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Journal

AIHA Journal, 41(5)

ISSN

1542-8117

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Publication Date

1980-05-01

DOI

10.1080/15298668091424861

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Peer reviewed

Since sulfate aerosol particles are an environmental factor of possible concern, laboratory studies are being conducted to determine their health effects. It is important in such studies that aerosols be controlled and monitored. Submicron sulfate aerosols at high (greater than 80%) and low (30-40%) relative humidities were generated and characterized in support of animal inhalation experiments. Aqueous solutions of ammonium sulfate and ferric sulfate were aerosolized with a compressed air nebulizer, dried, discharged and passed into an aerosol chamber. Aerosol characterization was performed using cascade impactors, electron microscopy, filter samples and an electrical mobility analyzer. Parameters measured included particle size distribution and mass concentration. Instruments used for sizing the aerosols were compared. The electrical mobility analyzer provided useful information on the time stability of the particle size and the mass concentration, but agreement between this instrument and electron microscopy or cascade impaction was poor.

Laboratory production of ammonium and ferric sulfate aerosols

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introduction

Particulate sulfate in the respirable size range can be expected to be present in the atmosphere in increasing amounts as the consumption of high-sulfur-content fuels increases. This fact, plus the realization that airborne sulfate levels are already a major factor in urban air pollution, serves as an impetus for inhalation toxicity studies on sulfate particulates.⁽¹⁾ Meaningful laboratory toxicity studies require realistic, well-characterized aerosols at various relative humidities. The behavior of certain sulfate salts as a function of ambient relative humidity adds to the complexities of aerosol generation and characterization in the laboratory.

This work concentrated on the generation and control of sub-micron diameter aerosol particles of ammonium and ferric sulfate in chambers at high and low relative humidities, and on the measurement of those aerosol properties believed to be most closely related to effects on health. Moderately large scale production of aerosol was required in order to obtain the maximum mass concentration consistent with the avoidance of significant coagulation.

The aerosols were to have mass median aerodynamic diameters between 0.1 and 1 micrometer in order to insure deposition in the lung and to mimic the air-pollutant sulfate aerosol. The size distribution was to be relatively narrow. For a log-normally distributed aerosol, a geometric standard deviation of less than about 2 would be desired for proper deposition in the lung. For example, a log-normally distributed aerosol with a count median diameter of 0.5 micrometer, a geometric standard deviation of 2 and a material density of 2 grams/cm³, would have a mass median diameter of 2 micrometers; that is, half of the mass would be contained in particles greater than two micrometers in diameter. Aerosols larger than a few microns in diameter could have preferential, and undesirable, upper respiratory

deposition. Particle shape was to be globular and single particles rather than fiber-like or agglomerated. The above criteria were to be satisfied for animal exposures in chambers operated at high (greater than 80%) and low (30 to 40%) relative humidities. Further, where possible, multiple methods were to be used for aerosol characterization and intra-instrument agreement obtained when using instruments with different principles of operation. For example, one should be able to reconcile a size distribution found via electron microscopy with one determined with a multi-stage impactor.

General descriptions of the laboratory generation and characterization of aerosols have been published.⁽²⁻⁴⁾ Generation and characterization of ammonium sulfate and ammonium bisulfate aerosols have been more specifically described.^(5,6) Our work is comparable to the first study⁽⁵⁾ but differs in that electron microscopy was used by us and our work included ferric sulfate. The second study⁽⁶⁾ used generation methods that involved thermal decomposition of ammonium sulfate; a different technique than used by us. These investigators performed electron microscopic observations and electrical aerosol analyzer measurements but did not directly compare the size distributions obtained by these two methods.

experimental work

generation of aerosols

The generation of relatively small sulfate aerosol particles in large quantities continuously for several hours was achieved by nebulizing aqueous solutions with a compressed-air atomizer. The nebulizer, a three-jet collision type, (Model 7330, Sierra Instrument Inc., St. Paul, Minnesota) has been described.⁽⁷⁾ By varying the concentration of a salt in the nebulizer, the size distribution, number and mass concentration of the dried atomized aerosol particles could

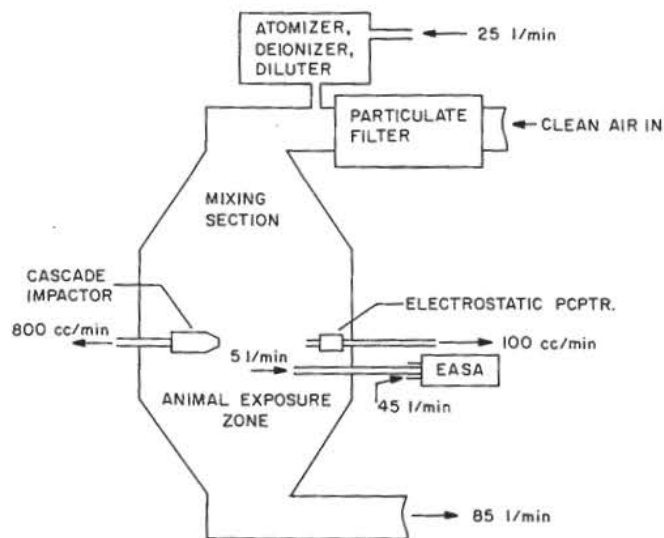


Figure 1 - Aerosol generation and animal exposure system. EASA is the electrical aerosol size analyzer.

be controlled.⁽⁸⁾ The commercial fluid atomization aerosol generator used utilizes follow-up inertial impaction and produces particles at concentrations up to 10^9 per cc. of output air. The device also contains a drying section and a radioactive charge neutralizer. Clean compressed air was passed through the atomizer at a flow rate of approximately 9 liters/min. Before being brought to charge equilibrium by passage through the 2 mCi⁸⁵Kr ion source, aerosols were diluted with up to 35 liters/min of filtered dry air to facilitate drying of droplets and reduce the rate of agglomeration of particles. The solution in the atomizer was kept at a constant level by slow infusion of fresh solution from a syringe mounted on a syringe pump. Dry aerosols were blown into a clean, 1 m³ volume, stainless steel chamber with a hexagonal cross section fabricated after the original University of Rochester design.⁽⁹⁾ The number and mass concentration of dried sulfate particles were controlled by adjustment of a second dilution with clean chamber throughput air.

Humidity and temperature control of air entering the aerosol chamber was accomplished by an automatic air conditioning unit (Bemco Inc., Pacoima, California). The unit has a refrigerant drier and steam injection system for humidity control with an air handling capacity of 2.8 m³/min. Refrigerant coils remove all moisture down to 2°C wet bulb temperature, while the adjustable injection system for humidity controls the relative humidity at room temperature to any value between about 30 and 90%. Temperature control is achieved through the use of high- and low-range heaters which bring the air temperature back up to the desired 22°-24°C for animal experiments.

characterization of aerosols

In the diameter size range of interest (0.1 to 1.0 micrometers), particle motion is significantly influenced by both Brownian bombardment by air molecules and by the particles' inertial properties. Size characterization therefore should include estimates of both the geometrical size and aerodynamic diameter since these two parameters will

determine the motion in an exposure chamber and deposition in the respiratory tract. Sizing methods used included electron microscopy for geometrical size, cascade impaction for aerodynamic size and electrical mobility analysis. Figure 1 shows the relationship of aerosol generation, characterization and animal exposure systems. For microscopy, ferric and ammonium sulfate particles were collected on carbon-coated electron microscope grids using an electrostatic precipitator operated at 100 cc/min⁽¹⁰⁾ (Aries Inc., Davis, California). Since the ammonium sulfate aerosols were unstable under the electron beam, electron microscope photographs were taken under low beam intensity to minimize particle decomposition. Photographs were made such that particles in the 0.01 micrometer size range could be seen. Magnifications of 28 to 36 thousand were obtained on prints from micrographs made with a Zeiss Model 9-S2 electron microscope. An internal magnification standard was derived from electron micrographs of carbon-coated formvar replicas of a diffraction grating (Ladd, Burlington, Virginia). The size distribution values, count median diameter and geometric standard deviation were determined by analysis of photographs (Figures 2 and 3) using a Zeiss TGZ-3 particle size analyzer. Median projected area diameter, mass median diameter, and geometric standard deviation of aerosols from 10% (w/v) ferric and ammonium sulfate solutions are shown in Table I. The cumulative size distribution of salt aerosols as plotted on log-probability paper (Figure 4) indicates that the data were essentially log-normally distributed.

A theoretical estimate of the size distribution of dried aerosol was made as follows. According to the manufacturer, the nebulizer-droplet size distribution, after the impaction stage, had a volume median diameter of 0.60 micrometers and a geometric standard deviation of about 1.65. These values were verified by nebulizing a test aerosol from an 8% sodium fluorescein solution and performing a particle-size analysis of the dried aerosol by electron microscopy. This calculated droplet size distribution for our nebulizer allowed us to project the expected size distributions of sulfate salts nebulized from aqueous solutions.

An instrument for estimating the mobility distribution of aerosols in an electrical field has recently become available⁽¹¹⁾ (Electrical Aerosol Size Analyzer (EASA) Model 3030 Thermo Systems, St. Paul, Minnesota). Since the electrical mobility is related to geometrical diameter and since the instrument obtains a sample rapidly and provides a near real-time output of data, this instrument was included in the sampling scheme. The instrument has a diffusion-charging section followed by a collector section that is increased stepwise in voltage to collect successively more of the charged aerosol. Beyond this collector is a filter that is grounded through a sensitive electrometer. Currents through the electrometer provide the basic output and the differences between currents obtained from adjacent collector voltages are used to determine the number of particles in each size interval. Though the instrument is typically operated using 10 size intervals all below 1.0

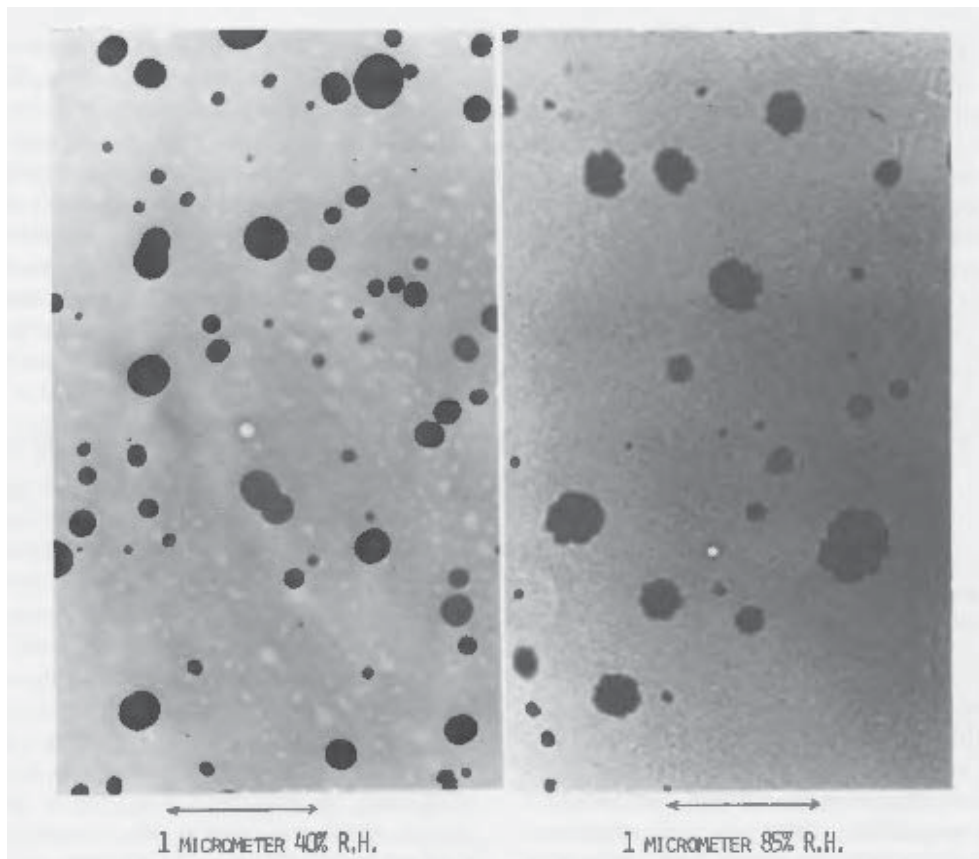


Figure 2 – Electron micrographs of ammonium sulfate aerosol sampled from Rochester style chamber. Aerosol was prepared by drying a nebulized solution (10% weight/volume) of the salt.

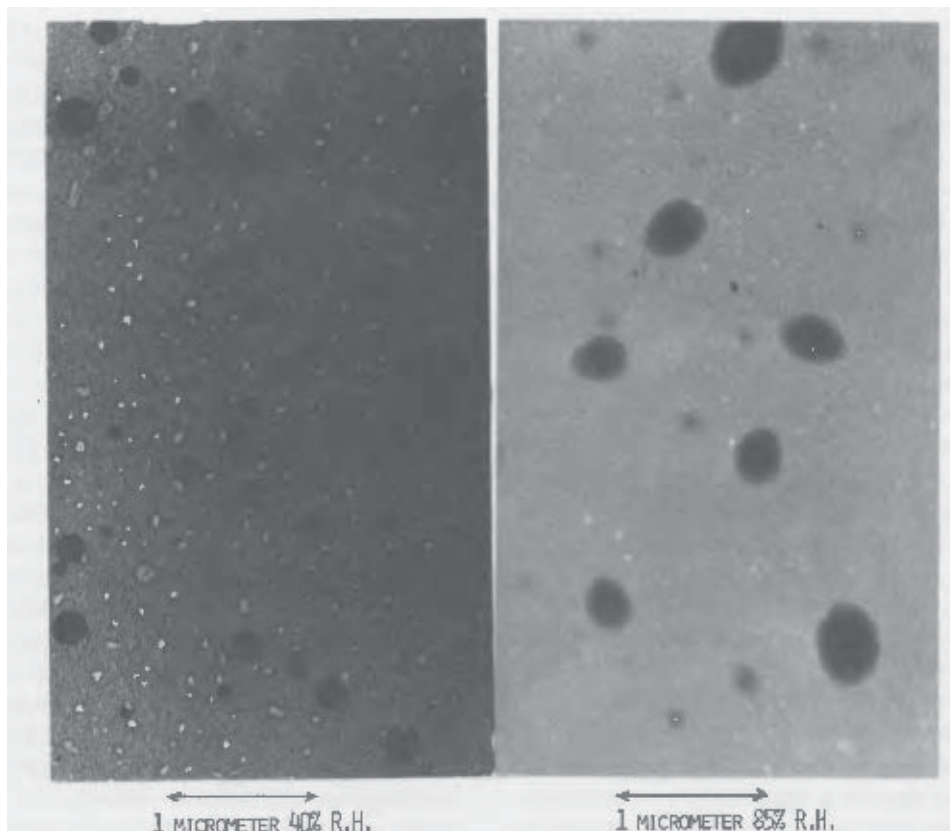


Figure 3 – Electron micrograph of ferric sulfate aerosol sampled from Rochester style chamber. Aerosol was prepared by drying a nebulized solution (10% weight/volume) of the salt.

TABLE I
Size Distribution, Count Median Diameter and Geometric Standard Deviation Determined by Analysis of Electron Microscopic Photographs Using a Zeiss TGZ-3 Particle Size Analyzer (40% R.H.)

Aerosol	Density gm/cm ³	Number of Particles Counted	Count Median Diameter Microns	Mass Median Diameter Microns	Expected Mass Median Diameter Microns	Aerodynamic Diameter Microns	Geometric Standard Deviation
Ferric Sulfate	2.1	409	.11	.22	.23	.32	1.67
Ammonium Sulfate	1.8	306	.11	.27	.25	.36	1.73

micrometer, internal losses of particles are size-dependent and must be dealt with by a set of correction factors.⁽¹²⁾ These correction factors can be quite large and it is not clear that they are independent of particle composition, relative humidity and other factors.⁽¹³⁻¹⁵⁾ If particle losses within the instrument are not variable with time, the data can be used to estimate both the size distribution and the airborne mass concentration.

Surface area, volume and mass distributions of the salt can also be estimated for smooth spherical aerosol particles by calculation. If the density of particles is known, the mass concentration can also be calculated. The correlation between mass concentration obtained from the EASA and filter weighing method (assuming chemical handbook values for particle densities) is shown in Figure 5. Though the absolute values for mass concentration differ considerably using the two methods, the EASA has been very useful for monitoring the stability of an aerosol during an exposure. Electric current readings from the instrument are very sensitive to the number of particles in the chamber and any change in the mass concentration can quickly be

detected. Also the calibration curve (Figure 5) can be used to convert EASA data into actual mass concentration, assuming the filter method yields correct values.

It was noticed that the voltage of the EASA charging screen increases by as much as 50% as the humidity increases from 40% to 80%. Also as humidity increases, higher current readings in each channel are obtained for the same concentration of salt aerosol. This effect may be caused by the reduced ion mobility resulting from the attachment of water molecules to the positive ions, so caution must be applied when the instrument is used in a situation where humidity is not constant. Dilution air drawn into the EASA was matched in humidity and temperature to the air in which particles were generated.

Figure 4 shows the size distribution of ferric sulfate and ammonium sulfate at low relative humidity according to EASA data. The count median diameters of the salts are quite different than those found by electron microscopy. This discrepancy has been reported and discussed previously.⁽¹³⁾

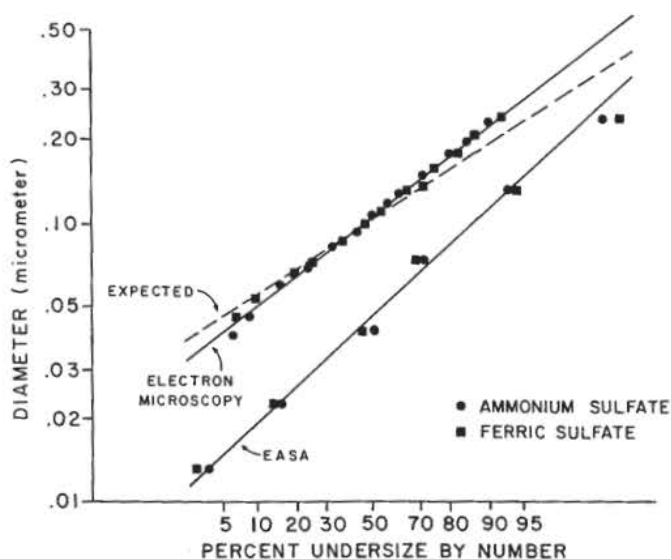


Figure 4 - Cumulative size distribution of ammonium sulfate and ferric sulfate generated from 10% weight/volume solution at 40% R.H. EASA count median diameter averages between .04 micrometer and .05 micrometer diameter. The expected distribution, shown by the dashed line, was determined from the known solution concentration and known droplet size distribution of the nebulizer.

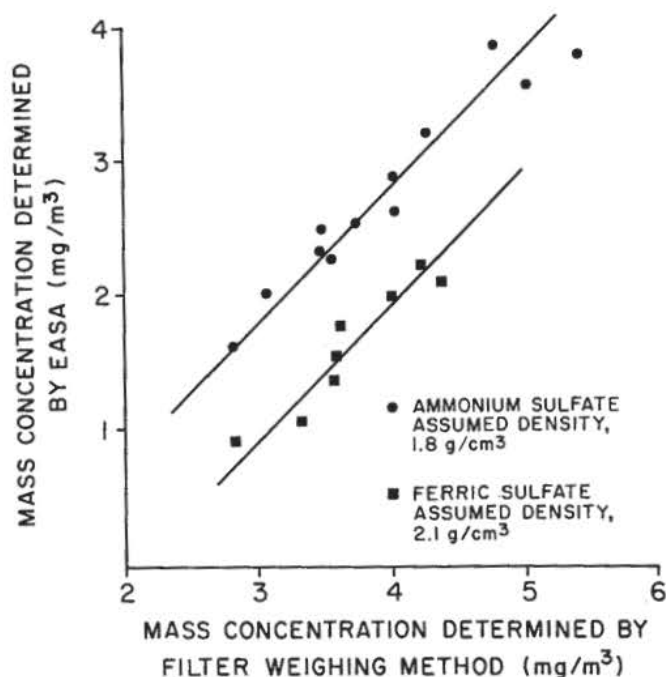


Figure 5 - The correlation between mass concentration obtained from the EASA and filter weighing method at low relative humidity (40% R.H.).

TABLE II
Size Distribution of Ammonium Sulfate and Ferric Sulfate Determined by Electron Microscopy and Seven Stage Impactors at 85% R.H.
 (all sizes are in microns)

	Ammonium Sulfate		Ferric Sulfate
	Expected	Impactor	Impactor
Count			
Median Diameter	.17	—	—
Mass Median Aerodynamic Diameter	.48	.50	.52
Geometric Standard Deviation	1.65	2.1	2.0

At high relative humidity, ammonium sulfate and ferric sulfate grow in size. According to Tang's⁽¹⁶⁾ calculation, the ammonium sulfate will grow by a factor of 1.5 at 85% R.H. To ensure accurate determination of the aerodynamic size distribution at high relative humidity, a seven-stage cascade impactor after the design of Mercer *et al.*⁽¹⁷⁾ (Aries, Inc., Davis, California) was used. This equipment can measure the aerodynamic size distribution of aerosol particles which range from 0.3 to several micrometers in aerodynamic diameter. Table II shows the close agreement of mass median aerodynamic diameter between the seven-stage impactor and that calculated from nebulizer performance data. The impactor was not used to measure low relative humidity aerosols due to the poor resolution of the impactor when collecting dry submicron particles.

The mass of salt aerosols per unit volume of air was determined by weighing filter samples. Providing that sampled air volume is accurately known and the filter has a high efficiency, this method is highly reliable. The flow rate through a filter tends to decrease as the particles load on the filter and increase its pressure drop. A calibrated critical limiting orifice (Millipore Corporation) was used in the sampling line to regulate air flow and minimize fluctuations. The orifice maintained a 9.8 L/min. flow when a pressure differential across the orifice of greater than 50 cm. of Hg was maintained.

At low relative humidity, immediately after sampling dry aerosol, the filter samples weighed essentially the same as after drying in an oven at 110°C. Drying was necessary, especially for high relative humidity samples since there are many states of hydration of ferric sulfate (Table III).

In order to determine the state of hydration of ferric sulfate that was generated into the chamber, a combination chemical titration and gravimetric method was used. A typical filter, for example, increased in weight from 36.05 mg. to 43.55 mg. after two hours sampling at 40 percent R.H. After drying at 200°C the weight changed to 41.47 mg. and the color of the deposit went from white to dark brown. The total net increase of weight over the clean filter, after dehydration was then 5.42 mg. The same filter was then chemically titrated for ferric ion and found to have 5.55 mg. of ferric sulfate. Based on these data, the ferric sulfate had 28 percent water which is equivalent to about 9 H₂O molecules per molecule of salt aerosol. The molecular formula was probably then Fe₂(SO₄)₃·9H₂O. Whether or not this state of hydration of ferric sulfate is ever present in the workspace or urban atmosphere is not known.

discussion

Ferric and ammonium sulfate aerosols generated by nebulization from 10% (w/v) aqueous solutions and sampled from the area of the chamber in which animals are exposed, had mass median aerodynamic diameters of about 0.5 micrometers at high (80-90%) relative humidity as determined by the cascade impactor. At low (30-40%) humidity the aerodynamic diameters as determined by calculation from electron micrographic sizes were 0.32 micrometers for ferric and 0.36 micrometers for ammonium sulfate. Estimates of the geometric standard deviations averaged 1.7 (Tables I and II). Good agreement on particle size was obtained between measurements by cascade impaction and electron microscopy; both measurements falling close to the particle size diameters expected from calibration of the nebulizer with sodium fluorescein.

Particles were typically singular and globular in shape (Figures 2 and 3), with a significant number of doublets and a few higher order multiplets present at low relative humidity. At low relative humidity the particles were probably crystalline and relatively dry except for water of hydration. At high relative humidity the aerosol particles

TABLE III
Selected Properties of Ammonium and Ferric Sulfate Salts

Formula	Density gm/cm ³	Crystal Form	Color	Notes
(NH ₄) ₂ SO ₄	1.8	Rhombic	White	Deliq. at 80% R.H.
Fe ₂ (SO ₄) ₃	3.1	Rhombic	Yellow	Hygroscopic
Fe ₂ (SO ₄) ₃ ·9H ₂ O	2.1	Rhombic	Brown	Deliq., dehydrates above 83°C.
Fe ₂ (SO ₄) ₃ ·10H ₂ O	2.1	Amorphous	Colorless to pale violet	
Fe ₂ (SO ₄) ₃ ·XH ₂ O				X=7 ¹ / ₂ , 7, 6, 4, 3, 2

appeared to be solution droplets. Ammonium sulfate collected at high humidity appeared as a crystalline-like residue that tended to decompose in the electron beam under high beam intensities.

The mass median aerodynamic diameter of the salt aerosol in the exposure chamber was stable up to an aerosol concentration of 4 mg/m³ of air. Above this concentration coagulation appeared to increase the mass median aerodynamic diameter significantly.

Each of the two sulfates have properties that complicated their generation into aerosols and the subsequent characterization. Ferric sulfate exists in a hydrated form after nebulization of an aqueous solution, and ammonium sulfate exhibits deliquescence above about 80% relative humidity.⁽¹⁶⁾ Such properties can lead to significant errors in interpreting filter sample weights or in sizing by electron microscopy. Further, to insure reproducibility of similar aerosols for laboratory experiments, chambers or other aerosol containment systems must have controlled temperature and humidity.

The methods described here appear to be adequate for generation and characterization of selected sulfate aerosols for animal inhalation experiments, provided proper care is taken in controlling relevant factors such as temperature, relative humidity, and solution concentration in the nebulizer.

acknowledgements

The authors are indebted to Judson Kenoyer and Robert Walters for review of the manuscript and to Lisa Lieberman and Pam Swick for preparation of the manuscript. The research was supported by the California Air Resources Board under contract number ARB-725.

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