

**Automated Optical and Chemical Characterization of Fine Airborne Particles by Size  
DOE STTR Project DE-FG-98ER86070  
Phase I Final Report**

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**Executive Summary**

Fine airborne particles contribute to urban and regional haze, influence global climate and are implicated in the impairment of human health. Knowledge of their composition and concentration is limited for lack of suitable monitoring technology. Needed are automated, high-time resolution measurement of the particle chemical composition, and size-resolved light scattering properties.

We have proposed a system that will provide immediate data on the airborne concentration of sulfates, nitrates and carbonaceous aerosols in three size classes, and on particle number and light scattering coefficient in thirty-two size channels. The components of our chemistry and detailed particle sizing system are a particle nitrate monitor, a particle sulfate monitor, a particle carbon monitor and a detailed particle size spectrometer. The feasibility of the nitrate monitor was shown prior to our Phase I application. The critical technologies for the other three components were tested through our Phase I work for this project.

In Phase I we constructed a system for particle sulfate and carbon monitoring based on our integrated collection and vaporization cell that was developed previously for nitrate monitoring. This was tested in the laboratory and the field. We found linear response to ammonium sulfate standards and laboratory ammonium sulfate aerosol with a detection limit at the 10 ng level. We found linear response to organic carbon standards and oxalic acid-containing aerosols, with detection limits comparable to those for sulfate. We tested the application of a low-resolution optical spectrometer for high-resolution size distribution and size-resolved nephelometry measurements through field tests in three locations in the US. We operated the particle chemistry monitors, optical spectrometer and multiwavelength nephelometer simultaneously over a four-day period in the Denver Colorado area. For these field measurements the sum of measured sulfates, nitrates and carbonaceous aerosol correlated with the particle volume from the size spectrometer with a value of  $R^2 = 0.99$  and a slope of  $1.2 \text{ g/cm}^3$ . These results meet the Phase I objectives for detection limits and sensitivity, and demonstrate the technical feasibility of our approach.

This technology is much less expensive than filter-based sampling as is currently done, and will provide an immediate, continuous data base for sulfate, nitrate, carbon concentrations, and particle volume and size. The approach for size distribution measurement relies on an inexpensive instrument, with sophisticated data reduction.

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### **Automated Optical and Chemical Characterization of Fine Airborne Particles by Size**

#### **1. Introduction**

The atmosphere contains many fine particles, loosely defined as those particles with diameters below a few micrometers. Concentrations range from hundreds to tens of thousands per cubic centimeter of air. Particle sizes range from a few nanometers in diameter to a few micrometers. Chemical constituents include sulfates, nitrates, organic matter and soot. Origins of these particles are varied. Some are directly emitted from anthropogenic sources such as combustion. Others are formed in the atmosphere by secondary processes, such as the photochemical reaction of anthropogenically emitted gases. Still others result from increased biogenic activity attributable to anthropogenic increases in carbon dioxide levels.

This complex mixture of airborne particles is of environmental concern in several arenas. On an urban scale, fine airborne particles are an air pollutant that has recently been related to health effects (EPA, 1996). On a regional scale they contribute to atmospheric haze which is of concern in our national parks (Malm et al, 1994). On a global scale, fine particles contribute to radiative forcing and influence global climate (Charlson *et al.*, 1991).

Chemical composition and size can help identify the sources from which particles are derived. For example, fine soot particles are associated with combustion sources such as diesel vehicles. Urban sulfates in the size range from 0.5 to 1  $\mu\text{m}$  are generally derived from heterogeneous transformation of sulfur dioxide (Hering and Friedlander, 1982). Nitrates in the size range from 1 to 3  $\mu\text{m}$  have been attributed to reaction of nitric acid with sea salt (Wall and John, 1988).

The magnitude of the optical effects, penetration into the lungs, the lifetime of particles in the atmosphere all depend strongly on particle size. Knowing the size distribution permits estimation of integral parameters such as total scattering, light scattering contributed by specific size ranges, total mass, mass in specific size ranges and aerosol surface available for heterogeneous chemistry. As it becomes necessary to reduce particle concentrations, data on particle chemical composition and size will become critical to identifying origins of particles, to assessing their effects, and to developing effective control strategies.

Automated methods, such as are now available for gaseous pollutants such as ozone and carbon monoxide, have made it possible to obtain high-time resolution ambient concentration data at reasonable cost. Equivalent, automated methods are needed for monitoring the chemical constituents of fine particles. Currently, particle chemistry is measured by manual, filter-based methods. Samples are collected on site and taken to the laboratory for analysis. The time resolution is 4 hours at best, and often results are not known for many months after sample collection. The high cost of this labor-intensive approach has greatly limited the amount of data collected.

As stated in the Phase I request for proposals, a monitor is needed for measuring several particle size ranges in aerosols and for characterizing the particle scattering and chemical composition within these size ranges (Topic 1b of technical topic descriptions). Submicrometer particles are of greatest interest for scattering visible light. The chemical species which comprise the majority of the submicrometer mass, and which were specifically identified in Topic 1b, are sulfate, nitrate and carbon. Thus our focus is on submicrometer aerosols, their size distribution, size-resolved light scattering, and the size-resolved concentration of sulfates, nitrates and carbonaceous aerosols.

## **2. Technical Approach**

Through Phase I and Phase II STTR research, we propose to develop a robust chemical speciation and particle sizing system that can provide particle chemistry with time resolution of the order of 5-10 minutes, and detailed particle size and light scattering information with a time resolution of 30 seconds. The particle chemistry includes nitrate, sulfate and carbon in each of three size classes. The detailed particle sizing provides particle number, volume and light scattering coefficient in 32 size bins. The higher size resolution data are combined to match the three size classes available for the chemistry.

Components of this system include four instruments: three size-resolved monitors for particle nitrate, sulfate and carbon, and one detailed particle size and light scattering spectrometer. Each is designed to be rugged, and suitable for long-term monitoring. Each has the potential for miniaturization and relatively low cost.

Our approach for particle chemistry is based on our automated particle nitrate monitor (Hering and Stolzenburg, 1998). With this technique, particles are collected in an integrated collection and vaporization cell (ICVC). They are analyzed in place at the nanogram level by flash vaporization and quantitation of the evolved vapors. Prior to collection, the aerosol sample stream is denuded to remove interfering vapors such as vapor organics, and then humidified to enhance particle collection. The denuded, humidified particles are collected by impaction onto a metal substrate. At the end of collection the cell is filled with a carrier gas, the substrate is heated

resistively, and the particles thermally decompose to vapors that are quantitated using a commercial gas phase analyzer. A unique flow system eliminates the need for valves on the aerosol transport line. For our nitrate monitor the substrate is heated in a nitrogen stream, with quantitation of the evolved nitrogen oxides by chemiluminescence. In our Phase I work we extended our approach for automated nitrate analysis to include particle sulfate and carbon analysis. This was done with a separate collection cell, by heating the substrate to a higher temperature, using a scrubbed air carrier gas, and analyzing the evolved sulfur dioxide and carbon dioxide.

Our chemical analysis approach offers several advantages. First, this approach can be used to provide quantitative data on the concentration of all major particle constituents, namely carbon as well as sulfate and nitrate. Second, it is amenable to measurement of these concentrations in several size ranges. Third, the method concentrates the aerosol before analysis and thus yields low detection limits with small pumping requirements. Fourth, the degree of concentration can be adjusted to achieve the needed detection limit and time resolution. Fifth, the system is rugged, and potentially quite compact.

Our approach for detailed particle sizing in a compact and robust package is an aerosol spectrometer that permits determination of the light scattering contributed by various size ranges of particles in the air. The technique utilizes a low-resolution optical bench, high-resolution pulse height analysis, and data reduction and calibration techniques which permit the high resolution determinations to be made. This technique will be cost effective and efficient. It will also be applicable to determination of other integral properties of the aerosol size distribution. Thus, it should be of use in monitoring the mass concentration of various size ranges of the ambient aerosol as well as the light scattering properties. The instrument will be light, compact and low power and thus suitable for use on sounding or tethered balloons. It could be used to characterize altitude profiles of desired parameters.

To summarize, our approach is a modular system with four components: monitors for particle sulfate, nitrate and carbon in three size classes, and an optical-based system for detailed particle size distribution measurement in 32 size classes. Such measurements are needed for mapping the concentration, size and composition of fine, airborne particles. Our approach has the potential to be small, rugged and cost-effective.

### **3. Phase I Objectives**

In our Phase I proposal we stated our Phase I technical objectives as follows:

*“Our long-term goal is to produce a compact monitor which provides size resolved light scattering and composition of the fine aerosol. Detailed sizing will be provided using a focussed cavity aerosol spectrometer; size-resolved chemistry will be provided through cascaded collection and vaporization cells with quantitation of sulfate, nitrate and carbon in airborne particles. The feasibility of this approach will be established in Phase I. Our objectives are:*

- (1) *to adapt our integrated collection and vaporization cell (ICVC) technology, which already provides nanogram detection of nitrates, to provide detection of sulfate aerosols at the nanogram level;*
- (2) *to adapt our ICVC technology for the analysis of carbonaceous aerosol with detection limit of the order of tens of nanograms;*
- (3) *to demonstrate that the focused cavity aerosol spectrometer is successful in determining the light scattering coefficient for different types of boundary-layer aerosol; and*
- (4) *to test the performance of our approach in the field by comparing the time-variation in ambient sulfate, carbon and nitrate concentrations determined with the ICVC system to particle light scattering determined with the aerosol spectrometer.*

*The above objectives focus on the issues we feel to be most critical to the development of this system. We have deferred the adaptation of the ICVC system for size-resolved particle chemistry to Phase II because this is a less critical issue. Because the system uses inertial collection, we expect it to be reasonably straightforward to cascade our cells to provide size-resolved data.”*

Each of our four objectives were met through a separate task. The approach, experimental methods and results for each task are described below.

#### **4. Task 1. Adaptation of the ICVC for Analysis of Sulfate Particles**

In this section we first provide the necessary background through a description of our ICVC system. We then describe the adaptation and testing for analysis of sulfates, and highlight our results.

##### *4.1. The Integrated Collection and Vaporization Cell for Automated Particle Chemistry*

A schematic of the instrument is shown in Figure 1. The system consists of pre-impactor, a carbon honeycomb denuder, a humidifier, a collection and vaporization cell, a nitrogen source, a chemiluminescence nitric oxide detector, vaporization electronics, pump, data system and various sensors, flow meters and valves. The denuder consists of an activated carbon honeycomb. The humidifier is a single tube of Nafion<sup>®</sup> surrounded by a jacket of water (Perma Pure) that is kept full by means of a water reservoir (not shown). The integrated collection and vaporization cell has a single orifice that operates under sonic flow conditions, with metal strip mounted below the orifice exit to collect the particles. The strip is held in place by metal mounting posts which provide the electrical contact as well as mechanical stability. The internal volume of the cell is approximately 15 cm<sup>3</sup>. These components are housed in a ventilated chamber to maintain ambient temperatures for the particle sampling. The carrier gas can be either nitrogen or scrubbed air. The gas analyzer is a standard commercial detector for nitrogen oxides, sulfur dioxide or carbon dioxide. The original vaporization electronics consisted of a bank of capacitors. More recently we have used a gel cell coupled with an infrared detector sensor. The current data system and control is PC based.

Our system has two modes of operation: sampling and analysis. During sampling particles are collected by impaction onto a small area at the center of the metal strip mounted inside the collection and vaporization cell. At the end of the collection period the instrument switches to the analysis mode. The particle deposit is vaporized in place by rapid resistive heating of the metal strip and the evolved vapors are transported by a carrier gas to a commercial gas phase analyzer. The resulting peak in the gas-phase concentration is integrated to give the mass of the nitrate collected. After the analysis is complete the system returns to sampling mode, and the cycle is reinitiated.

In the sampling mode the valve between the cell and the pump is open, while the valves between the cell and the gas analyzer and between the cell and the carrier gas source are closed. Ambient, particle-laden air is drawn through a pre-impactor, vapor denuder, humidifier and into the collection and vaporization cell. Because the particles are wet they do not bounce (Winkler, 1974; Stein et al 1994) and thus can be collected efficiently by impaction. The sample flow rate is controlled by the cell orifice.

In analysis mode the valve between the cell and the pump is closed, and the valves to the carrier gas source and to the gas analyzer are open. Carrier gas enters through the pumping port and through the orifice tube, and exits into analyzer. The gas is introduced to the cell slight excess of the flow required by the gas analyzer, and the slight excess flow is vented upwards through the sampling line. This arrangement eliminates the need for valves on the sample line. After a preset flushing time (typically 20 s) the collection strip is rapidly heated by an electrical current passed through the strip and the evolved vapors are quantitated by the gas analyzer. Then the system is returned to the sampling mode.

For nitrate measurement, the carrier gas is nitrogen and the gas analyzer is a commercial chemiluminescence nitrogen oxides analyzer. The analyzer is operated in NO<sub>x</sub> mode whereby the gas stream passes through a molybdenum converter for reducing higher nitrogen oxides. The resultant NO is detected based on the chemiluminescent reaction with ozone. This approach is similar to that of Yamamota and Kousaka (1992). For sulfate and carbon measurement we use a scrubbed air carrier gas, and two gas analyzers operated in series, as described below in our Phase I work. The first is a NDIR analyzer for CO<sub>2</sub>, the second is a pulsed fluorescence analyzer for SO<sub>2</sub>. This approach for sulfate analysis method was first described by Roberts and Friedlander (1978).

Typical collection times are 8-minutes, although sampling periods as short as 3-minutes have been used in regions of higher concentrations. The time currently required for the analysis step is 90 seconds, however this may be shortened. The heating of the metal substrate requires less than 1 sec, and with a suitable analyzer the resultant peak is approximately 5 seconds wide.

#### *4.2 Approach for Testing of Sulfate Analysis*

For sulfate analysis we replaced the NO<sub>x</sub> analyzer on our nitrate system with a pulsed fluorescence SO<sub>2</sub> monitor designed for ambient monitoring at the ppb level. Two types of monitors were used, a Horiba Model and a Thermo Environmental Instruments Model 43C. These were borrowed from the manufacturer. The pulsed fluorescence methodology is much

more robust than the flame-photometric detectors originally used for this type of analysis, and thus were considered the better choice for evaluation here.

We have used the flash-vaporization technique for aerosol sulfate analysis for more than twenty years, but these analyses were done in a glass cell to which samples were individually transferred after collection. Critical issues addressed to adapt this manual method to our ICVC are whether the analysis would tolerate repeated use of the same collection substrates, and whether SO<sub>2</sub>, which more readily deposits on surfaces than does NO, is not lost in the closer geometry of the ICVC.

In our Phase I proposal we stated that we would test the sulfate analysis by: (1) evaluating the analysis step of the ICVC using sulfate standards applied directly to the collection substrate and (2) evaluating the complete system using laboratory generated, monodisperse sulfate aerosols. Both tests were done, as described below. In addition we added the capability to readily display the shape of our analysis pulses on the computer screen so that adjustments to optimize this response could be readily made.

#### 4.3 *Experimental Methods*

Sulfate standards are applied to the collection strip as a 0.2  $\mu$ L to 0.8  $\mu$ L drop using a microliter syringe. The droplet is dried to mimic the aerosol deposit. After drying the deposited standard is analyzed in the ICVC using the automated system. Tests were done with the original glass cell used for manual sulfate analysis, and with the ICVC.

The configuration for aerosol tests is shown in Figure 2. Ammonium sulfate particles are generated by nebulization, and a mono-mobility size fraction was selected from the nebulized aerosol using a high-flow differential mobility analyzer. The particle concentration upstream of the collection cell was monitored with a condensation nucleus counter (CNC) and an LAS-X optical counter. The particle concentrations downstream of the collection cell were monitored with a second optical particle counter operated at low pressure. The LAS-X counter allowed us to correct for doublets, ie larger doubly charged particles in the test aerosol, while the CNC provided redundancy for evaluating counting efficiency, and for evaluating the response for particles below the optical counter detection limit.

#### 4.4 Results

The pulsed fluorescence analysis has an inherently lower response time than the chemiluminescence nitrogen oxide analysis due to the larger sensing volume (approximately 250 cm<sup>3</sup>). Thus the vapor pulse from the flash vaporization of the sample is spread out over a longer time period, and is lower in height. To compensate for the reduced sensitivity as compared to nitrate analysis, we adapted the cell to operate at a flow rate of 3 L/min instead of 1 L/min as used for nitrate. The ICVC was tested in this configuration. Also, it was found that the pulsed fluorescence analysis does not perform well in a nitrogen-only stream. Some oxygen is needed to quench background fluorescence. Thus we moved to a carrier gas of air, and to nichrome substrates which are more durable than the stainless steel employed for the manual sulfate analysis and for the nitrate analysis. Finally, we replumbed the analyzer with the critical orifice upstream of the detection chamber, so that it operated at a pressure of 300 torr. This reduced the residence time and decreased the peak width without reducing the height of the peak.

Results from the application of liquid standards are shown in Figure 3. The ICVC cell was operated with a nichrome substrate (a chromium nickel alloy), and with a 3 L/min orifice. At the same time tests were done with the original glass cell and a baked stainless steel substrate, exactly as is used for the manual analysis. It is apparent that both systems give the same result, despite the difference in geometry and substrate. The response of 6.5 SO<sub>2</sub> ppb-s/nanogramSO<sub>4</sub><sup>-</sup> is one-half of that calculated on the basis of the analyzer flow rate and SO<sub>2</sub> calibration, indicating that only half of the deposited sulfate is converted to SO<sub>2</sub> which is detected. Although quantitative

recovery is certainly more desirable, we note that the recovery from the manual system is also only 50%, and yet it has compared well with filter-based methods over the last 20 years.

The response to ammonium sulfate aerosols is shown in Figure 4. The aerosol volume from the DMA is calculated on the basis of the CNC counts of the generated aerosol, and on the diameter from the DMA. The deposited sulfate mass is calculated using the response curve of Figure 3, and the ppb-s integrals from the flash analysis of the substrate. As we have consistently found with the nitrate system, the response to actual aerosol is much more precise than for the application of liquid standards. The response is linear with concentration in the range up to 200 nanograms. The slope of the line is in the range of expected response. In Figure 4 the aerosol volume is shown in units of  $\text{cm}^3 \times 10^{-9}$  which is equivalent to particle mass in nanograms at a density of  $1 \text{ g/cm}^3$ . The theoretical slope is the product of the particle density and the fraction of the particle mass that is sulfate, or  $(1.77)(96/132)=1.3$ , compared to the 1.38 value measured. This discrepancy is likely due to error in accounting for the mass doublets in the test size distribution.

As part of the aerosol experiments, the cell collection efficiencies were measured by counting penetration with the downstream optical counter. For this cell operating at 3 L/min, the collection efficiency at and below  $0.2 \mu\text{m}$  is 90% as compared with the 98% valued for the 1 L/min cell. This is to be expected for because of the lower Stokes number for the larger jet at the higher flow. Results are shown in Table 1 below, with comparison to the previous results for 1 L/min cell. Consideration is being given to returning to the lower flow rate.

Table 1. Particle Collection Efficiency Measured with Laboratory-Generated Ammonium Sulfate Aerosols

Particle Diameter	Collection Efficiency	
	@ 1L/min	@ 3 L/min
0.1 $\mu\text{m}$	99.7 %	89.7 %
0.2 $\mu\text{m}$	99.8	91.0
0.3 $\mu\text{m}$	99.7	99.9
0.4 $\mu\text{m}$	99.7	99.9
0.8 $\mu\text{m}$	95.	99.8

## 5. Task 2. Adaptation the ICVC for Analysis of Carbonaceous Particles

### 5.1 Approach and Experimental Methods

Two  $\text{CO}_2$  detection methods were considered, flame ionization detection and nondispersive infrared absorption (NDIR). Flame ionization is the approach used for thermal analysis of filters, such as that performed commercially by Desert Research Institute (Reno NV) and Sunset Laboratories (Forest Grove OR). It has the advantage of lower detection limits, but requires a methanator with hydrogen carrier gas. NDIR is inherently more robust, but not as sensitive. We examined the NDIR first because of its obvious ease of use. After a survey of the market, we arranged to borrow an instrument, model LI-6252 from Li-Cor (Lincoln, NE). We first tested whether we could obtain a clear signal, and then we tested the system with oxalic acid liquid standards and oxalic acid-sulfate aerosol mixtures. Experimental methods were much the same as described in Section 5.1.3 above. Tests were done with oxalic acid, an organic acid common in urban atmospheres.

## 5.2 Results

The vaporization conditions developed for the sulfate analysis in the first task were just those expected to be needed for the carbon analysis, namely high temperature heating in a gas stream with oxygen. The NDIR detector selected has a cell volume of less than  $10 \text{ cm}^3$ . It was installed immediately upstream of the  $\text{SO}_2$  analyzer, so that with each sample flash two analyses are obtained, one for carbon and one for sulfate. The carrier gas used is air that had been passed through a bed of soda lime to remove most of the ambient carbon dioxide.

An example of the analysis signal from this combined system is shown in Figure 5. The results are for a sample of laboratory aerosol consisting of approximately equal masses of carbon and sulfate. For this particular example the sampled mass is 90 ng each of carbon and sulfate as estimated from DMA size, solution mix and LAS-X counts. The graph is taken from our on-line data acquisition system. Carbon dioxide concentration is the upper curve, and is displayed on the right-hand axis in units of ppm. Sulfur dioxide is taken from the 1-sec output of the ThermoEnvironmental 43C, and is the lower, histogram shaped curve with concentrations shown on the left-hand axis in units of ppb. The  $\text{CO}_2$  signal is sharp and quiet and allows us to readily distinguish an output of a few ppm above the 10 ppm background.

Sulfate and carbon responses were compared for a  $0.4 \mu\text{m}$  aerosol generated from a 25%/75% mixture of ammonium sulfate and oxalic acid. This yields approximately equal mass of sulfate and carbon. Results are shown in Figure 6 for a range of concentrations. Various cell configurations were tested with this system, with similar results. Also shown are data using both the capacitor flash electronics and a gel cell system with an imbedded infrared sensor for determining the end point of the heating. The points marked "Gel Cell FI-2" are from modification of the circuitry to allow higher temperature heating. The measured  $\text{CO}_2/\text{SO}_2$  ratio is 10:1, compared to an expected value of 8:1 (equal 96/12, the ratio of the molar masses). Calibration was also done with liquid standards, as with sulfates.

In Figure 7 the carbon from the flash analysis is compared to the sampled aerosol volume for this same 75/25 oxalic acid / sulfate mixture. These data were collected over various days, with different cells and flasher electronics, but were reduced with a common calibration constant. The slope of the line is  $0.21 \text{ ngC}/(10\text{-}9\text{cm}^3 \text{ aerosol})$ . The mass fraction of carbon is 14%, which yields a carbon mass to aerosol volume ratio of 0.26, if the aerosol is dry. More careful experiments are needed to determine the exact calibration factor, but clearly the system is capable of detecting carbon at the level of a few tens of nanograms.

## **6 Task 3. Demonstration that the Aerosol Spectrometer is Successful in Determining Light Scattering Coefficient**

### *6.1 Selection of the Optical Bench and Adaptation for Use in the Troposphere*

Figure 8 shows the layout of the optical bench used in Phase I. The bench was purchased from PMS Inc in Boulder for use in high altitude applications. The light scattered by particles out of the laser beam into coaxial cones of 45° half angle oriented perpendicularly to the laser and aerosol beam is collected and measured by two array photodiodes. The bench is sensitive to particles in the diameter range from 74nm to 1050 nm. This bench does not meet the cost-effective criteria for candidate benches described below. However, it has low-resolution. This means that the introduction of monodisperse aerosol into the viewing volume results in a population of pulses of many sizes as shown in Figure 9. Design trade-offs that allowed the bench to be useful for measurements made at 200m/s in the stratosphere resulted in this behavior.

Adapting the bench for use in the troposphere involved installation of a sheath air system that recirculates approximately 27 cm<sup>3</sup>/s of filtered air and draws 1.1 cm<sup>3</sup>/s of sample flow. This relative modest sample flow prevented coincidences between particles in the viewing volume and the large amount of filtered sheath air prevented recirculation of particles through the laser beam. The data acquisition rate was adjusted to permit adequate statistical samples to be collected without filling up the disk.

This optical bench had not been used prior to this application and it represents a new type. Therefore, it is not as well understood as its predecessor in spite of shared geometry.

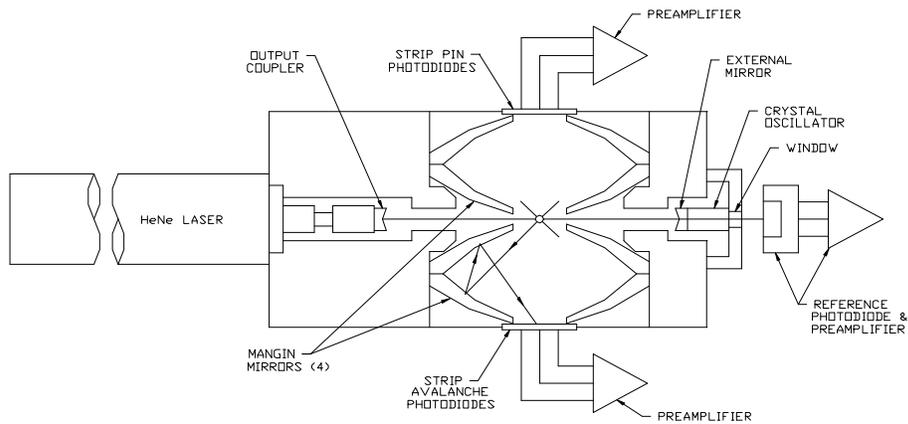


Figure 8. Schematic of optical bench used in Phase I. The bench is sensitive to particles in the 74 to 1050 nm diameter range and is low resolution in the sense illustrated by Figure 9.

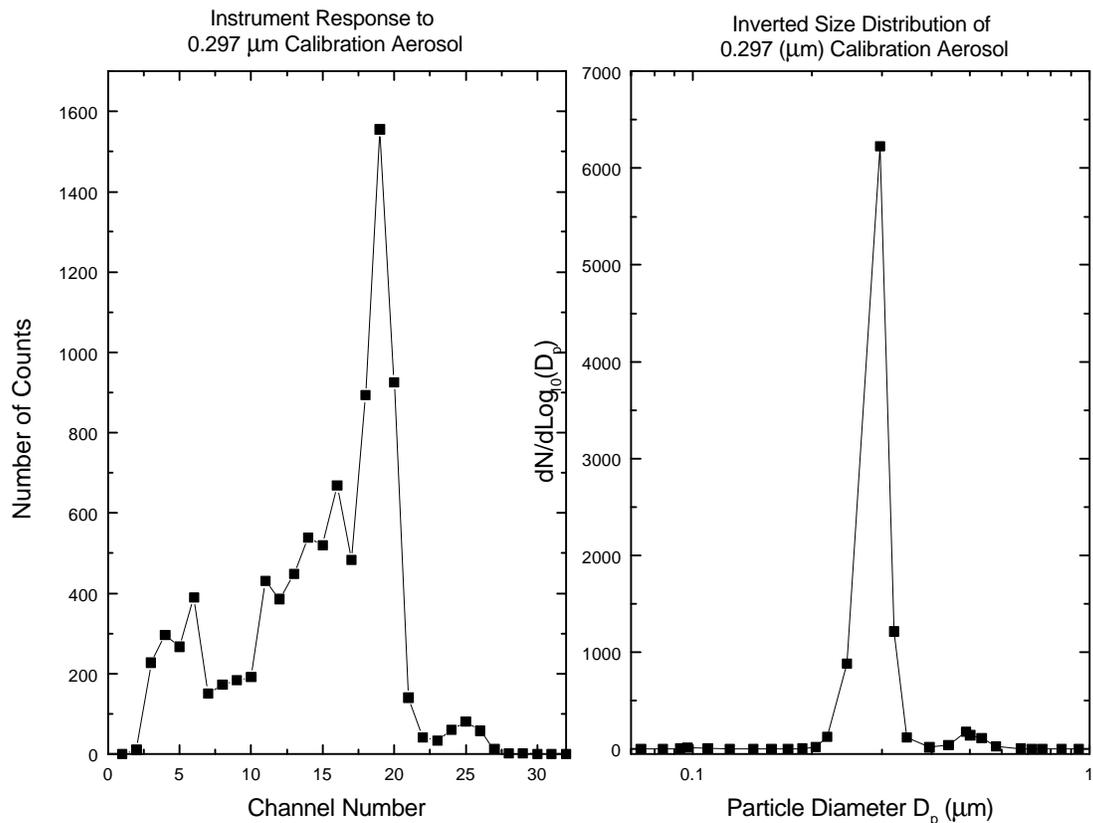


Figure 9. Left Panel: Pulse height distribution for a calibration with particles having a diameter of 0.297  $\mu\text{m}$ . Approximately half of the particles fall outside of the main peak seen in channels 18-20. The Peak around channel 25 includes the doubly charged particles having the same mobility as the main peak. Right panel : Size distribution resulting after inversion with the Twomey technique. The average diameter obtained by averaging the size distribution from the lower bound to the beginning of the doublets peak is within two percent of the diameter provided by the differential mobility analyzer.

## 6.2 Calibration of the Optical Bench

Twenty-eight, monodisperse calibration aerosols consisting of di(2-ethylhexyl) sebacate were generated using an atomizer and a differential mobility analyzer. The resulting pulse height distributions were modified to remove the impact of the doublets seen in Figure 7. Then the 28 normalized distributions were placed into a matrix describing the instrument response. Simultaneous measurements with a CNC counter permitted the detection efficiency of the optical bench to be determined as a function of particle size.

## 6.3 Data Reduction

A smoothed Twomey data inversion technique was used (Markowski,1987). The detection efficiencies were then applied to the inverted distributions to obtain the measured size distribution.

The convergence criterion was altered slightly and additional smoothing was performed using a 3 channel boxcar average.

#### 6.4 Field Comparisons: Marshall, CO:

Scattering predicted from the size distributions measured using the optical spectrometer is compared to nephelometer readings in Figures 10 and 11. The nephelometer was measuring submicron aerosol and data were supplied by John Ogren of NOAA CMDL.

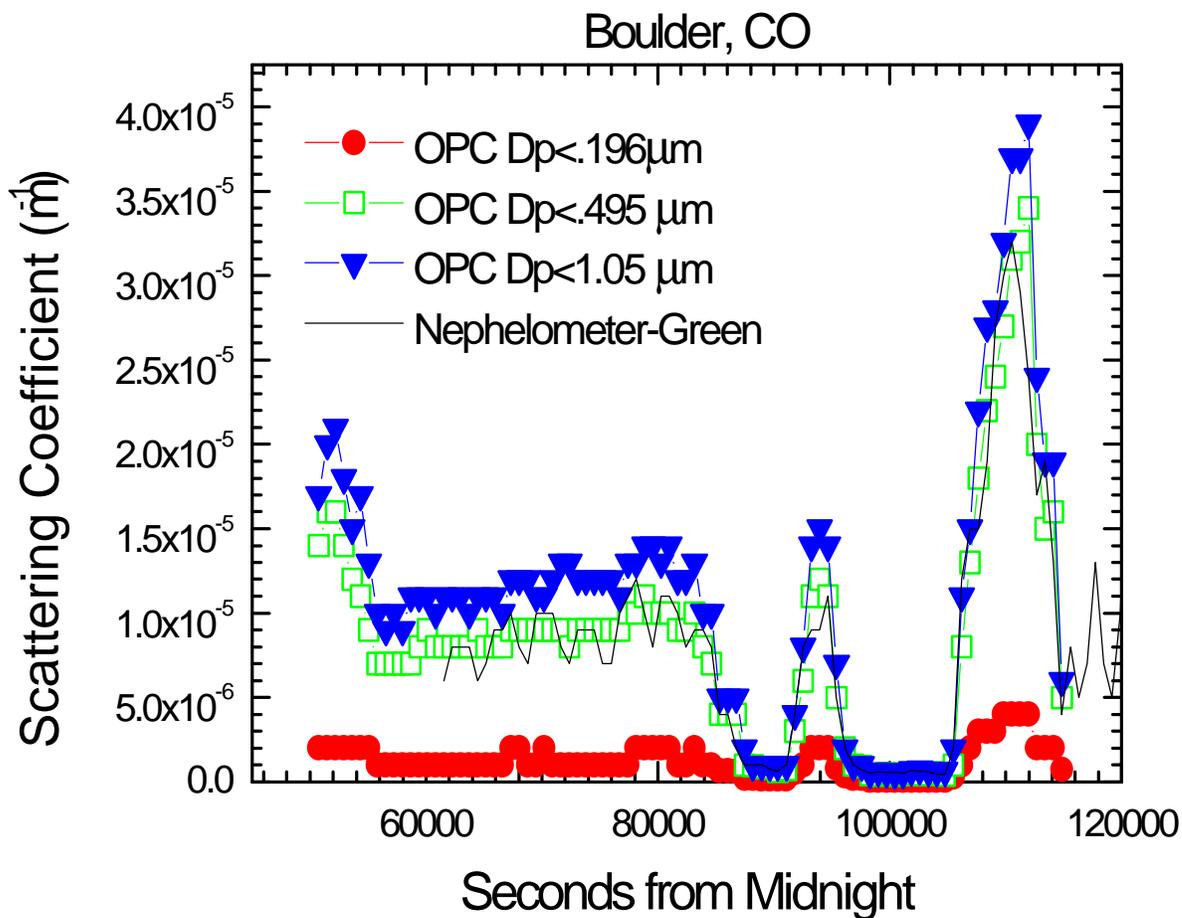


Figure 10. Scattering coefficient predicted from the size distributions determined using the aerosol spectrometer (OPC) and measured using a nephelometer. Note that particles smaller than 0.2 micron did not contribute much to the scattering and the dominant contribution is made by particles in the 0.2 to 0.5 μm diameter range.

The scatter plots shown in Figure 11 show that the scattering for the blue, green and red light predicted from the aerosol spectrometer size distributions exceeded that measured by the nephelometer by 10%, 20% and 25% respectively. The value of  $R^2$  for the regressions all exceeded 0.93. The scatter plot of aerosol mass determined by the ICVI against the volume predicted by the aerosol spectrometer also demonstrates an impressive correlation (Figure 15).

The aerosol spectrometer was calibrated at the site in Marshall and the nephelometer was checked with span gas shortly before the comparison. The aerosol sample for the spectrometer was drawn from the tube through which the nephelometer sample was drawn. The sampling arrangement was not isokinetic but corrections were calculated using the known flow rates and the geometry of the sampling configuration. The discrepancy between the nephelometer and the scattering predicted by from the spectrometer size distributions could be reduced by correcting the nephelometer reading for angular nonidealities (Anderson and Ogren, 1998). These nonidealities will be less than 10% in the case of the Marshall data since the scattering is dominated by small particles. But the corrections are in the right direction to reduce the small discrepancies and move the slopes of the scatter plots closer to one.

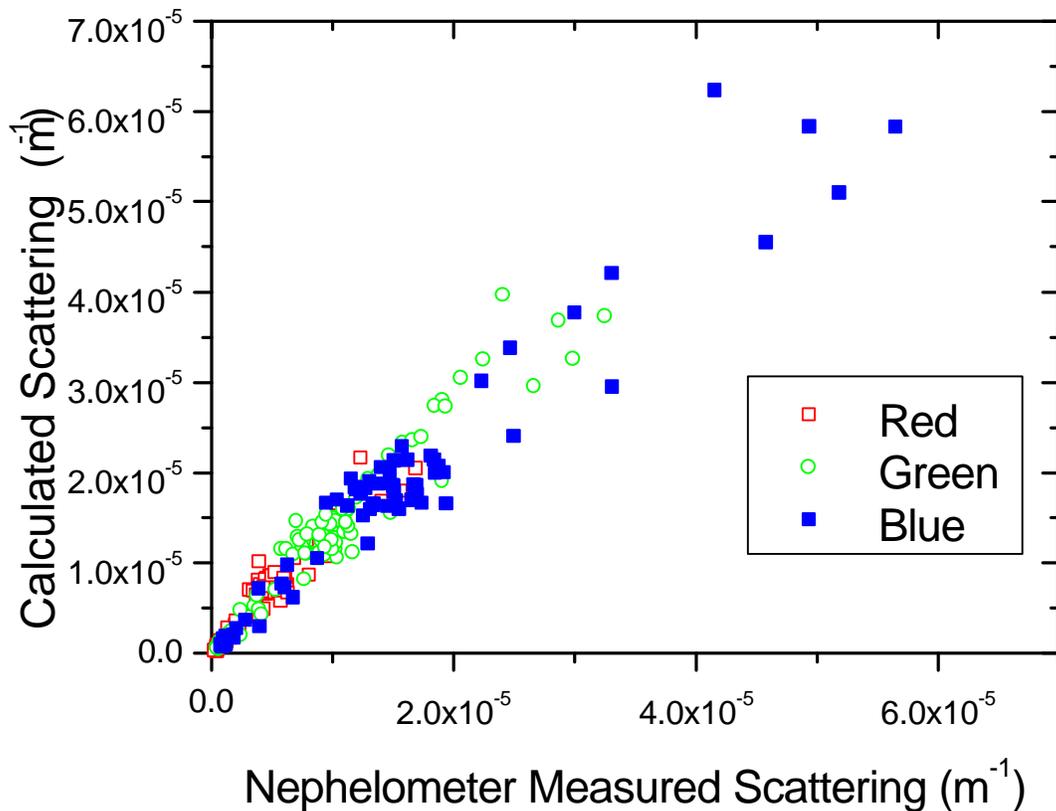


Figure 11. Scattering calculated from aerosol spectrometer measurements plotted against simultaneous nephelometer measurements. Values of  $R^2$  exceed 0.93 for the three curves. The slopes of the best-fit curves are 1.24, 1.19 and 1.09 for Red, Green and Blue respectively.

#### 6.5 Field Comparisons: Bondville, Il and SGP Site.

Additional comparisons were done at the Bondville site of the Illinois Water Survey and the DOE ARM program Southern Great Planes Site (SGP Site). At SGP the aerosol spectrometer was operated in an instrumented sea container next to a three color nephelometer. Isokinetic sampling was performed and the sample was drawn from the same tube carrying

particles to the nephelometer. Scheduling difficulties prevented a similar sampling arrangement at Bondville and due to the lack of a common sample line, those data are not presented. Figure 12 shows the comparison of the nephelometer reading with the scattering calculated to have originated from the same three size ranges. In the SGP comparison shown in Figure 12, the scattering predicted from the spectrometer size distributions exceeds that measured by the nephelometer. However, the correlation is still strong. The value of  $R^2$  resulting from plotting the predicted red scattering with the measured value is 0.89. That for green is 0.89, and that for blue is 0.83. Calibrations of the aerosol spectrometer and nephelometer spans were not done in the field this time. The fraction of the scattering contributed by particles larger than  $0.5 \mu\text{m}$  is much greater in these data than it was in the Marshall, CO case. The discrepancy between the total scattering reported by the nephelometer and that derived from the spectrometer measurements is also larger. Angular nonidealities increase for these larger particles and are likely to exceed 10%. Thus, the difference between the estimates of total scattering in the green would be ~43% of nephelometer reading.

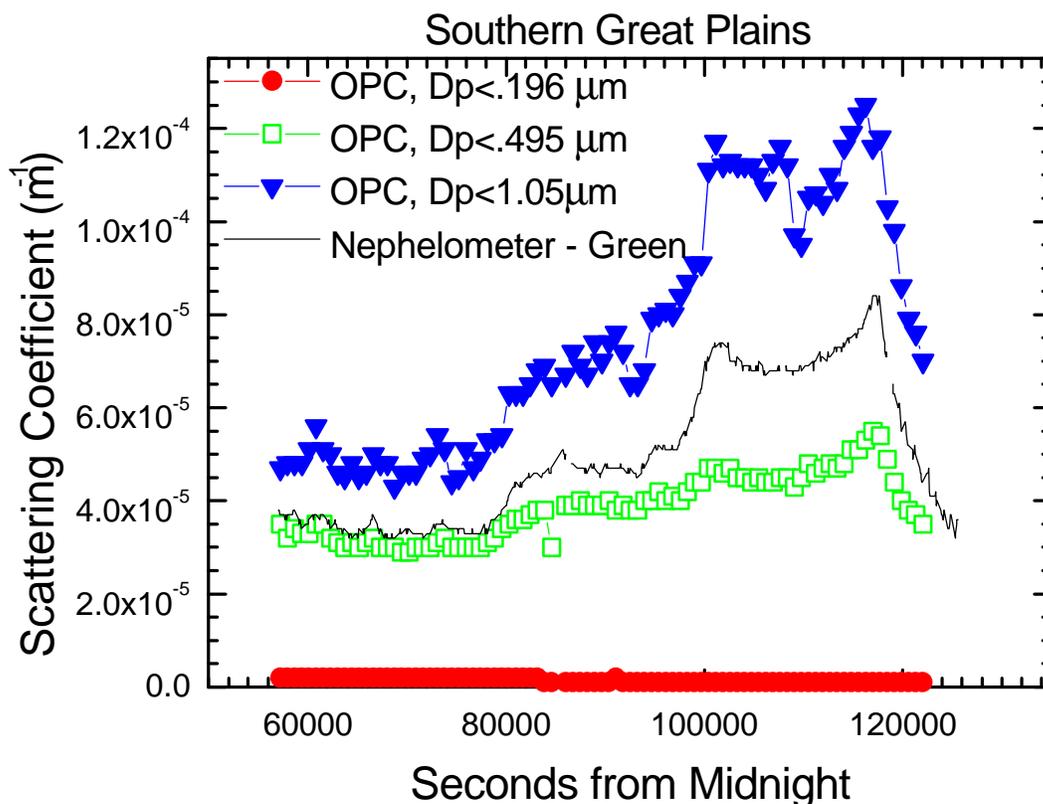


Figure 12. Comparisons between the scattering predicted from the size distributions measured by the aerosol spectrometer (OPC) and the scattering observed by the nephelometer.

Technical Feasibility. The data acquired at the Marshall, Bondville and SGP sites certainly demonstrate strong correlations between the scattering calculated from the spectrometer data and that measured by the nephelometer. In addition, Figures 9 and 10 demonstrate the ability of the

spectrometer to apportion the scattering among different size ranges. This apportionment was one of the main objectives of the RFP for Phase I.

The corrected ratio of spectrometer-estimated scattering to that measured by the nephelometer at SGP approaches 1.57, 1.43 and 1.26 for red, green and blue. These ratios are clearly larger than those for Marshall which were 1.24, 1.19 and 1.09. We do not know whether these discrepancies are caused by wandering instrument calibrations, systematic differences in the instruments' ability to handle particles between 0.5 and 1  $\mu\text{m}$  in diameter or the impact of different types of particles on the instruments. Optical benches similar to that used in the aerosol spectrometer were shown to perform well in the stratosphere after the eruption of Pinaubo when the stratospheric aerosol approached 1  $\mu\text{m}$  in diameter (Wilson, et al., 1993). Thus, there is no particular reason to believe that the optical spectrometer would be unable to handle these particles. In view of several years experience with robust optical spectrometers, we continue to believe that the discrepancy will shrink as we learn more about the data set. We look forward to better controlled experiments for exploring the differences and believe that a well designed system can live up to the promise of the Marshall comparison.

#### **7. Task 4. Demonstration of Performance and Data Consistency of Combined Systems under Field Conditions**

Measurements with the complete OPC, carbon, sulfate and nitrate system were conducted at the NOAA/NCAR site at Marshall Colorado, in collaboration with Dr. John Ogren of NOAA. The site is to the west of Denver, south of Boulder, with few local sources. As described above, nephelometry measurements were also made. Additional experiments were conducted with the sulfate system in the region of Waco Texas, (with partial support from Baylor University) and with the carbon and nitrate systems in Bakersfield California (with support for the nitrate measurements from California Air Resources Board).

Data for the period from 2100 December 15 through 1500 December 17 are shown in Figures 13 and 14. The individual species concentrations are shown by open symbols. The measured sulfate and nitrate mass are multiplied by 1.375 and 1.29 respectively to account for the ammonium cation, and the carbon mass is multiplied by 1.4 to account for the unmeasured oxygen and other noncarbon mass associated with the organic fraction. The dark points labeled "SpSum" are the sum of these values. The submicrometer particle light scattering is plotted on the right hand axis in units of  $\text{m}^{-1}$ , and correlates with the species sum.

Data for the same period are compared to the DU optical counter volume in Figure 14. In Figures 13a and 14a, at 0400 on December 16, we note a rise in the total fine particle concentrations at a time when the nitrate values were dropping, but when the particulate carbon increased sharply. For the period shown in 14b, the variability in particle concentration is mostly driven by variation in the nitrate concentration. Figure 14c shows data for an additional day, December 20, for which the nephelometry was not available. This period is of interest because the concentrations were lower, and the dominant species was sulfate. Yet the ratio between the species sum and the optical counter is the same as for the previous days.

The correlation between the species sum and the optical counter volumes is shown in Figure 15. Data are divided into three periods, corresponding to the three time series plots. We

found the data fell on a common line, even though the relative contribution of the nitrates, sulfates and carbon varied. Regression for the points of December 16 yields a correlation coefficient of  $R^2=0.988$ . The slope of the regression line is the indicated particle density. Our value of  $1.2 \text{ g/cm}^3$  is perhaps slightly low for dry particles, but does indicate that we have accounted for the majority of the fine particle mass.

In addition to the data shown, we tested for interferences through measurements on filtered ambient air in Marshall. We found no ( $<0.2 \mu\text{g/m}^3$ ) gas phase artifact for sulfate measurements, even without the denuder. For carbon it is necessary to denude the gas stream using an activated carbon denuder which brought the indicated carbon level to below  $0.4 \mu\text{g/m}^3$  for 8-min sampling. For measurements in Waco Texas, where the indicated ambient sulfate levels were relatively constant throughout the day, we varied the sample duration and found no measurable influence on the indicated levels.

## **8. Summary of Technical and Economical Feasibility**

The components of our chemistry and detailed particle sizing system are (1) particle nitrate monitor, (2) particle sulfate monitor, (3) particle carbon monitor and (4) detailed particle size spectrometer. The feasibility of the nitrate monitor was shown prior to our Phase I application. The critical technologies for the other three components were tested through our Phase I work for this project. Specifically, in our Phase I efforts we constructed and tested a system for particle sulfate and carbon monitoring, and we tested the application of a low-resolution optical spectrometer for high-resolution size distribution and size-resolved nephelometry measurements. These systems were tested in the laboratory, and in the field.

Specifically, we have demonstrated:

- (1) Linear response to ammonium sulfate standards and laboratory ammonium sulfate aerosol with a detection limit at the 10 ng level;
- (2) Linear response to organic carbon standards and oxalic acid-containing aerosols, with detection limits comparable to those for sulfate;
- (3) Detection of sulfate and carbonaceous aerosols employing gas analysis methods that are robust and economical, namely pulsed fluorescence for SO<sub>2</sub> and NDIR for CO<sub>2</sub>;
- (4) Favorable comparison between particle light scattering coefficients calculated from our optical spectrometer distributions to those measured by nephelometry at three locations;
- (5) Successful operation of all three chemical systems, the optical spectrometer and nephelometer at a field site near Denver Colorado; and
- (6) Consistency among particle chemistry data and particle volume data from the optical spectrometer in a field study near Denver Colorado.

Summary of technical feasibility: We have demonstrated in the laboratory that our ICVC approach meets our objectives for sulfate and carbon detection sensitivity. We have demonstrated that an aerosol spectrometer and associated data reduction techniques can be used to determine light scattering coefficient in the boundary layer and to apportion scattering among various size intervals. We have shown that our instruments produce consistent descriptions of the chemical, physical and optical properties of the aerosol and functioned reliably under field conditions.

Summary of economic feasibility: We have selected a measurement approach that is economical by comparison to single particle mass spectrometry systems, and that from the outset provides quantitative data on airborne concentrations.

Further, we note that the division of effort between the two institutions was exactly as planned. Our Phase I work plan contained four tasks, each focussing on one of the four objectives above. The first two were conducted by Aerosol Dynamics Inc. in our Berkeley lab facilities. The third was done by the University of Denver. The fourth task was a joint effort with both research groups working together in Denver. In addition to technical feasibility we have demonstrated a successful collaboration.

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