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FINAL REPORT

DOE CONTRACT EY-76-S-02-1248

"Electrical Charging of Small
Particles at Low Pressures"

The Tandem Differential Mobility Analyzer
Applied to
Studies on Particle Growth and Gas Phase Titration

P. H. McMurry and B. Y. H. Liu

Submitted by

Benjamin Y. H. Liu and K. T. Whitby

Particle Technology Laboratory
Mechanical Engineering Department
University of Minnesota
Minneapolis, Minnesota 55455

to

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PREFACE

This is the final report on DOE Contract EY-76-S-02-1248, entitled "Electrical Charging of Small Particles at Low Pressures". Various phases of the work performed under the contract have been reported previously. These are described in detail in the various contract publications listed on the following pages. The present report covers the work performed during the final year of the contract only. It deals with the tandem differential mobility analyzer (previously called the aerosol mobility chromatograph) and its application to studies on particle growth and gas phase titration. In addition, a Ph.D. thesis entitled "Aerodynamic Particle Size Measurement by Laser-Doppler Velocimetry", supported by this contract, was completed during the year. This is also being submitted as part of this final report.

LIST OF CONTRACT PUBLICATIONS

1. Liu, B. Y. H. and K. T. Whitby, "The Electrical Charging of Small Particles at Low Pressures", First Progress Report to AEC on Contract No. AT(11-1)--1248, Mech. Eng. Dept., Univ. of Minn., Mpls., MN (Oct., 1963). (COO-1248-1)
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THE TANDEM DIFFERENTIAL MOBILITY ANALYZER

APPLIED TO

STUDIES ON PARTICLE GROWTH AND GAS PHASE TITRATION

Prepared by

P. H. McMurry and B. Y. H. Liu

Particle Technology Laboratory
Mechanical Engineering Department
University of Minnesota
Minneapolis, Minnesota 55455

Experiments performed by

D. Y. H. Pui

Y. Kousaka*

P. H. McMurry

H. Takano**

*University of Osaka Prefecture
Mozu, Umemachi, Sakai
Osaka, Japan

**Doshisha University
Karasuma Imadegawa, Kamigyo-Ku
Kyoto, Japan

I. INTRODUCTION

Particle size changes are of fundamental importance in many aerosol systems. Ambient aerosols may shrink or grow with changes in humidity, and growth by gas-to-particle conversion is often a major factor in chemically reactive atmospheres. The formation and growth of primary aerosols in sources involves a complex series of processes including coagulation and condensation. The tandem differential mobility analyzer (TDMA) is an instrument which can precisely measure changes in the sizes of monodisperse ultrafine aerosols. [In a previous publication, Liu et al. (1978) referred to this instrument as the aerosol mobility chromatograph.] This instrument shows promise as a tool for studying these important phenomena.

A schematic diagram of the TDMA is shown in Figure 1. Note that the instrument consists of four essential elements. Differential mobility analyzer No. 1 (DMA1) (Knutson and Whitby, 1975) selects a monodisperse aerosol from a polydisperse aerosol. This aerosol is then modified by some process which may cause a change in particle size, and the new particle size is determined with the second differential mobility analyzer (DMA2) and an appropriate aerosol detector. In the studies reported in this report, either an electrometer current sensor (Liu and Pui, 1975) or a single particle condensation nucleus counter (Agarwal et al., 1977) was used as the detector, depending upon the required detection limit.

The TDMA has been used in well-controlled laboratory experiments as well as in field studies of ambient aerosols to investigate several problems involving particle growth. These studies can be divided into three basic categories:

- i. Laboratory studies of the growth of droplets or solid particles of known chemical composition with humidity changes. Experiments were performed with both internally and externally mixed aerosols.

- ii. Laboratory studies of the reaction between NH_3 (gas) and H_2SO_4 (aerosol).
- iii. Field studies of the effect of humidity on ambient aerosol particles of various sizes.

Results of these experiments are summarized in this report. Much of this work was exploratory, so the data reported here are mostly preliminary. Based on these results, however, it appears that the TDMA will provide new and quantitative data on aerosol formation mechanisms and gas-aerosol interactions.

II. DROPLET SIZE VERSUS RELATIVE HUMIDITY: LABORATORY STUDIES

When droplets consisting of aqueous solutions at a given humidity are exposed to higher humidities, they grow. Water-soluble crystals exhibit similar behavior, provided the new humidity is higher than the deliquescent point for the crystals. This process is well-understood theoretically (e.g., Junge, 1963), and droplet growth factors can be calculated with good confidence provided the requisite thermodynamic data are available. For most aerosols of practical importance where concentrations are very high, and where solutions generally consist of complex mixtures, these data are not generally available. In such systems, droplet growth factors can only be determined by measurement.

If the humidity around a droplet is decreased, it often will not shrink as much as would be predicted thermodynamically. This is known as the hysteresis effect (Junge, 1963), and is believed to occur because salts in the droplets become supersaturated rather than crystallizing once saturation is reached. The hysteresis effect is not observed for H_2SO_4 droplets, since H_2SO_4 does not crystallize at ambient temperatures. The effect is quite pronounced for salts such as NaCl or $(\text{NH}_4)_2\text{SO}_4$ which are normally crystalline at humidities below 75% and 80%, respectively. Thermodynamic properties of supersaturated solutions are generally not available, so hysteresis effects must generally be measured.

The TDMA has been used to measure aerosol growth and shrinkage with humidity changes in externally and internally mixed aerosols. An externally mixed aerosol is one which contains two distinct kinds of particles which are different chemically. Particles of internally mixed aerosols contain several compounds, and this chemical makeup is uniform for all particles.

II.1 Externally Mixed Solutions

The TDMA was originally proposed as a sulfuric acid detector (Liu et al., 1978). In this study, it was shown that monodisperse aerosols consisting of

a mixture of H_2SO_4 and K_2SO_4 particles (externally mixed) can be split into two distinct particle sizes by humidification. This occurs because H_2SO_4 and K_2SO_4 aerosols have different thermodynamic properties, and take up different amounts of water upon humidification. It was proposed that this technique could be used to distinguish pure H_2SO_4 from other particles in ambient air, provided the growth factors for H_2SO_4 are unique.

Pure H_2SO_4 particles were not detected in several spot checks of ambient Minneapolis air. This is not surprising. Studies of the reaction between H_2SO_4 particles and NH_3 (gas), reported in section III of this paper, indicate that H_2SO_4 particles should be rapidly neutralized for NH_3 concentrations typically encountered in ambient air. Pure H_2SO_4 particles should only be observed in close proximity to sources (e.g., catalyst-equipped automobiles) or in atmospheres with very low NH_3 concentrations. For a more detailed description of this study, the reader is referred to the paper which is included as an appendix to this section of the report.

II.2 Internally Mixed Aerosols

The experimental work described in this section was performed by Kousaka in the fall of 1976.

The effects of humidification and dehumidification on monodisperse aerosols consisting of internal mixtures of H_2SO_4 and $(\text{NH}_4)_2\text{SO}_4$ in various proportions were investigated. This work is related to work of Orr et al. (1958), Junge (1963), Charlson et al. (1974), Tang (1976), Ahlberg and Winchester (1978), and Tang et al. (1978). The Minnesota data were obtained using monodisperse particles as small as $0.05 \mu\text{m}$, which is a unique feature of this study. The range of droplet compositions and the small particle sizes used in these experiments have contributed new insights into the behavior of such aerosol systems.

II.2.1 Experiments

Two techniques were used to humidify and dehumidify the aerosols in this study. Using the technique shown in Figure 2, the aerosols were humidified (or dehumidified) by mixing with clean moist (or dry) air before entering the second differential mobility analyzer. While this technique insures that the particles will attain their equilibrium sizes before entering the classifier, it also results in dilution of the aerosol concentration by a factor of 10. To avoid this problem, the humidifier (dehumidifier) shown in Figure 3 was devised. In this case, aerosol humidification (or dehumidification) takes place within the classifier. Calculations for condensation and evaporation rates indicate that droplets should reach their new sizes approximately 0.02 sec after the humidity change. Since this is short compared to the three-second transit time through the classifier, this appears to be a reasonable approach. Also, experiments show that the data collected by the humidification systems in Figures 2 and 3 are in good agreement.

It should be noted that in the flow system of Figure 3, there is a slight increase in the volumetric flow rate through DMA2 due to addition of water vapor in the humidification chamber. This increase, which did not exceed 1.5%, was taken into account in reducing the experimental data from the system.

The aerosols used in these experiments were generated by means of the syringe pump atomizer described by Liu and Lee (1974). Aqueous solutions of H_2SO_4 and $(NH_4)_2SO_4$, mixed in various proportions, were atomized by the atomizer to obtain solution droplets containing the desired mixture. The droplets were then dehumidified and humidified as described above to study their hygroscopic properties.

Relative humidity, which is an important parameter in these studies, was measured by a hygrometer (Model 15-3001, Hygrodynamic, Inc., 949 Selim Road,

Silver Spring, MD 20910) or a thermo-electric dew-point indicator (Model 880, EG&G, Environmental Equipment Division, 151 Bear Hill Road, Waltham, MA 02154). Both instruments were calibrated periodically against a manually operated, standard dew-point indicator. The relative humidity was measured at the outlet of DMA2. Since the indicated value was found to be about 1.5% lower than the measured value at the inlet to DMA2, due to pressure drop in the system, the indicated value was corrected by this amount to obtain the relative humidity of the aerosol.

II.2.2 Results and Discussions

Some typical experimental results obtained by means of the procedures described above are shown in Figures 4 and 5. In Figure 4, the voltage-current curves obtained by the TDMA for the case of sulfuric acid particles are shown. It is seen that, as the relative humidity is increased, the peak in the electrometer current vs. collector rod voltage curve for DMA2 is shifted toward the right, indicating a growth in particle size with increasing humidity. However, in Figure 5, which applies to the case of $(\text{NH}_4)_2\text{SO}_4$ particles, the voltage-current curve remains stationary for the first four relative humidities of 16, 26.5, 49.5, and 62.5%. This indicates that the particle size did not change as the humidity was first increased. At a relative humidity of 79.5%, the curve shifts to the right, indicating the deliquescence of the particles at this humidity. With further increase in humidity to 86.5%, the curve continues to shift to the right, corresponding to the further growth of the $(\text{NH}_4)_2\text{SO}_4$ particles in the humid environment.

From curves similar to those shown in Figures 4 and 5, the particle size corresponding to the peak in the voltage-current curves can be determined as a function of relative humidity. The results are shown in Figures 6 through 10, and summarized and compared in Figures 11 and 12. It is interesting to note that there is no difference in the results when the corresponding systems in

Figures 2 and 3 were used, e.g., compare the data for INC-1 and INC-2, and those for DEC-1 and DEC-2. It should also be pointed out that in a few experiments, the flow rates through the DMA's were reduced to half of their normal values, and no difference was found in the experimental results. Furthermore, a few experiments were performed in which the residence time of the particles in the mixing chamber in the systems shown in Figures 2a and 2b was varied from 1 to 30 seconds. Again, no difference was observed. This suggests that the time to approach equilibrium is very short for the particles, and that there was indeed sufficient time for the particles to attain the final equilibrium size in all the experiments, including those obtained with the experimental systems shown in Figure 3, in which the approach to equilibrium occurred within the mobility tube of DMA2.

Referring to the experimental results in Figure 6 for sulfuric acid particles, we see that there is no difference in the measured particle size when the relative humidity around the particles is increased or decreased. However, in Figure 10, in the data for $(\text{NH}_4)_2\text{SO}_4$ particles, there is considerable difference in the results for increasing and decreasing humidities. With increasing humidity, there is no change in particle size until the relative humidity reaches the deliquescent point for $(\text{NH}_4)_2\text{SO}_4$. The deliquescent humidity for $(\text{NH}_4)_2\text{SO}_4$ agrees well with the literature value of 80% (Gillespie, 1928; Kracek, 1928). However, with decreasing humidity around the particles, there is a continuous decrease in particle size with decreasing humidity. $(\text{NH}_4)_2\text{SO}_4$ thus exhibits a large hysteresis effect, which distinguishes it from the non-hysteresis, reversible behavior of H_2SO_4 . The behavior of particles consisting of mixtures of H_2SO_4 and $(\text{NH}_4)_2\text{SO}_4$ are shown in Figures 7, 8 and 9. It is seen that the behavior is intermediate to those of H_2SO_4 and $(\text{NH}_4)_2\text{SO}_4$.

Experiment and theory for particle growth factors as a function of relative humidity are compared in Figures 13, 14, and 15. Comparisons are restricted to aerosols of H_2SO_4 , NH_4HSO_4 , and $(\text{NH}_4)_2\text{SO}_4$, since these are the only species in this study for which thermodynamic data are available. Agreement between observed and expected particle sizes is typically within 4%, indicating good agreement. Deviations between experiment and theory may be due to uncertainty in humidity measurements, or non-uniformities in the distribution of water vapor during humidification.

Further analysis of these data indicates that the area of the hysteresis curve can be used to evaluate the relative proportions of H_2SO_4 and $(\text{NH}_4)_2\text{SO}_4$ in the droplets. In Figure 16, hysteresis areas (normalized with respect to that for pure $(\text{NH}_4)_2\text{SO}_4$) are plotted as a function of the droplet composition. The concentration ratio $[(\text{NH}_4)_2\text{SO}_4]/\{[(\text{NH}_4)_2\text{SO}_4] + [\text{H}_2\text{SO}_4]\}$, the mole fraction of the H_2SO_4 - $(\text{NH}_4)_2\text{SO}_4$ mixture which is $(\text{NH}_4)_2\text{SO}_4$, was used as a measure of the droplet composition. Note that when this ratio equals zero (pure H_2SO_4), the normalized hysteresis area is zero, while for a value of unity (pure $(\text{NH}_4)_2\text{SO}_4$), the normalized area equals unity, as it must by definition. For intermediate compositions, there is approximately a linear relationship between these variables. Thus, by measuring the hysteresis area of an internally mixed aerosol known to contain H_2SO_4 and $(\text{NH}_4)_2\text{SO}_4$, the relative proportions of the two compounds can be obtained.

II.2.2 Summary and Conclusions for H_2SO_4 - $(\text{NH}_4)_2\text{SO}_4$ Study

The TDMA has been used to measure particle size shifts with humidity changes for internally mixed aerosols containing H_2SO_4 and $(\text{NH}_4)_2\text{SO}_4$ in various proportions. Theory and experiment are in agreement to within 4% for the growth of H_2SO_4 , NH_4HSO_4 , and $(\text{NH}_4)_2\text{SO}_4$ solutions as a function of relative humidity.

H_2SO_4 particle sizes follow the same path upon humidification and dehumidification. Particle sizes for compounds like $(\text{NH}_4)_2\text{SO}_4$, NH_4HSO_4 and other

intermediate mixtures which crystallize at low relative humidities, do not follow the same path upon humidification and dehumidification. For these substances, particle sizes tend to be larger than expected thermodynamically when the droplets are taken from regions of high to low humidities. This "hysteresis effect" occurs because the compounds remain in the liquid phase as supersaturated solutions, rather than crystallizing. It has been shown that this hysteresis area can be used to determine the composition of internally mixed $\text{H}_2\text{SO}_4-(\text{NH}_4)_2\text{SO}_4$ aerosols.

III. REACTION BETWEEN NH_3 (GAS) AND H_2SO_4 (AEROSOL): LABORATORY STUDIES

If H_2SO_4 aerosols are exposed to NH_3 gas, some NH_3 will be incorporated into the particles due to gas-aerosol collisions. While this process in itself will not have a significant effect on particle size, it will cause the composition of the droplets to change. If, after reaction with NH_3 , the droplets are humidified, they will grow to a new size which depends upon the fraction of the H_2SO_4 which was neutralized, as was discussed in the previous section. These differences in growth can be used to determine the extent, and thus, the rate of the reaction between NH_3 (gas) and H_2SO_4 particles.

III.1 Experiments

The experiments reported in this section were performed by Takano during the 1977-78 academic year.

A schematic diagram of the experimental apparatus used in the NH_3 - H_2SO_4 experiments is shown in Figure 17. Polydisperse H_2SO_4 aerosol was generated with a Collison atomizer and passed into DMA1, which selected particles of known size from the polydisperse aerosol. This aerosol was then exposed to NH_3 and some additional water vapor for a known residence time before flowing into DMA2. Molecular concentrations of NH_3 greatly exceeded those of H_2SO_4 , so that NH_3 was not depleted during the reaction. The humidity of the sheath air in DMA2 was varied with a bubbler. After exposure to the humidity in DMA2, the particles rapidly grew to a new size, depending upon NH_3 concentration, the residence time, and initial H_2SO_4 particle diameter. The new particle size was determined and used to estimate the extent of reaction.

The NH_3 was generated by vaporizing NH_4OH solutions of known concentration into the aerosol flow at a known rate. This was accomplished by connecting a syringe pump to the apparatus shown in Figure 18. By passing current through the resistance wire, the entering liquid is vaporized and added to the gas flow at a known and constant rate. Since NH_4OH solutions were used in these

experiments, both NH_3 and H_2O were added to the gas flow. Thus, by judicious choices of concentrations and flow rates, it was possible to set both the initial relative humidity and NH_3 concentrations.

Calibration of this device was checked only for humidity. Results of this calibration are shown in Figure 19. Notice that a known absolute humidity can be produced with uncertainties of ± 0.5 mm Hg for water vapor partial pressures ranging from about 1 to 20 mm Hg. An independent calibration check of this instrument was not done for NH_3 , although this is planned for future work. It is possible that some NH_3 was lost on the walls of the stainless steel generator. If this was the case, then actual concentrations would be lower than reported concentrations.

In all experiments, the $\text{NH}_3\text{-H}_2\text{SO}_4$ reactions took place at room temperature and about 10% relative humidity. Therefore, the important parameters for these experiments are the particle size during reaction, the reaction time, and NH_3 concentrations. A summary of the range of parameters studied in these experiments is given in Table 1. Additional data are presented in Appendix 2.

Selected results of these experiments are shown in Figures 20-26. These aerosols were initially exposed to NH_3 at low relative humidities (about 10%), and then exposed to the humidity shown on the ordinates after entering DMA2. For these data, the residence time between initial exposure of the particles to the NH_3 and entry into DMA2 was 4.0 sec, and the initial size of the H_2SO_4 particles was $0.053 \mu\text{m}$. The dashed lines on each figure represent growth of H_2SO_4 particles which were not exposed to NH_3 . Notice that this series of curves is quite similar to the hysteresis data described in the previous section (Figures 6-10) for solutions of H_2SO_4 and $(\text{NH}_4)_2\text{SO}_4$. It appears reasonable to estimate the degree of neutralization of the H_2SO_4 particles by comparing the area of these loops with the area of the pure $(\text{NH}_4)_2\text{SO}_4$ loops, as was done in Figure 16. This ratio, f , is plotted as a function of

ammonia concentration in Figure 27 for various initial particle diameters and reaction times. The linear relationship between f and $[\text{NH}_3]$ implies that the reaction rate is proportional to ammonia concentration, as expected. Observed reaction rates were about 1/3 the calculated transport rate of NH_3 to the particles. In Figure 28, the ammonia concentration required to achieve $f = 0.6$ is shown as a function of reaction time. The solid line represents the calculated time for 60% neutralization of $0.053 \mu\text{m H}_2\text{SO}_4$ (at 10% RH) particles by the indicated NH_3 concentrations. From these data, it is seen that $[\text{NH}_3]^{1/2}t^{-1}$, i.e., the product $[\text{NH}_3]t$ is approximately constant, as would be expected for a given degree of neutralization. This result implies that the extent of neutralization is approximately proportional to reaction time.

These data, plus additional data, are consolidated in Figures 29-32. Notice that there exists a critical NH_3 concentration above which no particle growth occurs after humidification up through 70% RH. By comparing these figures, it is observed that this critical concentration decreases with decreasing particle size. Data for the critical NH_3 concentration above which no particle growth occurs after humidification up through 70% are summarized in Figure 33 as a function of the initial H_2SO_4 particle diameters. The reaction time for these data was 4.0 sec; a similar complete set of data were not obtained for other reaction times, but this critical $[\text{NH}_3]$ should vary inversely with reaction time as shown above.

Also shown in Figure 33 is the calculated time for complete neutralization assuming transport limited reactions with 100% accommodation for NH_3 -droplet collisions. An appropriate transition regime expression (Bademosi, 1971) was used for these calculations. Note that observed critical NH_3 concentrations were, on the average, a factor of three greater than calculated concentrations for 100% neutralization. The primary uncertainty in our measurements was NH_3 concentrations. Reported concentrations were based on dilution ratio calculations

and not on measurements. It is possible that actual NH_3 concentrations were lower than reported, due to loss to the reactor walls. It is unlikely that actual concentrations were higher than reported, however, since considerable care was taken to insure against NH_3 contamination. It was therefore concluded that the rate for this gas-aerosol reaction is at least equal to one-third of the collision rate. Based on this analysis, Figure 34 shows the maximum time required to completely convert H_2SO_4 droplets of a given size at 50% relative humidity to $(\text{NH}_4)_2\text{SO}_4$.

III.2 Summary of NH_3 - H_2SO_4 Study

The TDMA was successfully used to measure the rate of reaction between NH_3 and H_2SO_4 . Preliminary results indicate that the reaction rate is at least equal to one-third of the collision rate between the NH_3 molecules and the droplets. The uncertainty in this result could be reduced considerably by measurements of NH_3 concentrations.

In principle, a modified version of the TDMA could be used for real time measurements of NH_3 concentrations. By titrating a monodisperse H_2SO_4 aerosol with ambient air containing NH_3 , one could detect the point of transition from growth to no growth upon humidification after known reaction times. Based upon the ratio of ambient to clean air present at this inflection point, and the known critical concentration of NH_3 at the inflection point, one could directly obtain ambient NH_3 concentrations. Preliminary design considerations indicate that this technique should function for NH_3 concentrations in the low ppb range.

IV. DROPLET SIZE VERSUS RELATIVE HUMIDITY: FIELD STUDIES

The TDMA was used to measure particle growth with humidity near a freeway in Minneapolis, and also in the "background" continental aerosol of rural Tennessee. In the freeway study, it was found that the aerosols are sometimes externally mixed. The Tennessee studies, however, showed that the continental aerosol was internally mixed, and that particle growth with humidity was usually independent of particle diameter.

IV.1 Freeway Study

The experiments reported in this section were performed by Kousaka during the summer of 1977.

The TDMA was used to measure particle size changes with humidity shifts for air sampled on Minneapolis freeways. In these experiments, freeway aerosol was collected with a bag sampler system located beside the freeway; this insured a constant aerosol during the course of a measurement. Aerosols in these studies often showed no growth when the relative humidity was increased from ~12% up to 90%. Occasionally the aerosol was observed to be externally mixed, consisting of a mix of hygroscopic and non-hygroscopic particles.

Sample data from this study are shown in Figure 35. At 17:25 on July 12, 1977, the aerosol consisted roughly of equal amounts of hygroscopic and non-hygroscopic particles, while only 15 minutes later, the hygroscopic component was absent. Particle growth curves for these and other data collected on the same day are shown in Figure 36. Note that the hygroscopic aerosol fraction appears to grow like H_2SO_4 .

Aerosol from the tailpipes of two automobiles was studied for comparison with the freeway aerosol. A catalyst-equipped 1976 Dodge Aspen was found to produce non-hygroscopic aerosols, while a 1973 Chevrolet Vega, also catalyst-equipped, sometimes produced hygroscopic aerosols which behaved like H_2SO_4 .

It is not surprising, therefore, that air sampled on a freeway would contain a mix of both types of particles.

In summary, in studies of freeway aerosols as well as in studies of two catalyst-equipped cars, aerosol was usually found to be non-hygroscopic. Hygroscopic aerosol which behaved like H_2SO_4 was occasionally detected in freeway air, and from one of the cars.

IV.2 Tennessee Haze

During the summer months, a haze layer often covers much of the eastern half of the United States. During stagnant conditions, severe visibility degradation has been observed (b_{scat} up to $6 \times 10^{-4} \text{ m}^{-1}$). This visibility degradation is not limited to urban areas, but rather covers rural areas as well. Evidence suggests that the severity of these episodes has increased with rising emissions from coal-fired power plants which are numerous in the area (Husar et al., 1979). Long-range transport with subsequent gas-to-particle conversion of emissions from such plants has been documented, and may explain the widespread distribution of the haze.

Researchers from the Particle Technology Laboratory spent the month of August, 1978, studying plumes from TVA coal-fired power plants as well as this continental haze. Measurements of particle growth-humidity behavior with the TDMA supplemented other aerosol and gas data collected routinely with the University of Minnesota Mobile Laboratory.

IV.2.1 Experiments

The experiments reported in this section were performed by McMurry during August, 1978.

The humidification and dehumidification systems used for these experiments are identical to that shown in Figure 3. Due to the relatively low aerosol number concentrations in ambient air, it was necessary to use a single particle condensation nucleus counter (Agarwal et al., 1977) as a detector after DMA2..

One problem which is encountered in experiments with ambient aerosols is dehumidification to low relative humidities. Due to the high moisture content often present in ambient air, diffusion dryers of a reasonable size are frequently not adequate. This problem was solved by using bottled N_2 for the sheath air. (In future work, bottled air rather than N_2 will be used.) The humidity content of the N_2 was extremely low, so the relative humidity of the sheath air plus sample air mixture could be made as low as several percent.

With one exception, these data were collected between midnight and sunrise. During this period, the winds are typically nearly calm, which eliminates the problem of fluctuating aerosol concentrations during the period of measurement. This is important, since a period of 3-4 hours is typically necessary to measure the growth properties of four particle sizes. Sampling during the day when transport from local sources is often a problem may necessitate collection of a large bag sample for the measurements. Due to particle losses on the bag surface, etc., this technique is undesirable.

IV.2.2 Results and Discussion

Particle growth data for the experiments summarized in Table 2 are shown in Figures 37-39. Notice that particle growth behavior tended to vary slightly from day to day. For the data in Figure 37, observed growth behavior agreed well with the theoretical curve for H_2SO_4 . In Figure 38, fair agreement was obtained when data were compared with the growth data for solutions of H_2SO_4 and $(NH_4)_2SO_4$ mixed in the proportion 1:3. Note that in this case, particle growth behavior was independent of the initial particle size. The data in Figure 39 are strikingly different. In this case, small ($\sim 0.05 \mu m$) particles behaved more like $(NH_4)_2SO_4$, while larger particles grew more like H_2SO_4 .

The difference in growth patterns for small and large particles in the August 8 and 9 data has several possible explanations. This effect may have

been due to preferential neutralization of small particles by ambient NH_3 , as would be expected from transport theory. This apparent difference in particle growth with size may also be an experimental artifact. If NH_3 became dissolved in the humidifier water during the time between experiments, it is possible that it re-entered the gas phase during the experiments, and reacted with the particles. Again, as was shown previously in this report, for a given reaction time, preferential neutralization of small particles would be expected. Due to instrument malfunctions which could not be solved in the field, it was not possible to determine whether this was an experimental artifact or a real effect.

The data of August 5 indicate that particle growth properties were independent of droplet size on that day. This tends to indicate that particle composition was independent of size for the droplet sizes considered. It is also possible to use these data to infer whether or not the aerosols are primarily internally mixed. In Figure 40, curves of number concentration after DMA2 are plotted as a function of voltage on DMA2 (V_2). In this plot, the number concentration was normalized with respect to the maximum number concentration observed during a particular number-voltage scan (N_{max}), and the voltage was normalized with respect to the voltage ($V_{2 \text{ max}}$) at which that concentration was observed. According to Knutson and Whitby (1975), if these aerosols are monodisperse, the data should fall on the theoretical curve given by the solid line. Notice that agreement between the normalized data and theory is very good. From this, we infer that the aerosol entering DMA2 was monodisperse. This is only likely if the aerosol is internally mixed. In externally mixed aerosols, monodisperse particles would grow to a variety of sizes after humidification. In this case, one would expect a much broader experimental peak, or perhaps several peaks, rather than the theoretical curve.

The conclusion that the haze aerosol is internally mixed and hygroscopic contrasts with results of the Minneapolis freeway study, where particles were externally mixed and primarily non-hygroscopic. This is consistent with the character of the two aerosols. Freeway aerosols are fresh from the source, and have not had time to coagulate and grow by gas-to-particle conversion processes which lead towards homogeneity in aerosol composition. The haze, in contrast, is probably largely secondary aerosol, and homogeneity is expected.

IV.3 Summary and Conclusions

The TDMA has been used to measure particle size-humidity relationships for submicron ambient aerosols as small as $0.02\text{ }\mu\text{m}$. These studies were done on freeway aerosols, and aerosols in the continental summer haze in Tennessee. Aerosol growth properties in these two studies were quite different. The haze aerosols were hygroscopic and internally mixed, while freeway aerosols were usually not hygroscopic. In the event that freeway aerosols had a hygroscopic component, they were generally externally mixed. The behavior of freeway aerosols was consistent with the behavior of automobile aerosols. The haze aerosols behaved much like mixtures of H_2SO_4 and $(\text{NH}_4)_2\text{SO}_4$ --likely components of secondary aerosols.

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Table 2. Summary of TDMA data collected in Tennessee haze - August, 1978.

Table 1. Summary of $\text{NH}_3\text{-H}_2\text{SO}_4$ Experiments

Initial H_2SO_4 particle size, μm	Reaction time, s	NH_3 concentrations, ppb
0.053	1.0	0.01, 0.1, 3, 12, 15, 17, 20
0.053	4.0	0.1, 2.0, 3.0, 10, 20, 30, 300
0.053	80.0	0.1, 0.8, 1.0, 5.0
0.074	4.0	0.1, 0.3, 2.0, 10, 80, 300
0.1125	4.0	0.1, 0.3, 2.0, 10
0.175	4.0	0.1
0.198	4.0	0.1, 0.3, 2.0, 10, 50, 60, 80, 100, 300

Table 2. A SUMMARY OF TDMA DATA COLLECTED IN TENNESSEE HAZE - August, 1978

Date	Time	Location	Initial particle diameters before humidification, μm	Supplementary data	Experimental details	Remarks
4-Aug.-78	15:00-17:00	12 miles at 215 from Cumberland city power plant - on well-ventilated hill - near Clarksville, TN	0.081	All UMML data* Filters: X-ray fluorescence (dichotomous) carbon analysis (Lawrence Berkeley Lab) light attenuation (U of M; LBL)	Bottled N_2 not used; lowest RH achieved = 25.8%	We were sampling in an area through which the plume had recently passed.
6-Aug.-78	00:00-08:00	Outlaw Airfield, Clarksville, TN	0.052, 0.076, 0.113, 0.172	All UMML data Filters: X-ray fluorescence (dichotomous) Impactor: low pressure cascade impactor - analyze for sulfur with- flash volatilization for 5 size cuts between 0.05 - 1 μm	N_2 used for DMA2 sheath air; ambient air for DMA1. In retrospect, it would have been better to use N_2 for DMA1 sheath air.	Haze data.
9-Aug.-78	22:00-03:00	Outlaw Airfield, Clarksville, TN	0.052, 0.076, 0.113, 0.172	All UMML data Filters: X-ray fluorescence (dichotomous) Impactor: low pressure impactor	N_2 used as sheath air for DMA1.	A new, fairly clean air mass moved in during the daytime on 8-Aug.-78. Aerosol accumulation modes dropped from about 25 $\mu\text{m}^3/\text{cm}^3$ on noon of the 8th to about 10 $\mu\text{m}^3/\text{cm}^3$ at midnight, when these experiments began.

*The UMML is the University of Minnesota Mobile Laboratory. Measurements of aerosol size distributions (electrical aerosol analyzer and optical particle counters), SO_2 , NO , NO_2 , O_3 , ANC (Aitken nuclei concentration), b_{scat} (the light scattering coefficient), SO_4 , and ambient temperature and relative humidity are recorded simultaneously.

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Figure 35. Aitken nuclei count measured after the second differential mobility analyzer (DMA2) as a function of DMA2 collector rod voltage. At 17:25, the aerosol consisted of roughly equal amounts of hygroscopic and non-hygroscopic aerosol, but at 17:40, the hygroscopic portion was absent.

Figure 36. Particle size achieved when freeway aerosols initially at 10% RH are exposed to the relative humidity shown on the ordinate. Note that two types of particles were present--those which grew like H_2SO_4 and others which did not grow with increased humidity.

Figures 37-39. TDMA data for the growth of Tennessee haze aerosol with humidity.

Figure 40. Number of particles (N) penetrating the second differential mobility analyzer (DMA2) (normalized with respect to the maximum number observed during a voltage scan N_{max}) versus the voltage on the DMA2 collector rod (normalized with respect to the voltage at N_{max}). The solid lines represent the theoretical curve for a monodisperse aerosol entering DMA2. This agreement between data and theory suggests the aerosol was internally mixed.

Figure 1. A schematic diagram of the tandem differential mobility analyzer (TDMA).

(a) Humidification

(b) Dehumidification

Figure 2. Flow systems used when aerosol was humidified or dehumidified before entering the second differential mobility analyzer (DMA2).

(a) Humidification

(b) Dehumidification

Figure 3. Flow systems used when aerosol was humidified or dehumidified inside the second differential mobility analyzer (DMA2).

Figure 4. Electrometer current measured after the second differential mobility analyzer (DMA2) as a function of the collector rod voltage on DMA2 for studies of H_2SO_4 growth with increased humidity. Particles of a fixed initial diameter were exposed to humidities shown in the key. Note that increases in humidity always resulted in particle growth.

Figure 5. Electrometer current measured after the second differential mobility analyzer (DMA2) as a function of the collector rod voltage for studies of $(NH_4)_2SO_4$ growth with increased humidity. Particles of a fixed initial diameter at 8% relative humidity were exposed to humidities shown in the key. Note that particles did not grow until exposed to a relative humidity of 79.5%, the deliquescence point for $(NH_4)_2SO_4$.

Figures 6-10. Plots of particle size changes with humidity changes for internally mixed solutions of H_2SO_4 and $(NH_4)_2SO_4$ in various proportions. The solid curves are drawn through data points obtained by increasing the humidity around the particles from about 8% to the value on the ordinate. The dashed curves are drawn through data points obtained by decreasing the humidity around the particles from about 95% to the value on the ordinate. The symbols in the key describe experimental procedure. For example, INC-2 indicates that particle humidities were increased using the second humidification system (Figure 3), while DEC-1 1/2 flow rate indicates that humidities around particles were decreased using the first dehumidification system (Figure 2), and the aerosol and sheath air flow rates through DMA2 were 1/2 and 5 lpm, respectively, 1/2 their normal values.

Figure 11. Particle diameters achieved when aerosols consisting of mixtures of H_2SO_4 and $(\text{NH}_4)_2\text{SO}_4$, internally mixed in various proportions, are exposed to relative humidities shown on the ordinate. The initial humidity in all cases was about 8%.

Figure 12. Particle diameters achieved when aerosols consisting of mixtures of H_2SO_4 and $(\text{NH}_4)_2\text{SO}_4$, internally mixed in various proportions, are exposed to relative humidities shown on the ordinate. The initial humidity in all cases was about 95%.

Figures 13-15. Comparison between experiment and theory for growth factors (D_p/D_0) of droplets containing H_2SO_4 , NH_4HSO_4 , and $(\text{NH}_4)_2\text{SO}_4$ solutions with humidity. In all cases, the droplets were initially exposed to humidities of about 8%. Humidities were increased to values shown on the abscissa before new droplets were measured. D_0 is the estimated diameter of the droplets at 0% relative humidity.

Figure 16. Relationship between area of the hysteresis loop (normalized with respect to that for pure $(\text{NH}_4)_2\text{SO}_4$) and the mole fraction of $(\text{NH}_4)_2\text{SO}_4$ in solutes consisting of H_2SO_4 and $(\text{NH}_4)_2\text{SO}_4$ mixtures.

Figure 17. Schematic diagram for NH_3 (gas)- H_2SO_4 reaction studies.

Figure 18. Diagram of NH_3 and absolute humidity generator. The syringe was mounted in a syringe pump, which forced NH_4OH solutions into a heated capillary tube. From this tube, the NH_4OH was vaporized at a known and constant rate into the aerosol flow.

Figure 19. Calibration curve for absolute humidity generator shown in Figure 18.

Figures 20-26. Variation of particle size with increased relative humidity for 0.053 μm H_2SO_4 (at 10% RH) particles exposed to various concentrations of NH_3 for 4 sec. The dashed lines represent growth of H_2SO_4 not exposed to NH_3 .

Figure 27. The area enclosed by growth curves for H_2SO_4 exposed to NH_3 and pure H_2SO_4 , normalized with respect to the area enclosed by growth curves for pure $(\text{NH}_4)_2\text{SO}_4$ and pure H_2SO_4 . By referring to Figure 16, the droplet composition, and hence the extent of reaction, can be estimated if this area ratio, f , is known. The linearity of these results supports the hypothesis that the reaction rate is proportional to ammonia concentration.

Figure 28. Ammonia concentration required to produce an area ratio of 0.6, for several reaction times. Note that this concentration varies inversely with time. In other words, the product $[NH_3]t$ is approximately constant for a given extent of reaction.

Figures 29-32. Particle growth factors (D_p/D_0) as a function of NH_3 concentration after a reaction time of 4 sec. The numbers on each curve represent the humidities to which the particles were exposed after reaction. D_0 is the estimated initial H_2SO_4 diameter at 0% RH, and D_i is the actual initial particle diameter at 10% RH.

Figure 33. Comparison between observed and calculated NH_3 concentrations required to completely neutralize H_2SO_4 particles of diameter D_p at 10% RH for a 4 sec. reaction time. The calculated line was obtained by assuming 100% accommodation for NH_3 (gas)-aerosol collisions.

Figure 34. Calculated values for the maximum time required to convert H_2SO_4 particles of indicated diameter to $(\text{NH}_4)_2\text{SO}_4$ for various NH_3 concentrations. Based on experimental data, a reaction rate equal to $1/3$ the collision rate was assumed. The H_2SO_4 was initially in equilibrium at 50% RH.

Figure 35. Aitken nuclei count measured after the second differential mobility analyzer (DMA2) as a function of DMA2 collector rod voltage. At 17:25, the aerosol consisted of roughly equal amounts of hygroscopic and non-hygroscopic aerosol, but at 17:40, the hygroscopic portion was absent.

Figure 36. Particle size achieved when freeway aerosols initially at 10% RH are exposed to the relative humidity shown on the ordinate. Note that two types of particles were present--those which grew like H_2SO_4 and others which did not grow with increased humidity.

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APPENDIX 1

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THE AEROSOL MOBILITY CHROMATOGRAPH:
A NEW DETECTOR FOR SULFURIC ACID AEROSOLS

B.Y.H. Liu, D.Y.H. Pui, K.T. Whitby and D.B. Kittelson
Particle Technology Laboratory
Mechanical Engineering Department
University of Minnesota
Minneapolis, Minnesota 55455

Y. Kousaka
University of Osaka Prefecture
Mozu, Umemachi, Sakai
Osaka, Japan

and

R.L. McKenzie
National Bureau of Standards
Washington, D.C. 20234

ABSTRACT

A new instrument has been developed at the University of Minnesota for measuring sulfuric acid aerosols. The instrument is called an Aerosol Mobility Chromatograph since it is based on the electrical mobility of aerosol particles and operates in a way similar to that of the conventional liquid or gas chromatograph. The particle diameter range of the instrument is from 0.005 to 0.2 μm . The instrument sensitivity for measuring monodisperse sulfuric acid aerosols is estimated to be 500 particles/ cm^3 at a particle size of 0.02 μm , when an electrometer current sensor is used as the particle detector. The corresponding mass sensitivity is 0.01 $\mu\text{g}/\text{m}^3$. When an expansion-type condensation nuclei counter is used as the particle detector, the number and mass sensitivities are improved and become respectively 50 particles/ cm^3 and 0.001 $\mu\text{g}/\text{m}^3$. With the use of a recently developed continuous flow condensation nuclei counter, the instrument sensitivities are further improved and become 0.5 particles/ cm^3 and 10^{-5} $\mu\text{g}/\text{m}^3$. Experiments are described: (1) demonstrating the operating principle of the Aerosol Mobility Chromatograph, (2) verifying the theoretical growth factor for sulfuric acid particles and (3) showing the feasibility of measuring low level sulfuric acid particles in a background of other types of particles.

INTRODUCTION

There has been considerable interest in recent years in the study of sulfur-containing particles in the atmosphere and many techniques have been developed for their measurement. Among the more widely used techniques are those for the measurement of sulfate using wet chemical analysis (Brosset and Fern, 1976; Appel et al., 1977). The sulfur content of particles can also be determined by X-ray fluorescence (Dzubay and Stevens, 1975; Dzubay, 1977). Recently, several techniques based on the use of the flame-photometric detector (FPD) have also been developed. The FTD, used primarily for gas measurements on SO_2 and H_2S , has been adapted for particulate sulfur measurement by several different schemes. In one scheme (Roberts and Friedlander, 1976; Husar et al., 1975; Tanner et al., 1977), the particles are collected, and then flash-volatilized and measured by the FPD. In a second scheme (Huntzicker et al., 1977), the SO_2 and H_2S gases are chemically scrubbed, leaving the sulfur-containing particles to enter the FPD and be detected. In a third scheme (Kittelson et al., 1977), the gaseous sulfur are not scrubbed, but the aerosol particles are electrostatically chopped. The resulting AC signal from the FPD is then measured with a lock-in amplifier. Other techniques that have been used include radioactive tracer (Forrest and Newman, 1977), micro-Raman spectroscopy (Etz et al., 1977), laser-Raman spectroscopy (Stafford et al., 1976), in-beam gamma-ray spectroscopy (Macias, 1976) and ion chromatography (Mulick, 1976). Table 1 summarizes the principal techniques used and their pertinent characteristics.

It is clear that while many techniques have been developed for particulate sulfur measurement, only a few can provide chemical speciation capabilities. Chemical speciation is important because of the different health effects of different sulfur compounds. Among the sulfur compounds of interest in health-effect studies, sulfuric acid is probably one of the most important because of its known irritant potential and effect on the respirable airways. In this paper, a new technique for the direct determination of sulfuric acid aerosols is described.

The instrument described in this paper for measuring sulfuric acid aerosols is termed an Aerosol Mobility Chromatograph (AMC), since it is based on the electrical mobility of aerosol particles and operates in a way similar to that of the conventional liquid or gas chromatograph. The

instrument is capable of measuring sulfuric acid particles in-situ, allowing both the concentration and size distribution of the particles to be determined. The sensitivity of the device for detecting monodisperse sulfuric acid aerosols is estimated to be $0.01 \mu\text{g}/\text{m}^3$ of sulfuric acid when an electrometer current sensor is used as the particle detector. With the use of a condensation nuclei counter, the instrument sensitivity is further improved and becomes $0.001 \mu\text{g}/\text{m}^3$. This paper described the operating principle of the AMC and the performance characteristics of a prototype instrument developed at the Particle Technology Laboratory, University of Minnesota.

OPERATING PRINCIPLE AND BASIC FEASIBILITY

The Aerosol Mobility Chromatograph operates by growing sulfuric acid particles in a humid environment and measuring the particle growth with a differential mobility analyzer. The growth of sulfuric acid and other hygroscopic particles in humid atmospheres is well-known and has been studied extensively by the use of the nephelometer (Covert, 1974; Charlson et al., 1974). However, in this paper, a precise particle size measuring device is used to more fully utilize the principle of particle identification by means of its hygroscopic properties.

To demonstrate the basic operating principle and feasibility, the system shown in Figure 1 has been developed. The purpose of the system is to show that H_2SO_4 particles in an aerosol containing a mixture of particles can indeed be separated from other non-hygroscopic, or less hygroscopic particles and be identified by the AMC principle. In the particular experiments performed, particles of H_2SO_4 and K_2SO_4 were generated by atomization with the use of two syringe-pump atomizers shown. The syringe-pump atomizer (Liu and Lee, 1976) was chosen because of its stability, i.e., its ability to generate a stable aerosol with a constant concentration and particle size distribution. Following atomization, the solution droplets were mixed and allowed to enter a diffusion dryer where the relative humidity was lowered to about 8%. The mixed aerosol was then passed through a Krypton-85 neutralizer (see Liu and Pui, 1974a for a description of the operating principle of the Krypton-85 neutralizer) to obtain a Boltzmann equilibrium charge on the particles, and then introduced into the first of

two differential mobility analyzers (DMA). In the first DMA, particles of H_2SO_4 and K_2SO_4 within a narrow size range were extracted according to their electrical mobility. This monodisperse aerosol was then humidified to about 53% relative humidity by means of a packed tower humidifier. The 53% humidity was sufficiently high to cause a significant growth in size for the H_2SO_4 particles, but not sufficiently high to cause the K_2SO_4 to deliquesce and grow. The size distributions of the H_2SO_4 and K_2SO_4 particles in this new humid environment was then measured with the second DMA, which functions as a particle mobility, and size, analyzer. The DMA used in these experiments were developed at the University of Minnesota and had been used for a variety of purposes including particle size classification, and monodisperse aerosol generation (Liu and Pui, 1974b; Liu et al., 1974; Liu and Kim, 1976; Liu et al., 1975). The operating principle of the device has been analyzed in detail by Knutson and Whitby (1975a and 1975b).

A variety of detectors can be used with the above described system to detect particles emerging from the second DMA. In the system shown in Figure 1, an electrometer current sensor is used which detects the singly charged particles emerging from the device by collecting the particles on an insulated filter and measuring the rate of charge collection by a sensitive electrometer. In Figure 2, the output of the electrometer current sensor is shown as a function of the applied voltage on the collector rod in the second DMA, the voltage on the collector rod in the first DMA being kept fixed in these experiments. Two curves are shown. The solid curve corresponds to the case where there is no humidification between the two DMA's. The peak in the curve indicates the monodispersity of the particles being produced by the first DMA and that of the particles being measured by the second DMA. However, if prior to entering the second DMA, the aerosol is first humidified as described above, the dotted curve shown in Figure 2 is obtained. The two peaks in the curve correspond to the two different sized particles present under the new humidity conditions. The peaks are quite distinct, indicating that the particles are now different in size. It should be further noted that, if the collector rod voltage is set to, say, the value corresponding to the second peak -- approximately 550 volts in the case shown -- the aerosol emerging from the second DMA would consist of H_2SO_4 particles only. The K_2SO_4 particles, being smaller in

size, would be rejected by the second DMA. By this means, the hygroscopic H_2SO_4 particles can be physically separated from other non-hygroscopic or less hygroscopic particles in an aerosol mixture. This particular property of the device is analogous to that of the conventional liquid or gas chromatograph in which physical separation of the molecular species also takes place on account of their different migration velocities through the chromatographic column. In the present case, the DMA functions as a chromatographic column with the different sized particle being separated according to mobility.

PARTICLE SIZE RANGE AND SENSITIVITY

The particle size range of the AMC is estimated to be from 0.005 to 0.2 μm diameter. The upper size limit is determined by the fact that in order for the first DMA to extract a monodisperse aerosol from a polydisperse aerosol according to electrical mobility, the particles must be singly charged. For particles in Boltzmann equilibrium (Liu and Pui, 1974c), multiple charging does not become a significant factor until the particle diameter approaches 0.1 μm . While the instrument will continue to function with appropriate corrections for multiple charging effects for particles up to 0.2 μm diameter, the effect of multiple charging on larger particles will become too large to be satisfactorily corrected. On the other hand, the lower size limit of the instrument is determined by the fact that for small particles, the fraction of particles that are electrically charged is small. Thus, the instrument sensitivity will rapidly diminish as the particle size is reduced. It is estimated that with the particle detectors now available, particles as small as 0.005 μm can be satisfactorily detected by the instrument with reasonable sensitivity.

The sensitivity of the instrument for detecting sulfuric acid particles is determined by the specific particle detector used. For the electrometer current sensor shown in Figure 1, the current, $I(\text{A})$, indicated by the sensor is related to the particle concentration, $N (\text{cm}^{-3})$ as follows,

$$I = q e N f \quad (1)$$

where $q (\text{cm}^3/\text{sec})$ is the aerosol flow rate entering the electrometer current sensor, f is the fraction of particles carrying either +1 or -1 unit of charge

and e (1.602×10^{-19} Coulomb) is the elementary unit of charge. For an aerosol flow rate of $q = 50 \text{ cm}^3/\text{sec}$, which is the standard flow rate used in the above described experiments, and a minimum measurable electrometer current of 0.001 pA , which is typical of the electrometer used in these experiments, the minimum measurable particle concentration is

$$N = 1.25 \times 10^2 / f \quad (2)$$

For particles in Boltzmann charge equilibrium and for sufficiently small particle sizes, the particles will be either electrically neutral or carry ± 1 elementary unit of charge. In which case,

$$f = N_1 / (2N_1 + N_0) \quad (3)$$

and

$$N_1/N_0 = \exp (-e^2/D_p kT) \quad (4)$$

where N_1 is the concentration of the singly charged particles of one polarity and N_0 , the concentration of the neutral particles, the aerosol being assumed to be monodisperse. In Eq.(4), D_p (cm) is the particle diameter, k is the Boltzmann's constant, and T is the absolute temperature.

Figure 3 shows the theoretical sensitivities calculated by means of the above equations. For the mass sensitivity, the calculations were made for unit density particles. However, the actual density of sulfuric acid will depend on the ambient humidity. For instance, for an ambient humidity of 50%, the density of sulfuric acid is 1.325 g/cm^3 and the droplet will contain 42.5% of sulfuric acid by weight. In which case, the sensitivity values shown in Figure 3 should be multiplied by $(1.325)(0.425) = 0.563$ to obtain the instrument mass sensitivity for sulfuric acid. It is interesting to note that the minimum number sensitivity of the instrument is about $500 \text{ particles/cm}^3$, whereas the minimum mass sensitivity is about $0.01 \text{ } \mu\text{g/cm}^3$ for monodisperse aerosols at a particle size of $0.02 \text{ } \mu\text{m}$.

In addition to the electrometer current sensor, other particle detectors can also be used. Using the CNC-2 Condensation Nuclei Counter manufactured by the General Electric Co., and assuming a minimum detectable particle concentration of 10 cm^{-3} for the CNC-2, the detection limit of the AMC for sulfuric acid particles is,

$$N = 10 / f, \text{ cm}^{-3} \quad (5)$$

In Figure 3 the calculated number and mass sensitivities of the AMC for the case of the General Electric CNC-2 are also shown. The minimum detectable mass concentration is seen to be about $0.001 \mu\text{g}/\text{m}^3$ for this case. Recently, a continuous flow, single-particle counting, condensation nuclei counter has been developed (Agarwal, Sem and Pourprix, 1977). This device, which is based on the earlier work on the continuous flow CNC of Bricard et al. (1976), is capable of measuring aerosol concentrations to a level of $0.01 \text{ particles}/\text{cm}^3$. With this device, the theoretical detection limit of the AMC for sulfuric acid aerosols of $0.02 \mu\text{m}$ diameter is about $10^{-5} \mu\text{g}/\text{cm}^3$. A prototype version of this single-particle counting, continuous flow, CNC was used in some preliminary experiments described later to demonstrate the feasibility of this approach.

EXPERIMENTAL VERIFICATION OF THE PARTICLE SIZE GROWTH FACTOR FOR SULFURIC ACID AEROSOLS

The ability of the AMC to identify sulfuric acid particles is based on the known response characteristic of sulfuric acid to ambient humidity. The growth in size of sulfuric acid particles with increasing humidity was studied in a series of experiments using the same apparatus shown in Figure 1. In these experiments, only sulfuric acid aerosol was generated and the atomizer for K_2SO_4 particles was turned off. By varying the humidity of the aerosol entering the second DMA, the change in particle size of sulfuric acid as a function of humidity could be measured. In Figure 4 the experimental results are compared with the theoretically calculated values using the equilibrium vapor pressure data for sulfuric acid given in the Chemical Engineers' Handbook (Perry and Chilton, 1973) and taking into account the Kelvin's effect. It should be noted that for the size range covered in these experiments, the Kelvin's effect was quite small for the curve on the left in Figure 4, while for the curve on the right, the Kelvin's effect is entirely negligible. It is seen that the agreement between theory and experiment is good. These results show that: (1) the change in particle size of sulfuric acid particles as a function of relative humidity can be accurately predicted from theory and (2) the experimental apparatus is functioning properly.

DETECTION OF LOW LEVEL SULFURIC ACID AEROSOLS BY THE AEROSOL MOBILITY CHROMATOGRAPH

So far we have not succeeded in detecting the presence of free sulfuric acid aerosols in the ambient atmosphere in Minneapolis. However, in a sequence of experiments performed over a period of one week, ambient aerosols were sampled into a plastic bag and a small quantity of sulfuric acid aerosol was injected into the bag. The presence of this artificially generated sulfuric acid aerosol in the natural, ambient aerosol background was detected by the AMC in a few cases. These experiments are described below.

For these experiments, the single-particle counting, continuous flow condensation nuclei counter was used as the particle detector. The ambient aerosol was sampled into a 0.2 m³ plastic bag. Then a small amount of sulfuric acid aerosol was generated by the syringe pump atomizer and injected into the bag. The mixed aerosol was then sampled by the AMC and measured. For the experiments that resulted in the detection of this injected H₂SO₄ aerosol, the results shown in Figure 5 are typical. It is seen that appearance of the H₂SO₄ peak is quite distinct and that the experimentally determined particle size growth factor of 1.38 agrees well with the theoretically calculated factor of 1.40. It should be mentioned that in a few experiments, the injection of H₂SO₄ aerosol into the bag did not result in the appearance of a new peak. It was postulated that for these experiments, there was sufficient ammonia present in the ambient atmosphere to neutralize the small amount of H₂SO₄ particles injected. However, further experiments are needed in order to confirm this hypothesis.

CONCLUSION AND FUTURE WORK

The Aerosol Mobility Chromatograph described in this paper has been developed as a means for measuring sulfuric acid aerosols on the basis of particle size change with relative humidity. We have demonstrated the basic feasibility of the concept, and verified the theoretical size growth factor for sulfuric acid particles. We have also shown that low level sulfuric acid aerosols can be identified by the AMC in the presence of other particles normally found in the ambient atmosphere. The prototype

instrument described in this paper is useful primarily for studying sulfuric acid aerosols in the laboratory. For actual ambient measurements, further improvement is needed. In addition, possible interference effects from other types of particles with varying degree of hygroscopicity must be worked out in detail. Some of these problems will be addressed in forthcoming communications.

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Figure 1. System demonstrating the principle of the Aerosol Mobility Chromatograph.

Figure 2. Output voltage-current curve for the Aerosol Mobility Chromatograph showing the separation of H_2SO_4 and K_2SO_4 particles.

Figure 3. Sensitivity of the Aerosol Mobility Chromatograph for monodisperse, H_2SO_4 aerosols using an electrometer current sensor or a condensation nuclei counter as the particle detector.

Figure 4. Size of H_2SO_4 particles as a function of relative humidity -- comparison of theory and experiments.

Figure 5. Output of the Aerosol Mobility Chromatograph showing the detection of H₂SO₄ in the presence of background particles.

Table 1. Principal Techniques for Particulate Sulfur Measurement.

<u>Technique</u>	<u>Element or Compound Measured</u>	<u>Working Range* or Detection Limit**</u>	<u>References</u>	<u>Comment</u>
1. Wet Chemical Analysis	$\text{SO}_4^{=}$		Appel et al. (1977)	
a. Methylthymol Blue		6-60 $\mu\text{g/ml}$ extract*	Brosset & Fern (1976)	
b. Barium Chloranilate		13-50 $\mu\text{g/ml}$ extract*		
c. Modified Brosset		3-13 $\mu\text{g/ml}$ extract*		
d. Brosset		0.2 $\mu\text{g SO}_4^{=} / \text{ml}^{**}$		
2. X-ray Fluorescence	S	10^1 - 10^3 ng/cm^2 or 10^1 - 10^3 ng/m^3 **	Dzubay & Stevens (1975) Jaklevic & Walter (1977)	
3. Flame-photometric Detector				
a. Flash Volatilization	S	0.06 $\mu\text{g/ml}$ extract**	Husar et al. (1975) Roberts & Friedlander (1976)	
b. Gas Scrubbing	H_2SO_4 & HSO_4^-	1 $\mu\text{g/m}^3$ **	Tanner et al. (1977)	
with Thermal Speciation	$\text{SO}_4^{=}$, H_2SO_4	1 $\mu\text{g/m}^3$ for H_2SO_4 **	Huntzicker et al. (1977)	
c. Electrostatic Aerosol				Meloy SA285 Detector with 1 ppb min. det. level
Chopping	S	0.3 $\mu\text{g/m}^3$ **	Kittelson et al. (1977)	
with Thermal Speciation	$\text{SO}_4^{=}$, H_2SO_4		McKenzie et al. (1976)	
4. Radioactive Tracer	Soluble Sulfate	1 $\mu\text{g S/6 in}^2$ filter**	Forrest & Newman (1977)	Sulfite is an interference
5. Micro-Raman Spectroscopy	HSO_4^- , $\text{SO}_4^{=}$, $\text{SO}_3^{=}$		Etz et al. (1977)	Lower Particle Size Limit: $\sim 1 \mu\text{m}$
6. Laser-Raman	$\text{SO}_4^{=}$	10 ppb**	Stafford (1976)	
7. Gamma-ray Spectroscopy			Macias (1976)	
8. Ion Chromatography	$\text{SO}_4^{=}$	0.3 $\mu\text{g/ml}$ extract**	Mulick (1976)	

APPENDIX 2

Additional data from the experiments on
the reaction between NH_3 gas and H_2SO_4 aerosols,
performed by Takano during the 1977-78 academic year.

These data supplement results which are shown in Figures 20-26. The experimental procedure for these experiments was discussed in Section III.1. Key experimental parameters shown on each graph include:

- c - the ammonia concentration, ppb
- D_i - the droplet size during reaction (at about 10% R.H.), μm
- t_r - time the H_2SO_4 particles were exposed to NH_3 before
entering DMA2