Reports

Spectroscopic Observation of Acid Sulfate in Atmospheric Particulate Samples

Abstract. *Infrared spectra of time- and size-classified atmospheric particulate samples collected with an inertial impactor reveal the presence of acid sulfate in the submicrometer-sized fraction. Although the degree of acidity is highly variable with time, the acidic nature of the particles is observed at all times of the day and may persist for several days in urban areas.*

As a result of growing concern over the adverse effects associated with particulate sulfates together with the calls for increased use of sulfur-containing coals brought on by recent economic and political events, increasing attention in recent years has been focused on (i) the development of the instrumentation necessary to assess the extent and severity of the problem and (ii) the study of the formation and transport of particulate sulfate in the atmosphere.

Techniques for the measurement of sulfur compounds in ambient air have been reviewed by Forrest and Newman (*1*). A complex analytical method in which ammonia titration is used for the measurement of strong acid aerosols has been described by Dzubay *et al.* (*2*). The detection of airborne acid sulfate particulates in the St. Louis area has been reported by Charlson *et al.* (*3*), using a technique based on the hydrophilic properties of the particles. Brosset and his co-workers (*4*) have reported the occurrence of two types of acid sulfate particles in samples collected on the west coast of Sweden. Recently, Leaky *et al.* (*5*) have described techniques for the characterization of sulfate aerosols using both pyrolytic and solvent extraction methods, and Huygen (*6*) has described a photometric method for the determination of sulfuric acid aerosol. In general, however, with the techniques used for the determination of airborne particulates it is not possible to measure the degree of acidity of the sample, and methods employed specifically for this purpose have serious drawbacks.

We report here the infrared spectroscopic observation of acid sulfate in samples of submicrometer-sized particles collected in urban areas, describe the temporal variation in the degree of acidity of these particles, and discuss briefly the implications of these observations in terms of possible mechanisms for the formation of particulate sulfate in the atmosphere.

Details of the atmospheric sampling, sample-handling, and spectroscopic procedures have been described elsewhere (*7*). Briefly, samples that are size- and time-classified are collected with a Lundgren type impactor and infrared spectra of the samples are obtained by use of KBr pellet techniques. In our earlier work (*7*) we have shown that the chemistry of airborne particulate material is dependent on the particle size, with large particles comprising primarily silicates and carbonates, whereas those particles less than a few micrometers in diameter are principally ammonium sulfate. These chemical differences become apparent in size ranges that correspond to the two main peaks of the bimodal particle volume distribution observed by Whitby *et al.* (*8*). The variations in chemistry with particle size are consistent with the notion that the large-particle size range is dominated by mechanically injected primary particulates, whereas the smaller-particle size range comprises, for the most part, secondary particulates formed in the atmosphere from gaseous precursors. The spectra of submicrometer-sized particles collected in the Chicago suburban area (*7*) were dominated by the infrared active vibrational modes, $\nu_3(F_2)$ and $\nu_4(F_2)$, for the tetrahedral ammonium ions which are observed at 3140 and 1400 cm^{-1} and sulfate ions which are observed at 1110 and 620 cm^{-1} (*9*) (see Fig. 1, curves a and q).

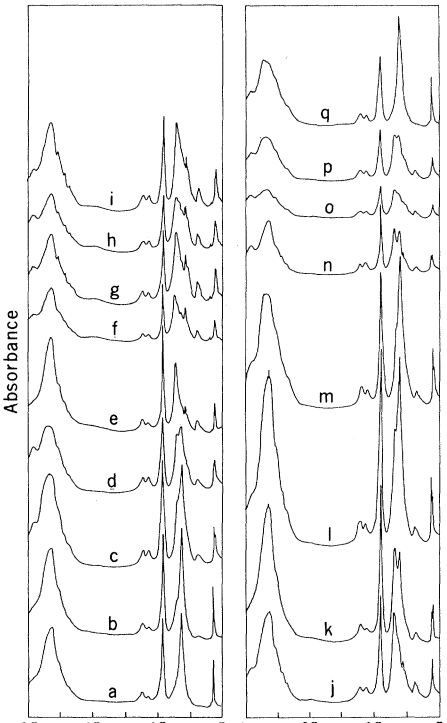

Fig. 1. Infrared spectra for a series of submicrometer-sized particulate samples collected in the City of Chicago. Each sample was collected over a 3-hour period, with starting times indicated in Table 1. All spectra were obtained with 8-cm^{-1} resolution and are plotted in the same scale in absorbance.

Subsequently, for a number of samples collected in Chicago and St. Louis, we observed significant variations in the sulfate bands. Figure 1 shows the nature of these spectral variations for a time sequence of 3-hour sampling periods for submicrometer-sized particles collected in stage IV of a Lundgren impactor during the period from 5 to 7 August 1973. The impactor was situated on the flat rooftop of an eight-story building in downtown Chicago; the air inlet was about 2 m above the roof (*10*). Data relevant to these samples are presented in Table 1. For the 21-hour period represented by curves a through g in Fig. 1, it is clear that a transformation occurs in the sulfate spectra. The two bands associated with the sulfate ion diminish in intensity and are replaced by a more complex band structure in which four prominent bands, at 1205, 1063, 869, and 600 cm^{-1} and two weaker bands, at 1118 and 675 cm^{-1}, are resolved. The remaining curves in Fig. 1 show the extent to which the spectral variations persisted over the next 30 hours with the simple sulfate spectrum again evident in curve q.

We attribute the spectral variations observed in Fig. 1 to changes in the degree of acidity of the samples. The frequencies of the four prominent bands correspond reasonably well with those reported for the bisulfate ion (*11*). The following assignments have been made: 1205 cm^{-1}, $\nu_4(E)$; 1063 cm^{-1}, $\nu_1(A_1)$; 869 cm^{-1}, $\nu_2(A_1)$; and 600 cm^{-1}, $\nu_3(A_1)$ or $\nu_6(E)$, or both. One can reproduce the general features of the spectra in Fig. 1 for atmospheric sulfate by mixing ammonium sulfate and sulfuric acid in various proportions, but the relative intensities of the bands are not in good agreement with those observed for the at-

Table 1. Summary of data pertaining to the samples for which spectra are shown in Fig. 1; ppm, parts per million.

Curve in Fig. 1	Sample information			Related environmental information* (averaged over sampling time)					
				Wind					
	Time sample collection started	Sample weight (μg)	Degree of acidity	Speed (km/hour)	Direction (deg)	Relative humidity (%)	SO_2 concentration (ppm)	CO concentration (ppm)	Coefficient of haze
a	20:00	443	Neutral	13.5	206	44	0.010	9.0	0.44
b	23:00	662	Weak	12.6	208	51	0.002	7.9	0.64
c	02:00	782	Weak	11.3	203	55		7.4	0.83
d	05:00	808	Moderate	12.8	205	53	0.010	9.7	1.29
e	08:00	543	Strong	22.6	210	44	0.010	8.8	1.20
f	11:00	444	Very strong	23.8	213	32	0.040	8.8	1.37
g	14:00	626	Very strong	24.5	204	30	0.020	9.0	0.87
h	17:00	516	Very strong	19.6	201	34	0.008	8.8	0.75
i	20:00	769	Strong	15.0	196	43	0.005	8.4	0.76
j	23:00	799	Strong	15.2	192	44	0.007	8.3	0.95
k	02:00	805	Moderate	13.3	199	47	0.008	6.6	1.09
l	05:00	913	Weak	13.9	187	49	0.006	9.3	1.48
m	08:00	802	Weak	17.2	211	45	0.024	9.3	1.54
n	11:00	360	Moderate	22.0	219	36	0.030	8.6	1.38
o	14:00	419	Strong	23.4	218	33	0.031	9.0	0.94
p	17:00	516	Moderate	21.3	206	37	0.011	8.6	0.68
q	20:00	584	Neutral	14.3	191	44	0.010	8.7	0.82

*Wind data are representative of the flow over the Chicago area. Relative humidity was measured at the sample collection site. Pollution parameters were obtained from the Chicago Air Sampling Network and are representative of conditions at the sampling site. There was no precipitation during the sampling period.

mospheric samples. We have found, however, that the spectra of aerosols created by bubbling clean air through dilute ammonium sulfate–sulfuric acid mixtures very closely reproduce the spectra of the atmospheric samples. A comparison of the spectra of atmospheric samples with spectra obtained with synthetic samples has led us to conclude that the weak bands at 1118 and 675 cm^{-1} are present when the sample is more acidic than ammonium bisulfate, that is, when the sample consists of a mixture of ammonium bisulfate and sulfuric acid.

Thus, the variations observed in the infrared spectra of samples of submicrometer-sized particles provide a sensitive indication of the degree of acidity of these particles and show that acidity may vary continuously over a wide range. At present, we can make only qualitative assessments of the acidity of atmospheric particulates (see Table 1). The absorbance of the acid sulfate bands is significantly different from the absorbance of corresponding bands in neutral sulfate and appears to vary with the degree of acidity. Thus, although absorbance measurements are used to determine neutral sulfate with reasonable accuracy in the range from about 5 μg to several hundred micrograms (as ammonium sulfate), absorbance cannot be used at present for the determination of acid sulfate because of the unreliability of standards for acid sulfate. Furthermore, effects that may be produced by collection of the sample are not easily assessed (*12*).

The specific occurrence of acid sulfate described above came near the end of a 9-day sampling period during an interval of moderate south-southwesterly winds over the Chicago area (see Table 1) such that our sampling site was downwind of an extensively developed industrial and commercial section of the city. Although the loading of atmospheric particulate in the submicrometer size range was quite high, sulfur dioxide concentrations and other indicators of air pollution were not unusual during the sampling period. The earlier part of the sampling period was characterized by light north-northwesterly winds with loadings of submicrometer-sized particulates typically resulting in sample weights in the range from 50 to 300 μg. The spectra of these samples show that, in addition to moderate to slight amounts of ammonium sulfate, significant amounts of hydrocarbon (as determined by the carbon-hydrogen stretching bands mear 2860 and 2920 cm^{-1}) were present. Hydrocarbon was not observed in the spectra of the samples containing acid sulfate (see Fig. 1), nor, as a rule, has it been observed in our other acidic samples.

Furthermore, as indicated in Table 1, the onset of acidity has been observed during both nighttime and daylight hours, with the frequency of occurrence of acid sulfate in all of our Chicago samples about equally divided between the two periods. In addition, although acid sulfate is most often observed during periods when the loading of submicrometer-sized particulates is high, strong acidity has been noted occasionally when the loading is low.

The occurrence of acid sulfate in urban Chicago is not infrequent. During the past 2 years, we have collected and analyzed over 250 samples from the city and have observed some degree of acidity 21 percent of the time. In the heart of the city acid was present in 33 percent of the samples, whereas at the University of Chicago, about 10 km south of the center of the city, acid was present in 11 percent of the samples. In both locations, temporal variations in the degree of acidity have been such that consecutive samples, each collected over a 3-hour sampling period, have changed from strongly acidic to neutral ammonium sulfate and vice versa.

We observed acid sulfate in about 8 percent of the samples collected at a site located approximately 13 km north-northwest of downtown St. Louis during a 24-day sampling period in August 1974. This incidence of acid sulfate is somewhat less than that reported by Charlson *et al.* (*3*), but differences in sampling location and dates of collection are too great to permit reliable comparison. The spectral characteristics of the acid sulfate observed in St. Louis and Chicago are very similar.

It is difficult to refrain from speculating about what these observations may indicate regarding the mechanism of formation of particulate sulfate. Certainly, if one accepts the premise that acid sulfate is a younger aerosol than neutral sulfate, it seems clear that reactions taking place during the night must be responsible for at least some sulfate formation although samples with a higher degree of acidity are observed during daylight hours, an indication that photochemical processes or a photochemically produced precursor may be involved. Less surely, the steady wind conditions that prevailed during the period of acidity described here and the general nature of the temporal and spatial variations in the degree of acidity suggest that the chemical reactions producing and neutralizing acid sulfate take place to a significant extent on a time scale of a few hours. The strong negative correlation between acid sulfate and hydrocarbon would appear to suggest either that hydrocarbon inhibits sulfate formation in some way or that the hydrocarbon species are too volatile in an acidic medium to remain associated with the acid sulfate particulates. Finally, as has been suggested by others (*13*) on the basis of an apparent upper limit for sulfate concentration in the atmosphere, the observation that the occurrence of acid sulfate is not closely linked with high concentrations of sulfur dioxide suggests that the formation mechanism is one in which other factors control the rate of sulfate formation.

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10. The building, located at 320 North Clark Street, is in a highly developed commercial area and is surrounded by structures of both greater and lesser height. Local meteorological measurements are highly influenced by these structures and do not accurately reflect the general movement of air masses over the city.
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12. The most important effects produced by impactor collection probably involve reactions between particles and changes in water content. Our samples clearly indicate that, in many cases, especially when the relative humidity is high, recrystallization of the sample occurs on the impaction surface; and, on analysis of the sample, its water content is presumably less than that of the ambient aerosol. On the other hand, reaction of the impacted sample with ammonia or sulfur dioxide in the air appears to be less of a problem than for filter samples.
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Early Irradiation of Matter in the Solar System: Magnesium (Proton, Neutron) Scheme

Abstract. *The occurrence of positive and negative* ^{26}*Mg anomalies in inclusions of the Allende meteorite is explained in terms of proton bombardment of a gas of solar composition. A significant fraction of* ^{26}*Mg in the irradiated gas is stored temporarily in the form of radioactive* ^{26}*Al by the reaction* ^{26}*Mg(p,n)*^{26}*Al. Proton fluxes of* 10^{17} *to* 10^{19} *protons per square centimeter per year at 1 million electron volts are inferred. Aluminum-rich materials condensing from the gas phase have positive* ^{26}*Mg anomalies, whereas magnesium-rich materials have negative* ^{26}*Mg anomalies. The proton flux required to account for the observed magnesium anomalies is used to investigate possible isotopic anomalies in the elements from oxygen to argon. Detectable isotopic anomalies are predicted only for neon. The anomalous neon is virtually pure* ^{22}*Ne from* ^{22}*Na decay. The predicted amount of anomalous* ^{22}*Ne is about* 10^{-8} *cubic centimeter (at standard temperature and pressure) per milligram of sodium.*

Gray and Compston (*1*) and Lee and Papanastassiou (*2*) have reported isotopic anomalies of Mg in inclusions of the Allende meteorite. Their observations are enigmatic because ^{26}Mg is sometimes enriched and sometimes depleted relative to ^{25}Mg. These investigators have presented ingenious explanations for their results. Following the suggestion of Gray and Compston (*1*), we will briefly consider the possible effects of proton bombardment. We believe that it is much too early to rule out any viable idea.

Protons in the energy range of galactic cosmic rays are undoubtedly capable of changing the isotopic composition of Mg by spallation in Al and Si. Judging from the well-studied system Ne-Na-Mg (*3*), one predicts that such protons will always lower the ^{24}Mg/^{26}Mg ratio, will leave the ^{25}Mg/^{26}Mg ratio virtually unchanged in Si-rich systems, and will perhaps decrease the ^{25}Mg/^{26}Mg ratio in Al-rich systems. However, one must posit vast numbers of galactic protons, on the order of 10^{21} to 10^{22} proton cm^{-2} with assumed cross sections σ of 10 millibarns, to account for the observed effects (*1, 2*). Depletion of ^{26}Mg is virtually ruled out. From this reasoning we conclude that protons in this energy range are not the cause of the observed Mg anomalies.

The effects of protons of intermediate energy, say 10 to 100 Mev, are difficult to evaluate at this time because of the plethora of possible reactions in Mg, Al, and Si for which cross sections are unknown. Below 10 Mev the number of possible reactions in these elements becomes much smaller, and (p,n) and (p,^{4}He) reactions are probably the most important ones. Here we will consider only (p,n) reactions in Mg. Reactions such as ^{27}Al(p,^{4}He)^{24}Mg and ^{26}Mg(p,^{4}He)^{23}Na, which have Q_m values (the mass threshold of a nuclear reaction, that is, the positive or negative change in mass between reactants and products) of +1.6 and −1.8 Mev, respectively, must eventually be considered.

The (p,n) reactions in the stable isotopes of Mg are "cyclic" as the reaction products ^{24}Al, ^{25}Al, and ^{26}Al decay by β^+ emission to the target nuclides from which they had been formed. If the radiation remains unchanged for periods longer than the mean lifetime of ^{26}Al, about 10^6 years, a steady state is reached after a few million years in which constant fractions of each of the stable Mg isotopes are "stored" temporarily in the form of their respective radioactive Al-precursors. Because of the very short mean lifetimes of ^{24}Al and ^{25}Al (3.0 and 10.4 seconds, respectively), the fractions of ^{24}Mg and ^{25}Mg so stored are negligibly small. Because of the cyclic nature of the (p,n) reactions, irradiation of solid grains containing Mg and Al does not result in isotopic anomalies in Mg, as all of the ^{24}Mg, ^{25}Mg, and ^{26}Mg atoms that are stored temporarily in ^{24}Al, ^{25}Al, and ^{26}Al are eventually (after a significant number of ^{26}Al half-lives) restored to the system.

We will consider therefore the effects of the irradiation of a "dust-free" gas (or plasma). When, after several million years, equilibrium is reached, the ^{26}Al/^{26}Mg ratio in the gas phase depends only on the proton spectrum and the excitation function ^{26}Mg(p,n)^{26}Al, which has a Q_m value of about 5 Mev (*4*). The ^{26}Al/^{27}Al ratio at equilibrium depends also on the Mg/Al abundance ratio in the gas phase, which we assume here to be 0.1, the solar value (*5*).

For the calculations we have assumed that the (differential) proton spectra are of the form $dF/dE = kE^{-\gamma}$, where dF/dE is the differential proton flux between E and $E + dE$ (in protons per square centimeter per year); k is a normalization constant; E is the kinetic energy of the protons (in millions of electron volts); and γ is a parameter representing the steepness of the energy distribution. We have used γ values of 2.5, 3.5, and 4.5, which cover present-day galactic cosmic protons and a substantial range of known γ values in present-day solar flares (*6*). The σ values for ^{26}Mg(p,n)^{26}Al were taken from Furukawa