CHEMICAL-ANALYTICAL TECHNIQUES
FOR AEROSOLS

by Roger L. Tanner and Leonard Newman

Atmospheric Sciences Division
Brookhaven National Laboratory
Upton, N. Y. 11973

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1 Introduction

Analysis of sulfate and other oxyanions of sulfur in airborne particles has attracted increasing attention from air pollution control authorities since evidence is mounting that sulfate is a more serious health hazard than its principal atmospheric precursor, sulfur dioxide (SO_2) (1). Furthermore, reduction in SO_2 emissions has not resulted in proportionate decreases in ambient sulfate concentrations in the USA as shown by Altshuller (2). Developing an effective control strategy for atmospheric sulfate will require, analogously to other secondary pollutants, a more thorough understanding of the generation, transport, transformation and removal processes of sulfur oxides in the atmosphere. Increased understanding of transformational aspects of this cycle will not be forthcoming from sulfate measurements alone--important as such measurements are. It will be necessary (a) to determine the specific chemical nature of the airborne sulfate, (b) to make these determinations as a function of particle size from molecular or cluster dimensions to the "boulder" regime ($> 10 \mu\text{m}$ diameter), and (c) to determine chemical composition as a function of particle size with a time discrimination of one hour or less.

We discuss recent progress in determining chemical composition of the sulfate fraction in ambient aerosol particles from a variety of sampling locations with suboptical size fractionation and time discrimination of one hour. Analyses for acid, ammonium, soluble sulfate and nitrate in acidic aqueous extracts of airborne particles have been used, according to the methodology of Brosset, et al. (3), to identify air masses in which the sulfate portion of the aerosol particles is dominated by sulfuric acid and/or its ammonia-neutralization products. Benzaldehyde and isopropanol extraction

techniques first described by Leahy, et al. (4) specifically separate sulfuric acid and bisulfates (in the absence of H_2SO_4), respectively, from sulfates in airborne particle samples collected on Teflon or treated quartz filters at the 10 μg sulfate level. Diffusion sampling (5) using the Sinclair diffusion battery (6) with filter collection and chemical composition determination of particles size-fractionated in the suboptical regime ($< 0.3 \mu\text{m}$) has been shown to be a valuable tool for characterizing the growth patterns and chemical evolution of very small atmospheric particles.

These analytical chemical, sampling and particle size discrimination techniques have been applied to samples collected in urban and rural ambient environments at both coastal and continental locations in connection with several sampling programs during spring, summer and fall, 1975. The emphasis in these studies was on developing analytical methods for chemically speciating sulfate in ambient airborne particles, applying these methods in field studies designed to characterize ambient sulfate particle composition as a function of particle size and meteorological variables, and then beginning to evaluate transport and transformational implications of the resulting data. In succeeding sections the analytical methods are described, followed by discussion of the results of some field studies employing these methods in the New York City and St. Louis areas and at General Motors' Milford, MI. proving ground.

2 Analytical Methods for Speciation of Airborne Sulfate

2.1 Extraction Methods for H_2SO_4 , Bisulfate

Two approaches have shown promise for sulfate species separation - thermal volatilization (7, 8) and solvent extraction. We have concluded after an extensive study (4) that the thermal volatilization approach by which H_2SO_4 is removed from heated surfaces in the presence of other airborne particles is a difficult and marginally successful approach to speciation; recoveries are

variable and extension to other sulfate species is not straightforward.

Barton and McAdie (8) have reported removal of H_2SO_4 from Nuclepore filters by extraction with isopropanol. Unfortunately isopropanol also completely dissolves ammonium bisulfate and part of the NaHSO_4 as shown by the work of Leahy, et al. (4) listed in Table 1. However, it is shown in that same table that benzaldehyde is the preferred extractant and does selectively remove H_2SO_4 in the presence of bisulfates and sulfates. Recoveries were nearly 100% for samples of ca. 250 μg aerosol H_2SO_4 .

Additional experiments were conducted to test the specificity of benzaldehyde with sulfuric acid samples at the μg level. Microgram-samples of $\text{H}_2^{35}\text{SO}_4$ were placed on a variety of filter materials and dried in vacuo at about 40°C , contacted with 10-15 ml of benzaldehyde, a portion of the extract back-leached into water, and the sulfate recovery determined by β -counting of the dried extract. As shown in Table 2, sulfuric acid was removed from Teflon (Mitex 5 μm and Fluoropore 0.2 μm) and H_3PO_4 -treated quartz filters with recoveries increasing from about 75% for 10 μg samples to about 95% for 100 μg samples. Determinations of non-radioactive sample recovery by turbidimetry were also consistent.

Ammonium bisulfate samples are clearly not extracted by benzaldehyde (Table 2, row 7) although for mixed H_2SO_4 - NH_4HSO_4 samples, the % NH_4HSO_4 co-extracted is about 5%. Methanol and isopropanol will quantitatively extract bisulfate in the presence of sulfates, but isopropanol is preferred since methanol will partially extract ammonium sulfate from the filter as well as bisulfates (4). Preliminary experiments have been conducted to determine the optimum procedure for determination of both H_2SO_4 and bisulfate on the filter sample: sequential extraction with benzaldehyde for H_2SO_4 , then isopropanol for bisulfate; or parallel extraction of two portions of the filter,

benzaldehyde for H_2SO_4 and isopropanol for the sum of H_2SO_4 and bisulfate with bisulfate calculated by difference. The latter procedure is experimentally simpler but optimization experiments are still in progress.

2.2 Chemical Composition from Soluble Ion Measurements

A second approach to sulfate speciation in use in our laboratories has been adapted from the approach of Brosset and coworkers (3) who have determined the acid and soluble ion content of acid aqueous extracts of airborne particle samples. The total titratable acid in an extract of the particle sample is determined by incremental titration with strong base with correction for the leach solution contribution. The data are plotted in exponential form (Gran titration (9)) as shown in Figure 1 to permit determination of strong acid ($K_a \geq 10^{-3}$) in the presence of weaker acids by extrapolation from early points in the titration curve. Determination of as little as 0.1 μeq (1 $\mu\text{eq} = 10^{-6}$ equivalent) with 10% precision is possible.

Optimization of procedures to reduce analysis time per sample for the Gran titrations has proceeded along two lines. Manual titration has been replaced by a coulometric titration (10, 11) of particulate acid using a PAR 179 Digital Coulometer (Princeton Applied Research, Princeton, N. J.) in control I mode, in which OH^- is generated at a Pt working electrode in 0.04 M KBr with a Ag/AgBr counter electrode and the pH continuously monitored by an Orion Ionalyzer (Orion Research Corp., Waltham, Mass.) with recorder. With proper stirring the titration can be conducted in 15 min or less with negligible operator attention. The data analysis is now being conducted on an HP 9101B Programmable Calculator (Hewlett-Packard Corp., Avondale, Pa.), using a modified linear regression program in which the raw mV data are converted to $10^{E/8}$ data and plotted vs. μeq of added base and the best fit straight line drawn by an HP 9125B Plotter (ibid.). Complete determination of strong acid in about 10 filter samples per analyst-day is possible.

The aqueous extract is further analyzed for ammonium by the indophenol colorimetric method (12), nitrate by hydrazine reduction, derivatization and colorimetry (13), and sulfate by turbidimetry (14). A portion of the 4 in. diameter filter samples is analyzed for total sulfur content of the airborne particle sample by the reduction $^{110}\text{Ag}_2\text{S}$ technique of Forrest and Newman (15). The combined sampling and analysis precision ($\pm 1\sigma$) for the wet chemical methods for ammonium, nitrate, sulfate and total sulfur is $\leq \pm 10\%$ at ambient levels.

Total soluble sulfur determinations have also been done on many samples using a new flash volatilization-flame photometric technique described by Husar, et al. (16) and by Roberts and Friedlander (17). The basis of this technique is the flame photometric measurement of sulfate which has been volatilized from a metal strip or boat by rapid heating to $\geq 1200^\circ\text{C}$ by capacitance discharge. This method has been modified in our laboratories (18) by reducing the volatilization chamber volume and introducing the use of a platinum boat-sample holder. The redesigned volatilization chamber has a very long sample boat lifetime, allows the use of dried room air to carry the volatilized sample to the detector, and results in an output signal peak proportional to the square of the quantity of volatilized sulfur (without peak integration). The minimum quantity determinable with $\pm 10\%$ precision is now about 3 ng S.

3 Field Experiments Featuring Chemical Composition Determination of Ambient Aerosol Sulfate

3.1 Brookhaven National Laboratory (BNL) Sampling.

A data summary showing the cation-anion balance on an equivalent basis in the soluble ion portion of extracts of selected airborne particle samples

collected at the BNL sampling site in 1975 (mostly at about 125m above ground level atop the Ace meteorology tower) is reported on Table 3. The data show that equivalents of $H^+ + NH_4^+$ are equal to equivalents of $SO_4^{2-} + NO_3^-$ within $\pm 20\%$ for most of the air masses sampled, independent of filter material used. The equivalents of H^+ may occasionally exceed equivalents NH_4^+ and particles may also be net basic to the pH 4 leach used and appear as a negative $[H^+]$ in the table. The precision limits for simultaneous sampling on identical filters are $\pm 10-30\%$.

This summary shows that sulfuric acid and/or its ammonia-neutralization products frequently dominate the sulfate portion of the ambient aerosol sampled at the semi-rural BNL location (on Long Island, 100 km ENE of New York City), since equivalents of strong acid and ammonium usually equal equivalents of sulfate and nitrate equivalents are only a few % of sulfate. This is consistent with the data of Brosset, et al. (3) taken at a rural location on the West Coast of Sweden, and also with the data of Charlson, et al. (19) obtained at both rural and urban sites in the St. Louis area.

Within experimental error, $(NH_4^+ + H^+)$ equivalents rarely exceed sulfate equivalents in airborne particle extracts, but 20-40% excess sulfate over $(NH_4^+ + H^+)$ equivalents is not uncommon especially when, as on the 10/15 sampling date, the air-mass back trajectory from BNL passed through the metropolitan New York area. Acid sulfate particles with equivalents of strong acid exceeding equivalents of ammonium are relatively rare in non-size-segregated airborne particle samples and appear to be confined to episodic conditions in stagnant air masses.

3.2 Comparison of Soluble Ion and Extraction Data for Acid Sulfate Particles.

We report in this section a comparison of the benzaldehyde extraction technique and soluble ion determinations of H^+ (Gran Titration), NH_4^+ and SO_4^{2-}

for determination of sulfuric acid in airborne particles. Nominally, for particle samples in which moles H^+ > moles NH_4^+ and moles $(H^+ + NH_4^+) \approx 2 \times$ moles SO_4^{2-} , sulfuric acid should be present in the particles and be detected by the extraction technique. Some of the airborne particles samples collected for our group on H_3PO_4 -treated quartz by Battelle Pacific Northwest Laboratory personnel flying in the St. Louis urban plume on Aug. 8 and 18, 1975 met the above criteria for the presence of sulfuric acid. The data from those experiments are shown in Table 4 (nitrate moles/ m^3 only $\approx$ 5% of sulfate).

During the 1430-1520, 8/8 sampling period moles H^+ exceeded moles NH_4^+ by 0.217, corresponding to $0.108 \mu\text{moles}/m^3 H_2SO_4$. This calculation assumes that H^+ and NH_4^+ are associated only with sulfate. Alternatively we may assume that NH_4^+ is present only as NH_4HSO_4 ($0.226 \mu\text{moles}/m^3$) and the additional sulfate is present as H_2SO_4 ($0.084 \mu\text{moles}/m^3$). The calculated value in the table is the average of these two values ($0.096 \mu\text{moles}/m^3$) and is in excellent agreement with the $[H_2SO_4]$ determined by benzaldehyde extraction and flash volatilization-FPD (16-18). A similar calculation for the 1530-1620, 8/8 period yields a calculated value of $0.106 \mu\text{moles}/m^3$ compared with $0.155 \mu\text{moles}/m^3$ by extraction. The extracted value may exceed the calculated value if the acid is inhomogeneously distributed in the sulfate-containing particles, however, the calculated $[H_2SO_4]$ should not (within experimental error) exceed the extracted value.

During 3 of the 8/18 sampling periods moles H^+ < moles NH_4^+ and, as expected, no sulfuric acid was observed. Moles H^+ did exceed moles NH_4^+ in the sampling period 1330-1420, 8/18 but moles $(H^+ + NH_4^+) < 2 \times$ moles SO_4^{2-} hence sulfate not associated with H_2SO_4 and its ammonia-neutralization products was present and the assumptions on which the comparison of calculated and extracted $[H_2SO_4]$ is made break down. We conclude that H_2SO_4 in airborne particles can be quantitatively determined by the benzaldehyde extraction method at the $5-10 \mu\text{g}/m^3$ level.

3.3 Intercomparison of Aerosol Sulfate Analysis Methods.

In connection with an extensive intercomparison study of methods for the physical and chemical characterization of atmospheric aerosols conducted by U.S. EPA/ESRL personnel at RAMS Stations #106 (St. Louis urban location) and #124 (rural location S. of St. Louis), manual dichotomous samplers (MDS) (20) operating in parallel at each site were used to collect 24 hr total, fine fraction, and coarse fraction samples during the period of 8/18 (Day 1) to 9/4/75 (Day 18). We obtained MDS fine fraction samples collected on Fluoropore (47 mm, Type FALP) at both sites on sampling days 1-6, 10, 16, and 18 as well as MDS fine fraction and total samples collected on H_3PO_4 -treated quartz filters at both sites on days 10, 16 and 18. From the resultant analytical data a direct comparison of sampling methods and sulfate analysis techniques was possible. In addition sulfate speciation data was obtained for some samples and the percent of sulfate in the fine fraction was determined.

A direct comparison of the turbidimetric sulfate data from samples collected on Fluoropore filters with data obtained by T. G. Dzubay of EPA/ESRL using X-ray fluorescence (XRF) (20), is shown in Table 5. Considering that the one σ precision for sampling and analysis by each of the two methods is ca. $\pm 10\%$, the agreement between methods is good. A linear regression plot of the turbidimetric data vs. the XRF data (x-axis) yields a slope, $a = 1.2$, an intercept, $b = -0.5 (\mu g/m^3)$ and a correlation coefficient $R = +0.955$, and indicates that the XRF data are $\sim 20\%$ low or the turbidimetric data are $\sim 20\%$ high.

Table 6 lists speciated sulfate analyses for 3 sampling days at both sites. As noted above, both total and MDS fine fraction samples were collected on acid-treated quartz filters and preserved in sealed plastic containers until analyses were performed. The data show that on the average more than 90% of the soluble sulfate is in the fine particle range. In fact, a plot of total sulfate vs. fine fraction sulfate yields the following linear regression statistics (defined above) when the origin is included: $a = 0.96$, $b = 1.18$, $R = +0.965$. Fine

fraction samples usually contain more strong acid than total particulate samples, indicating inhomogeneity in the distribution of extractable strong acid or base with respect to particle size, as originally noted by Junge and Scheich (21) and found as well by Marlow and Tanner (5) in smaller size ranges. Contributing to this apparent inhomogeneity is the presence of net-basic particles in the coarse particle range as noted below.

3.4 Lagrangian Experiments for Sulfate Speciation.

Several experiments have been conducted to document the chemical evolution of the sulfate portion of the ambient aerosol in an air mass as it passes from a source-dominant urban area downwind into a rural area. Ground sampling experiments were conducted utilizing simultaneous high volume sampling at an urban location (roof of U.S. ERDA's Health and Safety Laboratory, 376 Hudson St., New York) and at the BNL rural location, with wind speed and direction appropriate for transport of the New York urban plume to the BNL location in 4-6 hr. The data for the 9/10/75 Lagrangian experiment, shown in Table 7, include data taken aboard a ship traversing parts of the continental shelf 30-60 km S. of Shinnecock Inlet, Long Island.

The most noteworthy aspect of the data is their internal consistency. BNL #1 represents the regional background (about $3.5 \mu\text{g}/\text{m}^3$) before passage through urban New York since the air-mass backward-trajectory (22) passed N of the city and through upstate New York. The urban sulfate concentration increased during the day to from 50% to 200% larger than background and this increase is reflected in the concentrations measured at BNL (#2, 3 and 4) and offshore (OCEAN #1 and part of #2) during the period when the back-trajectory passed through the urban area 4-6 hr previously. During the sampling period for BNL #5 the winds had shifted to $190-210^\circ$ and the back-trajectories were S of New York through the Philadelphia-Baltimore area and it is not surprising that the regional sulfate background had increased by about 50% over that observed in BNL #1.

The concentrations of airborne particulate sulfur calculated as sulfate by three methods are in excellent agreement for most measurements. Occasional incursions of sulfur compounds not analyzed as soluble sulfate may be expected in airborne particles collected in an urban region; this would cause the total S measurements to exceed those of the other two techniques as in sample NYC #4. The observation of negative acid concentrations (i.e., net base present) in the urban samples, which are not present in the BNL samples, indicates that the urban source region probably contains large basic particles which are lost by sedimentation in the 4-6 hr transit time to the BNL location. In fact there is a moderate amount of titratable acid in the samples (BNL #2, 3, 4) with back-trajectories through the urban area, even though the sulfate concentration exceeds the sum of $[H^+] + [NH_4^+]$ by 40-100 neq/m³ (2-5 µg/m³).

This experiment is clearly valuable in simultaneously deducing the changes in the concentration and chemical composition of sulfate which are induced by passage of an air parcel through a large urban area, and possibly in distinguishing between the urban sulfate contribution and the regional background. The results of this and other experiments indicate that an increase of 4-8 µg/m³ of sulfate at the BNL site over regional background commonly occurs due to passage of an air mass through the New York urban area when the trajectory to BNL is reasonably direct and the transit time is of the order of 2-8 hrs. The changes in chemical composition of sulfate induced in the urban plume are more difficult to identify and quantify although the analytical techniques for doing so have now been developed. An experiment in which chemical composition changes in ambient aerosol sulfate could be quantitatively established is described in the next section.

3.5 Ambient Neutralization Rates of Sulfuric Acid Particles from Catalyst-Equipped Automobiles

One of the most promising applications of chemically speciated, size-

discrimination SO_4^{2-} measurements has been in the evaluation of the potential health hazard of acid sulfate emissions from catalytic converter-equipped automobiles. The GM Sulfate Dispersion Experiment (23) conducted at the General Motors Proving Ground at Milford, Michigan, during October 1975 was designed to quantitatively elucidate the potential hazard from the sulfate emissions of catalytic converter-equipped automobiles under ambient roadside conditions. It provided for the participation, in addition to the GM Environmental Sciences staff, of two branches of EPA's Environmental Sciences Research Laboratory (ESRL) and their contractors as well as independently supported groups such as Brookhaven National Laboratory (BNL). The BNL experimental work consisted of the collection of one hour HiVol samples on treated quartz filters at two locations (2 meters and 100 meters E of the roadway) and comparison of the analytical results with those from a background sample (30 meters W of the roadway). The downwind impact data are shown in Table 8.

Interpretation of the BNL data led to the following conclusions (24):

a) Sulfate emissions from the fleet of catalyst-equipped vehicles at the GM Sulfate Dispersion Experiment resulted in increased sulfate burdens of 3.2 to 6.2 $\mu\text{g}/\text{m}^3$ at the immediate roadside.

b) Comparison of total sulfur and sulfate data indicate that the auto emission of sulfur is in the form of sulfate.

c) Increases in total acidity and sulfuric acid concentrations downwind of the track strongly infer that the sulfate emission is in the form of sulfuric acid.

d) Ammonium increases downwind of the track, when coupled with increases in acidity and H_2SO_4 , strongly suggest that the emitted sulfuric acid is neutralized by ammonia with a resultant mean half-life for sulfuric acid particles of on the order of tens of seconds. This lifetime, not unexpectedly,

is apparently dependent on the ambient ammonia concentration.

Clearly the techniques are now available to establish the rate of neutralization of acid sulfate particles under ambient conditions (by a combination of field and laboratory studies) as a function of gaseous NH_3 concentration, particle size of emitted H_2SO_4 and relative humidity (controlling factor in growth rate). The evaluation of risk from H_2SO_4 emissions from converter-equipped automobiles and other sources is critically dependent on this ambient neutralization rate.

4 Particle Size Classification of Suboptical Particles by Diffusion Sampling.

4.1 Diffusion Sampling Methodology

The size discrimination innovations we discuss are in the use of a diffusion sampler consisting of a battery of diffusion cells designed by Sinclair (6). Each cell is a highly collimated hole structure of 14,500 stainless steel tubes of 0.22 mm diameter, creating a diffusion cell of ca. 10^3m equivalent length which is only 4 cm in diameter and 2.5 cm in length. Smaller particles diffuse preferentially to the walls, hence by sampling after increasing numbers of cells, removal of progressively larger particles is possible. Fractional penetration vs. log particle diameter curves can be calculated from the known conditions of volume flow, equivalent length and particle diffusion coefficients (5).

Sampling after increasing numbers of diffusion cells with a condensation nuclei counter (CNC) allows determination of particle size distributions. The innovation of Marlow and Tanner (5) is to use filter sampling and chemical composition determination after diffusion sampling using the apparatus in Figure 2. The difference between the chemical composition of untreated and diffusion processed

air after a given equivalent length of diffusion cells is the composition of the smallest particles (those captured by the diffusion battery). Furthermore, by comparing the chemical data for 2 (or more) simultaneously sampled ports, the composition of the fraction of particles sampled as defined by the difference in the fractional penetration curves (at the extant volume flow) can be determined. The product of the size distribution function (determined for $< 0.4 \mu\text{m}$ diameter particles by diffusion sampling-CNC or other means) and the appropriate fractional penetration curve for a diffusion-sampled port yields the size distribution of aerosol filter-sampled at that port.

4.2 Field Experiments Employing Diffusion Sampling

The results of preliminary experiments with the diffusion-sampling method at BNL (5) indicated that suboptical particles were frequently more acid than larger light-scattering particles; furthermore, passage of an air mass from a source region across a body of water to the BNL receptor site resulted in more acid particles in the suboptical size range than passage predominantly over land areas. It was hypothesized that lower ammonia concentrations over ocean areas decrease the neutralization rate of H_2SO_4 droplets hence increase the proportion of acid in particles of a given size.

It was desirable to test the method and the tentative conclusions derived therefrom in other sampling locations. Therefore, a nine-day, intensive, diffusion-sampling experiment was conducted at Glasgow, Ill., a rural location 120 km N of St. Louis, Mo., during the period of July 22-30, 1975, in coordination with the RAPS summer 1975 field program. Twelve hour samples were taken each day and night with the diffusion battery of Sinclair (6) sampling ambient air (samples designated PQU), diffusion processed air with a 50% penetration diameter ($d_{50\%}$) of $0.035 \mu\text{m}$ (PQDB₁), and diffusion processed air with $d_{50\%} = 0.13 \mu\text{m}$ (PQDB₂). Size distributions were also obtained using an

11-port screen-type diffusion battery (25) in conjunction with a condensation nuclei counter.

The sulfate concentration data presented in Figure 3 demonstrate the significant information readily accruable by the diffusion sampling method. Comparison of the data for unprocessed air (PQU) with that for air with the smallest particles removed (PQDB₁) demonstrates that, as expected, sulfate concentrations are equal within experimental error. This indicates that little sulfate mass is present in particles of diameter less than a few hundredths of a micron. However, comparison of PQU data with data from air with most suboptically sized particles removed (PQDB₂) indicates that of the order of 50% of the sulfate mass is found in particles with diameters less than the size limit for optical scattering techniques. Furthermore this fraction is not strongly dependent on the total sulfate concentration for the reported sampling period and location. There is no evidence in this Eulerian experiment of temporally dependent growth of sulfate within a given air mass into larger size fractions.

5. Summary

Techniques for sampling and analysis of airborne particles for the purpose of determining the chemical composition of the sulfate therein have been described. This analytical methodology has been applied to speciation of airborne sulfate in several locations and sampling regimens with time resolution of 1 hr or less and with size discrimination in the suboptical particle size range.

The significant results and conclusions of this study include the following:

- a) The benzaldehyde extraction technique has been shown to specifically determine sulfuric acid in the presence of bisulfates and sulfates at the 10 μg sulfate level by laboratory experiments and in field studies.
- b) The sulfate mass at the semi-rural BNL sampling site is frequently dominated by sulfuric acid and/or its ammonia-neutralization products.
- c) Aerosol sulfur and sulfate levels measured by several techniques under carefully controlled conditions may vary by as little as $\pm 20\%$.
- d) Aerosol sulfate fractions in the fine particle range are about 90% and may consist of $> 80\%$ ammonium sulfate.
- e) The portion of regional sulfate and New York City urban-induced sulfate in an air mass reaching the BNL sampling site was quantitatively documented.
- f) Emissions from a fleet of catalyst-equipped vehicles at the GM Sulfate Dispersion Experiment resulted in increased sulfate burdens of 3-6 $\mu\text{g}/\text{m}^3$ at the immediate roadside; the sulfur emission was in the form of sulfuric acid, the neutralization rate of which is dependent on the ambient ammonia concentration.

g) More acidic sulfate may be present in small particles at coastal receptor sites than at continental sites.

h) A significant portion (ca. 50%) of sulfate mass exists in the particle size region below $0.3\ \mu\text{m}$.

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TABLE 1

Extraction of Sulfate and Bisulfate
Species by Benzaldehyde and Isopropanol

<u>Extracted Species</u>	<u>Percent Extracted by</u>	
	<u>Benzaldehyde</u>	<u>Isopropanol</u>
H_2SO_4	110	103
NaHSO_4	N.D. ^a	36
NH_4HSO_4	N.D.	109
Na_2SO_4	N.D.	N.D.
$(\text{NH}_4)_2\text{SO}_4$	N.D.	N.D.

^aNone detected

TABLE 2 Benzaldehyde Extraction of H_2SO_4 and NH_4HSO_4 from Filters

<u>Amount</u>	<u>Sample</u>	<u>No. of Determinations</u>	<u>Filter Material</u>	<u>% Recovery</u>	<u>Method</u>
10 μg	H_2SO_4	2	Quartz	75	^{35}S
20-40 μg	H_2SO_4	2	Mitex 5 μm	71	^{35}S
30 μg	H_2SO_4	1	Fluoropore 0.2 μm	90	^{35}S
20-40 μg	H_2SO_4	4	Quartz	78	^{35}S
70-80 μg	H_2SO_4	4	Quartz	86	SO_4^{a}
100 μg	H_2SO_4	5	Any of the above	94 ± 8	^{35}S
10-70 μg	NH_4HSO_4	3	Fluoropore 0.2 μm	1.2	^{35}S
34 μg	NH_4HSO_4	2	Fluoropore or Quartz	111^{b}	^{35}S

a Soluble sulfate determined by turbidimetry.

b Extraction by methanol.

TABLE 3

Selected Chemical Composition Data
from Airborne Particle Samples Collected
at BNL, 1975.

Duration		Location	Filter Material	$[H^+]$ $\frac{\text{neg}}{3}$ m ³	$[NH_4^+]$ $\frac{\text{neg}}{3}$ m ³	$[SO_4^{2-}]^a$ $\frac{\text{neg}}{3}$ m ³	$[NO_3^-]$ $\frac{\text{neg}}{3}$ m ³
5/8	24 hr	BNL Tower	Mitex 5 μ m	33	74	125	13
5/14	24 hr	BNL Tower	Quartz	298	191	456	13
5/19	24 hr	BNL Tower	Fluoropore 0.2 μ m	141	339	432	7
6/9	24 hr	BNL Tower	Quartz	22	42	69	18
6/19	6 hr day	BNL Tower	Quartz	890	770	2010	60
7/1	24 hr	BNL Tower	Quartz	51	108	170	ND
7/8	24 hr	BNL Ground Level	Fluoropore ^b	85 $\pm$ 12	117 $\pm$ 40	241 $\pm$ 24	21
9/15	6 hr HiVol	BNL Tower	Quartz	20	33	86	6
10/15	3 hr HiVol	BNL Tower	Quartz	48	286	494	28
11/4	5 hr	BNL Ground Level	Quartz	-6	159	141	15
11/20	2 hr HiVol	BNL Tower	Quartz	40	228	419	12

a Soluble Sulfate by turbidimetry.

b Mean and 1 σ values for triplicate samples

TABLE 4

BNL Data From the St. Louis Urban Plume

Date	Sampling Interval	$[H^+]$ $\mu\text{mole}/\text{m}^3$	$[NH_4^+]$ $\mu\text{mole}/\text{m}^3$	$[SO_4^{2-}]$ $\mu\text{mole}/\text{m}^3$	$\emptyset\text{CHO-extd}$ $[H_2SO_4]$ $\mu\text{mole}/\text{m}^3$	Calculated * $[H_2SO_4]$ $\mu\text{mole}/\text{m}^3$
8/8	1430-1520	0.443	0.226	0.310	0.089	0.096
8/8	1530-1620	0.463	0.278	0.397	0.155	0.106
8/17	1230-1320	0.192	0.387	0.288	0	0
8/17	1330-1420	0.324	0.274	0.414	0	? *
8/17	1430-1520	0.222	0.337	0.367	0	0
8/17	1530-1620	0.124	0.244	0.255	0	0

* See text for explanation

TABLE 5

RAPS Sulfate Data from Fluoropore
Filters by Turbidimetry and X-Ray
Fluorescence

<u>Sample No. a</u>	<u>Turbidimetric Sulfate, $\mu\text{g}/\text{m}^3$</u>	<u>XRF Sulfur as Sulfate, $\mu\text{g}/\text{m}^3$</u>
201	7.07	4.90
801	2.30	2.10
202	11.8	9.46
802	4.90	4.09
203	24.0	20.1
803	NA ^c	21.0
204	26.1	23.5
804	25.7	21.2
205	15.2	14.3
805	7.74	10.9
206	6.42	6.35
806	NA ^c	4.32
210	11.8 ^b	12.9
810	10.8	11.3
216	29.9	23.4
816	29.5	18.7
218	17.1	13.3
818	19.8	NA ^c

^a 200 Series from urban site; 800 Series from rural site.

^b Sample collected on treated quartz.

^c Data not available.

TABLE 6

Comparison of Total and Fine Fraction

Airborne Sulfate

Collected on Treated Quartz

Sample No.-Fraction		$[H^+]$ as $H_2SO_4, \mu g/m^3$	$[NH_4^+]$ $\mu g/m^3$	Turbidimetric Sulfate $\mu g/m^3$	Nitrate $\mu g/m^3$
210	Fine	0.01	3.8	11.8	0.25
210	Total	-0.9	3.3	14.4	0.36
810	Fine	0.37	2.2	10.5	0.22
810	Total	0.23	2.7	10.7	0.17
216	Fine	1.57	13.1	28.3	0.36
216	Total	0.64	10.8	26.7	0.23
816	Fine	1.3	6.0	23.5	0.59
816	Total	2.8	3.7	26.9	NA
218	Fine	0.3	3.7	13.7	0.31
218	Total	-0.6	4.5	17.0	0.27
818	Fine	0.55	5.8	18.4	0.60
818	Total	0.32	5.0	15.0	0.44

TABLE 7

Speciated Sulfate Data from Lagrangian

Experiment Conducted Sept 10-11, 1975

Sample Description				[H ⁺]	[NH ₄ ⁺]	FVFPD [SO ₄ ²⁻]	Turbidimetric [SO ₄ ²⁻]	Total S as SO ₄ ²⁻	Nephelo- metric Mass,
Date	Time	Location	No.	neq/m ³	neq/m ³	neq/m ³	neq/m ³	neq/m ³	μg/m ³
9/10	1030-1150	NYC	1	-44	84	108	109	110	---
	1200-1320	NYC	2	-35	95	204	128	163	---
	1330-1450	NYC	3	-32	112	154	155	156	---
	1500-1620	NYC	4	-62	98	192	198	282	---
9/10	1003-1313	BNL	1	4	17	70	69	69	8.2
	1318-1611	BNL	2	22	32	108	122	129	8.5
	1615-1918	BNL	3	21	89	177	155	117	17.9
	1922-2226	BNL	4	33	78	184	206	126	28.4
9/10- 11	2230-0834	BNL	5	10	86	101	120	147	17.9
9/10	1252-1910	OCEAN	1	-7	28	118	101	NA	---
9/10- 11	1915-0400	OCEAN	2	9	66	132	142	NA	---

TABLE 8

Downwind Impact of Catalyst Sulfate
on Speciated Sulfate Concentrations

				Change in Concentration in Particles, $\mu\text{g}/\text{m}^3$			
Date - Sampling Position				Acidity as H_2SO_4	Extracted H_2SO_4	Ammonium	Turbid. Sulfate
10/6	(279)	100m	downwind	2.8	1.4	1.8	4.4
10/8	(281)	30m	downwind ^a	1.5	0	0.64	1.4
10/10	(283)	100m	downwind	1.0	1.7	0	1.2 ^b
10/21	(294)	100m	downwind	≤ 0	0	0.44	0.7
10/22	(295)	30m	downwind ^a	1.5	0.9	3.6	9.3

^a Data corrected for 3 hr sampling time vs. 2 hr experiment duration.

^b Based on average of BNL total S, GM BCA and EPA XRF data.

List of Figure Captions

- Figure .01 Gran Titration plot of aqueous extract of ambient aerosol particles collected at BNL, May 14, 1975
- Figure .02 Diffusion battery and 47-mm filter sampling apparatus for diffusion sampling of ambient aerosols.
- Figure .03 Sulfate concentrations in airborne particles from ambient and diffusion-processed air; 12 hr sampling (ca. 0800-2000 hr, 2000-0800 hr) at Glasgow, Ill., July 22-30, 1975; — = PQU, ····· = PQDB₁; ----- = PQDB₂.