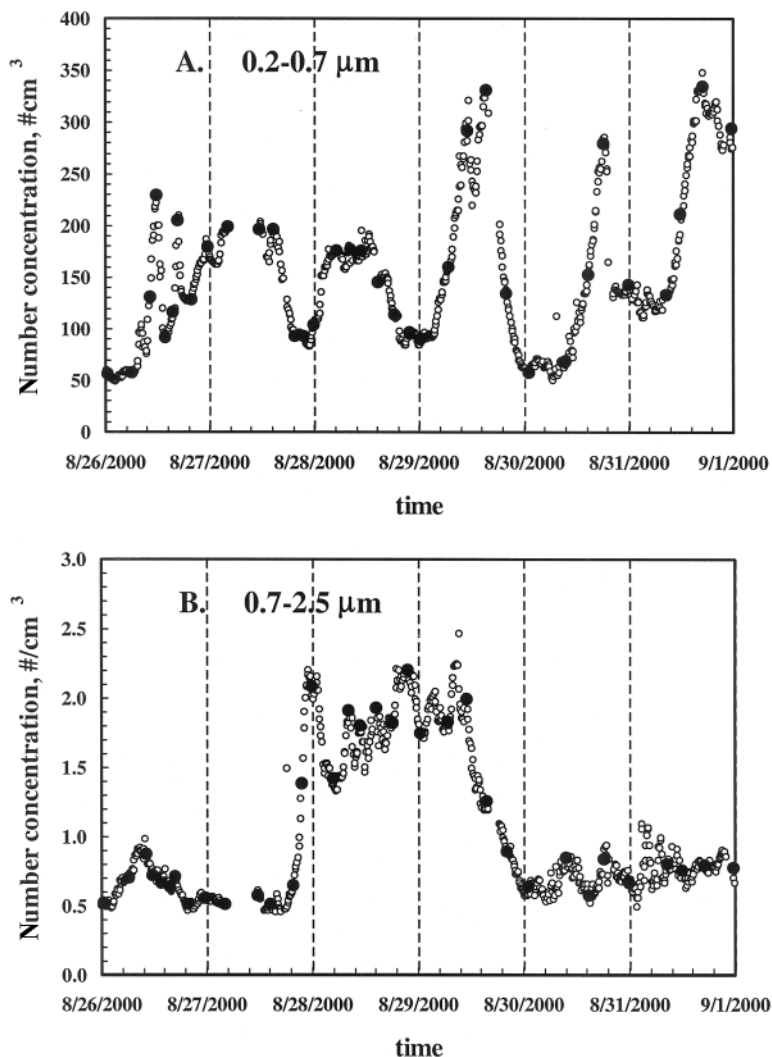


Figure 4. Six-day (8/26/00–9/1/00) portion of the aerosol concentration data during TexAQS 2000 experiment. The data obtained from the Lasair 1001 optical counter was binned into finer (0.2–0.7 μm , panel A) and coarser (0.7–2.5 μm , panel B) modes. Dashed lines correspond to midnights preceding the labeled day. Each vertical pair of dots corresponds to one aerosol sample stored for the analysis. Solid circles show individual samples actually analyzed.

particles are primarily modulated by gross changes in wind direction and speed. This observation is in accordance with the usual expectation that particle sources, their chemical composition, and atmospheric fates are quite different for submicron and supermicron particles (e.g., Seinfeld and Pandis 1998; Hinds 1999; John 2001). Coarser particles are usually generated by mechanical processes and consist of mineral dust, soil, sea salt, etc. Finer particles are formed mostly as a result of gas-to-particle conversion in technological and/or environmental processes (soot, ammonium sulfate, ammonium nitrate, VOCs, etc.).

To follow particle evolution events in both finer and coarser particle modes during the six-day period of 8/26/00–9/1/00, 35 representative samples were selected for CCSEM/EDX single-particle analysis. Solid circles in Figure 4 correspond to those

samples. Each tested sample grid was placed over a hole in a piece of copper foil of 4 cm^2 area and then was mounted in the microscope in a manner similar to the standard TEM sample mounting. This setup provides an exceptionally low background for electron and X-ray signals and allows satisfactory automated analysis of particles as small as 0.1–0.2 μm , including semi-quantitative detection of low-Z elements (Laskin and Cowin 2001).

Figure 5 shows typical SEM images taken from different areas of one individual aerosol sample. The density of particles deposited on a substrate by an impactor is not homogeneous, with the particle concentration being highest directly under the deposition nozzle. In the central area of the sample (area A, 0.1–0.2 mm diameter) the density of deposited particles is very high resulting in an overlap between particles observed in many

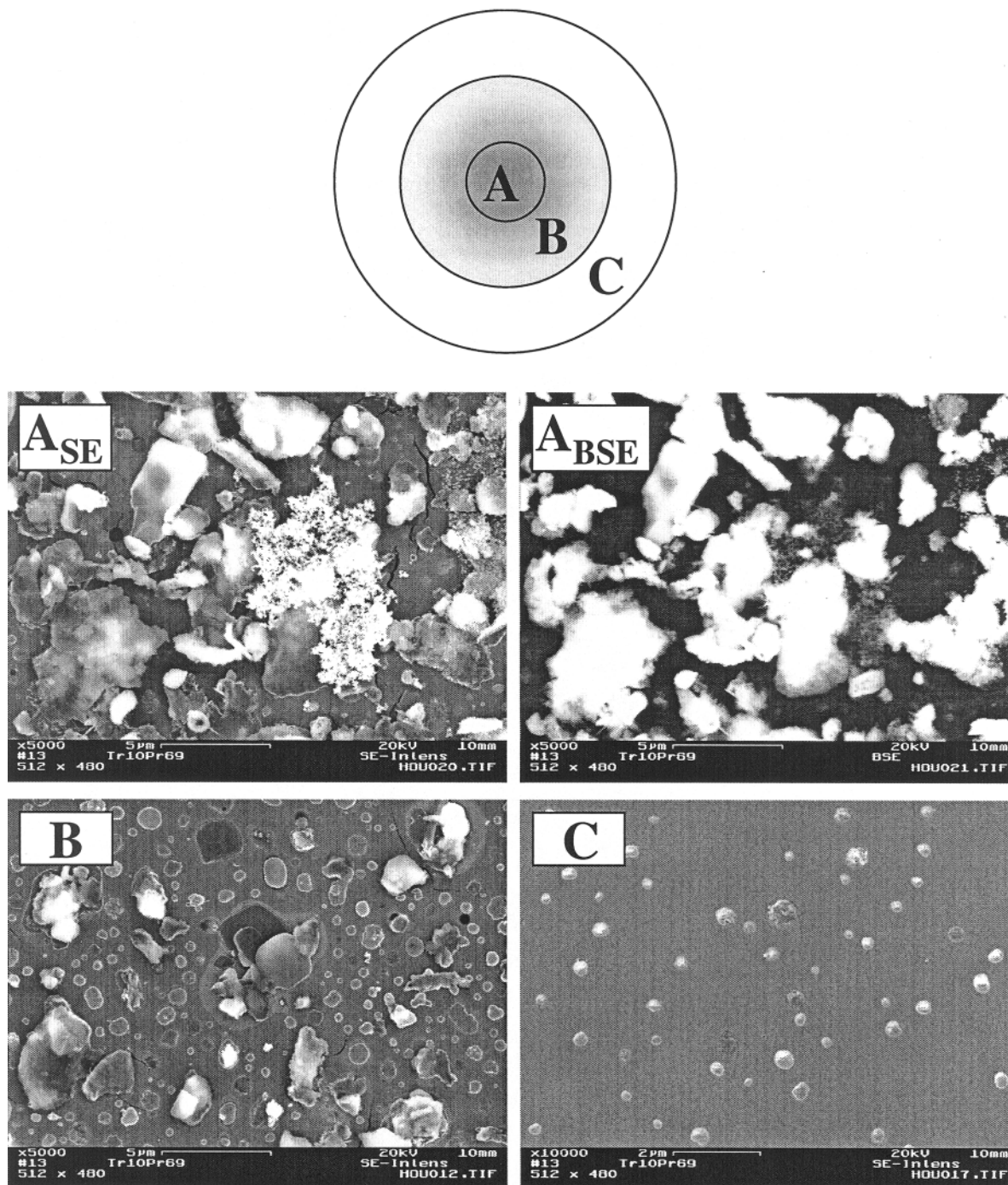


Figure 5. SEM images from different areas of an individual aerosol sample grid showing the spatial inhomogeneity of the deposition (schematically illustrated at the top). The panels labeled A_{SE} and A_{BSE} are the SE-Inlens and BSE images of the central area A; Panels B and C are SE-Inlens images of the annular areas B and C. See text for additional explanations. (Images are shown for the sample taken at 6:12–6:22 a.m. on 08/26/00.)

of the samples collected in Houston (1 slpm sampling flow, 10 min sampling). In this area single-particle analysis usually cannot be performed, though it is suitable for micro PIXE or other methods of microanalysis. The particle density in the annular area B (0.6–0.7 mm outer diameter) is typically most suit-

able for single-particle analysis. The large area C (1.0–1.2 mm outer diameter) has a very small number of particles larger than $0.2 \mu\text{m}$ and for time's sake was not analyzed in this work.

For automated imaging of particles over an extended period of time, the BSE signal is preferred over the SE signal because

of its high stability. However, low-Z compounds, particularly those with high carbon concentration, are almost invisible in the BSE mode due to their low backscattered electron yield. The two micrographs in Figure 5 (A_{SE} and A_{BSE}) show the same region imaged using the SE-Inlens (A_{SE}) and BSE (A_{BSE}) detectors. As can be seen, the big soot particle located just right off-center is clearly seen in the SE-Inlens mode, while it nearly disappears in the BSE mode. Therefore, imaging of particles was optimized using a mixed BSE and SE-Inlens signal. The SE-Inlens signal provides better imaging of low-Z particles while the addition of the BSE signal gives higher image stability over time. However, our experience showed that even with this approach the analysis was still biased toward detection of particles with higher Z elements. As a result, 0.2–0.3 μm particles with high carbonaceous content are usually underdetected by the microscope. Figures 5B and 5C (SE-Inlens imaging mode) show many nearly circular features that appear to have almost no vertical relief. These

indeed are very flat (nm) residues of volatile particles that from their shape seemed likely to have been liquid upon deposition even after passing through the drying tube and being dried out in the microscope chamber. These particles are not usually detected in the mixed image that is used for the particle detection and have a nearly negligible X-ray signal above the background. EDX analysis faintly shows sulfur in these residues, suggesting that these were probably sulfuric-acid rich aerosols.

The high electron transparency of the 50 nm carbon film makes EDX analysis feasible even at the very low intensities of X-ray signals typical for $\sim 0.2 \mu\text{m}$ particles, including semi-quantitative detection of carbon in carbon-rich particles (Laskin and Cowin 2001). Figure 6 shows examples of EDX spectra collected from different 0.2 μm particles compared to that from the carbon film itself. Even for such small particles, 5 seconds of X-ray collection time is enough to collect 1500–3500 photon counts from non-carbonaceous particles and 300–500 counts

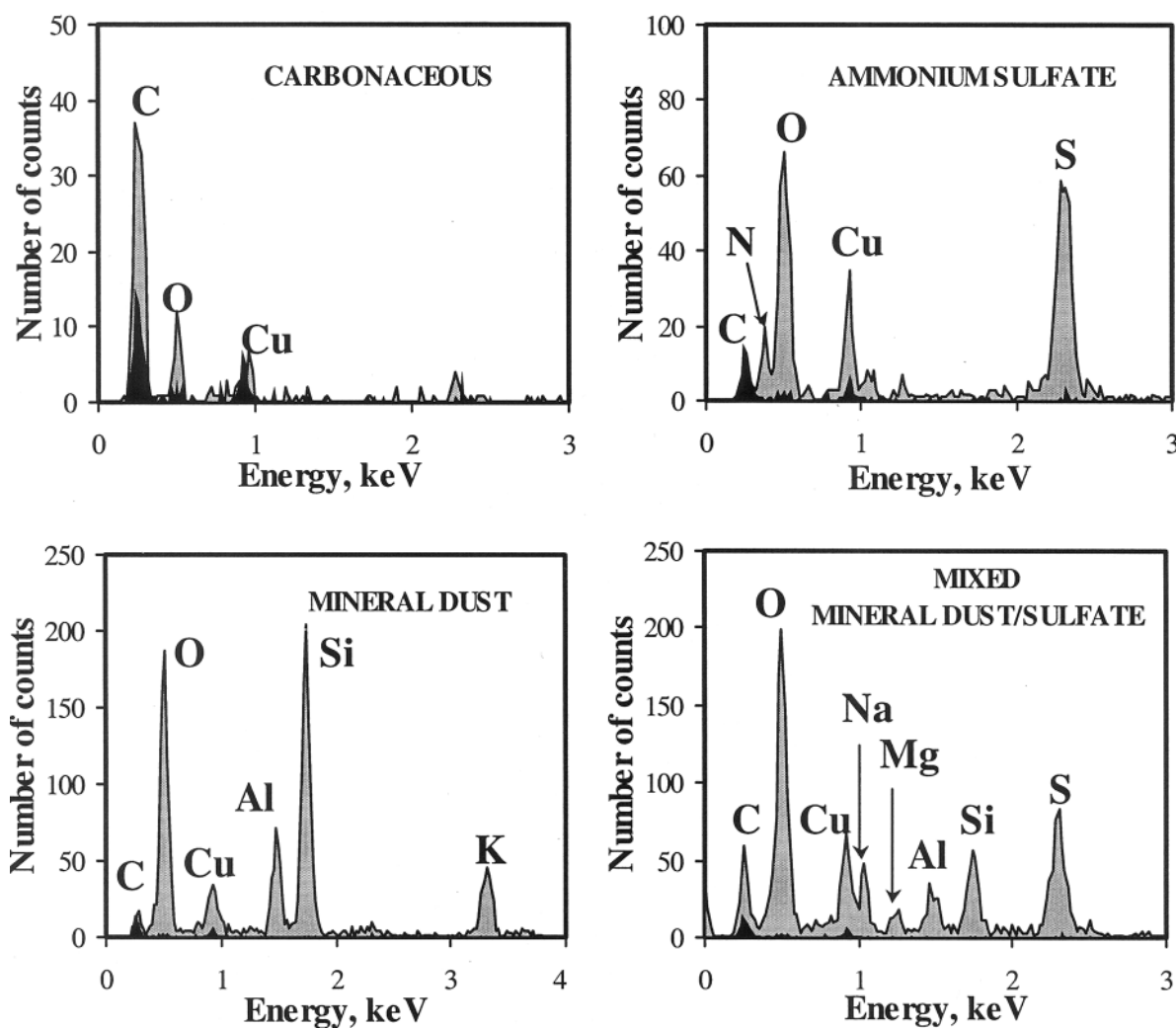


Figure 6. Typical spectra of individual 0.2 μm particles obtained in an SEM/EDX automated run (beam current 100–150 pA, acquisition live time 5 s). Carbon film background (black area) is shown for comparison; L_{α} peak of Cu at 0.930 keV is a background artifact.

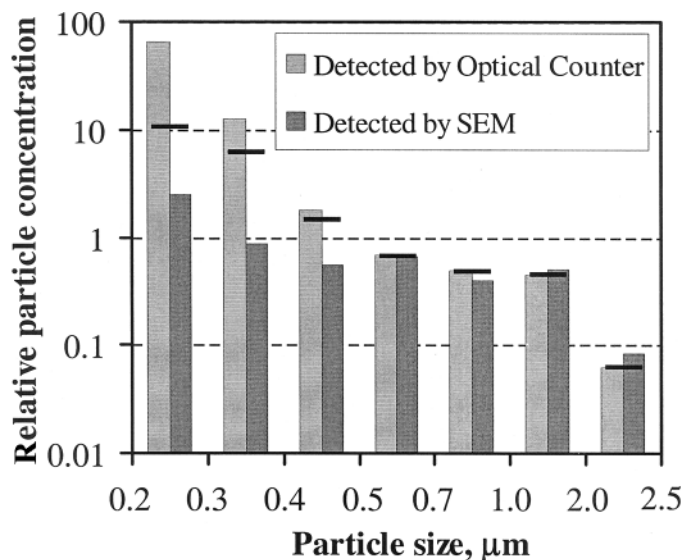


Figure 7. Particle size distribution of an aerosol sample detected by the optical counter in the field and by the electron microscope in the laboratory run. Size distribution is shown in relative values, normalized to the number of particles in the size range of 0.7–2.5 μm . Black horizontal bars show the values of the particle counter distribution multiplied by the size-dependent collection efficiencies of the TRAC impactor. (Sample taken over 6:12–6:22 a.m. on 08/26/00.)

from unmixed carbonaceous particles, sufficient to distinguish them from the carbon film background. The appearance of the L_{α} peak of Cu at 0.930 keV in the spectra arises from electrons scattered sideways by the particle that hit the copper grid and generate characteristic copper X-rays. However, we have demonstrated (Laskin and Cowin 2001) that while the level of the copper background varies as a function of particle size and composition, the carbon background from the film remains largely at minor level due to high electron transparency of 50 nm carbon film. Surprisingly, we were also able to detect even 0.2 μm ammonium sulfate particles, known to be very sensitive to electron beams (Post and Buseck 1984). This is probably due to our ability to use only 5 s of X-ray acquisition time, low beam current (100–150 pA), and the automated rastering of the beam over the particle during X-ray acquisition. Detection of ammonium sulfates in aerosol samples was also confirmed by the analysis of laboratory-generated ammonium sulfate particles. However, quantitative analysis of ammonium sulfate particles is still somewhat problematic. First, the transmission characteristic of the ATW2 window has a deep gap exactly at the K_{α} line of nitrogen. For this reason the nitrogen peak in spectra is always very low, even for materials with high nitrogen content. Second, the EDX-determined O/S mole ratio for ammonium sulfate is quite sensitive to the beam current and the analysis time. At the operating conditions presented here, the O/S ratio was close to 3 and at higher beam currents and longer times the O/S ratio was even lower. Ratios slightly closer to the correct one (O/S = 4) were obtained by reduction of beam current to 30–50 pA and for shorter analysis time. However use of these conditions results in poor imaging as well as in low

intensities of X-rays and thus is impractical for the automated particle analysis.

About 2000–3000 particles in each of the tested aerosol samples were analyzed for their size and chemical composition. Figure 7 shows typical particle size distributions in a single 10-minute period as detected by the optical particle counter in the field and by the CCSEM/EDX analysis of the corresponding sample. For comparison the size distributions are shown normalized to the number of particles counted in the size range of 0.7–2.5 μm (coarser particles). Particles in this size range are most likely mechanically generated nonvolatile particles, so they can be clearly detected and analyzed using CCSEM techniques. The normalization does not necessarily lead to agreement in each size bin in the coarser range, since the distribution between bins can be absolutely different. Therefore, the reasonable agreement between the two distributions (see Figure 7) supports the fact that indeed the CCSEM analysis covers the coarser particles fairly accurately. The black horizontal lines on the bars represent the number of particles one could expect to detect in a sample with the only losses due to the impactor transfer function. Their values were calculated by multiplying the measured deposition efficiencies of the impactor by the particle number concentration measured by the optical counter. As can be seen, the impactor efficiency alone cannot explain the undercount of the small particles (<0.5 μm) by the CCSEM. There are several other factors that can contribute to the observed discrepancy. As we have already pointed out, the spatial distribution of particles is not homogeneous, with the smallest particles scattered in a very wide area, larger than the area analyzed during the run. We have also mentioned that imaging of carbonaceous particles,

especially those with small size and high carbon content like soot, was far from ideal and therefore results in an analysis bias, undercounting this type of particles. For the same reason, the already discussed “non-vertical relief sulfur containing particles” were likely undercounted. Lastly, volatile and semivolatile particles like ammonium nitrate, sulfuric acid, or secondary organic aerosols of photochemical origin also contribute predominantly to the small sizes. These particles can be completely lost during collection or in the microscope vacuum chamber and thus cannot be analyzed. The aforementioned issues are substantial limits of the presented approach that could hardly be avoided at this time.

We have analyzed nearly 200 representative individual samples from the TexAQS 2000 field campaign for a total of nearly 500,000 individual particles. The information is so detailed and specific that only a fraction can be conveyed in this paper. For demonstration of the TRAC-CCSEM/EDX utility, we present here only a six-day fragment of the data with the aerosol composition gathered into several broad, very general particle-type classes for “finer” and “coarser” modes respectively.

In this work, we have used a somewhat subjective assignment of individual particles to aerosol classes, which was motivated by our specific observation of the aerosol composition. Analysis of the first TexAQS 2000 samples immediately showed that sulfur was the most common element in the Houston aerosol. In order to address basic partitioning of sulfur in the individual particles we applied the simple classification scheme shown in Figure 8. First we distinguished S-bearing and S nonbearing

particles. Then, among S nonbearing particles we have assigned those particles that meet the criteria of $[C] + [O] + [N] > 95\%$ and $[C] > [O] + [N]$ (atomic percent) to a high carbon content class (high-C), while the rest was assigned to another S nonbearing class (non-S). Between S-bearing particles we viewed particles that show the presence of S, O, and N only as ammonium-sulfate-like (ASL) particles. The remaining S-bearing particles (S_{nASL} -bearing) were subdivided into high carbon content sulfur bearing (C/S_{nASL} -bearing) particles, silicon containing sulfur bearing (Si/S_{nASL} -bearing) particles, and other sulfur bearing (other/ S_{nASL} -bearing) particles. Figure 9 shows an example of particle-type classification for the “finer” and “coarser” particles for just one 10-minute sample. Panel A illustrates classification results and relative particle populations in ASL, S_{nASL} -bearing, non-S, and high-C classes. Panel B shows further breakdown of the S_{nASL} -bearing class into three subclasses: C/S_{nASL} -bearing, Si/S_{nASL} -bearing, and other/ S_{nASL} -bearing.

In general, aerosols in the Houston area are often strongly “processed” with sulfur. Significant populations of sulfur-bearing particles were always identified in both particle modes. In the sample shown in Figure 9A, more than 90% of the coarser particles contain sulfur. Approximately a fourth of them are pure non-mixed ASL particles (23%) consisting of elements S, O, and N only. These particles are pure and/or mixed NH_4/SO_4 salts like $(NH_4)HSO_4$, $(NH_4)_2SO_4$, and $(NH_4)_3H(SO_4)_2$. The S_{nASL} -bearing (68%) are mostly the Si/S_{nASL} -bearing particles (62%), which correspond to the high silicon content particles (fly ash, mineral dust, soils, etc.) most likely mixed with H_2SO_4 and/or

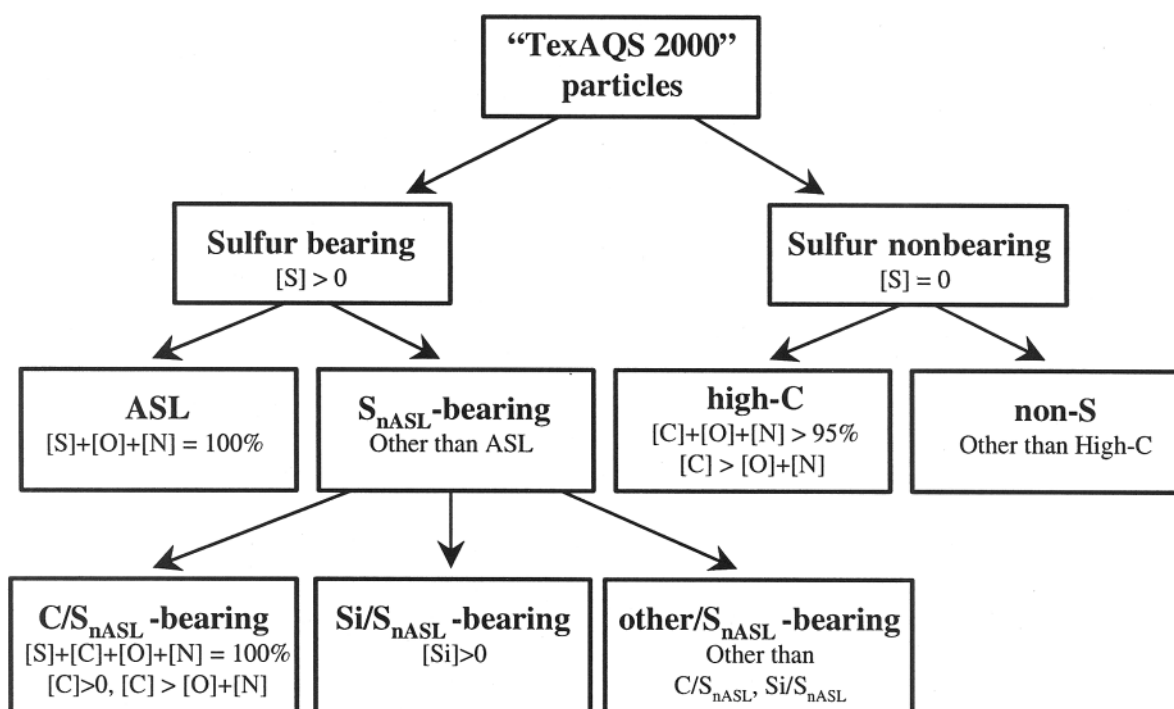


Figure 8. Simple classification scheme applied to “TexAQS 2000” particles. Labels of the particle classes are depicted by bold font. Applied class criteria are set for atomic percent and shown by regular font.

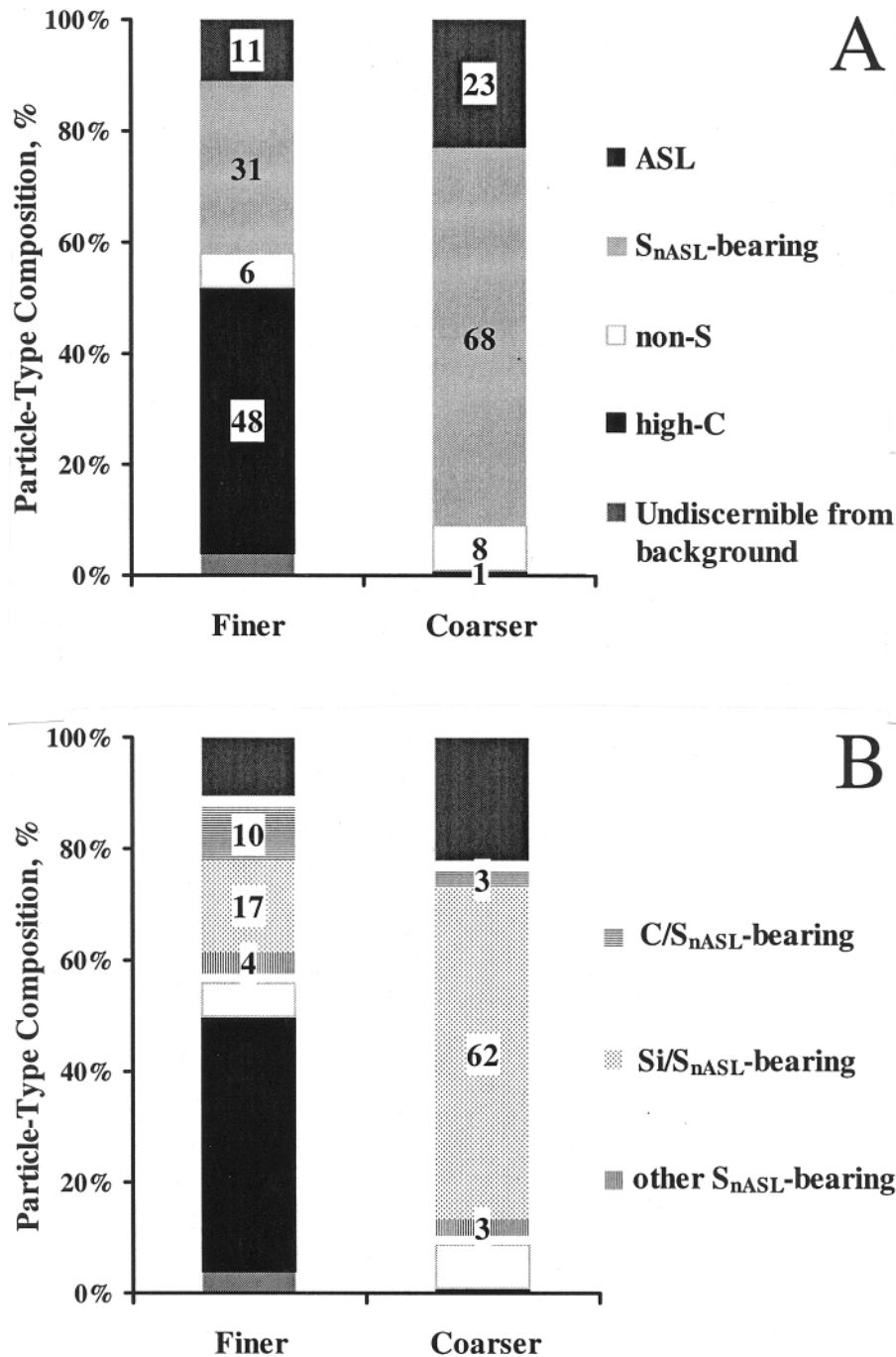


Figure 9. Particle-type classification for individual aerosol sample as detected by SEM/EDX analysis for “finer” (0.2–0.7 μm) and “coarser” (0.7–2.5 μm) particles. Panel A shows particle-type classification for four major classes. Panel B shows further breakdown of S_{nASL} -bearing class into three additional subclasses. (Sample taken over 6:12–6:22 a.m. on 08/26/00.)

NH_4/SO_4 salts. These mixed particles could be formed via direct coagulation, but for the humid Houston air, the particles are likely incorporated into water droplets, which may accumulate ammonia and sulfuric acid. When the particles dry out either in the ambient air or passing through the sampler drying tube, they become mixed/coated with ammonium sulfates. The C/S_{nASL} -

bearing particles contribute negligibly (3%) to the coarser mode. The finer particles in the same sample (see Figure 9) are mostly high-C particles showing the presence of C, O, and N only. They contribute 48% of the finer mode by number. The ASL particles and the S_{nASL} -bearing particles contribute to 11% and 31% respectively. Of the finer S_{nASL} -bearing particles (31%), most

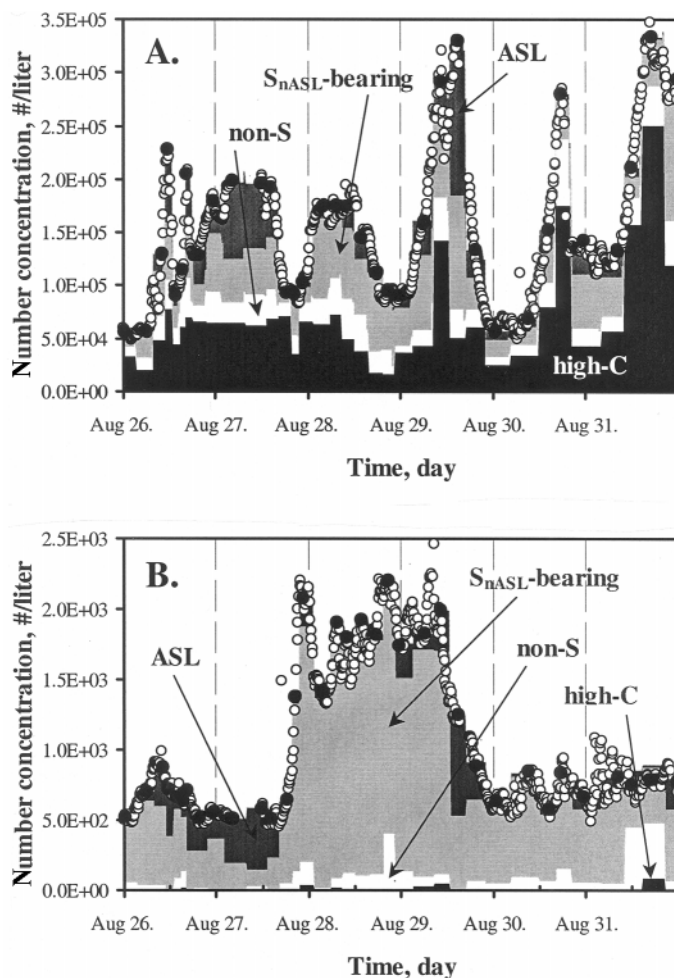


Figure 10. Time evolution of the particle composition for a six-day (8/26/00–9/1/00) portion of the Texas 2000 Air Quality Study as detected by CCSEM/EDX analysis for “finer” ($0.2\text{--}0.7\ \mu\text{m}$) and “coarser” ($0.7\text{--}2.5\ \mu\text{m}$) modes. Each pair of open circles corresponds to one individual sample stored for the analysis. Pairs of solid circles show those individual samples taken for the analysis. The area below the dots is painted with the respect to the relative particle populations determined by the analysis. Dashed lines correspond to midnights preceding the labeled day.

are the $\text{Si}/\text{S}_{\text{nASL-bearing}}$ particles (17%), however, the $\text{C}/\text{S}_{\text{nASL-bearing}}$ particles (10%) also contribute significantly in this case.

The individual particle analysis data allows a much more detailed classification of particles than that shown in Figure 9. Obviously, each of the presented subclasses can be easily subclassified again and again for more detailed and specifically focused information. For example, the high-C particles can be subclassified based on their C to O ratios and presence of trace metals. This should allow apportioning the high-C particles to different pollutant sources (diesel, coal burning, forest fires, etc.). Individual mineral types may be identified in further classification of Si-containing particles. Rare particles that are of health concern can be specifically mined out of the data set. In many samples, for example, we saw 1 to 10 distinct lead-containing particles, such as pure lead, lead oxide, lead sulfate, metallic lead-iron mix, and some others.

Figure 10 shows a rough pattern of the evolution of the aerosol composition for a six-day period (August 26–31). Open circles show particle number concentrations measured by the OPC when the samples were taken. Solid circles depict those samples that were analyzed. The area below the circles is “painted” proportionally to the relative particle populations as classified by the CCSEM/EDX analysis of the tested samples. For brevity, we again present particle-type composition data gathered into only four generic classes: ASL, high-C, $\text{S}_{\text{nASL-bearing}}$, and non-S particles (see Figure 8 to recall the classes). Prevailing diurnal cycles are obviously seen for the finer particles with the exception of August 26 (see Figure 10A). The finer particles tend to peak between noon and 2 p.m., with major contributions from high-C and ASL particles. This can be explained by daytime production of photochemical smog and/or soot from daytime vehicle emissions (high-C). ASL particles are formed by the

reaction of ammonia and sulfuric acid. The major route of sulfuric acid production is oxidation of SO_2 to SO_3 by OH radicals followed by the reaction of SO_3 with water, finally yielding H_2SO_4 (Finlayson-Pitts and Pitts 2000). This reaction sequence is also strongly enhanced by sunlight and contributes to the diurnal cycles of the ASL particles. While this paper does not show this information in detail, many of the fine S_{nASL} -bearing particles, from their morphology and detailed composition, look like ASL-coated particles (soot, fly ash, tiny mineral dust, etc.).

The coarser particles (see Figure 10B) are primarily non-ASL sulfur-bearing (S_{nASL} -bearing) particles. Similar to the case shown in Figure 9, the majority of the coarser S_{nASL} -bearing particles are Si/ S_{nASL} -bearing particles. They could be primarily associated with ASL-coated mineral dust particles. Sulfur nonbearing particles (non-S) are almost completely absent in the coarser mode. At the times of maximal ASL occurrence, their population often drops to near zero, such as near midday of August 27 and 29. This is probably because all the pre-existing coarse particles become mixed/coated with NH_4/SO_4 salts. During the presented six-day period, concentration of the coarser aerosol altered drastically only once, starting from the afternoon of August 27 when its concentration increased by factor of ~ 4 , remained almost unchanged for the next two days, and finally returned to the same level by the end of the day of August 29. This observation correlates well with the wind trajectories measurements (Berkowitz 2001), which indicate significant wind speed acceleration by the end of the day of August 27, and swift change in the wind direction on the afternoon of August 29.

In Figure 10 we combined OPC and CCSEM/EDX data sets in order to follow an evolution of the finer and coarser particle modes. This must be viewed cautiously, as generally speaking OPC size is not necessarily identical to the physical size measured by the SEM. Moreover, it can be additionally complicated by the fact that SEM measurement samples only two dimensions of 3D objects and thus tends to overestimate the size of flat-shaped particles. Therefore, such a combination of OPC and CCSEM/EDX datasets may be justified for particles in relatively broad size bins but not in narrow ones.

Although the TRAC-CCSEM/EDX approach has a number of limitations that will be discussed below, it is encouraging that the results shown in Figures 9 and 10 are in accordance with generally accepted expectations. We are in the beginning of correlating these results at their full level of analytical detail with the data available from other research groups (meteorology, trace gases, expected chemistry, etc.). The specificity and quality of the single-particle data will make it possible to track particle classes and sources as well as to follow the atmospheric processing of certain types of aerosols (e.g., Laskin et al. 2002).

However, we note that the TRAC-CCSEM/EDX data must always be assessed judiciously and their meaning should not be overestimated. This is especially true for Figure 10 where we combined OPC and CCSEM/EDX-TRAC data sets. In that

figure the information on the particle-type contribution given by the "painted area" should be treated as qualitative rather than quantitative. Figure 10 gives a clear indication of the general compositional structure and the differences in the two modes of aerosol that showed distinct time-resolved behavior. For example, one could learn the time of the maximal and minimal appearance of ASL, high-C, or any other particles and correlate these events with other field observations (meteorology, trace gas measurements, intensity of vehicle traffic, etc.). This can be done with the time resolution down to 10 minutes, if necessary. However, neither Figure 9 nor Figure 10 provides absolute data on the particle-type aerosol makeup. With some reservations this can be estimated from the data presented there, but then the estimated values must be used very cautiously since they might reflect a number of problems inherent with the TRAC-CCSEM/EDX approach.

First of all, as we mentioned earlier, volatile and many semi-volatile particles are not analyzed by the CCSEM/EDX. Their escape from the analysis definitely affects the absolute extent of the particle classes in the aerosol makeup, but not the relative partitioning of the detected classes. At this time, the loss of volatiles is a general limit of all EPMA methods. There are some recently reported efforts underway to address this issue and minimize loss of volatiles during the analysis using cryostages to freeze particle samples (e.g., Ro et al. 2001a, 2001b). However, no effort has yet been reported on the development of samplers that are able to collect and preserve volatile particles on chilled substrates. This task is one of our major priorities for further TRAC development and improvement.

The nonuniformity of particle deposition using a single round-jet impactor may result in differences of particle-type composition for each given area. Ideally, in order to obtain a representative view of the particle size and composition, the sample must be analyzed either entirely or across the deposition spot. As we already discussed, in analyzing our first TRAC dataset from the TexAQS 2000 study we have realized that for many episodes 10 minutes of sampling time was too long for the Houston area. This resulted in frequent particle overlap in the central spot of the probe, making that area unsuitable for single-particle analysis. In order to provide internal consistency for the analysis among consecutively collected samples we have chosen an annular area of $\text{ID} = 0.2$ mm and $\text{OD} = 0.6$ mm. The area excludes the central spot and the outer impactation area, which largely contains particles smaller than ~ 0.2 μm . This artificial arrangement may affect the relative abundance of particle classes compared to the case when the entire sample area is analyzed. However, the effect would be more dramatic for a detailed classification with many classes specified rather than for the coarse classification scheme presented here. There are several ways to avoid this problem in future sampling. First, a simple duty cycle mode can be implemented for TRAC operation in order to decrease particle density. During each sampling period the pump would be turned on and off several times, providing only part of the time for particle collection. Another way is to implement very slow

continuous motion of the substrate during the deposition. This would decrease sample density and also transform nonuniformity of the sample from a two- to a one-dimensional problem, so that complete analysis of the section across the motion path will be representative of the whole sample. Use of a micro-slit jet combined with continuous motion would effectively homogenize particle density over the entire sample, allowing analysis of randomly chosen sample areas. Single-spot TRAC operation and each of the aforementioned options might have strong advantages and disadvantages depending on the application and sampling environment. For instance, the micro-slit option with moving substrate would probably work best for sampling in areas similar to Houston, while the single-spot option is obviously the best way for frequent sampling on board research aircraft. Our current TRAC improvements include implementation of all the options listed above to make the device easily adjustable to different sampling conditions.

The use of the TEM grids opens up the possibility of including low-Z elements C, N, and O in particle classification, yet the accuracy of their detection is constrained by several factors. Detection of C is obviously limited by the carbon background from the film itself. Although the carbon film is very thin (~ 50 nm), its background in the X-ray spectra can be quite significant, especially for small particles (see Figure 6). The carbon background largely originates from electrons scattered sideways by the particle, impacting the adjacent carbon film at glancing incidence. The magnitude of the background signal is affected by many factors: particle composition, size, shape, general load of the sample, etc. Our studies of laboratory-generated aerosols (Laskin and Cowin 2001) shows that carbon background may be generally neglected only for particles larger than ~ 0.5 μm . For some applications it may be advantageous to use readily available silicon oxide films instead of carbon films. In this case, the carbon background will be traded for silicon and oxygen backgrounds.

Detection of N is complicated by the deep gap in the transmission characteristic of the ATW2 window that overlaps with the K_{α} line of nitrogen. This results in very low intensities of the nitrogen peak and, consequently, in difficulties in its accurate deconvolution. Nevertheless, we have demonstrated very accurate detection of elemental nitrogen during nitrate formation in sea salt particles (Laskin et al. 2002).

Detection of O is less problematic compared to C and N. However, an oxygen background originating from ice buildup on the EDX crystal can complicate it. In order to avoid this problem the crystal must be well maintained and conditioned quite frequently. Conservatively, all these limitations result in a *semi-quantitative* analysis of low-Z elements rather than in a quantitative one. Finally, detection of low-Z elements suffers most from sensitivity effects related to atomic number (Z) dependent electron scattering, absorption (A), and fluorescence (F). While ZAF corrections can usually be avoided for submicron particles mounted on the thin film, X-ray intensities of larger particles must be ZAF-corrected (Armstrong 1991). These corrections

are minimal for 1–2 μm particles but become very significant for particles with the size of a few microns.

As we noted before, the use of the mixed BSE/SE signal for particle image tends to underreport small carbonaceous and other light-element particles, which is also a limitation of the presented approach. Very recently we have upgraded our system with an option to mix BSE and TE signals for computer-controlled particle imaging. The initial results are very promising, and significant improvements are expected in the detection of small low-Z particles.

In this work, we have focused only on the CCSEM/EDX single-particle analysis of the TRAC collected samples. Although not presented here, we also have explored the use of other analytical techniques to address some specific questions. We have probed the surface composition of the collected aerosols with high-resolution time-of-flight secondary ion mass spectrometry (TOF-SIMS). This includes nanometer depth-resolved analysis of the aerosols, probing organic and inorganic overlayers. Hydration reactivity of the field-collected aerosols of certain types has been studied using an “environmental” SEM (ESEM) that allows imaging at up to 10 torr total vapor pressure of water. Additionally, after the first deployment of the TRAC at the skyscraper site in Houston, very recently we have also successfully deployed it on board a G-1 research aircraft for continuous aerosol sampling with 1-minute resolution over the Seattle metropolitan area (PNW 2001). The results are yet to be published.

Finally, we would like to report that there is an effort underway to reduce drastically the size and weight of the TRAC system in order to make the instrument more robust and versatile. The next generation of the instrument is currently in the last stages of development. The new TRAC device is packed inside an approximately seven-inch cube, has a load of 560 samples, and is operated from a pocket PC. The new instrument runs off 12 V, consumes 8 W of power, and is suitable for battery operation in remote areas.

SUMMARY AND CONCLUSIONS

A practical Time-Resolved Aerosol Collector (TRAC) has been developed for continuous sampling of aerosols in field experiments. Samples are collected using an impactor for extended time periods at short-enough intervals (down to 1 min) to follow time-dependent variations in aerosol composition. The aerosol collector is optimized for use of grid-supported thin films as substrates, opening up the possibility of including light elements such as C, N, and O, an important constituent of fine particles, in reported CCSEM/EDX results. The CCSEM/EDX analysis of the TRAC-collected sequential samples is capable of following general time evolution of the nonvolatile aerosols featuring size- and time-resolved single-particle data.

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