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A GENERATOR FOR THE PRODUCTION OF SULFURIC ACID-COATED DIESEL SOOT AEROSOLS

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Abstract—Diluted diesel engine exhaust was mixed with sulfur trioxide and the resulting acid-soot aerosol characterized. The generation system, which is suitable for inhalation toxicology studies, was characterized at a soot concentration of approximately 0.5 mg m^{-3} and H_2SO_4 coating levels from 0 to 5 mg m^{-3} . Aerosol characterization included measurement of particle size (cascade impactor + electrical aerosol analyzer tandem sampler) and acid-soot association (electron microscopy of BaCl_2 -coated sample grids).

The mass distribution of both acid-coated and uncoated diesel soot was unimodal and approximately lognormal. The acid coating increased both the size and monodispersity of the soot aerosol. The mass median Stokes equivalent diameter and geometric standard deviation were $0.12 \mu\text{m}$ and 2.4 for the uncoated soot, and $0.28 \mu\text{m}$ and 1.9 at $5.0 \text{ mg m}^{-3} \text{H}_2\text{SO}_4$. Approximately 95% of the soot particles were coated with H_2SO_4 ; the remainder appeared uncoated. Some H_2SO_4 droplets without a visible nucleus were also observed.

Key word index: Diesel soot, sulfuric acid, aerosols, air pollution.

INTRODUCTION

The diesel engine meets many needs in the transportation industry and in other areas. However, concern about the effects of emissions from the diesel has led in recent years to an increase in research and regulatory activity. The particulate emissions are of special concern since they play a role in urban area visibility degradation, and may have adverse health effects.

Under certain circumstances, diesel soot aerosols may be expected to be associated with H_2SO_4 . In the atmospheric environment, SO_2 may be oxidized on the surface of solid soot particles (Novakov *et al.*, 1974) or in liquid droplets containing suspended soot particles (Benner *et al.*, 1982), with the resultant formation of H_2SO_4 . Such particles may exist in urban areas which have both widespread use of diesel engines and significant SO_x emissions. Acidic soot aerosols are also expected to be present in some underground mining environments. About 60% of U.S. mine diesels are estimated to use exhaust oxidation catalysts to reduce CO and HC emissions. Unfortunately, use of the catalyst promotes oxidation of a significant fraction of the exhaust SO_2 , resulting in mine H_2SO_4 levels of several mg m^{-3} (French and Mildon, 1984). Some of this H_2SO_4 is likely to be coated on the exhaust soot aerosols.

H_2SO_4 -coated diesel soot particles have small aerodynamic sizes and an insoluble core. Therefore, inhalation of these particles may result in sustained contact of H_2SO_4 with deep lung tissues. Since there is the potential for substantial human exposure in the en-

vironments above, the inhalation toxicology of this pollutant combination is of concern.

The present work describes an H_2SO_4 -coated diesel soot generation system and a limited physical characterization of the aerosol produced. The authors are not aware of any previous publications on the generation of acid-coated diesel aerosols, although other workers appear to have produced an acid-coated propane soot (Britton and Clarke, 1980; Brorström-Lundén and Lindskog, 1985) or acetylene soot (Thomas *et al.*, 1974) in the course of their experiments.

Although the present work is concerned only with the physical characterization of H_2SO_4 -coated diesel soot aerosols, we note the increasing evidence for the reactivity of H_2SO_4 with some of the components of diesel exhaust, to produce products of unknown toxicity (Schuetzle, 1983; Wall and Hoekman, 1984).

METHODS AND MATERIALS

A diagram of the system used to generate the H_2SO_4 -coated diesel soot aerosols is shown in Fig. 1. The engine (an 817 cm^3 displacement, single-cylinder, direct injection unit) was operated at constant speed (1800 r.p.m.) and load (78% of maximum). The loading method was a direct-coupled generator with a resistive electrical load. Monitoring instrumentation allowed the continuous measurement of intake and exhaust pressures and temperatures, engine r.p.m. and generator load. The fuel used was Phillips No. 2 Diesel Control Fuel, which was purged with N_2 upon receipt, and kept under positive N_2 pressure in a constant temperature environment.

The exhaust leaving the engine was allowed to age for a residence time typical of automotive exhaust systems (0.2 s),

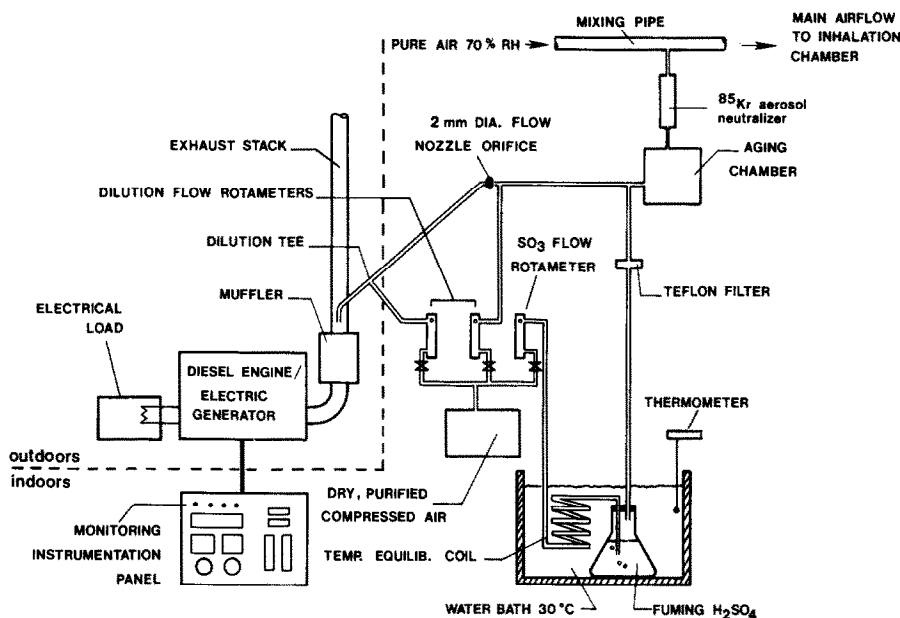


Fig. 1. Schematic diagram of the H_2SO_4 -coated diesel soot generation system.

and then a portion of the total exhaust was split off and diluted immediately with dry, purified air. A flow-nozzle orifice in the diluted exhaust line controlled the flow of dilute exhaust as required for the experiments. Following the orifice, the exhaust was again diluted with purified air. The overall dilution of the exhaust, including both dilution steps, was 1:9. This ratio was determined by measurement of dry CO_2 volume fractions in raw and diluted exhaust using a Perkin-Elmer Model 1100 medical mass spectrometer, and calculation according to the method given by MacDonald *et al.* (1980).

Prior to entering the aging chamber, the dilute exhaust was contacted with SO_3 vapor, injected as a centered, cocurrent jet. The SO_3 was obtained by bubbling dry, purified air through 450 cm^3 of fuming H_2SO_4 contained in a glass flask. As the purified air had been dried by a number of steps, including passage at 8 atm pressure through a Type 5A molecular sieve bed, the atmospheric pressure dewpoint was below -73°C . The extremely dry air was necessary to inhibit nucleation of H_2SO_4 prior to mixing with the diluted exhaust. The mass concentration of H_2SO_4 in the inhalation chamber was adjusted by varying the flowrate of air bubbling through the fuming H_2SO_4 . A temperature equilibration coil brought the carrier air to bath temperature prior to entering the fuming acid flask. The fuming H_2SO_4 used was obtained by mixing equal volumes of 20% free SO_3 fuming H_2SO_4 and 96% reagent-grade H_2SO_4 , and was about 3% free SO_3 . This reduced strength was more convenient for the carrier flowrates and H_2SO_4 concentrations in use. Even at the reduced strength, the mass of SO_3 contained in the fuming acid was several orders of magnitude larger than the mass of SO_3 consumed during a typical 5-h experiment. This design feature enhanced generator stability by minimizing the effects of SO_3 depletion. A Teflon filter, mounted in the Teflon line leading to the SO_3 injection jet, removed any spray droplets exiting the fuming H_2SO_4 bubbler.

At the point of SO_3 mixing, the dilute exhaust had cooled to 33°C and its relative humidity was 42% (at 33°C). The dilute exhaust flow was still somewhat pulsatile in nature at the SO_3 injection point, and the Reynolds number based on the mean flowrate was about 2000. Therefore, SO_3 mixing conditions were turbulent.

In the mixing region, injected SO_3 reacted rapidly with

H_2O vapor in the dilute exhaust to produce H_2SO_4 vapor. Since the hydrophobic diesel soot particles were insoluble and not wetted by the H_2SO_4 , high initial H_2SO_4 saturation ratios, above the homogeneous nucleation threshold, were required to acid-coat the particles. At the initial H_2SO_4 mixing ratios used in these experiments (10^{-6} to 10^{-5} moles H_2SO_4 mole air $^{-1}$), both homogeneous and heterogeneous nucleation are expected (Hoppel, 1975). The relative rate of these processes would depend on the concentration, size and surface characteristics of the diesel particles, the relative humidity, the H_2SO_4 vapor concentration, the effects of nearby surfaces, and other factors.

The stainless steel aging chamber, with a mean residence time of 1.4 min, allowed time for completion of the H_2SO_4 nucleation and condensation processes, cooling of the aerosol to room temperature, and particle coagulation to the desired size. The aerosol exiting the aging chamber was brought to Boltzmann charge equilibrium by passage through a ^{85}Kr aerosol neutralizer before mixing with the main airflow leading to the inhalation chamber.

The mixing of the dilute exhaust and inhalation chamber air supply flows resulted in a final dilution step of 1:15, for an overall exhaust dilution ratio of 1:135. All aerosol characterization was conducted in the animal breathing zone of the inhalation chamber, which had a mean residence time of about 3 min. For all experiments, the purified air entering the inhalation chamber was maintained at room temperature (24°C) and 70% relative humidity (r.h.).

Sulfate levels in the inhalation chamber breathing zone, for uncoated and acid-coated diesel soot aerosols, were determined by collection of aerosols on acid-washed Pallflex (Pallflex Products Corp., Putnam, CT) T60A20 Teflon-coated glass fiber filters. Filters were extracted in distilled water by mechanical agitation for 30 min, and analyzed for sulfate by ion chromatography. Selected samples were then re-extracted for 30 min using 60 (vol.) % isopropanol-40% distilled water solution. The isopropanol-water extraction solution increased the recovery of sulfate from uncoated diesel soot samples by about 50%, but did not enhance the recovery of sulfate from H_2SO_4 -coated samples.

The association of H_2SO_4 with the soot particles was investigated using a BaCl_2 coating method (Ayers, 1978). Samples of uncoated and coated soot aerosols were collected

on carbon-coated electron microscope grids using a point-to-plane electrostatic precipitator (Morrow and Mercer, 1964). An approximately 0.03- μm thick coating of BaCl_2 was then applied to the grid using a vacuum evaporator. Due to the known volatility of H_2SO_4 under vacuum (Gras and Ayers, 1979), this step was carried out as rapidly as possible. The evaporator vacuum was 1.5E-05 mm Hg, and the 0.03 μm coating thickness value was calculated from the known mass of BaCl_2 evaporated and the source-to-grid distance, assuming a point source of BaCl_2 . Grids were transferred after coating to a constant-humidity chamber, either 75% r.h. (high humidity development) or 20% r.h. (low humidity development) for 1 h. This 1-h development period provided the moisture and time needed for the Ba^{2+} in the BaCl_2 coating to react with available SO_4^{2-} on the particles, to form an insoluble BaSO_4 'reaction ring.' Upon removal from the development chamber, grids were examined and photographed in a Zeiss Model EM-10/CR transmission electron microscope.

The coated and uncoated soot aerosols were sized using a Sierra Model 210K 8-stage cascade impactor, sampling in tandem with a Thermo-Systems, Inc. Model 3030 electrical aerosol analyzer (EAA) (Cheng *et al.*, 1986). In the present work, use of an impactor alone would not be satisfactory as the majority of the aerosol would penetrate to the final filter and the sizing data would not be sufficiently detailed in the smaller size range. A low-pressure impactor would provide the necessary small-particle sizing but sample volatility at the low operating pressure becomes a concern. Use of the EAA downstream of the impactor provides the necessary small-particle sizing at a pressure near atmospheric. The upstream impactor allows for the collection (and size separation) of large particles which might artifactually influence EAA readings. The use of the EAA can be restricted to particles < 0.4 μm diameter, where it can more accurately measure volume distributions (Mulholland *et al.*, 1980).

To prepare the tandem sampler, the backup filter and filter supporting screen were removed from the Sierra impactor, and the unit was loaded with preweighed, high vacuum silicone grease-coated aluminum foil collection substrates. In this impactor, a portion of each collection substrate makes physical contact with the lower surface of the previous impactor stage. Therefore, to prevent weighing errors caused by grease adhering to upstream stages, the coating was applied to jet impingement (non-contact) areas only. The impactor was operated at a reduced flowrate of 7 $\ell \text{ min}^{-1}$ to minimize particle bounce and wall losses.

Downstream of the impactor, the aerosol stream was split. Part of the flow went to the aerosol inlet of the EAA through a short line of stainless steel tubing; the balance of the flow was filtered and monitored with a calibrated rotameter. The EAA sheath air was obtained from a matched clean-air inhalation chamber maintained at the same temperature and r.h. as the aerosol chamber, and was restricted slightly in order to achieve the necessary flow through the impactor. At the impactor sampling flow of 7 $\ell \text{ min}^{-1}$, the pressure drop across the impactor was 0.05 atm, resulting in an EAA inlet pressure of 0.95 atm. The reduced pressure inside the EAA analyzer tube was monitored with a vacuum gauge and held constant during each sampling run. Aerosol flow and total flow mass flowrates were reduced slightly in order to maintain the volumetric flows through the EAA at their standard sea level values of 4 and 50 $\ell \text{ min}^{-1}$. In a similar manner, the charger sheath air rotameter of the EAA was recalibrated at the lower pressure, and maintained at 1 $\ell \text{ min}^{-1}$. When sizing the coated soot aerosol, dilution of the aerosol was required, so a calibrated capillary diluter with an experimentally-measured dilution ratio of 1:13.8 was inserted between impactor and EAA. This brought total electrometer currents into the 4–12 picoampere range for all sampling runs.

To characterize the coated soot aerosols, the system was first conditioned by passing SO_3 through it for several hours. The SO_3 was then cleared from the system and the diesel

engine was started. Approximately 30 min after a steady-state exhaust temperature had been achieved, and the chamber soot concentration had stabilized as indicated by an infrared light-scattering mass monitor (GCA Corp. Model RAM-1), a filter gravimetric sample was taken. The SO_3 flow was then resumed and allowed to stabilize. Parallel filter and impactor/EAA samples, or parallel filter and electrostatic precipitator samples were then drawn from the inhalation chamber. In order to obtain enough sample on the impactor stages for reliable gravimetric analysis, the impactor/EAA tandem sampler was allowed to operate for 3–5 h. The EAA sizing procedure was performed at approximately 40-min intervals during the sampling period; the size distributions reported herein represent the mean of the EAA data. Following the completion of the characterization period, the SO_3 was again allowed to clear from the system, and a final filter gravimetric sample was taken. In general, the engine soot output was quite stable over the course of a run, and the initial and final gravimetric samples agreed within 20%.

RESULTS

When samples of uncoated diesel soot aerosol were collected on electron microscope grids, coated with BaCl_2 , and developed at 75% r.h., no evidence of barium sulfate reaction rings around the particles was seen. Ion chromatograph analysis of uncoated diesel soot samples extracted in 60% isopropanol/40% H_2O gave an apparent particulate sulfate content of 1–2%. The actual particle sulfate content may have been less due to possible SO_2 oxidation on the filter media; the SO_2 level in the inhalation chamber (as measured with a pulsed fluorescent instrument) averaged about 0.1 ppm.

Addition of SO_3 to the dilute exhaust led to acid-coated particles and produced observable reaction rings. Electron micrographs of the coated diesel soot aerosol, at H_2SO_4 levels of 0.13 and 3.0 mg m^{-3} , are shown in Figs 2 and 3. A barium sulfate reaction ring was observed around 95% of the soot particles at both levels of acid; the remainder of the particles appeared to be uncoated. The grid samples of the soot + 0.13 mg m^{-3} H_2SO_4 atmosphere were developed at high (75%) r.h., and the various simple-shaped particles visible in the background of Fig. 2 are recrystallized BaCl_2 . No such recrystallization occurred during the low (20%) r.h. development process, applied to the soot + 3.0 mg m^{-3} H_2SO_4 samples (Fig. 3). The mass of sulfate per particle increased with both H_2SO_4 concentration and the size of the soot particle. Sulfate particles without a visible nucleus were also visible in some micrographs.

The mass distribution of Stokes equivalent diameter, for the uncoated and coated diesel soot particles, is shown in Fig. 4. The impactor cutpoints (the Stokes equivalent diameter that is collected with 50% efficiency) were calculated from:

$$d_{50} = \sqrt{\frac{9\eta W St_{50}}{C_c \rho_p V_o}}$$

where d_{50} = 50% Stokes cutpoint (cm)

η = air viscosity at the local jet temperature of stage ($\text{g cm}^{-1} \text{ s}^{-1}$)

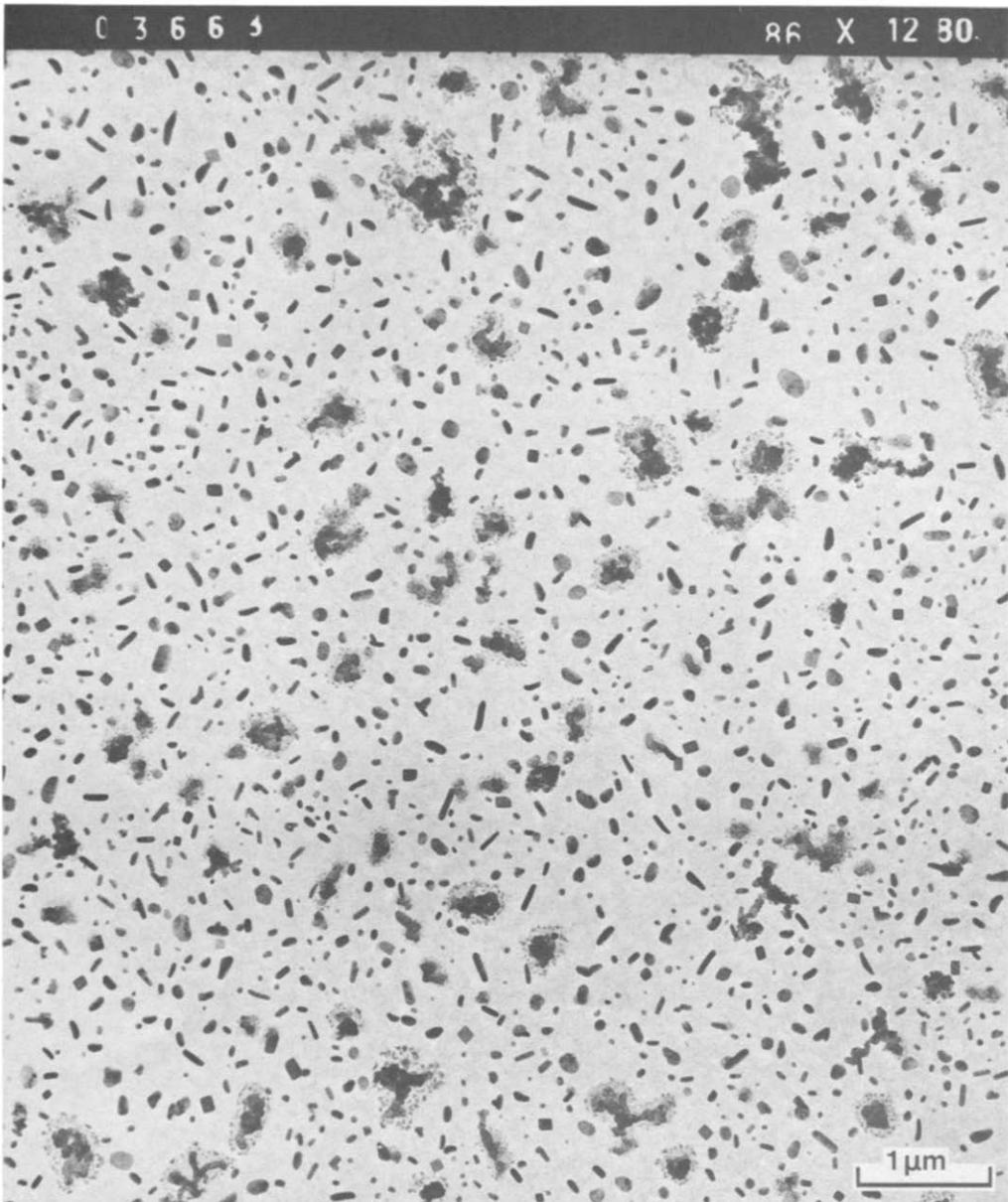


Fig. 2. Electron micrograph of 0.4 mg m^{-3} soot + 0.13 mg m^{-3} H_2SO_4 aerosol sample, coated with BaCl_2 and developed at 75% r.h.

W = slot width of impactor stage (cm)

St_{50} = Stokes number at 50% collection efficiency

C_c = slip correction factor, evaluated at d_{50} and the local jet pressure of stage

ρ_p = particle density (g cm^{-3})

V_o = jet velocity of stage (cm s^{-1}).

The impactor stage Stokes numbers at 50% collection efficiency were obtained from the theory of Rader and Marple (1985). Comparison between aerosol mass concentration at the EAA inlet, and calculated EAA aerosol volume, gave an apparent particle density of 1.24 g cm^{-3} for the uncoated soot particles; this value

was used in the calculation of d_{50} . Since the theoretical density of H_2SO_4 droplets in equilibrium with 70% r.h. is close to 1.24 g cm^{-3} , this density was also assumed for the acid-coated soot particles. The calculated 50% Stokes cutpoint for the last impactor stage was $0.3 \mu\text{m}$ at the sampling conditions employed; particles smaller than this passed through the cascade impactor and were sized by the EAA.

Since the EAA was operated below normal atmospheric pressure, the channel size boundaries and conversion constants were shifted from the atmospheric pressure values. The problem has been examined theoretically by Ogren (1980). The EAA channel boundaries and conversion constants were recalculated

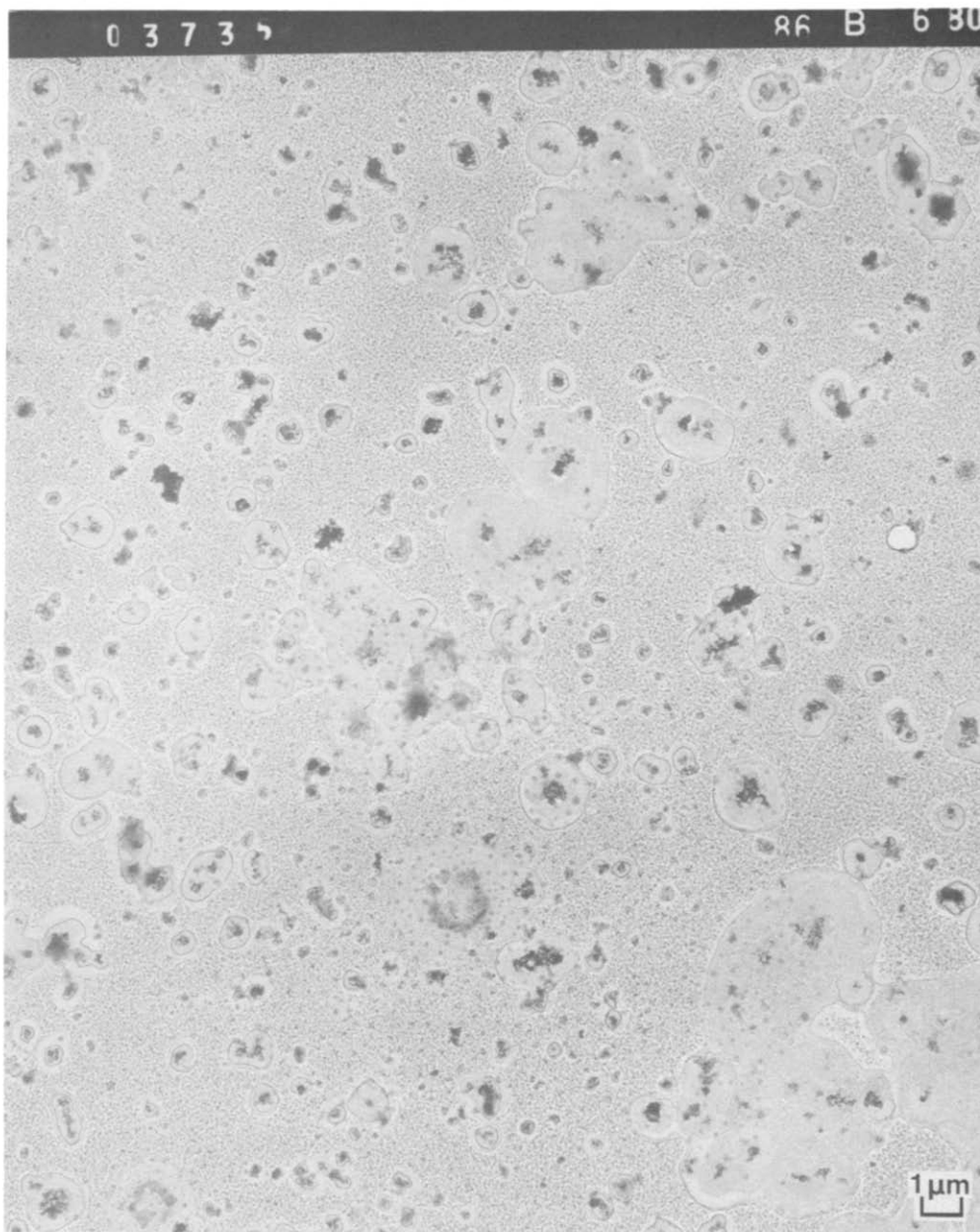


Fig. 3. Electron micrograph of 0.4 mg m^{-3} soot + 3.0 mg m^{-3} H_2SO_4 aerosol sample, coated with BaCl_2 and developed at 20% r.h.

lated for an EAA inlet pressure of 0.95 atm using Ogren's results for constant volumetric flowrates through the EAA. The theoretical corrections to the atmospheric pressure parameters were small. The recalculated channel boundary mobility diameters were about 2–5% larger than the corresponding atmospheric values, while the recalculated conversion constants were about 2–8% smaller.

Several simplifying assumptions were made in the preparation of the normalized mass distribution of Stokes equivalent diameter shown in Fig. 4. The particle property measured by the EAA is the electrical

mobility equivalent diameter. This may be defined as the diameter of a sphere with the same electrical mobility as the particle in question, when subjected to the same charging conditions. The equivalent Stokes diameter of a particle is the diameter of the sphere which has the same density and terminal settling velocity as the particle in question. For the acid-coated soot aerosols, the electrical mobility diameter was assumed equal to the Stokes diameter, since the acid coating should be sufficient to render the particles spherical.

For the uncoated soot particles, the Stokes equi-

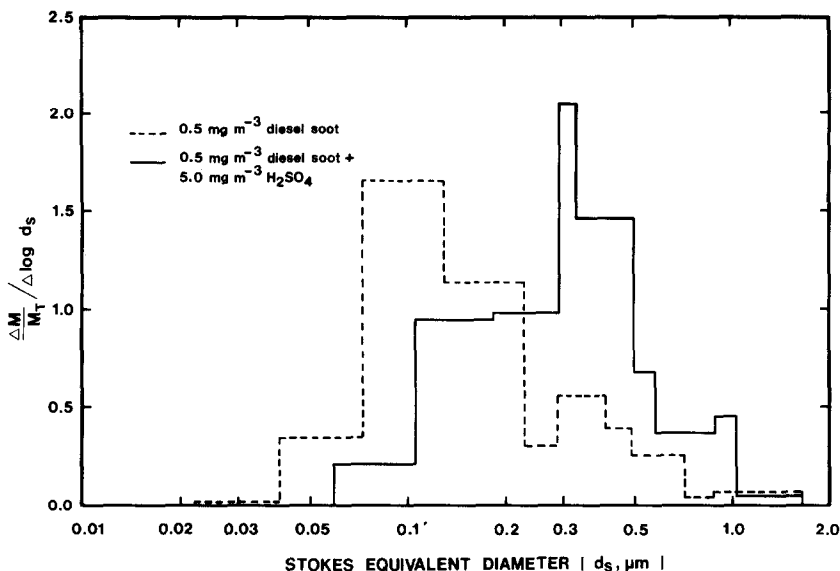


Fig. 4. Mass distributions of coated and uncoated diesel soot, as measured with the impactor + EAA tandem sampler.

valent diameter was estimated from the measured electrical mobility equivalent diameter using the following relation:

$$d_s = \frac{d_{em} C(d_{ve})^{3/2}}{C(d_{em}) C(d_s)^{1/2} \chi^{3/2}}$$

where d_s = Stokes equivalent diameter (μm)

d_{em} = electrical mobility equivalent diameter (μm)

$C(d_{ve})$ = slip correction factor, evaluated at the volume equivalent diameter of the particle

$C(d_{em})$ = slip correction factor, evaluated at the electrical mobility equivalent diameter

$C(d_s)$ = slip correction factor, evaluated at the Stokes equivalent diameter

χ = dynamic shape factor of the particle.

Based on microscopic examination of a 'typical' diesel soot particle, Yu and Xu (1986) estimated a dynamic shape factor of about 1.5. However, when placed in the electric field of the EAA analyzer, most diesel soot particles are expected to orient in such a manner as to reduce their shape factor (Hansson and Ahlberg, 1985). In this work, a dynamic shape factor of 1.3 was assumed for the irregular soot particles.

The volume equivalent diameter, defined as the diameter of a sphere with the same density and volume as the particle, was calculated from:

$$d_{ve} = \frac{d_{em} C(d_{ve})}{\chi C(d_{em})}$$

The mass concentration of aerosol at the EAA inlet was taken to be the difference between the total gravimetric mass concentration found in the inhalation chamber and the mass deposited in the impactor. Aerosol wall losses in the impactor and the short

stainless steel connecting lines were estimated at less than 5% and were neglected. Aerosol density was assumed constant with particle size; the aerosol mass concentration in any given EAA size range was presumed equal to the product of EAA volume fraction in that size range and EAA inlet mass concentration.

As shown in Fig. 4, the sizing results indicated a mass distribution which was probably unimodal for both coated and uncoated soot aerosols. The mass median Stokes diameter was $0.12 \mu\text{m}$ for the uncoated soot aerosol at a chamber mass concentration of 0.5 mg m^{-3} . When this soot aerosol was coated with 5.0 mg m^{-3} of H_2SO_4 , the mass median diameter increased to $0.28 \mu\text{m}$.

DISCUSSION AND CONCLUSIONS

The coating of electron microscope samples with BaCl_2 has been shown to be a useful aid in the characterization of sulfate-coated aerosols. The 'pure' sulfate droplets seen in some of the electron micrographs could have several possible sources. They could be sulfate droplets formed in the combustion process (Khatri *et al.*, 1978), H_2SO_4 aerosols formed from the reaction between SO_2 and O_3 in the point-to-plane precipitator corona (Kim *et al.*, 1984), or H_2SO_4 aerosols formed by homogeneous nucleation in the acid-coating section of the generator. As the 'pure' sulfate particles were not observed in BaCl_2 -coated samples of the diesel soot-alone atmosphere, the latter source is considered most likely.

The apparently uncoated soot particles comprised about 5% of the total number of diesel particles, at both the 0.13 and 3.0 mg m^{-3} H_2SO_4 levels. Such particles either had no acid coating, or had reaction rings that were too thin to be visible. These particles

may be due to resuspension of uncoated diesel particles (from previous runs) from surfaces downstream of the H_2SO_4 condensation zone. Another possibility is that the H_2SO_4 nucleation and condensation processes were completed before full soot- H_2SO_4 vapor mixing could be accomplished.

Barium sulfate reaction rings were observed around the particles even when the BaCl_2 -coated grids were developed at 20% r.h. (Fig. 3). Since water is required for the development of the reaction rings, and the development humidity is below the deliquescence points of ammonium bisulfate, ammonium sulfate and letovicite, this would suggest that the sulfate coating was predominantly unneutralized H_2SO_4 (Ono, 1978).

The mass distribution of both coated and uncoated diesel soot aerosols was unimodal and was found to be well approximated by a lognormal distribution function. The uncoated diesel soot aerosol had a mass median Stokes equivalent diameter of $0.12\ \mu\text{m}$ and geometric standard deviation of 2.4 at a concentration of $0.5\ \text{mg m}^{-3}$ in the inhalation chamber. When this aerosol was coated with $5.0\ \text{mg m}^{-3}\ \text{H}_2\text{SO}_4$, the size increased to $0.28\ \mu\text{m}$ M.M.S.D., and the G.S.D. decreased to 1.9.

Due to the non-ideal size classification characteristics of the impactor and EAA, estimates of the geometric standard deviation must be considered as approximate only. However, it appeared that the acid coating increased the monodispersity. Such an improvement in monodispersity is expected as the smaller soot particles should grow more rapidly than larger particles during the H_2SO_4 condensation process. Assuming the H_2SO_4 and soot densities to be similar, and the volumes of soot particle and acid coating to be additive, one expects an 11-fold increase in aerosol volume, or a 2.2-fold increase in the diameter of average mass, assuming aerosol number concentrations to be comparable. The mass median Stokes diameter increased by close to this amount (2.3-fold), while the calculated increase in the mobility equivalent diameter of average mass was larger, approximately 2.9-fold.

The described generation system has proven to be a useful tool for investigating the inhalation toxicity of air pollutant mixtures containing acid-coated diesel soots, as well as the study of aerosol coating processes. Further work in this area, including a more detailed physical and chemical characterization, would allow for optimization of generation techniques for this type of aerosol, as well as permitting a better understanding of its role in atmospheric pollution reactions.

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