

Major surprises and departures from the models developed here may occur, and indeed might be expected on the basis of earlier experience. Theoretical models for the martian ionosphere failed totally to account for the initial data obtained by Mariner 4 (13). If the models for Jupiter suffer a similar fate at the hands of Pioneer 10, we may look forward to an exciting era in an expanded arena of planetary aeronomy.

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Sulfuric Acid-Ammonium Sulfate Aerosol: Optical Detection in the St. Louis Region

Abstract. *Nephelometric sensing of the deliquescence of ammonium sulfate produced by the reaction of sulfuric acid or ammonium bisulfate aerosol with ammonia provides a means for detecting these substances in air. Field experiments show them to be the dominant substances in the submicrometer, light-scattering aerosol in the St. Louis region.*

Atmospheric H_2SO_4 aerosol, present as droplets of the acid and its products of neutralization with NH_3 mixed with other substances, have proved to be difficult to detect and quantify by traditional air-sampling methods (1). Knowledge of the existence of these compounds is important for an understanding of the natural sulfur cycle, atmospheric optics, acid rain, and health effects due to air pollution. Almost all the sulfate data in existence today are for the anion alone and provide no information regarding the attached cation. Nonetheless, the important properties of sulfates (toxicity, water solubility, refractive index, particle state and shape, and acidity) depend on the molecular composition and not on the anion alone. The recent CHES (Community Health and Environmental Surveillance System) report (2), linking SO_4^{2-} with effects on health, cannot be adequately understood unless the molecular forms of the compounds are known. Furthermore, control of the SO_4^{2-} may depend on the molecular form.

Not least among the analytical problems is the reactivity of H_2SO_4 with

or on sampling surfaces and with NH_3 to which the sample is probably exposed when handled. As a result, it is attractive to consider in situ methods of analysis which do not require the removal of particles from the air.

Our purposes in this report are to describe a method for sensing aerosols of H_2SO_4 , NH_4HSO_4 , and $(NH_4)_2SO_4$ and to present atmospheric data taken in and near St. Louis, Missouri. The basic apparatus, a humidograph (3), measures the dependence of the light-scattering coefficient of the particulate matter (b_{sp}) on the relative humidity (RH). This system can be operated with the injection of a few parts per million of NH_3 into the sample flow, causing the reaction of H_2SO_4 and NH_4HSO_4 to form $(NH_4)_2SO_4$. Both H_2SO_4 and NH_4HSO_4 aerosols exhibit a monotonic humidogram (the curve of light scattering versus humidity) in which b_{sp} increases continually with increasing RH as a result of the hygroscopic nature of these materials. The $(NH_4)_2SO_4$ humidogram, however, has an inflection point at about 80 percent RH owing to its deliquescent property (4). Aerosol particles of a deliquescent salt remain

Table 1. Effect of NH_3 addition on the ambient air humidogram.

Category	Location and date			
	Tyson Hollow, 21 to 27 September 1973 (88 pairs of measurements)*		St. Louis University, 27 September to 2 October 1973 (258 pairs of measurements)*	
	Number of mea- surements	Percent- age of total	Number of mea- surements	Percent- age of total
Category A: Monotonic before addition of NH_3 ; NH_3 caused an inflection at about 80 percent RH	46	52	22	8.5
Category B: Inflection at about 80 percent RH prior to NH_3 addition; NH_3 enhanced the inflection	22	25	5	1.9
Category C: Inflection at 80 percent RH; no change with NH_3 addition	19	22	64	24.8
Category D: Monotonic curve; no effect with NH_3 addition	1	1	167	64.8

* Not all measurements are included here owing to the fact that a measurement of the effect of the addition of NH_3 was not carried out after each ambient measurement.

dry if the RH is less than that over the saturated salt solution and grow suddenly to solution droplets when the RH exceeds this value, causing a sudden increase in b_{sp} , followed by an inflection point in the humidogram. If $(\text{NH}_4)_2\text{SO}_4$ is present as 30 to 50 percent or more of the mass of submicrometer particles, an inflection point can be seen; however, if it is only a trace constituent, the humidogram is dominated by other substances.

To our knowledge, no substances other than the two acid sulfates could (i) form an aerosol at normal conditions, (ii) be found in normal air as a major fraction of the submicrometer particles, (iii) have a monotonic humidogram before the addition of NH_3 , and (iv) have an inflection point at 80 percent RH after reaction with NH_3 .

The light-scattering technique does not make it possible to sense all particle sizes equally because of the dominance of particles 0.1 to 1.0 μm in diameter in this optical process (5). Fortunately, most products of the conversion of gas to particles in air accumulate in this size range (6), so SO_4^{2-} from SO_2 oxidation is normally found in the same range of particle sizes sensed by light scattering.

This system was operated at one rural and two urban sites in and near St. Louis between 22 August and 5 October 1973, with NH_3 addition after 21 September. The Washington University site, 12 km west of the Arch, is located in a college-residential area on a soccer field, whereas the St. Louis University site, 3 km west of the Arch, is much closer to the congested central city and nearby industry. The rural site at Tyson Hollow, 35 km west-southwest of the Arch at an altitude of about 200 m, receives air from the city with north to east winds and air from sparsely populated areas with other wind directions. Humidograms were made automatically every half hour and more frequently when NH_3 was used.

The data with no NH_3 addition showed an inflection point at about 80 percent RH between 25 and 41 percent of the time, regardless of the site, an indication that the submicrometer particles were frequently rather pure $(\text{NH}_4)_2\text{SO}_4$. Table 1 shows the effects of NH_3 addition on the humidogram, and the four categories of response are illustrated in Fig. 1. The response of pure H_2SO_4 is nearly identical to that of category A.

We conclude from these data that

the aerosol is totally dominated by SO_4^{2-} at Tyson and is strongly influenced by SO_4^{2-} at the other sites. For about 50 percent of the measurements at Tyson, the substance was not deliquescent until NH_3 was added, thus indicating a substantial fraction present as H_2SO_4 or NH_4HSO_4 .

Estimates of the submicrometer mass concentration of SO_4^{2-} may be made from the light-scattering coefficient (5), and the fraction of SO_4^{2-} may be estimated from the humidogram, both of which may be compared to mass and chemical determinations by other means. Between 1015 C.D.T. on 30 August and 0915 C.D.T. on 31 August

1973 at Washington University, the mass concentration smaller than 2 μm was determined by other workers with a size-segregating sampler and subsequently analyzed for various elements by x-ray fluorescence (7). The light-scattering coefficient at 525 nm was $1.2 \times 10^{-4} \text{ m}^{-1}$, corresponding to a submicrometer mass concentration of about 40 $\mu\text{g}/\text{m}^3$. The measured mass concentration smaller than 2 μm was 26 $\mu\text{g}/\text{m}^3$ (7). We estimate that about 30 to 50 percent (or 10 to 20 $\mu\text{g}/\text{m}^3$) of the aerosol was $(\text{NH}_4)_2\text{SO}_4$ from the observation that during this period the humidograms had a consistent and repeatable inflection point at about 80 percent RH. The concentration of sulfur (as the element), determined from x-ray fluorescence, was $3.1 \pm 0.7 \mu\text{g}/\text{m}^3$, which was the highest concentration of any element (7). This amount of sulfur corresponds to $13 \pm 3 \mu\text{g}/\text{m}^3$ as $(\text{NH}_4)_2\text{SO}_4$, which compares favorably with the estimate from the humidogram.

This method can be further quantified if repetitive humidograms are used to indicate the end points in a gas-phase titration with NH_3 . A preliminary uncalibrated experiment showed that a small flow of NH_3 could be added without causing an inflection point to appear. The addition of more NH_3 created an inflection point, and the addition of still more caused the inflection point to be enhanced. The first end point (corresponding to the depletion of H_2SO_4) occurs when the humidogram first shows an inflection point, and the second occurs where it exhibits no further enhancement with increased NH_3 flow. This aerosol-phase titration depends only on the ability to detect an inflection point in the humidogram and not on a correlation of the light-scattering coefficient with mass.

These observations not only show that H_2SO_4 and its neutralization products with NH_3 exist and often dominate the submicrometer aerosol in and near St. Louis, but also they suggest that these substances are normal intermediates in the cycling of sulfur through the atmosphere. Moreover, the lack of dependence of composition on wind direction or synoptic condition suggests that these substances are regionally distributed and are not an urban entity. At Tyson, for example, humidograms for stale city air were not systematically different from those for rural air. This finding is in agreement with studies of the ratio of SO_2 to SO_4^{2-} (8) and with the lack of varia-

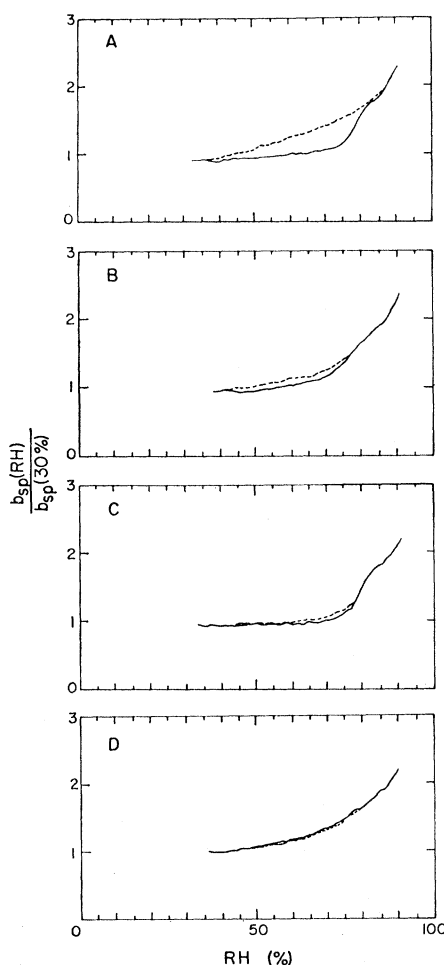


Fig. 1. Four classes of humidograms from Table 1. (Dashed curve) Before NH_3 addition; (solid curve) after NH_3 addition. (A) Monotonic (hygroscopic) curve; NH_3 caused an inflection point at 80 percent RH (deliquescence): 23 September 1973, 1208–1219 C.D.T., Tyson. (B) Inflection point at 80 percent RH enhanced by NH_3 addition: 21 September 1973, 2030–2047 C.D.T., Tyson. (C) Inflection point at 80 percent RH and no or little enhancement caused by NH_3 addition: 24 September 1973, 2245–2303 C.D.T., Tyson. (D) Monotonic curve unaffected by NH_3 addition: 28 September 1973, 0500–0518 C.D.T., St. Louis University.

tion in the concentration of sulfur compounds taken with a 2-hour sequential sampler (9).

We cannot now state quantitatively how much of the SO_4^{2-} aerosol is natural; however, on the basis of the known source strengths of sulfur compounds in this region, it seems likely that human sources of SO_2 dominate. The sources of SO_2 (mainly fossil-fuel power plants) are located on a spatial scale of from 10 to 100 km in Missouri and the surrounding states. The removal distance for SO_2 and its oxidation products is of the order of 1000 km (10), so that any site in the region is continually under the influence of a large number and variety of sources.

It is intriguing to speculate that these compounds, which dominate the light-scattering hazes in eastern Missouri, may also extend to the entire Midwest. Such visible, turbid air is noted in summer from perhaps Topeka, Kansas, to the East Coast and from Chicago, Illinois, to Little Rock, Arkansas (11), and only really disappears with massive intrusions of Canadian air in winter. Until more studies of these acid aerosols are available, their real and potential effects can only be matters for speculation. The utility of control strategies for particulate matter in cities [including sulfates, which are alleged to have effects on health (2) and which may be mainly regional and not urban] will be even less certain than the preliminary results presented in this report (12).

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Dexamethasone Stimulation of Murine Mammary Tumor Virus Expression: A Tissue Culture Source of Virus

Abstract. *In mouse cell lines derived from mammary adenocarcinomas, the synthetic steroid dexamethasone stimulates production of murine mammary tumor virus. Viral RNA and antigens are increased as much as 20-fold, and culture fluid supernatants from steroid-treated cells contain type B particles with reverse transcriptase. These cells provide a possible tissue culture source of this virus and a model system for studying the mechanism of action of corticosteroids and the regulation of transcription of integrated viral DNA.*

Studies on the etiology of mammary tumors have relied largely on the mouse model system in which the murine mammary tumor virus (MMTV), an RNA-containing virus with a reverse transcriptase, is an important factor in naturally occurring mammary adenocarcinomas (1). Expression of MMTV in mouse tissues other than mammary glands is frequently recognized (2), and virus production in vivo is generally associated with epithelial tissues. In an effort to study the virus-cell interaction in greater detail, several cell lines that are derived from spontaneous mouse mammary tumors and contain relatively low levels of MMTV have

been established (3-5). We found that clonal cell populations from one of these MMTV-positive tumor cell lines (CCL-51) had markedly different amounts of MMTV RNA and virion protein, but comparable amounts of MMTV DNA as measured by nucleic acid association reactions (6). These results and the widespread presence of MMTV DNA in different mouse strains (7, 8) suggested that although MMTV was present in all murine cells, its expression might be regulated by cellular control mechanisms acting at the level of MMTV RNA transcription from DNA.

In addition to the virus, a second

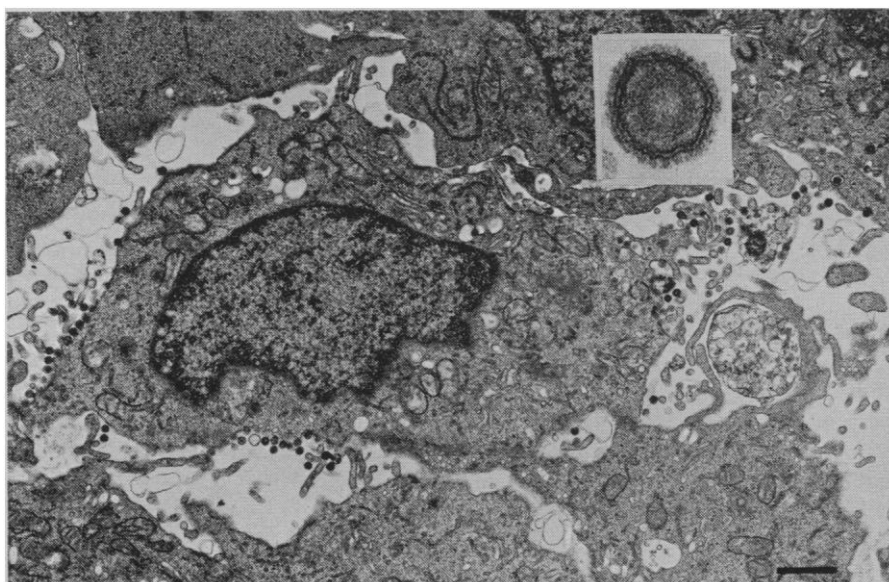


Fig. 1. Electron photomicrographs of dexamethasone-treated L8A Cl 11. Cells treated with dexamethasone for 72 hours were processed as described (18). Many type B particles are seen associated with the plasma membrane, apparently having completed the budding process. Intracytoplasmic type A particles were rare. Typical MMTV surface projections are seen on the particle in the inset. Bar, 1 μm ; inset, $\times 115,000$.