CHAPTER VI.

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I. GENERAL CONSIDERATIONS

At the present time, air pollution measurements are made by many analytical methods involving numerous analytical parameters and techniques. The data generated from these analyses are used by various researchers, Federal, State and local agencies, industry, and others to make very important, and oft times very expensive, decisions in the field of air pollution control. In general, the data are used to:

- Evaluate trends in environmental quality as necessary to assess the effectiveness of pollution abatement programs,
- Identify problem areas requiring stricter pollution control regulations and other remedial actions,
- Identify compliance with and violations of ambient environmental quality standards and source emissions standards,
- Characterize the health, ecological and economic effects of specific pollutants entering and in the environment; trace the interaction, movement, and fate of specific pollutants entering and in the environment (i.e., research monitoring).

Without the assurance that the measurements obtained truly describe the existing condition under observation, the validity of any conclusion must remain doubtful. Typical of questions asked during decision making processes are:

(1) Are the data valid?

(2) What method was used to collect the data?

(3) What is the interrelatability between various methods?

(4) Can I compare data from one study with data from another study if the methodology was different?

(5) Was the method calibrated correctly?

(6) What air monitoring instrumentation should be purchased to measure pollutants to determine compliance with implementation plans?

Other numerous specific questions could be presented, but the one main concept to be remembered is that any decision based on ambient air monitoring data, whether it be in the field of air quality management, standard setting, compliance, enforcement, or criteria development, is only as good as the validity of the data used to make the decision.

Attacking this area of the usefulness and interrelatability of air monitoring data is not a simple problem. The EPA has recognized this problem for at least the six criteria air pollutants and has developed its proposed equivalency regulations to help solve this problem (attachment O).

Future monitoring research activities should probably be directed toward the development and thorough laboratory and field evaluation of analytical methods capable of analyzing specific air pollutants at very low concentrations. Wherever possible, continuously monitoring instrumentation and techniques are desirable. However, the resource requirements of continuous monitors, (both in man-years of effort and dollars) may not always permit the use of continuous monitors, especially for a large network operation. In addition, there may not be a need for continuous data during a specific project. Hence, there will always be a need for well-defined integrated methods which collect periodic samples for later analysis.

II. ANALYTICAL METHODOLOGY

The current status of ambient air monitoring technology is the subject of several recent review articles. These articles briefly address the various types of pollutant monitors available for the analyses of pollutants present in the ambient air or emanating from stationary and mobile sources. The analytical principle behind the monitoring system is also discussed and the commercial sources are listed. It is not the intent of this conference to go into great detail about the various analytical instruments and methods available so these review articles are appended and appear as attachments 1, 2, 3, and 4 to this paper.

It is the intent of this conference to address the biological effects of salts and oxides of sulfur and nitrogen and the rest of the analytical considerations will be directed toward these substances.

A. Sulfur Compounds

Forest and Newman (attachment 5) have prepared a critical review of ambient air monitoring for sulfur compounds. Hollowell, et.al. (attachment 6) discusses the current instrumentation available for continuous monitoring of SO_2.

1. Sulfur Dioxide:

The problem of interrelatability of air monitoring data collected by different people employing different analytical techniques is best exemplified by sulfur dioxide monitoring activities. At present there are over 60 sulfur dioxide monitors available from 30 instrument manufacturers involving 13 distinctly different principles of operation. It is difficult enough to interrelate data from different laboratories using the same analytical principle much less different laboratories using different principles of operation. Until the results of the EPA "equivalency program" are available, one should always proceed with caution when interchangeably using data from different studies. The analytical principles behind the various SO_2 continuous monitors involve electro-conductivity, colorimetry, coulometry (amperometric), electrochemical transducers, flame photometry, or flame photometry-gas chromatographic systems, non-dispersive spectrometry, dispersive absorption spectrometry, correlation spectrometers, second-derivative spectrometers, condensation nuclei counters, and several newer techniques still under investigation such as mass spectrometry, chemiluminescence, and a combination of mercury substitution-X radiation. Newer techniques still under study are some laser techniques, Raman scattering techniques, microwave spectroscopy, and Fourier-transform spectroscopy.

For periodic sampling of SO_2, two methods have been most widely used. These are the West-Gaeke colorimetric procedure and the relatively non-specific hydrogen peroxide method. All of the data collected by the National Air Surveillance Network was collected by the West-Gaeke procedure.

2. Total Particulate Sulfate:

No instrumentation for continuously monitoring total particulates sulfate is commercially available. The usual approach is to collect the sulfate on one of various available filters followed by chemical analysis by any one of a variety of chemical methods. The great body of sulfate data collected by the NASN was obtained using glass fiber filters followed by analysis using the methylthymol blue procedure. The glass fiber filter are efficient, inert, and have small pressure drops across them but usually contain large amounts of residual sulfate that can be reduced by prewashing. Additionally, numerous investigators have shown that glass fiber paper has the tendency to absorb SO_2 due to its alkalinity and convert part or all of it to sulfate during the course of sampling. The amount of sulfate formed seems to vary with sampling time as well as manufacturer, grade, pretreatment of filters, etc. A blank correction is always necessary when running sulfate analyses on particulate samples collected on glass fiber filters. (See attachment 7).

As stated before, the NASN uses the methylthymol blue method of analysis for sulfate. The various CHESS studies historically used the turbidimetric procedure and switched to the methylthymol blue method in September 1971. At that time analysis of the same sample by the two methods gave results in agreement with each other within the realm of experimental error.

In the turbidimetric procedure, an aqueous extract of the sample is treated with barium chloride in the presence of Sulfaver, a stabilizing agent, forming barium sulfate crystals of uniform size. The absorbance of the barium sulfate suspension is measured by a spectrophotometer or filter photometer. The sulfate ion concentration is determined by comparison to a previously determined standard calibration curve.

In the automated methylthymol blue procedure for sulfate, the filter extract sample is first passed through a cation-exchange column to remove interferences. The sample containing sulfate is then reacted with barium chloride at a pH of 2.5-3.0 to form barium sulfate. Excess barium reacts with methylthymol blue to form a blue-colored chelate at a pH of 12.5-13.0. The uncomplexed methylthymol blue color is gray; if it is all chelated with barium the color is blue. Initially, the barium chloride and methylthymol blue are equimolar and equivalent to the highest concentration of sulfate ion expected; thus the amount of uncomplexed methylthymol blue, measured at 460 nm, is equal to the sulfate present.

3. Sulfuric Acid:

The analysis of sulfuric acid aerosol in the presence of SO_2, SO_3, other particulate sulfates, and other probably interfering pollutants such as ammonia is a very complex problem. To date, commercial instrumentation for routine monitoring of sulfuric acid aerosol has not been developed. Numerous manual methods involving filtration followed by either chemical or microscopic analysis have been presented but no one method has gone unchallenged or is generally acceptable by the scientific community. The limitations of the various methods are adequately described in attachments 5 and 8.

4. Nitrogen Dioxide:

It is now a well-known fact that the Federal Reference Method for NO_2, the Jacobs-Hochheiser method, has been found to be totally unacceptable for use. Unfortunately, when the Air Quality Criteria Document for nitrogen oxides was issued there was no acceptable method for demonstrating the equivalency of two or more measurement methods. The two most frequently utilized measurement methods were the continuous Griess-Saltzman method and the Jacobs-Hochheiser method which utilized a 24-hour bubbler system. Both methods were internally consistent but they did not agree well with each other. Because the National Air Sampling Network and a series of key health studies utilized the cheaper Jacobs-Hochheiser 24-hour bubbler method, this method was designated as the Federal Reference Method for nitrogen dioxide measurement. Unfortunately, when adequate nitrogen dioxide permeation tubes became available, our laboratories found that the Federal Reference Method was not acceptable because of a variable collection efficiency. This finding required that the Agency designate acceptable monitoring methods and to reassess the primary ambient air quality standard for nitrogen dioxide, the air monitoring data base for our Air Quality Control Regions, the emissions standards for light duty motor vehicles and the need for control of nitrogen oxide emissions from stationary sources.

When the original Federal Reference Method was retracted, three tentative candidate methods were proposed to serve during an interim period while all candidate methods were being thoroughly evaluated. These candidate methods are the continuous chemiluminescent method, the continuous Griess-Saltzman method and the 24-hour arsenite bubbler method. The latter two methods depend upon the same diazotization reaction but differ in the pH of the collection media, the elapsed time prior to analysis and the use of a stabilizing agent. The present

Air Quality Standard for nitrogen dioxide is based upon an annual average pollutant concentration and both continuous and short-term integrated methods (e.g., 24-hour bubbler methods) can be used to demonstrate achievement of the annual standard. However, if an air quality standard based on shorter term exposure is adopted, then a continuous monitoring method will be needed to measure compliance. In that case the 24-hour bubbler methods, which are cheaper and easier to operate, can be used to identify problem areas requiring continuous monitors and to satisfy some implementation plan needs.

Let me briefly summarize our current information about the measurement of nitrogen dioxide. First, the recently retracted Federal Reference Method which assumed a constant collection efficiency of 35 percent is not tenable because the true collection efficienncy is very high at low concentrations of nitrogen dioxide and quite low at high concentrations. Since nitrogen dioxide concentrations may vary a great deal during the 24-hour sampling period, there is no easy way to adjust for a variable collection efficiency over a 24-hour sampling period. Ignoring the latter problem, the usual result of the variable collection efficiency error would be to underestimate the true exposures at concentrations greater than 120 $\mu g/m^3$ and overestimate exposures at lower levels. In general, the shape of the collection efficiency curve suggests that the overestimation problem would be more severe. Another problem is that nitric oxide has proven to cause a significant positive interference with the retracted method.

Our laboratories are evaluating five other measurement methods including the three tentative candidate methods previously mentioned. This evaluation should allow our Agency to designate a scientifically defensible measurement method and to relate that method to the continuous Saltzman method and to the arsenite bubbler method. The latter task is necessary because the Saltzman method was employed in many of the health studies upon which the primary standard was based and because the major portion of our meager national air monitoring data base depends upon the arsenite method. In brief, it seems that the continuous Saltzman method may have problems in that measurements at low ambient concentrations are unreliable and ozone exerts a worrisome negative interference. A number of investigators outside of government disagreed with us and feel that the Saltzman method is quite reliable. The arsenite bubbler method has a stable 85 percent collection efficiency over a wide-range of nitrogen dioxide concentrations. However, interferences caused by gases commonly present in urban air handicap this method: carbon dioxide causes a positive interference and nitric oxide a negative interference. These worrisome interferences vary depending on the absolute concentrations of the interfering gases and the ratio of their concentration to that of nitrogen dioxide. The triethanol amine guaicol sulfite (TGS) method appears quite promising even though it is not one of the three proposed candidate methods. The TGS method has a stable 93 percent collection efficiency. No interferences caused by ambient pollutants have been identified and the collection media has good stability after sampling. The continuous chemiluminescent method avoids many of the problems inherent in wet chemical procedures but most instruments thus far evaluated either suffer from early production problems or require highly qualified field operators. However, the chemiluminescent approach retains a great deal of promise. To establish a new reliable reference method which is properly standardized and field tested will require another year with collaborative field testing occupying the last six to nine months.

5. Particulate Nitrate:

Many of the same type problems associated with the analysis of particulate sulfate are applicable to the analysis of particulate nitrate. The particulate nitrate can be collected on any of a number of various filter media and subsequently analyzed by any one of a variety of chemical methods. The NASN employs a glass fiber filter to collect the particulates, including the nitrates and then analyzes the nitrate by the hydrazine reduction method. Essentially the water soluble nitrate ions are reduced to nitrite ions. The nitrite ions formed are then used to diazotize an aromatic amine which is then reacted with a coupling reagent to form an azo dye that is analyzed colorimetrically. This is essentially the same reaction used to analyze NO_2 in the ambient air.

III. PARTICLE SIZE OF PARTICULATE SULFATE AND NITRATE

Measurement of the concentration and particle size distribution of atmospheric sulfate, nitrate, chloride, phosphate, and ammonium ion have been reported by Lee and Wagman (attachments 9 and 10) in Cincinnati, Chicago, Fairfax (Ohio) and Philadelphia. The results indicate that the average sulfate mass median diameter were nearly equivalent (0.42μ) for Cincinnati, Fairfax and Chicago despite large differences in sulfate concentration and heterodispersity. A slightly higher MMD (0.62μ) was noted for Philadelphia. In general the MMD for sulfate increased with increasing relative humidity.

Nitrate, chloride, and ammonium ions present in particulate matter were predominately associated with sub-micron particles while the MMD of the phosphate particles was greater than 3μ.

Lundgren (attachment 11) collected particles from the air at the Riverside Campus of the University of California. The average MMD found for sulfate was 0.3μ (range 0.1-0.6) and for nitrate was 0.8μ (range 0.6-1.8). These observations essentially agree with previous data presented by Lee and Wagman. Additionally, Lundgren demonstrated a strong relationship between gaseous PAN, particulate nitrate, and aerosol light scattering. High concentrations of ammonium nitrate particles, mainly in the 0.5-2μ diameter size range were found in the atmospheric particulate samples collected on days of very high smog (very limited visibility). This seems to agree with the report of Gordon and Bryan (attachment 12) that ammonium sulfate comprises approximately 10-15 percent of the total air-borne particles in samples collected in Los Angeles during 1971-1972.

Lee, et.al. (attachment 13) collected particulates in hot, concentrated automobile exhaust as well as in cold diluted exhaust. Most of the sulfate, nitrate, chloride, and lead were found in particles predominately sub-micron in diameter. The particle size distributions of sulfate and nitrate were dependent on engine operating conditions with the particle size decreasing with increasing road speed and exhaust temperatures.

IV. MONITORING DATA

A. Trend Data

The volume of aerometric and emission data available in the National Aerometric Data and Emission Banks prohibits their total inclusion in this paper. Requests for any data included in the banks can be made to the Monitoring and Data Analysis Division, OAWP, EPA, Research Triangle Park, N. C. 27711 - attention Mr. Robert Neligan. Attachment 14 represents the first annual report on air quality and emission trends. A quick examination of the report yields the following.

Figure 4-1 on page 4-4 gives the nationwide emissions for HC, CO, NO_x (1940-1970).

Figure 4-2 on page 4-4 gives the nationwide SO_2 emissions for SO_2 (1940-1970).

Figure 4-10 on page 4-15 - composite annual means of SO_2 at 32 NASN stations.

Figure 4-11 on page 4-15 - composite average maximum daily SO_2 concentrations at 32 urban NASN stations.

Figure 4-12 and 4-13 on page 4-19 - Regional companions for annual average and daily maximum SO_2 concentrations.

Figure 4-15 through 4-17 gives trend lines for NO, NO_2, and NO_x at CAMP sites.

The air quality data from the NASN and contributing state and local networks for SO_2 for the years 1969-70-71 appears as attachment

15; total suspended particulate data for 1969-70-71 are given in attachment 16; and for non-metallic inorganic ions (ammonium, fluoride, nitrate, and sulfate) as attachment 17. A companion booklet for NO_2 is not available since most of the data collected during the period was collected by the now discredited Jacobs-Hochheiser procedure.

It should be pointed out that at 196 NASN sites the NO_2 samples were simultaneously collected by both the Jacobs-Hochheiser procedure and the arsenite method. The ratios of paired 24-hour data for the two methods ranged from 0.8 in Yellowstone Park, Wyoming (a background site) to 6.3 in Newark, New Jersey. The average ratio for the 196 sites was 2.0.

B. Atmospheric Sulfur Dioxide and Sulfate

Two papers have recently appeared (attachments 18 and 19) which attempt to use the NASN data to determine what, if any, relationship exists between SO_2 and sulfate. One paper by Altshuller incorporates NASN data from 20 sites (14 East of Mississippi River) for the years 1964-1968. It was found that for SO_2 levels between 6-80 ug/m^3 the relationship between SO_2 and sulfate could be defined by the following equation with a correlation of 0.82.

$$\text{Sulfate} = 0.144 SO_2 + 4.92$$

For concentrations of SO_2 above 100 ug/m^3, no relationship was found.

The second paper by Frank incorporated data from 1964-1970 from 62 NASN sites. When the data was statistically tested for trends, it was found that SO_2 was decreasing significantly while the sulfate did not exhibit any trend. It was additionally demonstrated that the percentage of sulfate in the particulate matter was increasing. Summarizing the data available for 1969-1970 the following patterns of SO_2 and sulfate are observed.

		SO_4			
		Increasing	No Change	Decreasing	Total
SO_2	Increasing	2	0	4	6
	No Change	2	1	2	5
	Decreasing	19	9	24	52
	Total	23	10	30	63

Essentially Frank's conclusion is that there is no general empirical relationship between SO_4 and SO_2 which tends to be in opposition to Altshuller's finding.

C. Atmospheric Nitrogen Dioxide and Nitrate

A similar comparison of NASN data between NO_2 and nitrate is not possible at this time because of the difficulties in the NO_2 measurement process. However, if the NASN annual average data available for the year 1970 for nitrate is pooled on a state by state bases, Figure 1 results. Figure 2 represents the 90th percentile of nitrate data for the same year (i.e. 90% of all nitrate values were below the reported number).

D. Additional Comments on NASN Operations

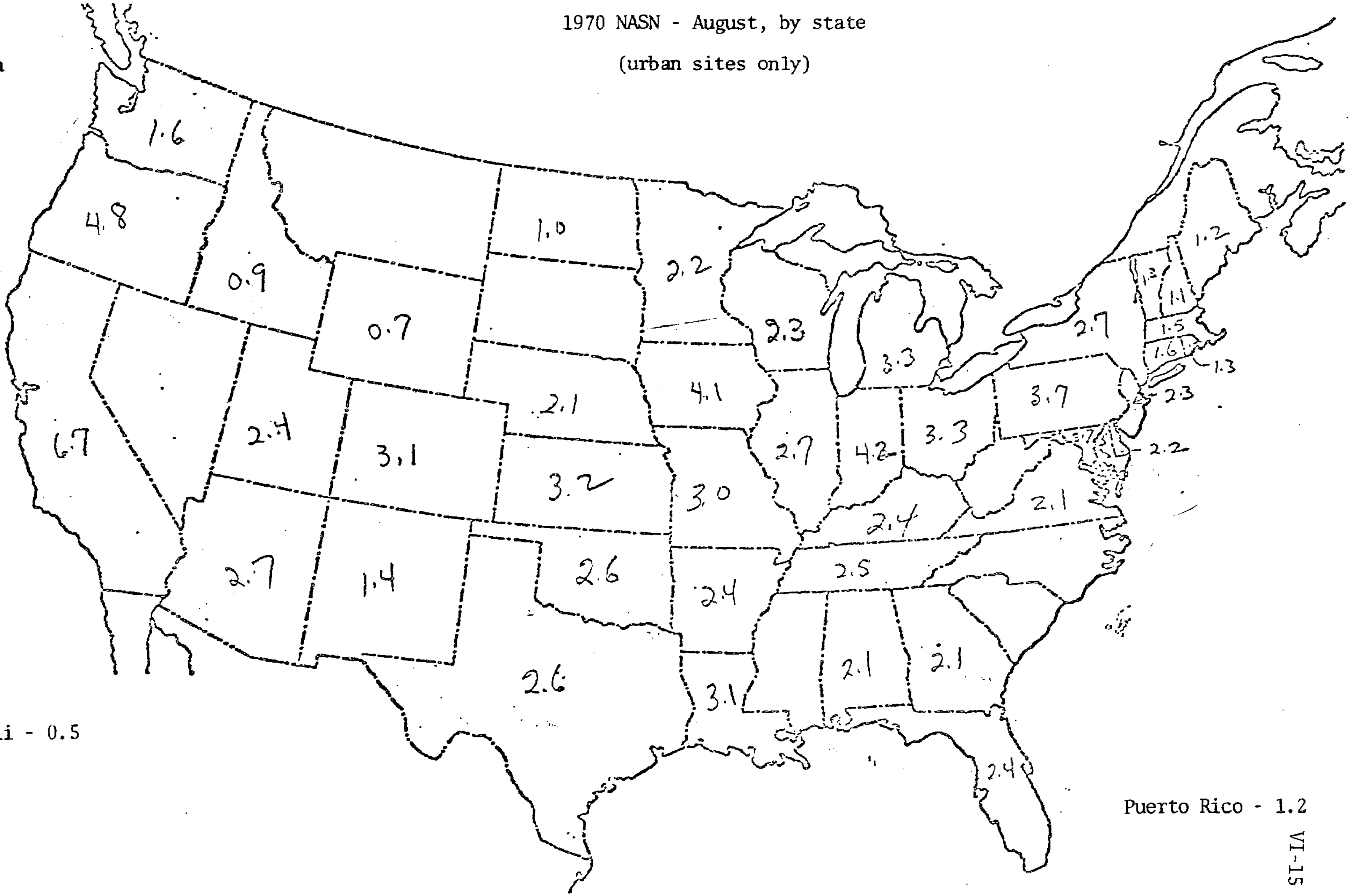
A decision has been made within EPA to decentralize the responsibilities for the operation of the NASN from the Quality Assurance and

ANNUAL AVERAGE SUSPENDED PARTICULATE NITRATE LEVELS (ug/m^3)

1970 NASN - August, by state

(urban sites only)

Alaska
0.7



Hawaii - 0.5

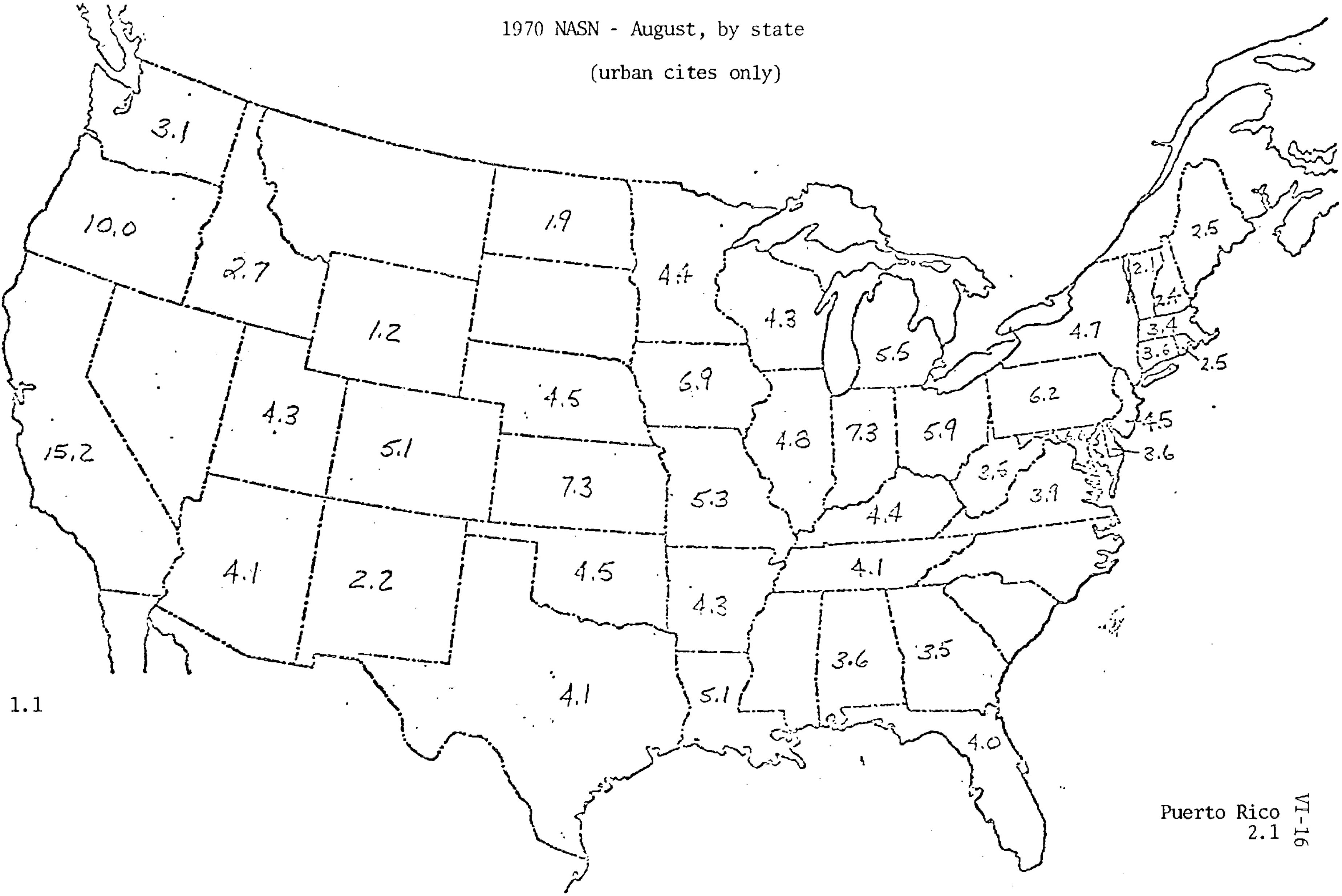
Puerto Rico - 1.2

90th PERCENTILE SUSPENDED PARTICULATE NITRATE LEVELS (ug/m^3)

1970 NASN - August, by state

(urban cites only)

Alaska
1.2



Hawaii 1.1

Puerto Rico
2.1

Environmental Monitoring Laboratory (QAEML) to the ten EPA Regional Offices. The Regional Offices will assume responsibility for all NASN sites within their Region in January 1974 and perform all analysis for suspended particulates, sulfur dioxide, and nitrogen dioxide. The role of QAEML in NASN activities in the future will be to provide technical assistance to Regional Offices, perform specialized analyses such as the trace metals, anions, organics, and Benzo(a) pyrene, and to develop and operate a quality control program for the Regional, state and local laboratories to assure the validity of the data collected both on the NASN and networks initiated in support of State Implementation Plans.

In addition, the responsibility for the operation of the Denver, Cincinnati, Philadelphia, and Chicago CAMP sites has been switched from QAEML to the Regional Offices. The St. Louis CAMP site was incorporated into the RAPS program while QAEML retained responsibility for the Washington, D. C. and Durham CAMP sites.

V. NON-URBAN MONITORING DATA

The annual average total suspended particulate (TSP) level at all NASN non-urban stations is 35 ug/m^3 for the time period 1964-1972. The yearly average TSP level of all the NASN non-urban stations ranged from 8 ug/m^3 at Yellowstone, Wyoming (1967 and 1968) to 110 ug/m^3 at Cape Hatteras, N. C. (1972). The pooled annual averages for these stations (1964-1972) ranged from 10 ug/m^3 at Yellowstone to 69 ug/m^3 at Cape Hatteras.

The daily 24-hour SO_2 levels measured at NASN non-urban sites ranged from less than the minimum detectable limit (26 ug/m^3) of the analytical method to 71 ug/m^3. Non-urban NO_2 data are not available again because of the faulty methodology.

The annual average sulfate level at all NASN non-urban stations is 5.6 ug/m^3 for the time period 1962-1970; for nitrate the annual average is 1.59 ug/m^3; and for ammonium the annual average is 0.30 ug/m^3.

The yearly average sulfate level for all non-urban NASN sites ranged from .5 ug/m^3 at White Pine Co. Nev. (1967) to 14.0 ug/m^3 at Calvert Co. Md. (1968); the pooled annual averages for sulfate levels (1962-1970) at all non-urban NASN sites ranged from 1.6 ug/m^3 at Butte Co. Idaho, Glacier National Park, Montana, and Black Hills National Forest, South Dakota to 10.0 ug/m^3 at Calvert Co. Maryland.

The yearly average nitrate level for all non-urban NASN sites ranged from 0.08 ug/m^3 at Glacier National Park, Montana (1962) to 3.34 ug/m^3 at Cape Hatteras, North Carolina (1970); the pooled annual averages for nitrate levels (1962-1970) from all non-urban NASN sites ranged from 0.13 ug/m^3 at Glacier National Park, Montana, to 1.81 ug/m^3 at Delaware County, Iowa.

The yearly average ammonium levels range from below the minimum detectable limit of the analytical method at six non-urban NASN sites to a high of 12.3 ug/m^3 at Kent County Delaware in 1964; the pooled annual averages for ammonium levels (1964-1970) from all non-urban NASN stations ranged from 0.06 ug/m^3 at Yellowstone National Park, Wyoming and Curry County Oregon to 0.82 ug/m^3 at Kent County Delaware and Washington County Rhode Island. In general, the ammonium levels seem to be much too low to be of any use as a data base in the significant deterioration problem.

An inspection of the data demonstrates that the air over the eastern United States contains more sulfate and nitrate ions than does the rest of the nation. Recent studies indicate that the threshold health effect caused by sulfate occurs at approximately 8 ug/m^3 for 24 hours. At present, nine non-urban NASN stations have annual average sulfate levels in excess of this 24-hour threshold value. These sites are predominately located in the eastern United States. Based on these observations, it is safe to say that these stations have already suffered significant deterioration and provided there is no known source of sulfate in the immediate area.

The <u>nitrate</u> issue presents a more difficult problem in that we don't know the threshold health effect level of nitrate. But it is generally conceded that both nitrate and sulfate particles in ambient air are predominately small particles in the respirable range that could contribute to health effects and additionally cause a reduction in visibility.

LIST OF ATTACHMENTS

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3. Stevens, R. K. and O'Keeffe, A. E. "Modern Aspects of Air Pollution Monitoring," Anal. Chemistry, 42, p. 143A (1970).

4. Nader, J. S. "Developments in Sampling and Analysis Instrumentation for Stationary Sources," Journ. Air Poll. Cont. Assn., 23, p. 587 (1973).

5. Forrest, J. and Newman, L. "Ambient Air Monitoring for Sulfur Compounds - A Critical Review," Journ. Air Poll. Cont. Assn., 23, p. 761 (1973).

6. Hollowell, C. D., Gee, G. Y., and McLaughlin, R. D. "Current Instrumentation for Continuous Monitoring for SO_2," Anal. Chem. 45, p. 63A (1973).

7. Lee, R. E. and Wagman, J. "A Sampling Anomaly in the Determination of Atmospheric Sulfate Concentration," Am. Ind. Hg. Assn. Jour., 27, p. 266 (1966).

8. Urone, P. "Source and Ambient Air Analysis of SO_3 and H_2SO_4," unpublished report from Univ. of Florida, Gainesville, Fla., November 1973.

9. Wagman, J., Lee, R. E., and Axt, C. J. "Influence of Some Atmospheric Variables on the Concentration and Particle Size Distribution of Sulfate in Urban Air," Atmos. Envir., 1, p. 479 (1967).

10. Lee, R. E. and Patterson, R. K. "Size Determination of Atmospheric Phosphate, Nitrate, Chloride, and Ammonium Particulate in Several Urban Areas," Atmos. Envir., 3, p. 249 (1969).

11. Lundgren, D. A. "Atmospheric Aerosol Composition and Concentration as a Function of Particle Size and Time," Jour. of Air Poll. Cont. Assn., 20, p. 603 (1970).

12. Gordon, R. J. and Bryan, R. J. "Ammonum Nitrate in Airborne Particles in Los Angeles," Env. Sci. and Technology, 7, p. 645 (1973).

13. Lee, R. E., et. al. "Concentration and Particle Size Distribution of Particulate Emissions in Automobile Exhaust," Atmos. Envir., 5, p. 225 (1971).

14. Publication No. EPA-450/1-73-001a. "The National Air Monitoring Program: Air Quality and Emission Trends Annual Report," 1, U. S. EPA, OAWP, OAQPS, Research Triangle Park, North Carolina, August 1973.

15. "Air Quality Data for Sulfur Dioxide for 1969, 1970, 1971," APTD-1354, U.S. EPA, OAWP, Research Triangle Park, North Carolina, November 1972.

16. "Air Quality Data for Suspended Particulates 1969, 1970, 1971," APTD-1353, U.S. EPA, OAWP, Research Triangle Park, North Carolina, November 1972.

17. "Air Quality Data for Non-Metallic Inorganic 1969 and 1970," APTD-1466, U.S. EPA, OAWP, Research Triangle Park, North Carolina, June 1973.

18. Altshuller, A.P. "Atmospheric Sulfur Dioxide and Sulfate," Envir. Sci. and Tech., 7, p. 709 (1973).

19. Frank, N. H. "Temporal Relationship of Sulfate, Sulfur Dioxide and Total Suspended Particulate," In-house report, U.S. EPA, OAWP, Research Triangle Park, North Carolina, August 1973.

ADDENDUM TO CHAPTER VI.

SULFATE EMISSIONS

A. Stationary Sources

1. Emission Data

Very little information is readily available on the sulfate content of particulate emitted from various stationary sources. That which is available is sparse and is included as a relatively minor part of other studies. Furthermore, in many instances, although the analytical data are valid, there are reservations about the sampling procedures used and the degree to which the integrity of the particulate has been maintained. The information which follows is presented as it relates to H_2SO_4, most likely the principal constituent of the total sulfate compounds, and to SO_2 and SO_3 which are the immediate precursors to the formation of H_2SO_4, subsequent inorganic and possible organic sulfates, and other sulfur compounds.

Table II-1 shows the emission of sulfur without abatement associated with various source industries as reported by the National Academy of Engineering.[1]

TABLE II-1

ESTIMATED NATIONWIDE SULFUR EMISSIONS WITHOUT ABATEMENT

	Annual		(Millions of Tons)
	1970	1980	1990
Power plants (coal & oil)	20	41.1	62.0
Other coal combustions	4.8	4.0	3.1
Other petroleum combustion	3.4	3.9	4.3
Metallic ore smelting	4.0	5.3	7.1
Petroleum refinery	2.4	4.0	6.5
Miscellaneous sources	2.0	2.6	3.4
TOTAL	36.6	60.9	86.4

Sulfur, contained as an impurity in fuels, is converted almost quantitatively (90+%) during the combustion process into SO_2 and SO_3. About 98% of the effluent sulfur is released as SO_2 and the remaining, 1 to 2% as SO_3. Since most combustion effluents contain some water vapor, the SO_3 rapidly reacts with the water molecules to form H_2SO_4. Additional processes which may act to convert SO_2 to SO_3 are alkali and ferrous metal sulfate decompositions(2) and heterogeneous catalysis by vanadium pentoxide and nickel oxides which are found in residual fuel oils(3).

The ASME(4) reports the H_2SO_4 dew point as approximately 240°F for 1 ppm and 270°F for 10 ppm. At these temperatures, the $H_2SO_4 \rightleftarrows SO_3 + H_2O$ equilibrium is more than 99+% toward H_2SO_4(5). The SO_3 formed will rapidly convert to H_2SO_4 if cooled and exposed to any water vapor. Walden(6) and a number of other investigators have shown that generally about 2% of the emitted sulfur is $SO_3(H_2SO_4)$. When this ratio is applied to the combustion source emission of Table II-1, Table II-2 results.

TABLE II

ESTIMATED COMBUSTION SOURCE EMISSIONS OF $SO_3(H_2SO_4)$ WITHOUT ABATEMENT

	1970	1980
	(ton,	annual)
Power plants (coal & oil)	400,000	820,000
Other coal combustion	96,000	80,000
Other petroleum combustion	68,000	78,000

The SO_3 emissions measured by Walden(6) using Method 6 of the NSPS in a contact sulfuric acid plant indicate that the 2% relationship may be valid for sulfuric acid manufacture. Therefore, it is estimated that the miscellaneous SO_3 (H_2SO_4) emissions are at 40,000 tons per year for 1970. Very little data on SO_3 emissions from the remaining classes of sources are available. Most of the SO_2 emissions in refineries come from burning various fuels and waste streams to produce heat. Therefore, the SO_3/SO_2 ratio is assessed at 2% for other combustion sources and SO_3 emissions are estimated at 48,000 tons in 1970. The small amount of data on metallic ore smelting indicates that the SO_3 levels are near 2% of the SO_2 levels. Their contribution is estimated at 80,000 tons annually (1970). This offers a potential 1970 nationwide emission of approximately 732,000 tons of SO_3 (H_2SO_4) annually.

2. Measurement Techniques

The major portion of the existing analytical methodology for SO_3 (H_2SO_4) emissions from stationary sources is based on the dew point of SO_3 being somewhat higher than the water dew point in the stream. A typical combustion effluent will have a water dew point of between 100°F and 140°F. The dew point for SO_3 varies from 240°F at 1 ppm to 280°F at 20 ppm.(4) The condensation techniques generally cool the effluent gas to 170 to 200°F and collect the aerosol H_2SO_4 by impaction or filtration. Analysis can be by sulfate specific Barium chemistry (colorimetric, potentiometric, titration with indicator, gravimetric) SO_2 is not collected in this technique and thus the two species are readily separated.

Condensation methods depend on the presence of water or water vapor to form H_2SO_4 and are thus restricted to "moist" sample streams.

The second major SO_2 collection technique is absorption which depends on the solubility of H_2SO_4 in aqueous solution. Environmental Protection Agency source method 6(7) uses 80% isoproponal in water to trap the SO_3 from combustion sources. Several investigators have shown that some higher alcohols inhibit the oxidation of dissolved SO_2 to SO_3. The combination of two IPA bubblers followed by a filter is nearly quantiative for SO_3. The dissolved SO_2 is removed by immediate purging with clean air. Gillham(9) indicates that the conversion rate ($SO_2 \rightarrow SO_3$) is approximately 25%/24 hours. Arthur D. Little(10) was unable to get more than 1%/24 hour conversion in a similar time period. The reason for this difference is not known.

The greater number of collection schemes proposed and used by Monsanto Corporation, Shell Research and Development Company, Chemical Construction Corporation, and EPA methods 6 and 8 are all modifications and subsets of one or the other of the two basic techniques. The principle (varient) being that EPA method 6, the Reich test, and the Shell methods assume SO_3 to be in the vapor phase and treat it as a gas during sampling. EPA NSPS method 8(8), the Monsanto method, and the Chemico methods assume that the SO_3 is in the condensed form as an aerosol and attempt to isokinetically sample it as a particulate. The collection schemes vary from cyclones and filters to midget impingers, midget bubblers, lamp sulfur absorbers, and condensation coils with sintered glass frets. Flint(11) indicates that 80% IPA filled bubblers have efficiencies of 42-46% and the in line filter at about 18% for essentially quantitative recovery. Walden(5) has tested the midget impingers and found them relatively constant at about 90% for the first impinger and 95% maximum for two in series. The midget bubblers were quite variable between 58% at 5 liters/min. and 93% at 0.5l/min. for two in series. The larger lamp sulfur absorbers appear to be quite constant at about 95% over the range of flows. Hissink(12) has indicated that controlled condensation with a filter for collection is essentially quantitative when the filter temperature is below 100°C. Walden(6) has shown that the controlled condensation approach produces substantially lower (slope 0.45) values than the IPA method in power plants, sulfuric acid plants, and smelting operations. Where as the SO_2 values given by the same apparatus give a slope of 0.99 and show excellent correlation.

At this time, no other test or verification or comparison data on any other test method is available for SO_3 or H_2SO_4 aerosols.

B. Mobile Sources

1. Emissions

Sulfate from mobile sources has not been considered significant due to the low levels of sulfur in refined fuels.

From the 1971-2 Bureau of Mines study gasoline contains 0.044 wt% sulfur for regular grade and 0.039% for premium. This leads to an estimate of 220,000 tons of sulfur per year nationally (as SO_2) or 0.8% of the total national emissions.

Locally, there may be a problem in that southern California has exceptionally high levels. These are the only areas where this is so, but the average concentration there is 0.15% in regular and 0.09% in premium. Assuming the worst case, this could account for about 36,000 tons of sulfur oxides/year as SO_2.

Sulfur contents of fuels from other sources also are not significant due to low usage rates and the low levels (2% maximum) in almost all mobile fuels.

2. Measurement Techniques

Sulfur is normally measured in the fuel by one of several methods: x-ray ASTM P-2622, lamp ASTM P-1266, and bomb P-129 among others.

Little work has been done on direct sulfate products from mobile sources. Usually any such analysis has been in conjunction with trace metal analysis of particulate matter collected on filters. X-ray techniques are most often used, but occasionally, wet chemicals have been employed. X-ray fluorescence techniques yield qualitative data in very little time, but are difficult with leaded fuels due to peak overlaps of lead and sulfur. Lead sulfate compounds[13] have been identified in automotive exhaust particulates.

The direct analysis of sulfur on tailpipe emission is usually done flame photometrically. Extremely high sensitivity is required because of the very low levels.

C. References

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III. AMBIENT SULFATE CONCENTRATIONS

A. National Air Surveillance Network

The most extensive body of 24-hour integrated sulfate (sulfuric acid and sulfate salts) measurements collected and analyzed by a common procedure has been compiled by the National Air Surveillance Networks (NASN). Sulfate data have been collected nationwide since 1957 by a network which has grown to include approximately 250 sites both urban and non-urban. The operation of the nationwide network depends on the services of a volunteer operator at each site to collect the sample on the designated sample date and mail the collected sample back to EPA for analysis. The schedule for sample collection was one 24-hour integrated sample collected randomly once every two weeks. Beginning in 1972, samples were collected every twelfth-day.

1. Spatial Patterns

In general the highest concentrations of sulfate in suspended particulate matter observed from 1957 through 1970 occurred in the industrial northeast.[1] The maximum 24-hour average sulfate concentration observed during this period in over 35 thousand samples was 197 $\mu g/m^3$ in a particulate sample of 425 $\mu g/m^3$ at Charleston, West Virginia, on September 24, 1967. The 1970 nationwide annual average sulfate concentration at the urban locations was 10.1 $\mu g/m^3$, and the non-urban average was 6.3 $\mu g/m^3$.[1] Table III-1 presents the urban and non-urban cumulative frequency distribution of annual sulfate averages. The number of stations included in these summaries varies from year-to-year depending upon the number

Table III-1. URBAN CUMULATIVE FREQUENCY DISTRIBUTION OF ANNUAL SULFATE AVERAGES

YEAR	TOTAL STATIONS	ug/m^3					
		< 5.0	< 10.0	< 15.0	< 20.0	< 25.0	< 30.0
1957	33	17	57	87	93	97	100
1958	49	6	54	77	98	100	100
1959	43	19	44	79	98	100	100
1960	61	13	33	72	93	100	100
1961	68	12	32	72	91	97	100
1962	79	16	52	81	96	97	100
1963	90	12	54	81	96	98	100
1964	100	23	66	84	95	97	100
1965	119	12	50	78	97	99	100
1966	99	21	53	84	98	99	100
1967	121	25	60	87	97	98	100
1968	146	21	60	85	96	99	100
1969	171	12	47	87	96	99	100
1970	164	9	53	84	95	98	100

NONURBAN CUMULATIVE FREQUENCY DISTRIBUTION OF ANNUAL SULFATE AVERAGES

YEAR	TOTAL STATIONS	ug/m^3		
		< 5.0	< 10.0	< 15.0
1965	25	40	88	100
1966	27	48	96	100
1967	26	50	92	100
1968	25	48	88	100
1969	22	36	91	100
1970	25	36	87	100

of stations in the network in a given year, the number of stations collecting the required number of samples, and the number having the proper distribution of samples throughout the year. For example, Table III-1 shows that in 1970, 84 percent of the 164 stations (138 stations) had an annual average less than 15 μg/m^3. The non-urban portion of the table shows that in every year since 1965, the annual average for non-urban stations was below 15 μg/m^3, with an annual average for all stations about 6 μg/m^3.[1]

2. Seasonal Patterns

Figure III-1 is a smoothed plot of the sulfate data showing seasonal urban and non-urban patterns. The sulfate patterns in the urban atmosphere prior to 1966 show a high winter -- low summer relationship. However, the seasonal sulfate pattern after 1965 shows no consistent winter/summer relationships. The non-urban pattern reveals a slightly higher summer lower winter cycle.[1]

Figure III-2 is a smoothed plot of the sulfate data showing long term patterns. It appears that there are no marked long term trends in the sulfate data. This fact can also be seen in Table III-1 where the percentage of stations within each cell changes only slightly from year -to-year, inspite of control techniques which were in general use in the urban areas since 1967.[1]

3. Empirical Relationship to Sulfur Dioxide

Beginning in 1962, and continuing to the present, the National Air Surveillance Networks have collected simultaneous ambient measurements of 24-hour sulfur dioxide and suspended sulfate in various cities. The earlier data (before 1968) demonstrated with a correlation coefficient above 0.75 that with increasing amounts of SO_2 the levels of the suspended sulfate aerosol increase. However, as the SO_2 levels diminish and approach the minimum detectable limit, there are residual amounts of sulfate present in ambient suspended particulate matter. The more recent data do not show the same degree of association, which may be attributable in part to the decrease in SO_2 concentrations across the country. For example, correlating individual 24-hour SO_2 measurements for the NASN data collected in 1967, 1968, and 1970 resulted in correlation coefficients above 0.5 in only 35%, 18% and 7% of the sites, respectively.[1]

For comparison purposes Table III-2 is constructed analogously to Table III-1, which shows the cumulative distribution of annual SO_2 averages. This table, by the way of contrast, illustrates the downward shift in SO_2 concentrations. Figures III-3 and III-4 can be compared with Figure III-1 and III-2, respectively. Note that urban SO_2 demonstrates a high winter, low summer pattern, corresponding to the winter heating season and increased home fuel usage. Seasonality exists at non-urban SO_2 sites as well as urban environments, presumably an influence thereof, but the winter to summer differences are not pronounced.[1]

4. Sample Collection and Analysis

Samples are collected with a high-volume sampler by drawing air through a glass fiber filter at a rate of from 40 to 60 cubic feet per

TABLE III-2. URBAN CUMULATIVE DISTRIBUTION BY PERCENT

YEAR	TOTAL STATIONS	(µg/m^3-Annual SO_2 Averages)				
		< 20	< 40	< 60	<80	<100
1962	33	36.4	60.6	69.7	72.7	84.8
1963	26	15.3	30.7	49.9	57.5	76.7
1964	33	12.2	45.5	57.6	69.7	100.
1965	34	29.4	44.1	64.6	76.4	100.
1966	45	24.5	48.9	62.2	73.3	77.7
1967	47	21.3	48.9	68.1	74.5	100.
1968	98	34.7	64.3	76.5	86.7	94.8
1969	109	39.5	73.5	86.4	94.7	97.4
1970	97	54.6	84.5	91.7	96.9	100.
1971	71	66.2	90.1	98.5	100.	

NONURBAN CUMULATIVE DISTRIBUTION BY PERCENT

YEAR	TOTAL STATIONS	(µg/m^3-Annual SO_2 Averages)		
		< 10	<20	<30
1968	5	40.0	100.	
1969	6	50.0	83.0	100.
1970	3	100.		
1971	9	100.		

minute. The collected particles are extracted by refluxing with 40 ml of distilled water in a 125 ml flask of an 8% section of the "exposed" glass fiber filter. The extract is then cooled and filtered. The sample and flask are washed with a small amount of water. The filtered extract and washers are combined and the volume is made up to 50 ml with water. The 50 ml sample is then mixed and used for the analysis.

The sulfate ion in the filtrate is determined by the methylthymol blue method with an Auto-Analyzer*. The filtrate is reacted with a reagent consisting of equal parts of methylthymol blue dye and barium chloride, kept at a pH of 2.8 to prevent the formation of a chelate complex from the dye and the barium. Any sulfate ion in the sample reacts with the barium, leaving an excess of methylthymol blue dye that is proportional to the amount of sulfate present. The pH is then raised to 12.4 at which point the barium not removed by the sulfate forms a chelate complex with the methylthymol blue dye and the excess dye turns yellow. The intensity of the yellow color is then determined colorimetrically at 480 millimicrons.

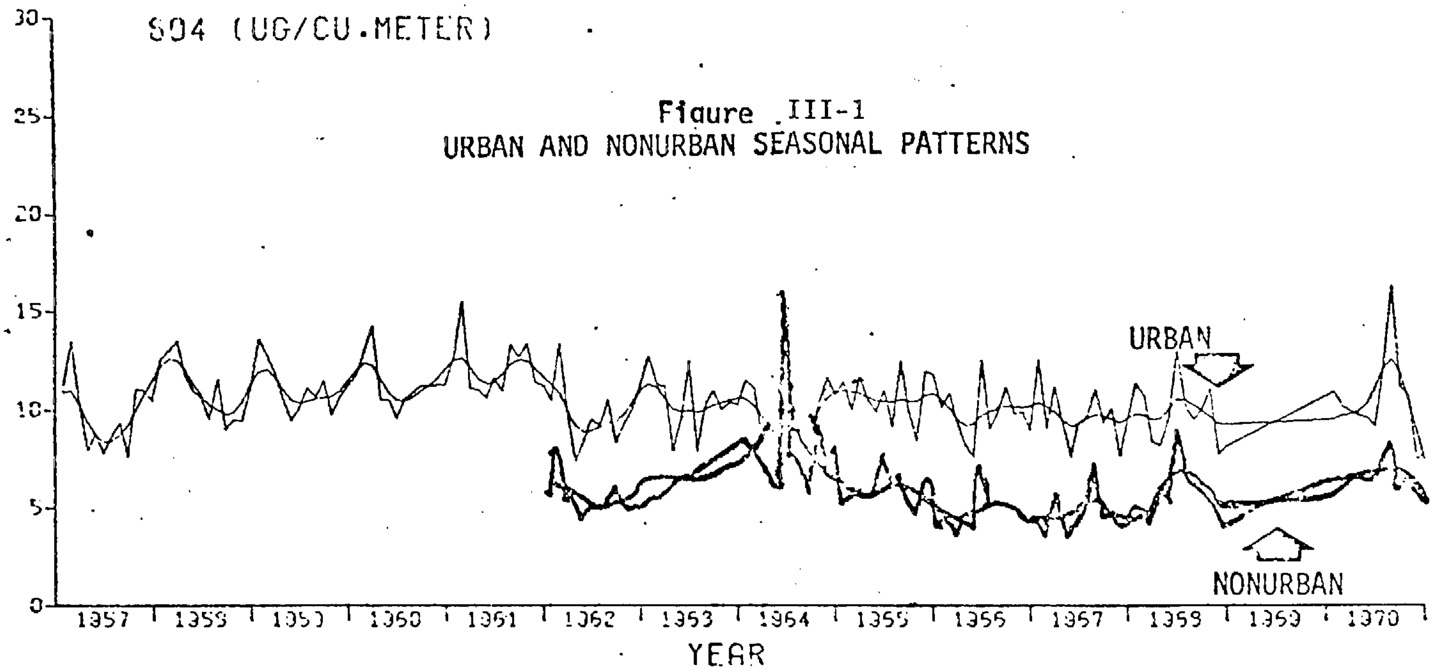
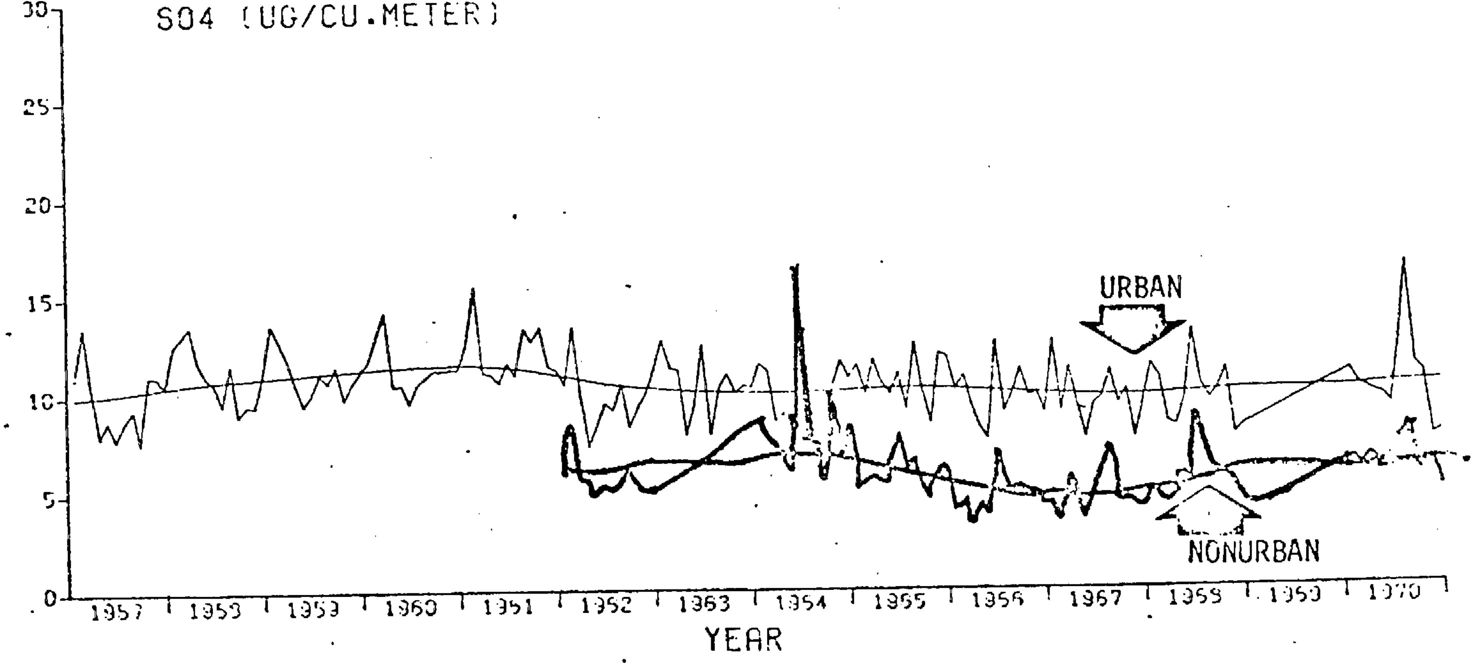


Figure III-1
URBAN AND NONURBAN SEASONAL PATTERNS

Figure III-2
URBAN AND NONURBAN LONG TERM PATTERNS



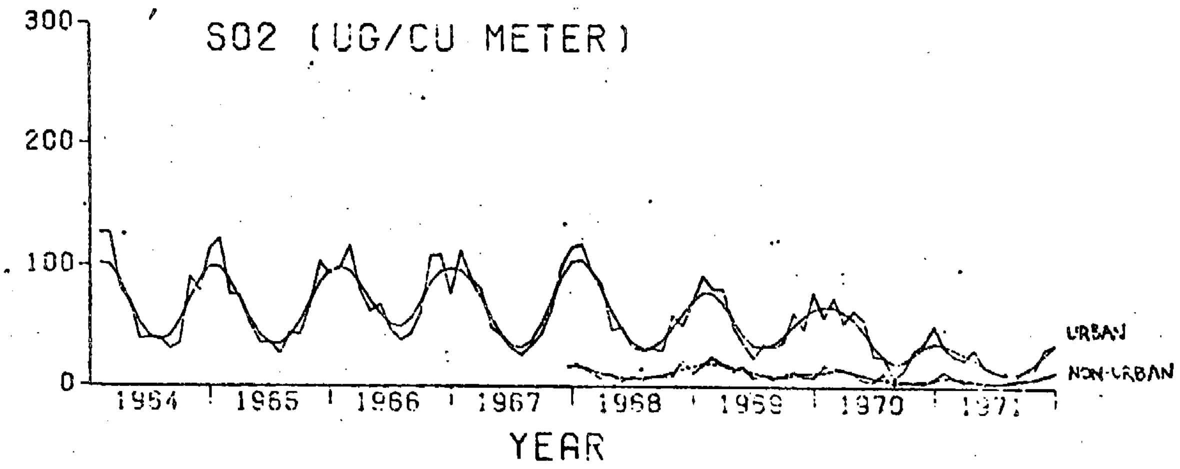
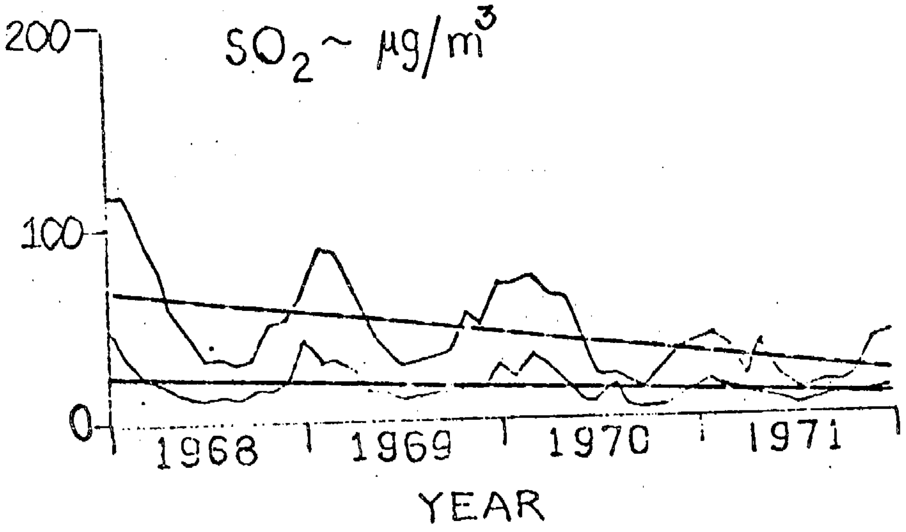


Figure III-3. SEASONAL PATTERNS OF SULFUR DIOXIDE CONCENTRATIONS

Figure III-4. LONG-TERM VARIATION IN NASN SO_2 CONCENTRATIONS



B. Review of Measurement Techniques

Since there is no room for improvement in all our analytical methods, whenever one speaks of analysis one talks about problems. The two main problems in the determination of atmospheric sulfate reside in collection and in analysis. Sulfate in terms of total atmospheric sulfate, sulfuric acid and other various types of sulfates is discussed.

1. Total Sulfate

Collection. Usually on glass fiber sheets and occasionally with cascade impactors, etc. Difficulty lies in the report that the concentration of sulfates in air depends on the sampling volume. This result has been explained on one hand as due to the catalytic oxidation of SO_2 to SO_4 -- at the surface of the collecting area and on the other hand as due to interferences in the analytical method arising from other substances also extracted from the glass fibers. Information is not generally available on the specific conditions required and the extent to which SO_2 could be converted to $SO_4^=$ on filters.

Analysis. A large number of methods of analysis for total atmospheric sulfate are available. A critical study and comparison of these methods is not available. Some of the techniques and their problems are shown in Table III-3.

2. Automated Total Sulfur Monitor

Particulate sulfur collected on millipore filters can be analyzed with X-ray fluorescence. The filter is irradiated in the analyzer with X-rays from an X-ray tube and photons emitted by sulfur are sensed with a lithium drifted silicon detector or a crystalline grating spectrometer. Analysis time is presently 30 minutes per sample if a complete elemental analysis is performed using a lithium drifted silicon detector. If only sulfur data are needed, the analysis is performed in 10 minutes. Up to 30 samples can be automatically analyzed without operator intervention. An automatic sampling station allows one to make collection intervals as short as two hours if diurnal variations are needed.

Sulfuric Acid

Collection. Usually on glass fiber filters and occassionally on paper or membrane filters, in impingers, containing aqueous solutions or dry impingers in cascade centrepetors, or, by sonic impaction on copper discs or planchets.

Analysis. Table III-4 gives a fairly concise list of most of the techniques in use to determine H_2SO_4. Obviously with the separation of H_2SO_4 from other sulfates, the various methods described in the sulfate section can be used.

A measuring method for strong acid aerosol has been developed by Brosset of Sweden[5] and Liberti and coworkers of Italy. Aerosol is collected in water, and then a titration is performed to distinguish between strong and weak acid. The method is specific to strong acid, but is not able to distinguish between various strong acids, nor is it very sensitive. A method more specific for sulfuric acid is the collection of particulate on a hi-vol filter followed by heating the filter after returning to the laboratory and detecting the SO_3 which evolves. This method requires making the rather questionable assumption that the H_2SO_4 does not react with anything between the time it reaches the filter and the time of laboratory analysis.

The most reliable procedure for determing acid mist should be the direct determination in the field in order to minimize reaction losses which occur between times of collection and analysis. Reliable commercial instrumentation is not presently available, and for this reason prototypes are now being developed by the Field Methods Development Section of Chemistry and Physics Laboratory. One devide under development uses a moving filter tape for collection followed by a heater for driving off SO_3 which in turn is sensed by a flame photometric detector. The measuring concept is identidal to the laboratory procedure described above. but reaction losses are minimized by the short (five minutes) time period between collection and analysis. A second technique uses a gas phase titration with ammonia to determine strong acids. The ammonia is measured with a chemiluminescent analyzer. Qualitative response to H_2SO_4 aerosol has been obtained. Research leading toward prototype development is being pursued. The method is sensitive only to strong acids, but it does not distinguish between H_2SO_4 and HNO_3.

3. Miscellaneous Sulfates

With collection on glass fiber paper and controlled vaporization of the sample into a computer-controlled, high resolution mass spectrometer, compounds such as H_2SO_4, $NH_4 HSO_4$, $(NH_4)_2 SO_4$ and $NaHSO_4$ have been characterized and assayed. Because of the temperatures involved in the vaporization the integrity of the sample is the big problem. Numbers will be readily obtained, but their accuracy might be a real problem.

4. General Difficulties

Sulfate

Collection of sulfate from all types of polluted air without formation of artifact sulfate during collection.

Water-insoluble sulfates not extracted in analytical procedure.

Problem in all collection methods is that the integrity of the sample must be proven and this integrity must have a reasonable shelf life.

Problem of field monitors is their expense, maintenance, rapid instrument obsolescence and field calibration. This problem is considerably enhanced with monopollutant analyzers.

H_2SO_4

In collection on glass fiber filters, these fibers may catalyze the oxidation of SO_2 to SO_3 and can also neutralize the H_2SO_4 at the surface of the glass fiber sheet.

In collection of particulate H_2SO_4 in aqueous solutions and in extraction of particulate H_2SO_4 with water, it is possible that dissolving basic particles will neutralize some of the H_2SO_4. Thus, an apparent H_2SO_4 is obtained and not a "true" H_2SO_4. However, it is argued by some that the apparent H_2SO_4 more closely approximates the effective H_2SO_4 than does the "true" H_2SO_4. This problem in collection would be even more serious in monitoring methods consisting of short-time collection and elution, where the precision would vary over a wide range dependent on the amount of soluble basic material caught with each batch of H_2SO_4.[2,3]

In any methods involving heat, artifact formation could ensue. Thus, ammonium sulfate would be measured as H_2SO_4. Other compounds, such as organic sulfates, sulfonates, sulfites and sulfones could interfere in this way dependent on the conditions and the method used.[3]

Table III-3

TECHNIQUES FOR DETERMINATION OF ATMOSPHERIC SULFATE

I. Turbidimetry and Nephelometry

- A. Methods
  1. Ba salt
  2. 4-Amino-4'-chlorobiphenyl
  3. 2-Aminopyrimidine
- B. Advantages
  1. Simplicity
- C. Disadvantages
  1. Possible interference from colloidal organic matter, filter media and colored material
  2. Coprecipitation problem
  3. Poor reproducability

II. Colorimetry with Color Decrease

- A. Methods
  1. Barium rhodizonate
  2. Morin or hydroxyflavone and thorium
- B. -
- C. Disadvantages
  1. Difficulties in precision with a subtractive method
  2. Lack of sensitivity

III. Colorimetry

- A. Methods
  1. Barium chloranilate
     - a. Cation interference
     - b. Centrifugation or filtration needed
     - c. Phosphate, oxalate and bisulfite interfere
     - d. Thought by some to be one of the best methods
  2. Methylthymol blue
     - a. Interfering heavy metals have to be removed by ion-exchange chromatography
     - b. Filtration of barium sulfate necessary
     - c. Range 0.3 to 45 μg SO_4^{-}/m^3 of air

Table III-3 Continued

d. Interference by oxidation of dye in alkaline solution.
e. Precision at lower concentrations needs more study since this appears to be a possible weakness
f. Colored blank interferes

3. Reduction to H_2S and reaction with N,N-dimethyl-p-phenylenediamine to give methylene blue

   a. Complicated procedure

4. Reduction to H_2S and reaction with ferric ion and o-phenanthroline to give the ferrous o-phenanthroline complex

   a. Complicated procedure
   b. Nitrite and other H_2S precursors interfere

IV. Quenchofluorimetry

A. Methods

1. Morin or hydroxyflavone with thorium

B. Advantages

1. Simplicity
2. Sensitivity potential high

C. Disadvantages

1. The difficult problem of measuring a decrease in fluorescence

V. Fluorimetry

A. Methods

1. Reduction to hydrogen sulfide and reaction with a non-fluorescent mercury derivative of a powerful fluorogen to give that fluorogen

B. Advantages

1. High order of sensitivity

C. Disadvantages

1. Complexity of procedure

VI. Ring Oven

A. Methods

1. Barium chloride - potassium permanganate

Table III-3 Continued

B. Advantages

1. Simplicity

C. Disadvantages

1. Precision depends on technique and eye of the experimenters
2. Interferences are phosphate, oxalate, sulfite

VII. Polarography

A. Methods

1. Indirect with lead or barium nitrate

a. Filtration or centrifugation necessary with consequent problems of adsorption and poorer precision

2. Direct square-wave polarography

a. Ion exchange chromatography necessary to remove interferences

VIII. Atomic Absorption

A. Methods

1. Barium
2. Lead
3. Calcium

B. Advantages

1. The measurement sensitivities of the metals used to precipitate sulfate are of value in this method

C. Disadvantages

1. All the usual problems of indirect methods and especially those involving precipitation with excess metal salt followed by subsequent measurement of residual cation

2. Usual interferences and especially the strong interference from phosphate in the calcium method.

IX. Gas Chromatography

A. Methods

1. Reduction to H_2S and measurement of the H_2S by gas chromatography with flame photometric detectors.

Table III-3 Continued

X. Potentiometry and especially Selective Ion Electrodes

  A. Methods

    1. Direct selective sulfate detector

      a. I know of no satisfactory detector of this type. However, the field is advancing rapidly so a satisfactory electrode could be developed soon.

    2. Indirect ion selective electrode for sulfate

      a. Lead selective electrode

        1. Most potential at moment
        2. Method involves titration with a lead salt
        3. Interferences would be any other anions that could precipitate lead. For the method to be workable the effect of these interfering anions would have to be cancelled.
        4. Reasonable sensitivity

XI. Flame Photometry

  A. Methods

    1. Similar to IX but essentially aspiration of sulfate solution into a hydrogen-rich flame and measuring the emission

  B. High Sensitivity

  C. Disadvantage

    1. Other sulfur compounds would contribute to the total sulfate

XII. X-ray Fluorescence

  A. Methods

    1. Essentially another laboratory method to measure sulfur. If all the sulfur were present as sulfate, this might be a good way to measure it.

  B. Disadvantages

    1. Other sulfur compounds would be measured
    2. Expensive instrumentation not available to most labs

  C. Advantages

    1. Fast method of analysis. Because of sophisticated instrumentation a good method for laboratory collection in the field and analysis in a central laboratory

Table III-4

Determination of Atmospheric H_2SO_4

I. Colorimetry

A. Methods

1. Vanadate

a. Simple procedure
b. Sensitive to 5 μg H_2SO_4
c. Average error 9.3%

2. Barium chloranilate

a. H_2SO_4 separated from other sulfates by elution with isopropanol
b. Filtration necessary
c. Colored material in the extract interferes, as does any anion which precipitates barium

3. West-Gaecke method

a. Procedure consists of evaporation of H_2SO_4, reduction with copper and determination of SO_2 colorimetrically
b. Complex procedure
c. Ammonium sulfate is also measured

4. Other colorimetric and fluorimetric methods described in the sulfate section could be used once H_2SO_4 is separated from other sulfates

II. Coulometry

A. Methods

1. As in IA3 but SO_2 titrated

III. Flame Photometry: As above but SO_2 measured with flame photometer

IV. Titrimetry

A. Methods

1. Sodium hydroxide residual titration method
2. Tetraborate residual titration method
3. Separation of H_2SO_4 by diffusion at elevated temperatures and titration with barium perchlorate using thoron I as indicator

V. pH Method: Especially measurement of pH and correlation of this with the H^+ ion concentration

VI. Square-wave Polarography: Volatile H_2SO_4 separated by diffusion and determined. Method more rapid than titration.

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ADDENDUM TO CHAPTER VI.

Summary Report on Atmospheric Nitrates

SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

1 SUMMARY

Nitrogen is a principal constituent in the earth's atmosphere. The most common forms of nitrogen found in nature are nitrogen gas, oxides of nitrogen, organic nitrogenous compounds, ammonia, nitrites, and nitrates. Nitrate salts and oxides represent the final stage in the atmospheric oxidation of gaseous oxides of nitrogen, starting with the formation of nitric oxide. Nitrogen oxides play a principal role in secondary aerosol formation, and hence urban smog.

There is an abundant amount of nitric oxide (NO) and nitrogen dioxide (NO_2) of natural origin in the atmosphere. In the lower atmosphere, NO is created thermally in flames, explosions, and electric discharges. In the upper atmosphere, NO is formed through the photodissociation of N_2 and O_2, followed by combination of N and O. For the purpose of this report, the vertical transport of NO from the upper atmosphere to the lower troposphere can be considered negligible. Nitrates observed in urban areas result principally from the conversion of nitrogen oxide emitted from man-made sources. Only a small fraction is emitted directly as nitrates.

Nitrogen oxides emissions in the U. S. result primarily from the combustion of fossil fuels in boilers, furnaces, and internal combustion engines. Practically all man-made emissions from non-combustion sources are from the manufacture and use of nitric acid. Currently, the stationary and mobile sources each contribute approximately 50% of the oxides of nitrogen emissions from man-made sources.

Nitrate is formed in urban area atmospheres mainly as peroxyacetyl nitrate (PAN) vapor, with a lesser amount formed as inorganic nitrates salts in the aerosols. In outlying areas, the formation of nitric acid and nitrate salts may well exceed the formation of PAN-type compounds. Nitrites also are formed in the atmosphere, but the concentrations are much lower than that for nitrates. The chemical path from NO to nitrates in the atmosphere may be extremely complex, and is not well understood, although the photochemical production of NO_2 has been studied extensively. A wide variety of organic and inorganic nitrate compounds might be formed, including intermediate species which may be unstable and highly reactive. A number of these compounds have been found in laboratory experiments, but few have been detected in the ambient atmosphere. Organic nitrates are formed by the combination of NO_2 with oxygenated radicals. Peroxy radicals yield PAN, which measurements show to be the predominant nitrate in urban atmospheres. Inorganic nitrate begins with the reaction of NO_2 with ozone, and is thought to proceed through an intermediate nitric acid species which, in the presence of other solubles, will be neutralized to yield various inorganic nitrates. It seems probable that PAN in the air is slowly taken up by aerosol droplets and hydrolyzed to nitrite in solution, which is then oxidized to nitrate. Thus, the ratio of inorganic nitrate to organic nitrate in a polluted air mass should increase slowly as the air moves away from the urban generation area. One might expect also that the chemical characterization of nitrate aerosols might vary from one urban area to another, depending upon precursor emission and their rate of emission.

The majority of the nitrate concentration data available in the U. S. has been acquired by analysis of particulate matter samples obtained using the Hi Vol sampler with glass fiber filters. Nitrates in this incidence are defined as those nitrates that are removed from suspended particulate matter, having a size range of 0.3 to 10 μm in diameter, collected on glass fiber filters. Such a technique provides only a limited indication of the nature of the air sample. Fully satisfactory methods for routine use in measuring particulate nitrate, PAN, nitric acid, nitrous acid, nitrogen dioxide, and nitrogen pentoxide are not yet available.

The arithmetic mean for nitrates as measured at the NASN stations with the Hi Vol sampler for a 5-year period (1966-1970) for those urban sites where all data were available ranged from 0.57 to 7.57 $\mu g/m^3$--the highest being in Los Angeles and the lowest in Concord, New Hampshire.

Nitrate measurements made at CHESS stations show large temporal and spatial variations. In Chattanooga, Tennessee, observed 24-hour average concentrations varied from below the detectable level to 107.3 $\mu g/m^3$, and the monthly arithmetic mean varied from 0.3 to 24.9 $\mu g/m^3$. The overall monthly urban averages varied from 1.3 to 7.2 $\mu g/m^3$.

Available data are not sufficient to describe diurnal variations; however, limited data and theoretical considerations suggest that significant diurnal cycles may occur, similar to that of ozone, particularly in the Los Angeles area. If this were the case, the daily maximum concentration should be significantly higher than the annual average--possibly orders of magnitude higher. Since nitrates in the atmosphere are primarily secondary aerosols resulting from chemical transformation processes, their distribution represents the conjugate of all sources in the area, and would extend beyond the actual source boundaries. Vertical distribution and dispersion would be directly influenced by meteorological conditions.

Data on the size distribution of nitrates in the atmosphere are limited. Available data indicate that the nitrate aerosol particles are normally 2 µm or less in diameter. Particle sizes in coastal areas are probably larger.

Atmospheric analyses have generally revealed oxidation products equivalent to only about half of the suspected emissions. Available data suggest that NO_2, N_2S, HNO_3, HNO_2, PAN, and particulate nitrates are taken up by such surfaces as leaves and soil at a greater rate than had heretofore been recognized. These removal mechanisms, coupled with the transformation processes would help to explain a diurnal cycle. The other principal removal mechanism is precipitation. In areas with little rainfall, such as Los Angeles in the summer months, dry removal processes must play a primary role. Millions of tons of nitrate containing aerosols reach the earth's surface each year from these removal mechanisms. The nitrogen content in runoff is highly variable depending upon the duration and intensity of rainfall, land use, topography, physical characteristics, and antecedent conditions. The rough average is 2-3 mg/l. In some cases, runoff adds enough nitrogen to surface waters to produce algal growth.

The residence time for nitrates in the atmosphere will vary depending upon the predominant removal mechanisms. Actual data on residence times are not available. Since the particle sizes are primarily sub-micrometer, they will remain suspended for periods on the order of days, and hence will be transported several hundred kilometers, unless contained by terrain and meteorological features--such as is the case with the Los Angeles Basin. Consideration of removal mechanisms and the physical properties of the aerosol suggest residence times of 2 to 10 days.

Nitrates and nitrites are found in varying concentrations in most foods, and in water. Tobacco smoke contains higher concentrations of nitrogen compounds than does polluted air. The highest amounts are in the form of total oxidizable nitrogen oxides and methylnitrite. A dimethylnitrosamine has been found in cigarette smoke. Nitrosamines have been reported in a number of foods, but at much lower concentrations than nitrate and nitrite. Nitrates and nitrites are used in curing meats; the Food and Drug Administration has established tolerance limits of 200 ppm for nitrites and 500 ppm for nitrates for this purpose. The Public Health Service has set 10 mg NO_3 per liter as the maximum permissible level for drinking water.

The ubiquity of nitrate in man's environment make possible his exposure to these substances through a variety of routes of entry into the body. Water and foods have long been recognized as the principal routes of entry. It is difficult to estimate the combined level of exposure of man to nitrate-nitrite. The question of exogenous sources versus endogenous production further complicates the problem. Nitrate and nitrite salts are readily adsorbed through the stomach. A rough estimate of nitrate in the average daily diet is 200 mg. Since nitrate and nitrite salts are readily soluble in water and serum containing systems, and are rapidly adsorbed when ingested, it seems likely that they also would be rapidly absorbed through the respiratory tract after deposition in the alveolar region of the lung. The question thus arises concerning the amount of nitrate absorbed in this manner as compared to that via ingestion. Using a standard respiratory volume per day, and assuming exposure to nitrate concentrations of 3-5 $\mu g/m^3$ for 12 hours per day, the calculated retained inhaled nitrate would be 21.5 μg. This is substantially less than 1 percent of the body burden if water alone is considered. It therefore appears unlikley that inhaled nitrates would contribute substantially to the body burden of nitrate-nitrite, and hence to the toxicity resulting from methemoglobinemia and its consequent effects. However, if the preliminary correlations found between nitrate and respiratory symptoms are correct, and they are causally associated, then airborne nitrate may be an important respiratory irritant.

The extent to which nitrate may be harmful to human health is dependent upon its reduction to nitrite, or the possible conversion to nitrosamines. Nitrate itself is relatively nontoxic, being rapidly absorbed and rapidly excreted. Nitrite when reaching the blood stream reacts with hemoglobin to form methemoglobin resulting in a decrease in the oxygen-carrying capacity of the blood. Infants, less than 3 months old, are particularly susceptible to methemoglobinemia. A number of cases, resulting in death, have occurred from nitrite formed from nitrate in water. A lesser number of cases have occurred from ingestion of vegetables having a high concentration of nitrites.

Epidemiological studies in Czechlosovakia and Poland implicated atmospheric nitrate as the etiologic agent in methemoglobinemia; however, these studies were not conclusive since the nitrate concentration in drinking water was not considered. Studies in the U. S. have associated airborne nitrates with aggravated asthma attacks. These preliminary data suggest that certain nitrate compounds found in urban atmosphere may be either direct or indirect respiratory irritants; however, more information is needed for confirmation.

Nitrosamines have been shown to be potent carcinogens in animal experiments. N-nitrosamines are formed by reaction between nitrous acid and tertiary and secondary amines. The reaction is dependent upon the concentration of nitrite, the pH of the medium (acidic), and the reacting amine, and cofactors such as formaldehyde, thiocyanate, and chloral. Laboratory experiments with animals suggests rather strongly that such reactions can take place in the mammalian stomach. Nitrosamines have been shown to be effective carcinogens in animals by all routes of administration. The formation of a carcinogen in one tissue may lead to tumor formation in an entirely different tissue. A slight change in the molecular structure of the nitroso compounds may cause a significant change in the carcinogenic activity. Nitrosamines are highly unstable. They have not been found, and it is unlikely that they will be found in the atmosphere; however, the possibility cannot be ruled out at this time. There is much that is yet to be learned concerning the chemical characteristics of atmospheric aerosols.

There is substantial evidence that some human cancers, particularly those of the respiratory tract, are more frequent in urban than in non-urban areas. There is some evidence to suggest that this "Urban factor" may in part be due to air pollution. The polycyclic aromatic hydrocarbons known to be present in urban air have long been suspect as the responsible agents, but a possible role for nitrosamines should be investigated when and if they are detected in the atmosphere.

The most significant effect of the alteration of the nitrogen cycle by man, through fertilization and waste disposal practices, is the eutrophication of lakes, rivers, and esturaries, and the contamination of drinking water supplies. Eutrophication may have beneficial results by increasing the productivity in the receiving bodies of water. However, in many areas, the excess of nitrates (or other nutrients) results in excessive growth of algae and other aquatic plants which reduce the oxygen supply in the deeper water. This condition may significantly affect marine life in the water systems. Nitrate in rainfall may contribute approximately 10 percent of the nitrate loading in surfaces waters.

High levels of inorganic nitrate found in ambient air do not have adverse effects on plant life; however, plants will accumulate high concentrations of nitrate under certain conditions. This has resulted in cases of acute nitrate poisoning of domestic livestock. Extensive damage to crops and ornamental plants has resulted from exposure to PAN.

Nitrates contribute to the initial corrosion of metals, but are not considered a major problem. High nitrate levels in Los Angeles have resulted in failure of electronic components through stress corrosion cracking.

Information concerning primary emissions of nitrates from stationary sources is lacking. The major source of nitrates in urban atmospheres is the conversion by atmospheric reactions of oxides of nitrogen emitted from the combustion of fossil fuels in stationary and mobile sources. Oxides of nitrogen (primarily NO) are produced in the combustion process by two mechanisms. The first is the fixation of atmospheric nitrogen, which has an exponential dependence on temperature and a lesser dependence upon the oxygen supply. The second mechanism is the oxidation of chemically bound nitrogen in the fuel itself in which the rate of oxidation is nearly temperature independent, but is strongly dependent upon the availability of oxygen. It has been estimated that approximately 50 percent of the NO_x produced by the combustion of heavy oils and coal is created by the conversion of the bound nitrogen. The formation mechanisms provide the basis for control strategies. The general control techniques are known, however, application to practical combustion systems is uncertain. Experience to date is almost exclusively with utility boilers.

Federal emission standards have been promulgated for new utility boilers greater than 25 MW for all fuels. Boiler manufacturers are currently selling units guaranteed to meet these standards. Federal emission standards are being proposed for stationary gas turbines fired with natural gas or fuel oil. Emission standards have not been proposed for other stationary sources. Standards for oxides of nitrogen emissions from mobile sources have been established.

The primary source of nitrates from industrial processes is fertilizer manufacturing. Data are limited as to the actual nitrate emitted. Nitric acid plants emit up to 10 ppm of HNO_3 mist, but the major contribution to the atmospheric nitrate loading is probably from the conversion of NO_x to nitrate. No proven control process is available. Advanced waste treatment processes are being developed which include nitrogen-removal by ammonia-stripping, ion-exchange, biological nitrification and break-point chlorination. The effectiveness of these processes vary depending upon the quality of the water involved, where they are used, and their location in the treatment sequence. Pilot studies have indicated that a substantial increment of organic nitrogen in the effluent from an activated sludge plant could be removed by filtration. The problems associated with the handling of runoff and solid waste are equally as complex--not the least of which is economics.

Although data are limited, it does not appear that significant amounts of nitrate are emitted directly from mobile sources. Atmospheric loading from mobile sources results primarily from the emission of oxides of nitrogen (principally NO) which is then converted to nitrates in the ambient atmosphere. Control strategies consist of modification of conventional internal combustion engines with oxidation catalyst, and the introduction of alternative combustion engines. Statuatory emission standards for mobile sources have been established at 0.4 g/mile to be achieved by 1977.

Nitrate and oxides of nitrogen concentrations in the atmosphere are not linearly related. An acceptable level of nitrate in the atmosphere has not been established, and the data to do so are not adequate at this time. Further, it is not known as to what extent it would be necessary to reduce oxides of nitrogen emissions in order to achieve an acceptable level of nitrate.

2 CONCLUSIONS

The total nitrogen cycle of the earth is still not well understood. The distribution and rate of transfer within and between the lithosphere, atmosphere, and hydrosphere can be estimated only within very broad limits. The only quantities thought to be known reasonably well are the amount of nitrogen in the atmosphere and the rate of industrial fixation. With the very limited available information, it is difficult to determine precisely the extent to which man's activities may influence the total nitrogen cycle. There is no clear evidence to indicate that these activities tend to deplete the earth's nitrogen supply in the same manner that has been argued in the case of oxygen. There is, however, rather conclusive evidence that man has significantly altered the distribution and chemical characteristics of nitrogen compounds in some of those regions in which he lives. Some obvious and undesirable effects of this alteration have been observed, and speculations made on more subtle effects that may be even more significant. Hence assessment can only be partially complete. Based upon available data, a number of conclusions can be reasonably drawn:

(1) There are three major activities by which man has significantly altered the nitrogen cycle on a local scale: combustion of fossil fuels, industrial fixation of nitrogen, and the generation and disposal of waste materials.

(2) All of the above activities at present are essential to man's existence and well-being; therefore feasible corrective actions must be based on management practices which in most cases are technology dependent.

(3) The atmospheric nitrate concentration in certain urban regions in the U. S. has been increased by orders of magnitude on a temporal basis as a result of the combustion of fossil fuels. The areas affected may extend several hundred kilometers beyond the urban boundaries.

(4) Nitrates in the urban atmospheres are due primarily to atmospheric chemical transformations of oxides of nitrogen. The secondary nitrate-containing aerosols are normally found in a size range of less than 1 μm in diameter, except possibly in maritime areas; therefore, they are respirable particles, of a size range which affects visibility, remain suspended in the atmosphere for several days, and are involved in precipitation processes.

(5) Nitrates in urban atmospheres consist of a wide range of inorganic and organic compounds. The present monitoring system is inadequate to characterize these compounds.

(6) Studies have shown a statistical association between nitrates, as measured in the atmosphere, and the aggravation of asthma. These results suggest that some nitrate compounds may be a direct respiratory irritant, although this has not been shown conclusively. Specific nitrate compounds have not been identified as causal agents.

(7) Certain species of nitrates found in urban atmosphere are known to cause damage to sensitive agricultural crops and ornamental plants.

(8) The nitrate concentration in precipitation in urban areas is generally higher than in non-urban areas.

(9) The nitrate concentrations in some surface waters in the U. S. have increased significantly as a result of discharges of municipal waste water; runoff from agricultural land and urban areas; animal wastes, refuse disposal and precipitation. Precipitation nitrate accounts for approximately 10 percent of man-made contributions to surface waters. This has resulted in eutrophication of lakes and streams, with associated major shifts in aquatic life and production of algal blooms. Nitrates in well water in many parts of the U. S. exceed the PHS standard of 10 mg/l.

(10) The uptake efficiency of nitrogen by plants is less than 50 percent. The probability of loss of nitrogen from the soil increases with intensified agriculture. Portions of the natural organic nitrogen, as well as industrial nitrogen applied as fertilizer, will be lost. The amount and rate of loss varies depending upon soil conditions, biotic species, rainfall, agricultural practices, etc. The contribution of nitrate in precipitation to nitrate concentration in plants is small compared to that from application of nitrogen containing fertilizers. The changes in the nitrogen cycle resulting from agricultural activities do not appear to be permanent or irreversible.

(11) The nitrate-nitrite content in foods used by man and domestic animals varied widely. Some of the variability may be attributed to fertilization practices; and to processing, handling, storage, and preparation practices. Certain foods and tobacco contain small concentrations of nitroso compounds which have been shown to be carcinogens in animals.

(12) Methemoglobinemia in humans (principally infants) and domestic animals has been associated with excess nitrate in water and food, but not in the atmosphere. The contribution from inhalation is small except in cases of occupational exposure.

(13) Nitrosamines have been shown to be potent carcinogens in animals. Ingestion of nitrite with certain secondary amines can lead to the formation of the carcinogenic nitrosamines in animals. This information suggest that these compounds in foodstuffs may contribute to the occurrence of human cancer, although this has not been shown.

.3 RECOMMENDATIONS

Nitrate is one of the end products of urban aerosol and smog formation, although it is not known what extent the oxides of nitrogen precursors serve as the universal controlling factor. The bulk of the available data only provides an estimate of the water soluble nitrates collected on a glass fiber filter. Based upon laboratory experiments and theoretical considerations, it is known that a wide variety of nitrate compounds may occur in the ambient atmosphere of urban areas and that these may be transported for hundreds of kilometers from the source area. The exact chemical nature of these nitrate compounds has not been determined. The controlling rate factors for urban aerosol formation are not well known. It is known that the rates of reaction are concentration dependent, but they are not linearly related. Knowledge concerning these factors is particularly important to the question of control strategies. Present capability is inadequate to provide the necessary data to characterize and understand the nature and extent of aerosol formation in ambient urban atmospheres in general, and the role of nitrates in particular. Available data indicate that atmospheric nitrates may act as direct respiratory irritants, and theoretical considerations suggest that they may contribute to the increased incidence of human cancer observed in urban areas; although the specific compounds which may serve as the causal agents, and their threshold values, are not known. Concentrations of these specific compounds have not been measured in the ambient atmosphere. The above are important gaps in our knowledge concerning nitrates in the atmosphere. Insight into these problem areas is essential if prudent decisions concerning the control of urban smog formation and its undesirable consequences are to be made. The following research and interim action programs are recommended.

(1) The present oxides of nitrogen air quality and emissions standards for stationary and mobile sources should be achieved within the shortest time frame feasible consistent with economic and social constraints. Based on possible health effects, specific emphasis should be given to those geographical areas which currently experience annual average nitrate concentrations on the order of 3 to 5 $\mu g/m^3$ or greater.

(2) An adequate routine monitoring system for nitrates should be developed and implemented. This will require the development and evaluation of suitable nitrate measurement techniques. Information concerning size distribution and chemical characterization should be either implicit in the concentration measurement or these parameters should be studied directly. Standard siting, sampling, preparation and analysis procedures should be established for the monitoring network.

(3) An extensive research effort is recommended to obtain an understanding of the nitrate aerosol formation, transport and removal processes in urban atmospheres. Particular emphasis should be given to determining the controlling rates of reaction as a function of precursor concentrations, and the transfer mechanisms (atmospheric removal) between the atmosphere, water, and soil. An integral part of this effort should be the chemical and physical characterization of nitrate aerosols in the different urban areas. Specific emphasis

should be given to carcinogenic compounds. It should also include the extent to which atmospheric removal processes contribute to the eutrophication of our surface waters.

(4) The question of the contribution of urban air pollution to the prevalence of human cancer and respiratory diseases is paramount. An integrated clinical, epidemiological, and toxicological research program is recommended to resolve the question of the "urban factor" in general, and the cause and effect relationship of inhalation of specific compounds in particular. This program should address specifically the questions of whether or not certain nitrate compounds observed in the atmosphere serve as direct respiratory irritants, and whether or not they contribute to human carcinogenicity, mutagenicity, and teratogenicity.

(5) Suitable strategies and technology for the control of primary nitrate particulate emissions, and the processes of secondary nitrate aerosols, should be developed. The program should include the development and implementation of interim measures to control the oxides of nitrogen emissions from the combustion of fossil fuels. Knowledge obtained from the research effort recommended above will be necessary to select the appropriate control strategy and to determine the level at which emissions should be controlled. The ultimate solution must address the problem of alternative energy sources. Nitrates in the atmosphere resulting from industrial product sources can best be controlled on the basis of emissions, equipment performance, and disposal standards.

SUMMARY OF NERC/RTP CURRENT RESEARCH ACTIVITIES RELATING TO NITRATES

A number of research projects currently are underway at the National Environmental Research Center, Research Triangle Park, either in-house or via contract, which will provide further insight into the problems relating to nitrates in the atmosphere. These are described briefly.

1 MEASUREMENT AND ANALYSIS

A study is underway to improve and optimize electrometric methods for measurement of nitrate and sulfate in particulates, to evaluate the effects of substrates and environmental conditions on collection of nitrates on filters, and to evaluate laboratory analysis methods for atmospheric nitrates. An ion selective electrode nitrate monitor, designed to provide a real-time indication of nitrate concentration averaged over 1 to 3-hour periods, has been developed and is now being evaluated.

2 HEALTH EFFECTS STUDIES

All ongoing CHESS studies include daily measurements of suspended nitrate levels and consider adverse health effects associated with this pollutant. Contracts have been awarded for studies on the relative toxicity of the respirable fraction of total suspended particulate (TSP), sulfates, and nitrates, and to study the effects of controlled exposure to sulfates and nitrates on environmental responses.

3 FORMATION AND DECAY OF POLLUTANTS

The research program in Formation and Decay of Pollutants has included the formation, decay and transport of nitrates as one of its major areas of concentration. The majority of the projects in this program can be expected to have some bearing on our understanding the nitrate problem. A number of projects are devoted mainly to nitrates, and are discussed below:

(1) An intramural research program on nitrogen compound photochemistry is being conducted in the EPA Research Triangle Park Laboratory. At present the principal research facility being used is a long path infrared photochemical reactor which is coupled to a Fourier Transform Spectrometer. Information is being acquired on nitrite photolysis, PAN production, nitric acid formation, and other topics of interest. These intramural nitrate studies will be extended to the large 500 cubic foot irradiation chamber which is presently being put into operation. The experimental studies are complemented by an intramural modeling program in which the experimental observations are fit into the overall chemical kinetics scheme by which pollution photochemistry is quantitatively described.

(2) Field measurements of nitrates are being carried out concurrently with the intramural laboratory studies. First, there is an intramural field program which was conducted in 1973 at Pasadena, California, and will be continued in 1974 at Houston, Texas, and St. Louis, Missouri. This program includes the measurement of gaseous and particulate nitrates. Secondly, there is a field program being conducted under contract with the Battelle Institute. This program is specifically addressed to the problem of accounting for the fate of all the nitrogen compounds emitted into the air.

(3) A program specifically addressed to the chemistry of the PAN compounds is being sponsored at the Illinois Institute of Technology Research Institute. The program is aimed at development of a better understanding of the fate of the PAN's in the air.

(4) Several of the aerosol characterization projects within the program are addressing the question of the nitrate component of the aerosols. Grants at the University of California, the University of Minnesota, Washington University, St. Louis, and the University of Washington are all contributing to development of the knowledge of nitrate aerosols. Under an interagency fund transfer from EPA, the Brookhaven National Laboratory is studying the formation of nitrates in power plant plumes.

(5) An outdoor smog chamber facility is being established at the University of North Carolina for study of aerosol formation in polluted air. A special effort will be devoted to the identification of the gas-particle interactions in the air. Nitrate formation will come into this project strongly. A close cooperation is being initiated between EPA personnel and the University of North Carolina personnel. The EPA role will be mainly to bring its long path infrared competence and facilities to bear on the study of the gas-particle interactions, while the University of North Carolina role will be the operation of the facility and the characterization of the particulate reaction products.

(6) A pollution up-take project is being initiated intramurally. In this study an attempt will be made to identify the rates at which

nitrogen containing compounds can be lost to surfaces in urban and rural areas. The gas-surface interaction facility of the Chemistry and Physics Laboratory Materials Section will be applied in the study. Initially the study will be addressed to the relative rates of loss of various pollutants to surfaces under controlled laboratory conditions.

4 CONTROL TECHNOLOGY

1 Stationary Sources

The Control Systems Laboratory R&D program is composed of four major research categories: (1) field testing and surveys, (2) process research and development, (3) fuels research and development, and (4) fundamental combustion research. Field testing and surveys includes studies designed to determine what can be done today to control NO_x emissions. This work is conducted on commercial equipment and is generally performed by research and development organizations familiar with the specific combustion systems being studied, and often with the financial and technical assistance of the manufacturers, users, and trade associations. In addition to developing trends and providing directional recommendations for industry to minimize emissions with today's technology, the work also defines where the research and development efforts should be concentrated by developing emission factors as a fraction of equipment type and size, and fuel consumed. The field testing and survey studies are the initial efforts in the development of control technology and are designed to provide the state of the art in control of NO_x emissions from today's commercial combustion systems.

1.1 Processes--Process research and development work involves studies with commercial or prototype combustion systems to develop cost and design information for the application of the optimum NO_x control technology to classical combustion systems (existing and new). The specific objective in this area is to develop design and operational guidance manuals that can be used by manufacturers and users to control NO_x emissions by combustion modification techniques. The results of the studies in this category provide the basis for the demonstration of combustion control technology. As in Field Testing and Surveys, these studies involve industry participation.

1.2 Fuels--Fuels research development studies are conducted in versatile experimental combustion systems and are designed to develop generalized combustion control technology which is applicable to the optimum control of NO_x emissions from the combustion of both conventional fuels and fuels of the future (e.g., coal derived fuels). These engineering research and development studies will provide the future goals for NO_x control and will generate the necessary technology to be applied in the Process Research and Development area.

1.3 Combustion --Fundamental combustion studies are basic investigations of the chemistry and physics of pollutant formation in combustion systems. The results of the work provide the fundamental understanding required for the generation of optimum NO_x control technology in the Fuels Research and Development studies and for the general application of the optimum NO_x control technology in Process

Research and Development. This understanding will be developed from experimental studies in idealized combustion systems. The results will provide the fundamental basis for mathematical simulations of pollutant formation and control during combustion.

1.4 Combustion Flue-Gas--Combustion flue-gas treatment processes to remove NO_x are under development. The control of NO_x emissions by combustion modifications can be limited by special process requirements for very high temperatures, limited space restrictions, or possibly the inherent fixed nitrogen content of the fuel. Flue-gas treatment techniques, including selective catalytic reduction, aqueous alkaline scrubbing, and other selective adsorption and absorption techniques, are under development.

1.5 Nitric Acid--Nitric acid manufacturing processes emit small quantities, but high concentrations of NO_x. By 1975, control using molecular sieves will be demonstrated in a form which is applicable to new and existing ammonia oxidation process nitric acid plant industry sources. Molecular sieves should permit a reduction in NO_x emissions by at least an order of magnitude below the level attainable with existing technology.

1.6 Planned Research and Development--It is imperative that a better data base for fine particulate, including specific species of nitrates, from stationary sources be developed. A standard analytical scheme is under development and will be utilized to develop this data base during all future sampling of stationary sources - especially as related to EPA demonstrations of control technology.

1.7 Problem Areas--In order for the Agency to make decisions with respect to the control of nitrates, it is necessary to establish immediately a better data base on the physical and chemical characterization of fine particulate emissions from stationary sources.

Strategy and methods for the control of gaseous precursors of secondary fine particulate matter, as well as nitrates, emitted by stationary sources must be developed. Before the magnitude of the necessary effort here can be determined, we must know the level of control required.

2 Mobile Sources

Research is currently underway to measure nitrate emissions directly from raw vehicle exhaust. These efforts involve filtration of particulate matter and wet chemical analysis for nitrate by colorimetric methods. The sensitivity of this method is less than one microgram per milliliter of extraction solution. So far, no nitrate has been positively detected by this approach, due probably to the sampling technique and lack of program coordination with the vehicle testing operations. Both catalyst-equipped and conventional automobiles are being investigated for direct nitrate emission and the effect of various types of control devices on the nature of the particulate emissions.

During the course of the above work, efforts were made to adapt existing chemical analysis procedures to the routine measurement and possible monitoring of vehicles for nitrate emissions. Some procedures show good results and have possibilities for the incorporation into a certification procedure for automotive exhaust.

Work is currently underway to investigate the particulate emissions from catalyst-equipped vehicles designed to meet the 1976 emission standards. These vehicles were equipped with oxidation-type catalysts designed to reduce CO and hydrocarbon emissions, but may, in fact, increase the emission of oxidized species like sulfuric acid, nitric acid, sulfate, and nitrate. Particulate emissions from these cars are being analyzed to determine if this is so. Also, work with the reductive type-catalysts like Ni-Cu used for the reduction of NO_x gases emissions is anticipated. In the latter case, besides the determination of the effectiveness for reducing NO_x emissions, a program for determining the presence and concentration of ammonia from these reductive catalysts will begin.

Some exploratory work has begun on the collection and analysis of particulate matter from aircraft turbine engines mounted on a test stand. There were some problems with the original collection system, but with an improvement in this an active program can be initiated to collect and analyze by particle size classes the emitted particulate matter for nitrate.

CHAPTER VII.

THEORY OF FORMATION AND PROPERTIES OF PHOTOCHEMICAL AEROSOLS

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Presented at the Conference on Health Effects of
Atmospheric Salts and Gases of Sulfur and Nitrogen
in Association with Photochemical Oxidant

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CHAPTER VII.

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1. Introduction

Ever since Tyndall's classical experiments in the 19th century on aerosol optical behavior, it has been known that exposure of reactive gases to light can produce copious quantities of airborne particles (Mohnen and Lodge, 1969). More recent observations have led investigators to speculate that the sunlight induced chemical reactions are responsible for a major fraction of intense haze observed over cities such as those in southern California. The link between photochemical reactions in polluted air was demonstrated in the early 1950's by Haagen-Smit and co-workers and was explored by a number of investigators including Stephens, Hanst, and Renzetti and Doyle (for a review, see Leighton, 1961). With the requirements for specific air quality standards on particulate matter becoming more stringent, there is increasing activity devoted to photochemical aerosol research. While new laboratory experiments have been reported, major new field studies have been implemented to characterize atmospheric haze formation in greater detail. Perhaps best documented of these is the 1969 Pasadena Smog Aerosol Study, reported in Aerosols and Atmospheric Chemistry (Hidy (ed.), 1972). This project was an exploratory program, but a much larger study, as yet incomplete, was undertaken in 1972 under sponsorship of the California Air Resources Board to study aerosol behavior in several California locations.

Photochemical aerosols in the atmosphere require at least an operational definition. Certainly such a definition can be derived in a straightforward way in controlled laboratory experiments by studying irradiated mixtures of gases. However, in the atmosphere such a definition becomes much more difficult because of the complexities of air chemistry constituting a mixture of processes that are both sunlight induced and non-photochemical in nature. The traditional definition of photochemical aerosols in the atmosphere are particles in air that are related to hazes formed in a time scale of hours in daylight. Perhaps the best documented example is the intense haze formation associated with photochemical smog over Los Angeles. To illustrate this phenomenon, let us pause for the showing of a short film of smog evolution produced by the U.S. Forest Service and the University of California Riverside Statewide Air Pollution Research Center and the University of Calif., Los Angeles. (Note in this film the development of the smog aerosol during the day and the extensive light scattering associated with the airborne particles.)

The crux of photochemical aerosol behavior in a polluted atmosphere is the quantitative description of the chemistry (composition) and physics of this airborne material. In this lecture, we shall review briefly the accumulated knowledge on the physical and chemical nature of urban haze, identified as material associated with photochemical smog. The common observational denominators for such observations are then summarized for a framework to test hypotheses for interpretation based on our knowledge of chemistry. After reviewing the constraints on atmospheric aerosol formation, placed by aerosol physics, the second part of these discussions is of the current knowledge of formation mechanisms of urban photochemical aerosols. The mechanistic information places heavy reliance on chemical identification of "photochemically" important aerosol constituents and the information derived from laboratory experiments and educated guesses. These results are used to construct tentative hypotheses about the formation of hazes during photochemical smog development.

2. Atmospheric Observations

Virtually all of the information that is believed to be relevant to photochemical aerosol behavior is derived from the study of the Los Angeles atmosphere. For purposes of discussion, let us consider first the data characterizing of the aerosol physical properties, then the aerosol chemical properties.

Physical Properties. Over the years in which photochemical smog has been identified as such in Los Angeles, the visibility has degraded steadily despite a marked decrease in total mass concentration of airborne particles. This change is believed to be related to shifts in a key parameter, the aerosol size distribution. Shown in Table 1 is a list of important physical parameters related to the size distribution, $n(v)$. These six properties with the mass density ρ_i and the index of refraction characterize the aerosols. For urban atmospheric aerosols, the average density is approximately 1.7, and the (real part of the) index of refraction is believed to be 1.4 - 1.5.

Table 1

PHYSICAL PROPERTIES OF AEROSOLS

1. Size Distribution Function	$n(v)$	$(\frac{\text{\# of particles}}{\text{volume-particle volume}})$
2. Total Number Concentration	$N = \int_{0}^{v'} n(v)dv$	$(\frac{\text{\# of particles}}{\text{volume of gas}})$
3. Surface Area per Unit Volume	$S \sim \int_{0}^{v'} v^{\frac{2}{3}} n(v)dv$	$(\frac{\text{particle surface area}}{\text{volume of gas}})$
4. Volume Fraction	$(\phi) = V \sim \int_{0}^{v'} vn(v)dv$	$(\frac{\text{particle volume}}{\text{volume of gas}})$
5. Mass Concentration	$m = \int_{0}^{v'} \rho_i v_i n(v_i)dv_i$	
	$= \bar{\rho}\, V$	$(\frac{\text{mass}}{\text{volume of gas}})$
6. Light Scattering -- Extinction Coefficient	$b_{scat} \sim \int_{0}^{v'} F(r,\theta,v,\ell)v^{\frac{4}{3}} n(v)dv$	

$F(r,\theta,v)$ = complicated function of index of refraction (r), angle (θ), and wavelength (ℓ) of incident light, and particle volume.

As an illustration of the size distributions measured in urban and non-urban locations several cases are shown from the 1972 California Aerosol Characterization study in Figure 1. An automobile dominated site is the Harbor Freeway, a desert background site is the Goldstone station, and a marine air dominated site is Pt. Arguello. Spectra showing aerosol growth by atmospheric chemical transformations are represented by the Pomona data. Note the strong similarity in the distributions above a diameter of 0.1 μm, indicating the relative lack of sensitivity to changes in this kind of plot. Note also the power law forms of the "average" distribution function.

Differences in aerosol size distributions are more sharply contrasted by the second and third moments of the size distribution, as pointed out by Whitby and others. This will be shown in the graphs - Figs. 2 and 3. In the extreme size ranges of < 0.1 μm and > 1.0 μm diameter are seen the influences of combustion aerosols and "natural" sources like windblown dust and sea salt.

Evidence suggests that the atmospheric chemical transformations are concentrated in 0.1 - 1.0 μm range, where a strong effect is seen in the Pomona data. Interestingly enough, however, if the existing particles are removed, the reactive gases produce large quantities of nuclei upon irradiation (Fig. 3A), as observed by Husar et al. (1973).

The influence of changes in the spectrum in presence of smog taken for Pasadena in 1969 by Whitby and colleagues are shown for a different set of data in Figure 4. Here the growth of particles in the size 0.1 to 1.0 μm range is indicated as the day progressed.

The link between the accumulation of material by physical or chemical processes in the submicron range and the light scattering (causing visibility change) is shown in Figure 5. The change in b_{scat} with size for aerosol distributions taken in 1969 in Pasadena were calculated from scattering theory by Charlson and colleagues. These data provide strong evidence, phenomenologically, that the sharp changes in light scattering calculated from the changes in the size distribution can readily be related to the visibility variation in the Los Angeles area.

The observations taken in Pasadena during 1969 gave a first glimpse of the relationship between changes in gaseous photochemical pollutants and

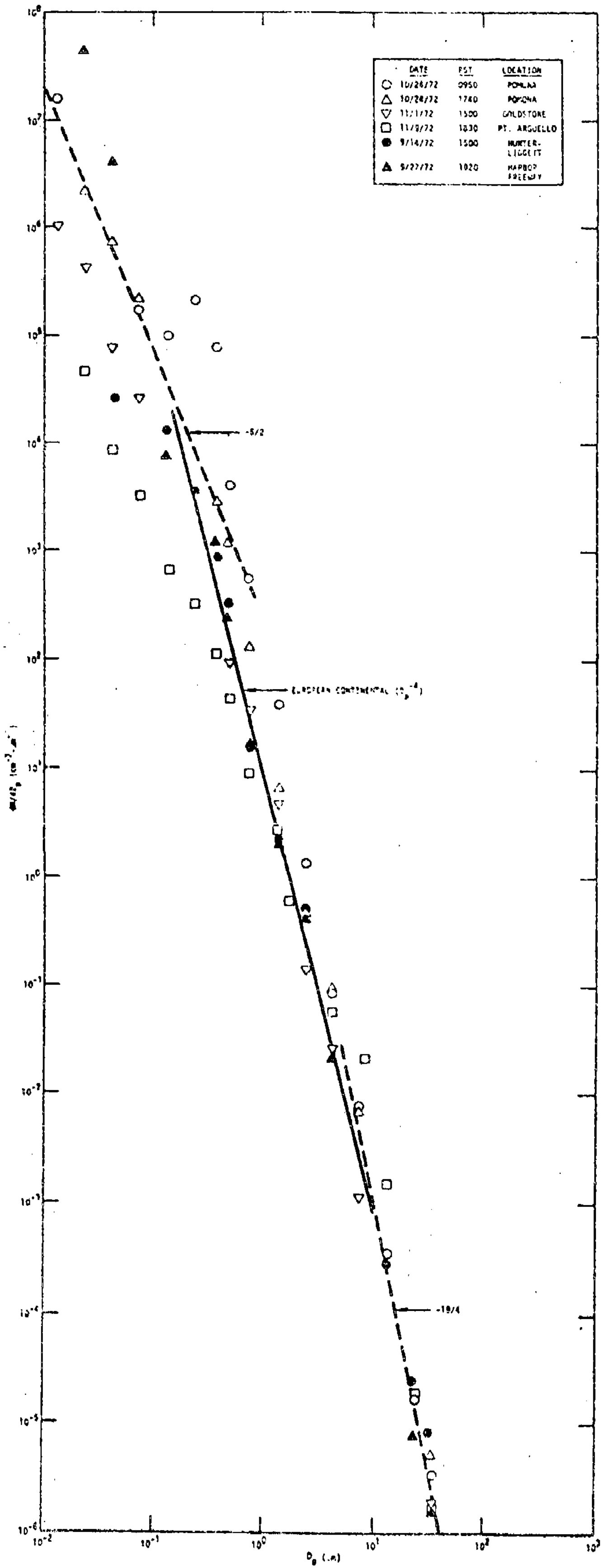

DATE
PST
LOCATION
○ 10/24/72 0950 POMONA
△ 10/24/72 1740 POMONA
▽ 11/1/72 1500 GOLDSTONE
☐ 11/9/72 1030 PT. ARGUELLO
● 9/14/72 1500 HUNTER-LIGGETT
▲ 9/27/72 1020 HARBOR FREEWAY
-5/2
EUROPEAN CONTINENTAL (D_p^{-4})
-19/4
dN/dD_p ($m^{-3} \cdot m^{-1}$)
D_p (m)
10^8
10^7
10^6
10^5
10^4
10^3
10^2
10^1
10^0
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
10^{-2}
10^{-1}
10^0
10^1
10^2
10^3

Fig. 1

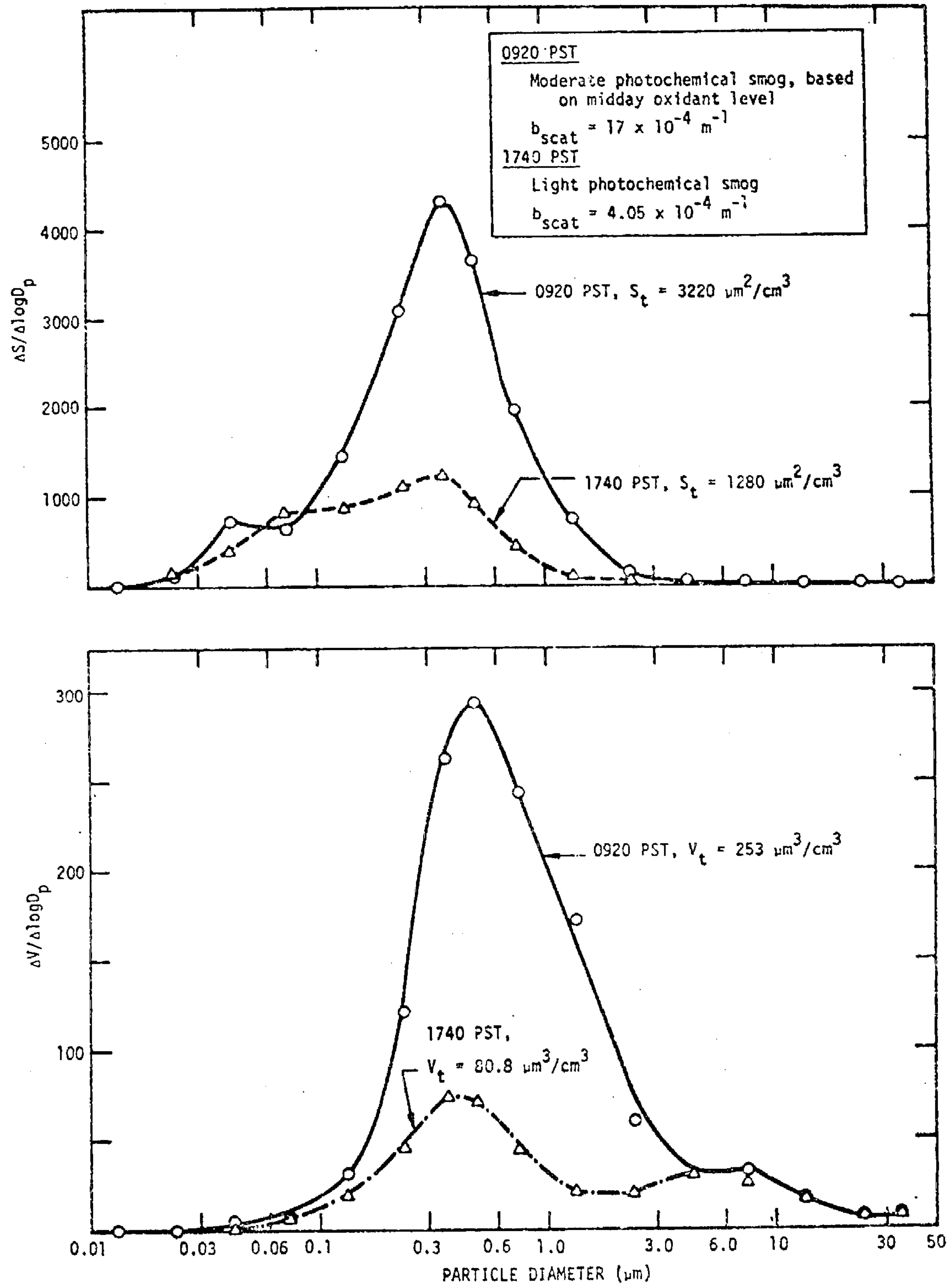


Fig. 2 Surface and Volume Distributions Taken at Pomona on October 24, 1972

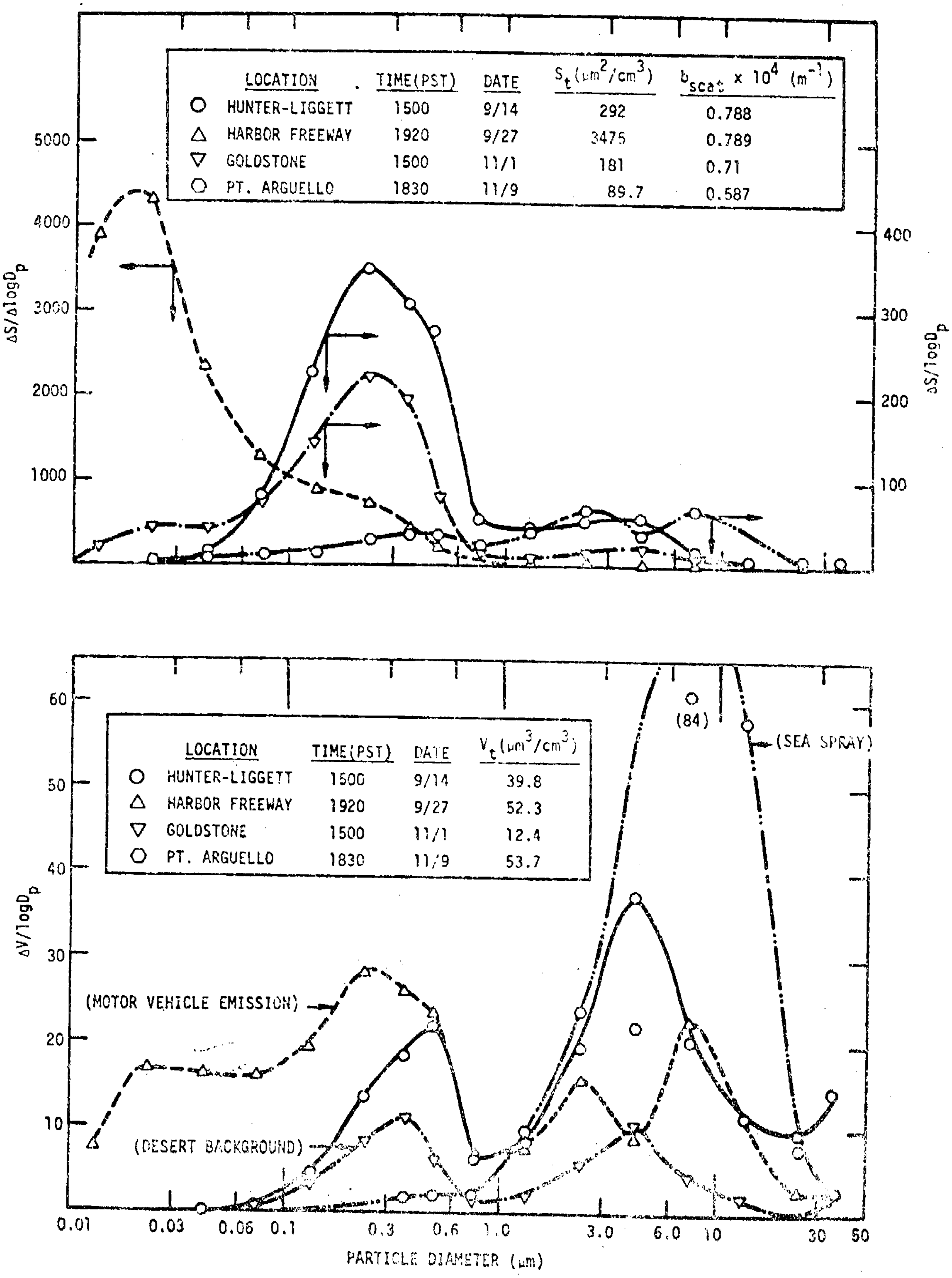
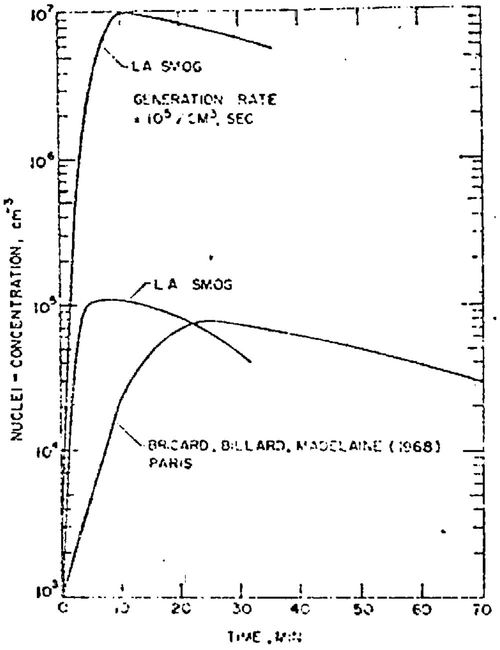


Figure 3 Comparison of Surface and Volume Distributions for Background and



The change of the total number concentrations in an irradiated, initially particle-free container: The initial concentration rise is due to nucleation and the subsequent decay is due to coagulation.

Fig. 3a

(from Husar et al.)

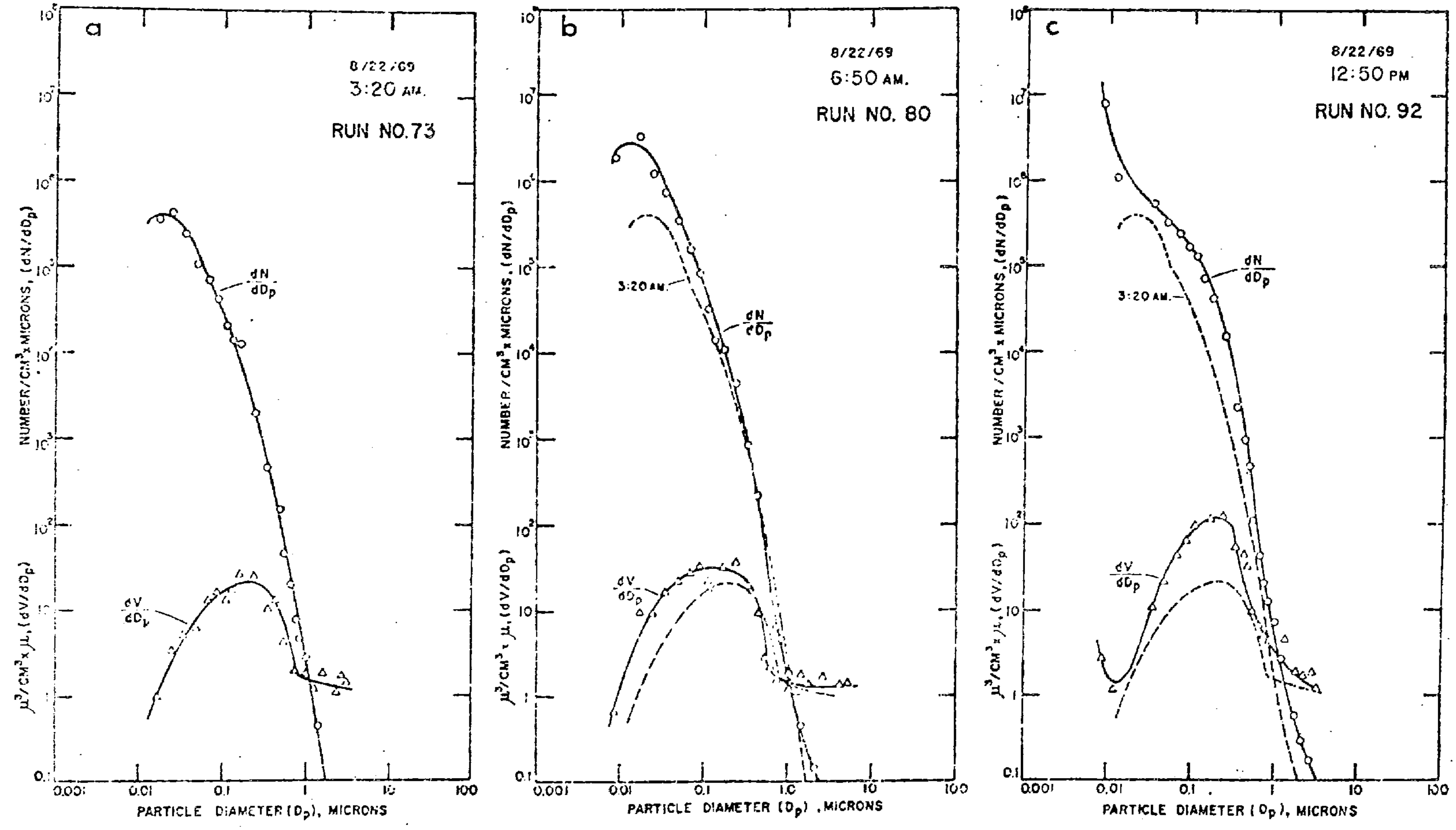


Fig. 4 Change in Aerosol Distribution during the Day in Pasadena (from Whitby *et al.*)

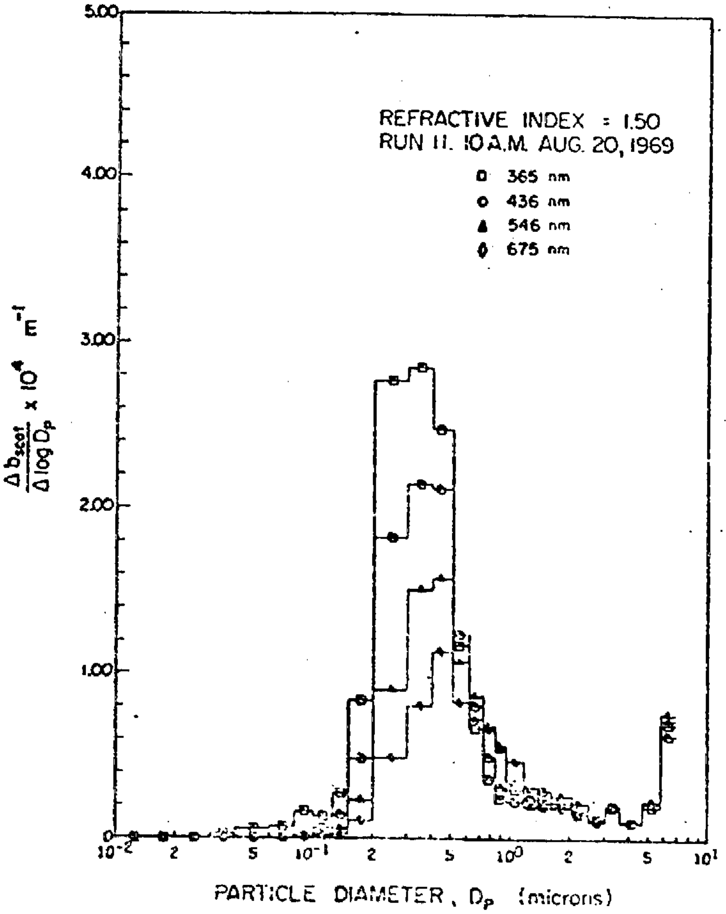


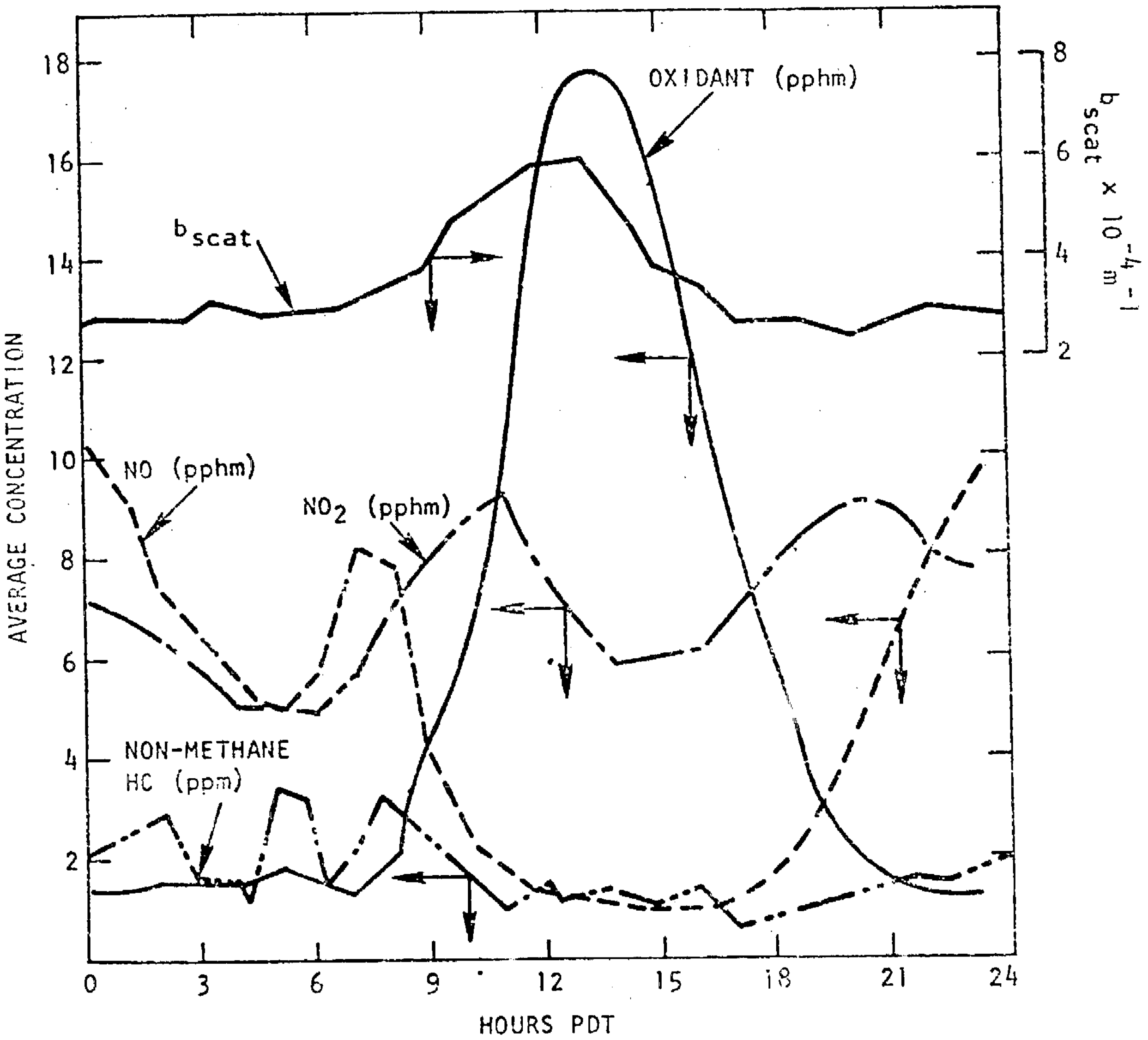
Fig. 5 - $\Delta b_{scat}/\Delta \log D_p$ as a function of particle diameter for a particle refractive index of 1.50 (linear-log plot). (From Charlson et al.)

changes in aerosols. Examples of such data are given in Figures 6 and 7. These data are composite averages taken for three different days. They suggest that the pattern of change in b_{scat} corresponds to change in oxidant level. The diurnal patterns of the moments S, ϕ, and N in Fig. 7 suggest that the behavior of the total number of particles (dominated by < 0.1 μm material) differs from ϕ and S, which are dominated by particles > 0.1 μm. The diurnal changes similar to peak ozone level are in the larger particles.

Like most cases of observations of natural phenomena the data taken in Pasadena were shown to characterize only a part of combinations of diurnal behavior of smog. For example, the results taken at a number of locations last summer indicated that the b_{scat} vs. O_3 correlation is not well established as a general rule (Fig. 8, for example). Examination of the "autocorrelation" of these parameters and others such as ultraviolet radiation show complex relationships that are not understood at present. Some examples taken in Pasadena on 9/20-21/72 are shown in Figs. 9 and 10. This was a day that had low relative humidity and mild smog, as characterized by the ozone level. Here the aerosol behavior during a thirty hour time lag interval shows a correlation pattern where u.v. radiation and ozone either lead or lag the b_{scat} significantly by several hours.

Chemical Properties. Perhaps more important than the physical changes to photochemical aerosol identification is the chemical composition of the aerosol. In particular, the evidence accumulated over many observational programs strongly points to the compounds of sulfur, nitrogen, and carbon as those of greatest significance in relation to smog. The Los Angeles aerosol long has been known to be rich in nitrate and organics and has significant quantities of sulfate despite the low levels of total sulfur in this urban atmosphere.

A typical breakdown of the chemical constituents of the Los Angeles aerosol is listed in Table 2. Most of this data comes from the California Air & Industrial Hygiene Laboratory and associated institutions. The importance of carbon and sulfur is indicated, but the nitrate levels were lower than often reported in this instance. Other data for key constituents of the Los Angeles aerosol are shown in Table 3. These results were obtained from analysis of 24 hour hi-vol filter samples during the 1972 program.



OXIDANT (pphm)
b_{scat}
NO (pphm)
NO_2 (pphm)
NON-METHANE
HC (ppm)
AVERAGE CONCENTRATION
$b_{scat} \times 10^{-4} m^{-1}$
HOURS PDT
18
16
14
12
10
8
6
4
2
8
6
4
2
0
3
6
9
12
15
18
21
24

Figure 6

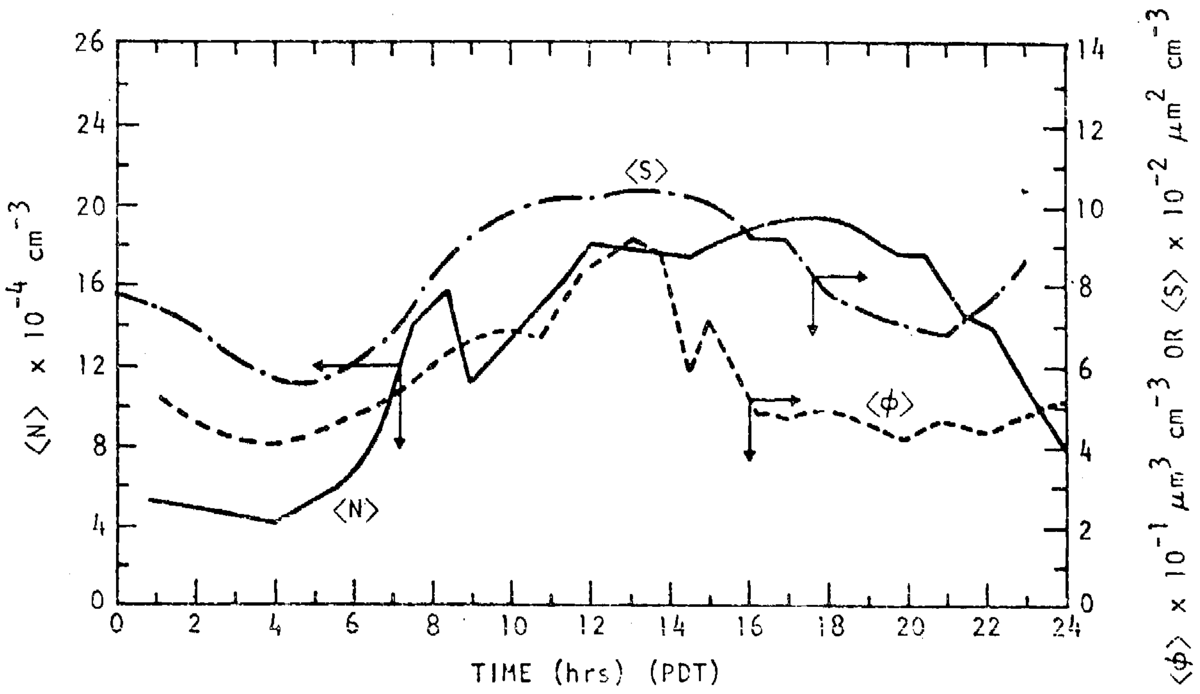

26
24
20
16
12
8
4
0
0
2
4
6
8
10
12
14
16
18
20
22
24
TIME (hrs) (PDT)
⟨N⟩ × 10⁻⁴ cm⁻³
14
12
10
8
6
4
2
0
⟨ϕ⟩ × 10⁻¹ μm³ cm⁻³ OR ⟨S⟩ × 10⁻² μm² cm⁻³
⟨S⟩
⟨N⟩
⟨ϕ⟩

Figure 7

Fig. 8

COMPARISON BETWEEN PEAK OZONE CONCENTRATIONS AND PEAK b_{scat} DURING INTENSIVE EPISODES

Date	Location	Time of O_3 peak*	Peak O_3 (pphm)	$b_{scat} 10^4 (m^{-1})$ at peak O_3	Time of b_{scat} Peak*	Peak $b_{scat} \times 10^4 (m^{-1})$	O_3 Conc. (pphm) at b_{scat} peak
8-11	San Pablo	1236	2.3 (Mast)	1.15	same	--	--
8-15	San Pablo	-	-	-	1310	.346	2.2
8-22	SFOAP	1550	2.29	0.608	2050	0.836	0.77
9-1	Fresno	1320	22.2	1.61	1200	1.76	18.6
9-7	Fresno	1240	13.1	0.896	0920	1.85	4.71
9-14	Hunter-Liggett	1800	12.1†	0.76	1120	0.964	10.6
9-20	Harbor Freeway	1150	4.64	2.86	same	--	--
9-27	Harbor Freeway	1120	0.90	2.84	1050	3.51	0.555
10-5	Pomona	1020	8.06	2.86	0840	5.0	2.54
10-11	Pomona	1520	11.9	1.02	1020	3.15	4.9
10-13	Pomona	1120	11.9	5.37	0950	7.58	6.52
10-17	Pomona	1620	7.22	2.97	0950	4.75	0.49
10-20	Pomona	1220	1.87	2.16	1630	4.17	0.335
10-24	Pomona	1400	24.2	8.2	1020	17.1	8.7
11-1	Goldstone	1510	5.94	0.669	1740	0.721	5.19
11-3	Goldstone	1550	4.91	0.295	2330	0.615	3.68
11-9	Pt. Arguello	1250	4.96	0.991	1210	1.03	4.79

*PST

†Ozone level ranged from 11 to 12 from 1331 to 2205 PST during this run

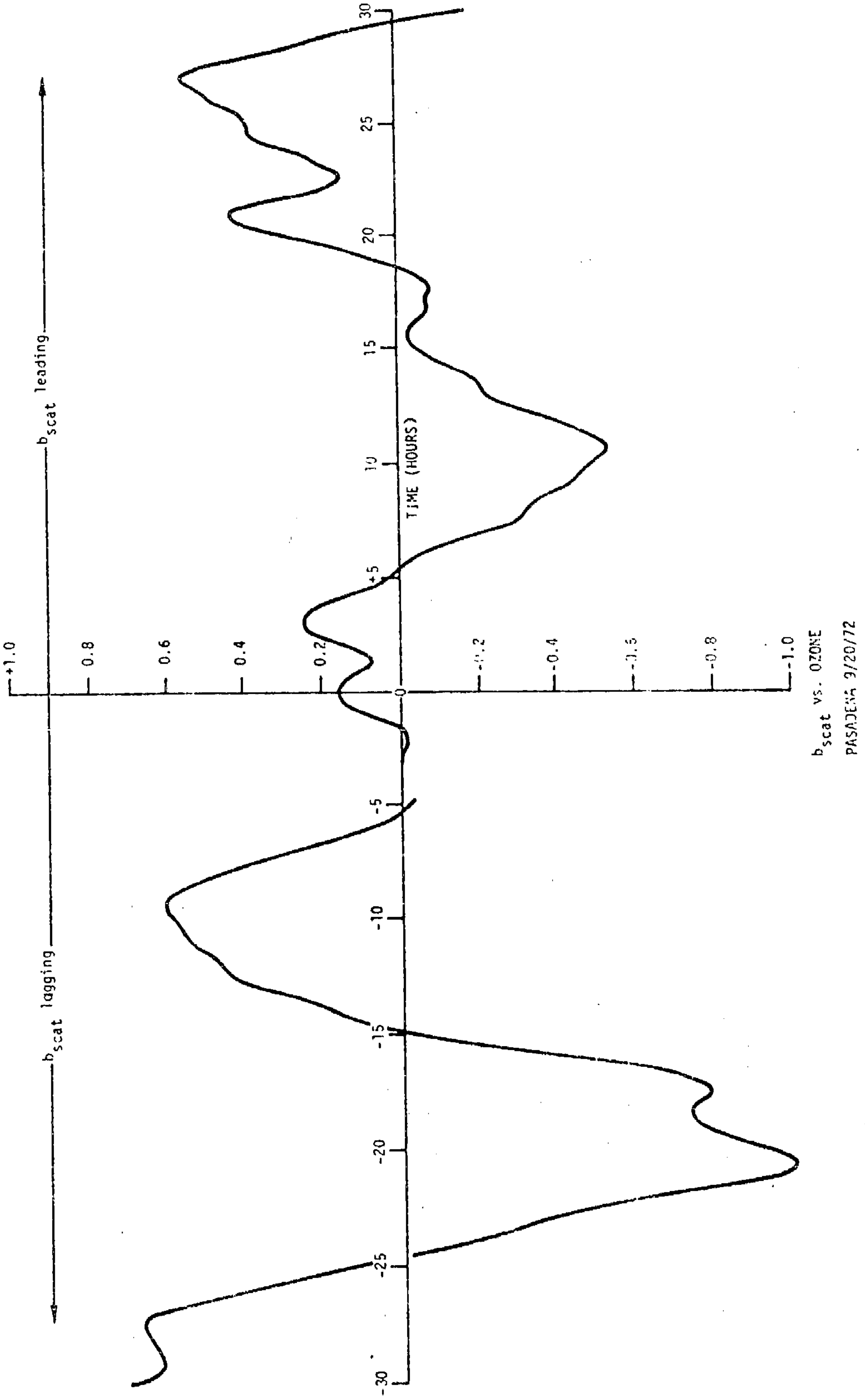
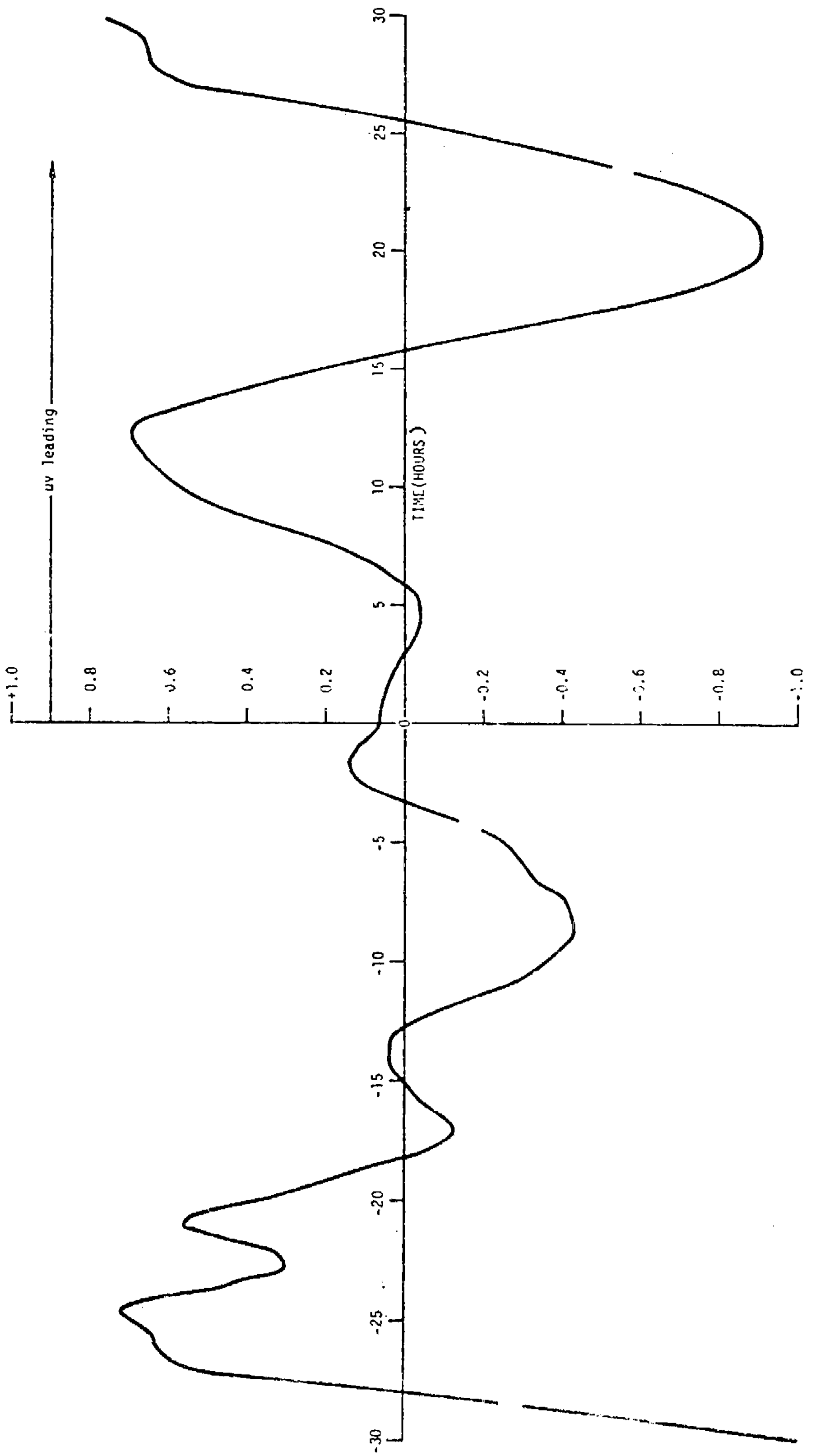

b_{scat} leading
b_{scat} lagging
TIME (HOURS)
-30
-25
-20
-15
-10
-5
0
5
10
15
20
25
30
+1.0
0.8
0.6
0.4
0.2
-0.2
-0.4
-0.6
-0.8
-1.0
b_{scat} vs. OZONE
PASADENA 9/20/72

Fig. 3



ULTRAVIOLET RADIATION vs. b_{scat}
Pasadena 9/20/72

Fig. 10

Table 2

PERCENTAGES OF SEVERAL ELEMENTS IN PASADENA PARTICULATE MATTER

(Average 0900-2000, Sept. 3, 1969)

Element	%
C	19
N	> 5
Na	1.02
Mg	1.1
Al	0.80
S	> 5
Cl	0.07
K	0.32
Ca	0.99
V	0.01
Mn	0.03
Fe	3.16
Cu	0.03
Zn	0.18
Br	0.6
I	0.006
Ba	0.04
Pb	3.3

(From Friedlander, 1973)

Table 3

HIGH-VOLUME SAMPLER CONCENTRATIONS ($\mu g/m^3$)

	PA	MG	RV
		10/4/72	
NO_3^-	7.19 ± 0.54	13.1 ± 1.4	15.4 ± 1.2
SO_4^{-2}	3.9 ± 0.1	6.2 ± 1.5	5.8 ± 1.4
CEO*	3.1 ± 0.2	4.8 ± 0.4	4.8 ± 0.2
NH_4^+	4.17 ± 0.4	6.39 ± 0.32	6.61 ± 0.33
$\frac{NO_3^- + SO_4^=}{NH_4^+}$	2.7 (3.2)	3.0 (3.2)	3.2 (3.2)
Mass	69.5 ± 7.6	137.0 ± 15.0	134.0 ± 15.0
NO_3^-/Pb	4.73	7.66	8.7
SO_4^{-2}/Pb	2.56	3.63	3.28
NO_3^-/Mass	0.103	0.096	0.115
SO_4^{-2}/Mass	0.056	0.044	0.043

*Cyclohexane extractable organics

CEO here represents the cyclohexane extracted organics which were found to be a small fraction of the total organic carbon. In these cases the stoichiometry shows that NH_4^+ would balance $SO_4^=$ and NO_3^- for ammonium salts. However, this was not the case in the earlier data (Table 2).

An illustration of the breakdown by identified compound of organic material is Table 4. These results of Schuetzle indicate the analytical power of high resolution mass spectroscopy (HRMS). Another new analytical technique of great importance for identification of valence state of airborne material is photoelectron spectroscopy (ESCA).

In Table 4, the oxygenated compounds as acids and aldehydes are identified, but probably represent only a fraction of the total organic carbon. The differences in sulfate compounds have been suggested by HRMS but recent work at the University of Washington indicates Schuetzle's assignments are ambiguous. According to R. Knights, HRMS at this time can give only total sulfate with confidence. The presence of a variety of different sulfur and nitrogen compounds in the Los Angeles aerosol has been deduced by ESCA measurements, discussed for example by Novakov (e.g., Hidy, 1972).

The chemical analysis of size fractions of the Los Angeles aerosol has suggested that certain constituents are concentrated in different ranges of sizes. Fig. 11 illustrates this for urban aerosols in Los Angeles. The carbon, nitrate, and sulfate material are found in the smaller sizes. Here the anthropogenic "primary" material and the material derived from "secondary" chemical transformations are shown schematically to be concentrated in a range of importance for visibility effects as well as for penetration into the lower respiratory system.

By choosing suitable tracers for material from certain sources, such as lead for automobile exhaust, one can construct an inventory of aerosols based on the chemistry. Such an inventory is shown for the Los Angeles aerosol in Fig. 12. This π diagram is estimated for collected aerosol mass equilibrated to air at less than 50% relative humidity based mostly on the 1969 and earlier results. In the upper half are the secondary constituents and in the lower half are the primary constituents. The great importance of secondary production to L.A. haze is readily illustrated

Table 4

COMPOSITION OF SOME ORGANICS IN AEROSOLS IN RANGE $D_p < 1$ μm;
LOS ANGELES AREA AVERAGE OF FOUR SAMPLES
TAKEN IN LATE MARCH 1972
(After Schuetzle)

Compound	% by Wt.
Total Acids (as acetic acid)	1.9
Organic Acids (c > 10)	0.98
Adipic Acid	0.65
Adipaldehyde	0.73
Glutaric Acid	0.39
Glutaraldehyde	0.72

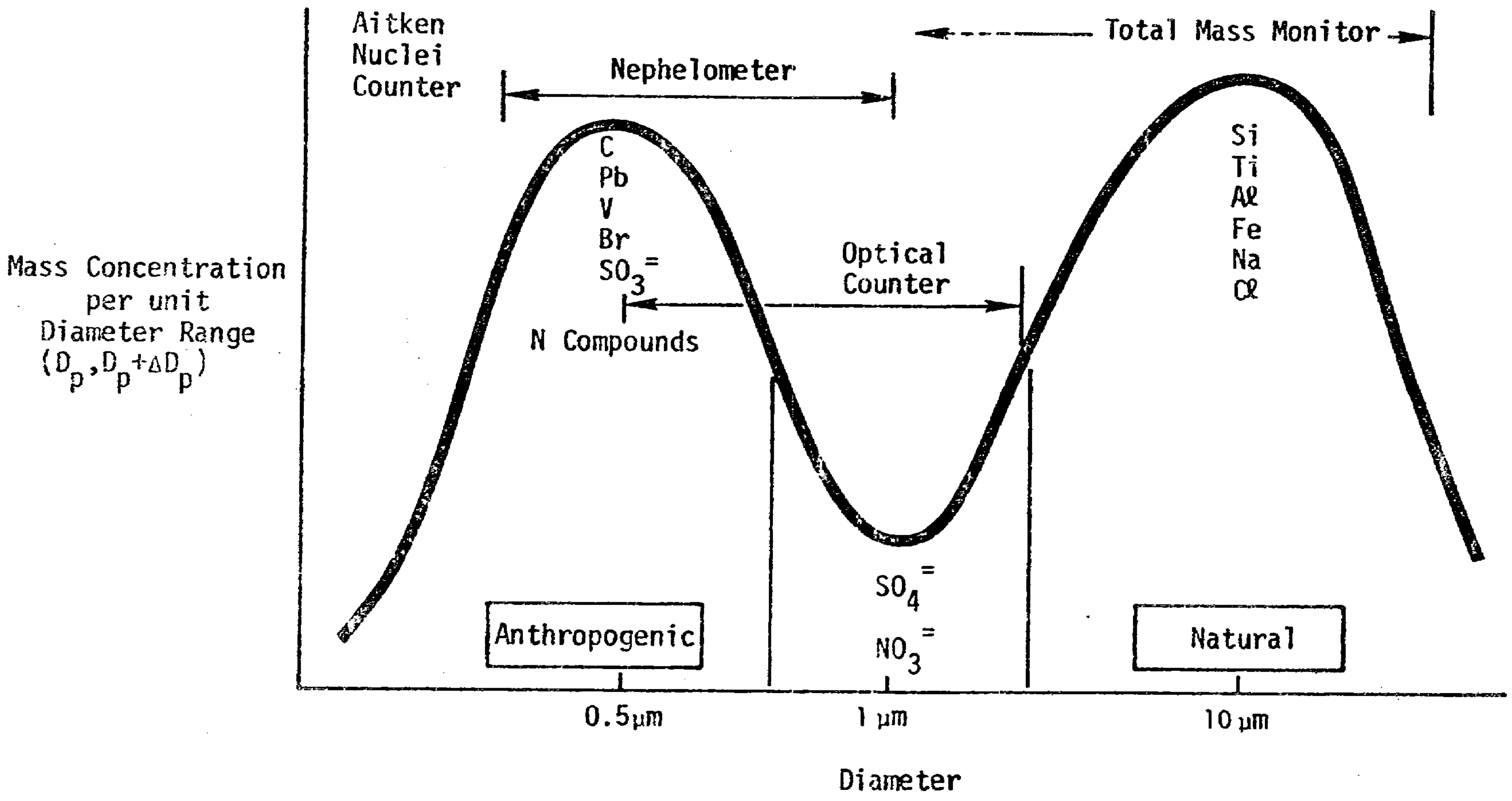


FIGURE 11 SCHEMATIC PRESENTATION OF BIMODAL MASS DISTRIBUTION

π MODEL OF AEROSOL SOURCES IN LOS ANGELES

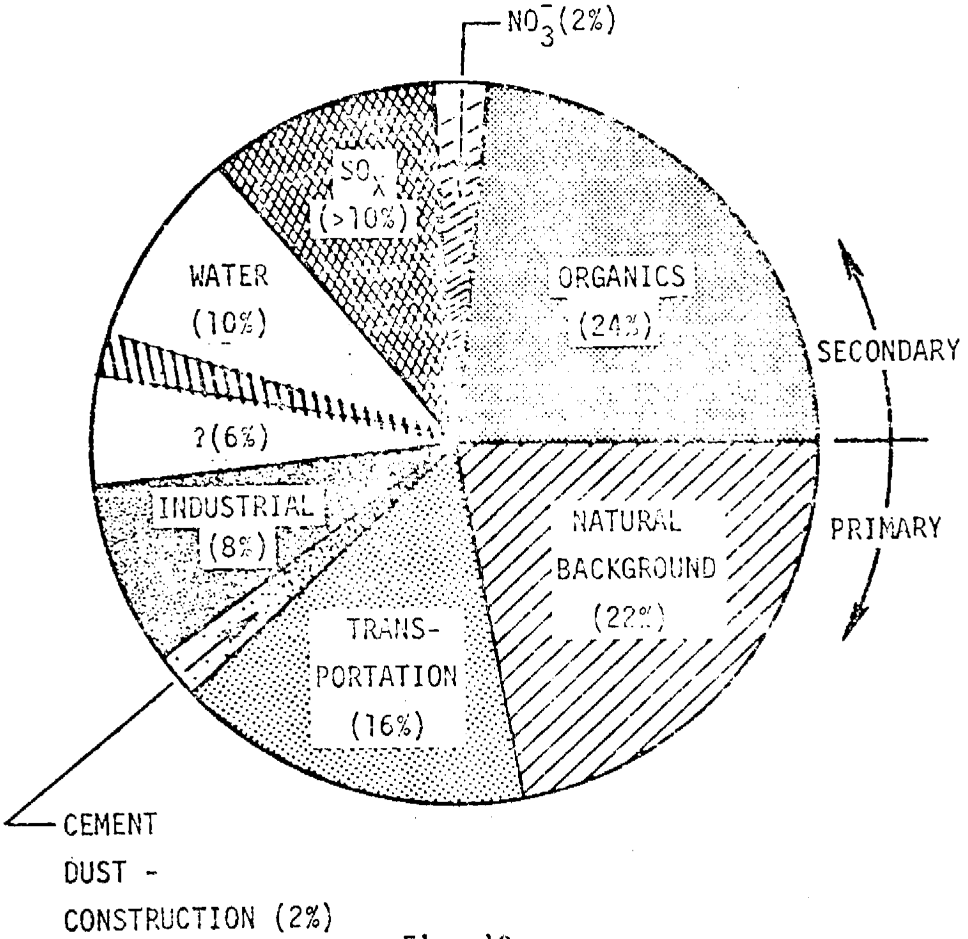


Fig. 12

be it from photochemical or nonphotochemical origins. Here, the nitrate is illustrated as ~ 2% based on data in Pasadena in 1969. However, most data for nitrate in Los Angeles would indicate a nitrate concentration of 10-20%. Perhaps half of the aerosol collected comes from the polluted atmosphere itself and most of this will be concentrated in the submicron particles.

Using the tracer calculations, combined with knowledge of emissions from different sources, estimates of the contribution of atmospheric reactions can be made. For sulfate and nitrate, there exist no major primary sources in Los Angeles except possibly for the motor vehicle. However, carbon is more complex. One calculation of the balance of carbon was attempted by Friedlander (1973). Shown in Fig. 13 is his estimate of the primary sources and of the secondary contribution. Based on this estimate more than half of the aerosol carbon in this Pasadena sample is attributed to atmospheric transformations. These reactions are essentially unknown at this time.

Like the trace gases in the atmosphere, the chemical components of the aerosol vary strongly by day. The variation of the carbon, sulfur, and nitrogen compounds is of particular interest because of the chemical changes projected for the atmosphere. Examples of measurements of changes in oxidized sulfur (S^+) and reduced sulfur (S^-) are shown in Figs. 14 and 15. These data are for material < 0.6 μm diameter collected by AIHL and on cellulose membrane filters in series with an impactor, and they were analyzed by Novakov and his staff. In Fig. 14, results for a location next to the Harbor Freeway are drawn. Note the high concentration of S^- compared with S^+. The S^- has morning and evening peaks accompanying heaviest traffic; however, S^+ peaks in midday with the SO_2 concentration.

The data taken at Pomona are contrasted with material sampled at the Freeway. Here the S^+/S^- ratio is much higher at Pomona and significantly more S^+ is observed, probably as $SO_4^=$. There is an early peak with a midday peak in S^+ with the SO_2 increase.

The Pomona sample was taken on a moderately smoggy day with relative humidity higher than 50-60%. However, the humidity was $\lesssim$ 40% at the Harbor Freeway with a very low oxidant level (lower than measured at several remote

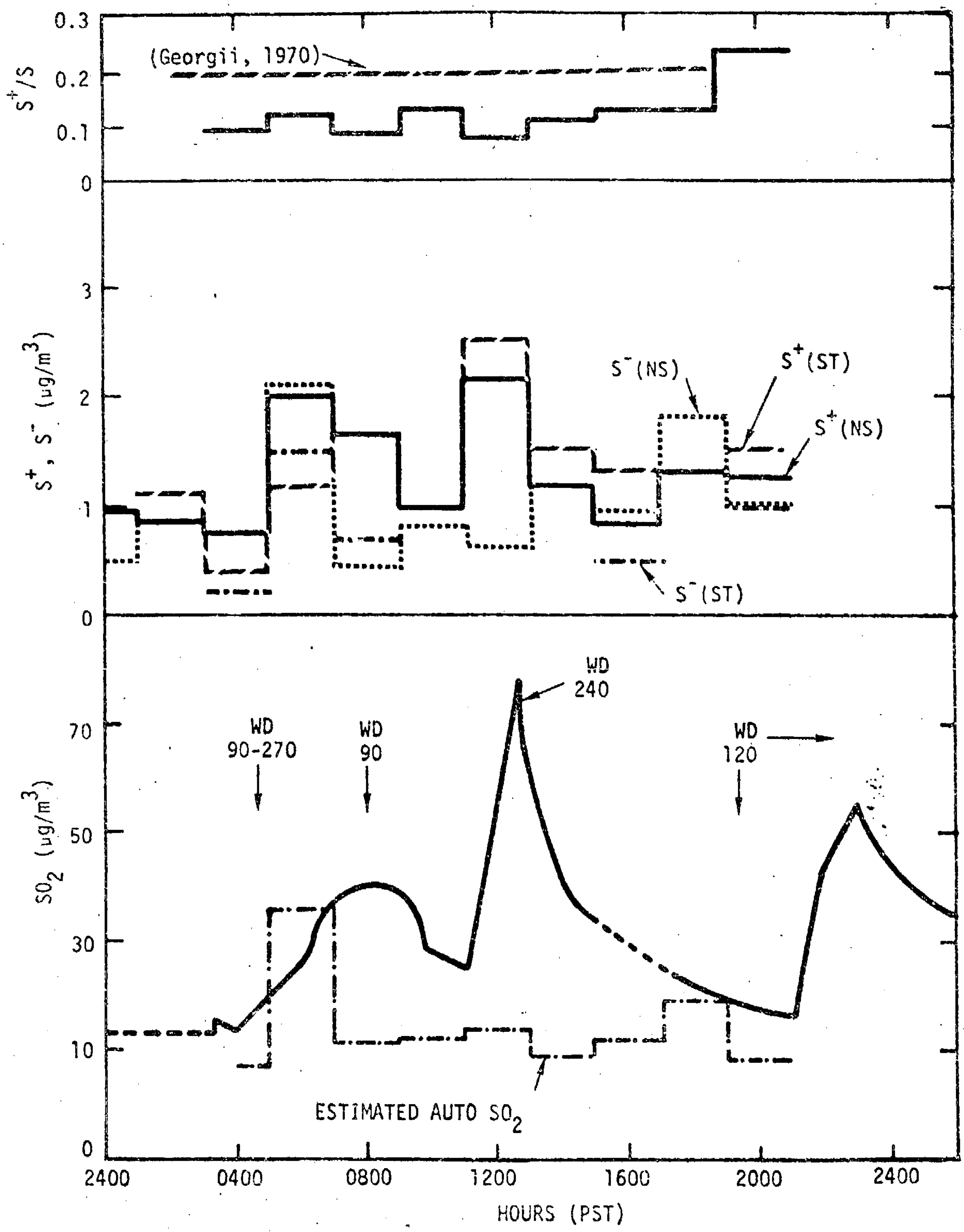
Fig. 13

CARBON BALANCE

Pasadena Aerosol, 9/3/69

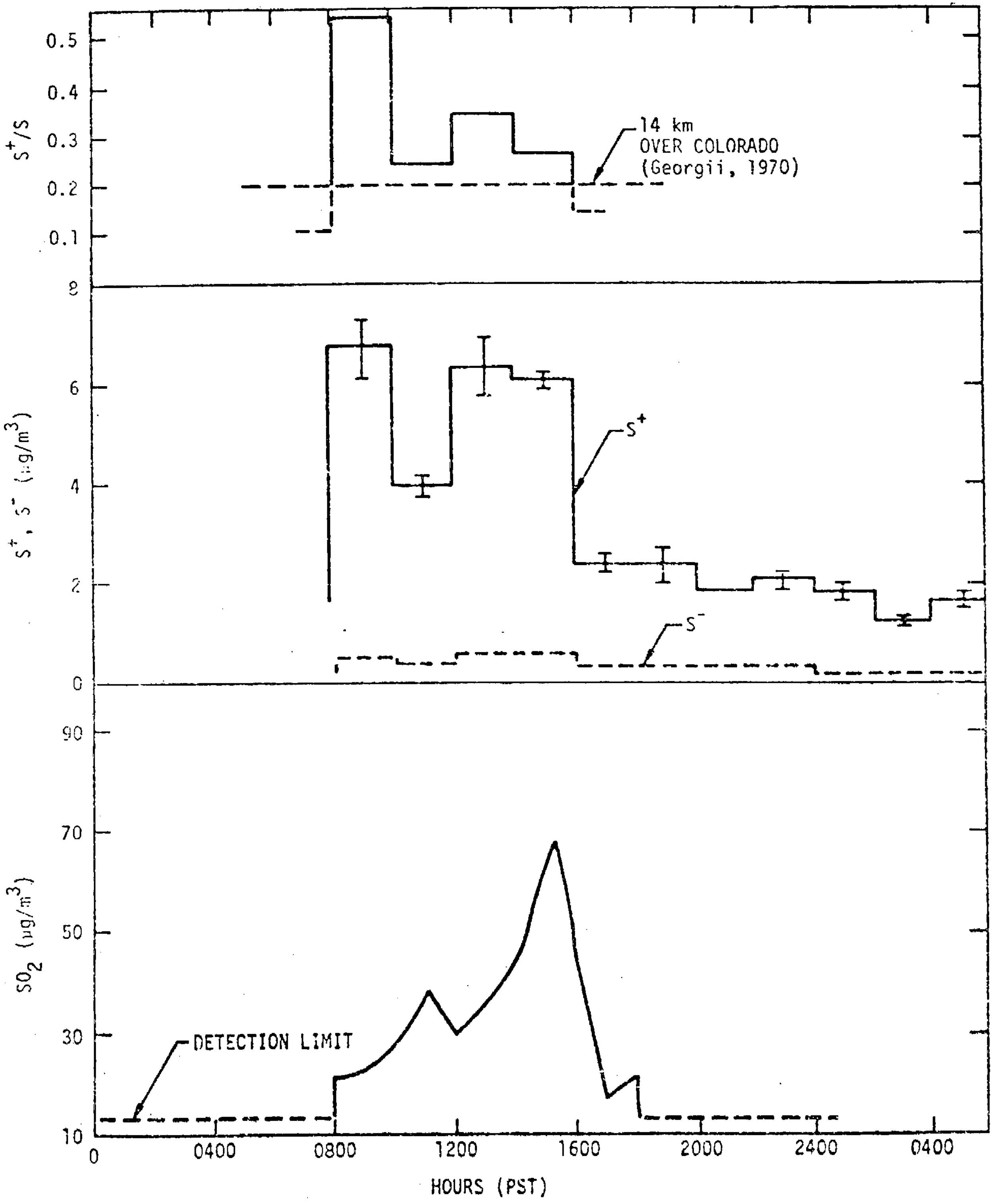
Source	C, % as carbon	C, % in compounds	Remarks
Automobile Exhaust	--	3.3	Carbon assumed to be 90% of tar
Tire Dust	1	2.1 (mostly Butadiene	
Diesel Exhaust	1.8	--	Scaled up from Lemke, et al (1971)
Aircraft Emissions	2.7	--	"
Atmospheric Conversion	--	8.1	By difference, hence a maximum value
Total	5.5	13.5	

(From Friedlander, 1973)



a. Harbor Freeway — September 20, 1972

Figure 14 SO_2 and Particulate S^+ and S^-



c. Pomona — October 24, 1972

Figure 15 SO_2 and Particulate S^+ and S^- (Contin.)

sites!) The difference in conversion ratio S^+/S, S = gaseous sulfur, is striking between Pomona and the Harbor Freeway. This difference is believed to be partly the result of injections of fresh material near the collector and partly to variations in conversion rate of S to S^+ by atmospheric transformation. In particular, this evidence combined with other information, including the data in Table 3, led investigators to speculate about the relative importance of humidity and photochemistry in conversion processes in terms of sulfur chemistry (e.g., Hidy et al., 1973).

In any case it is of interest to note that the conversion of S to S^+ is documented to be $\gtrsim 0.1$, whereas nitrate and carbon conversion is more like 1% with considerably less documentation.

The role of water in aerosol behavior has long been described in terms of changes in visibility, related to relative humidity. Recently, investigators in Europe have measured changes in weight of droplets of salt and material from the atmosphere with changes in relative humidity. Furthermore, Charlson et al., have measured directly changes in light scattering of aerosols as a function of humidity. Last summer, a new technique for observing semicontinuously liquid water content in aerosols was developed. An example of the diurnal changes in aerosol water content with total mass concentration in moderate Pasadena smog is indicated in Fig. 16. Here the water content systematically changes with mass concentration and with ozone, not shown here. These changes were observed over a steady decrease in relative humidity from 75% in the early morning to 55% by mid-day. Part of this change can be attributed to equilibration of the hygroscopic aerosol with water vapor, but part of the effect may be related to non-equilibrium effects; water may actually play an active kinetic role in the chemistry.

It is interesting to note that the extinction coefficient, b_{scat}, measuring aerosol light scattering was satisfactorily correlated with liquid water content, as shown on Fig. 17. This sample correlation is taken over a range from the Rayleigh scattering limit of a "dry" desert aerosol to cases of very high water content in Pomona.

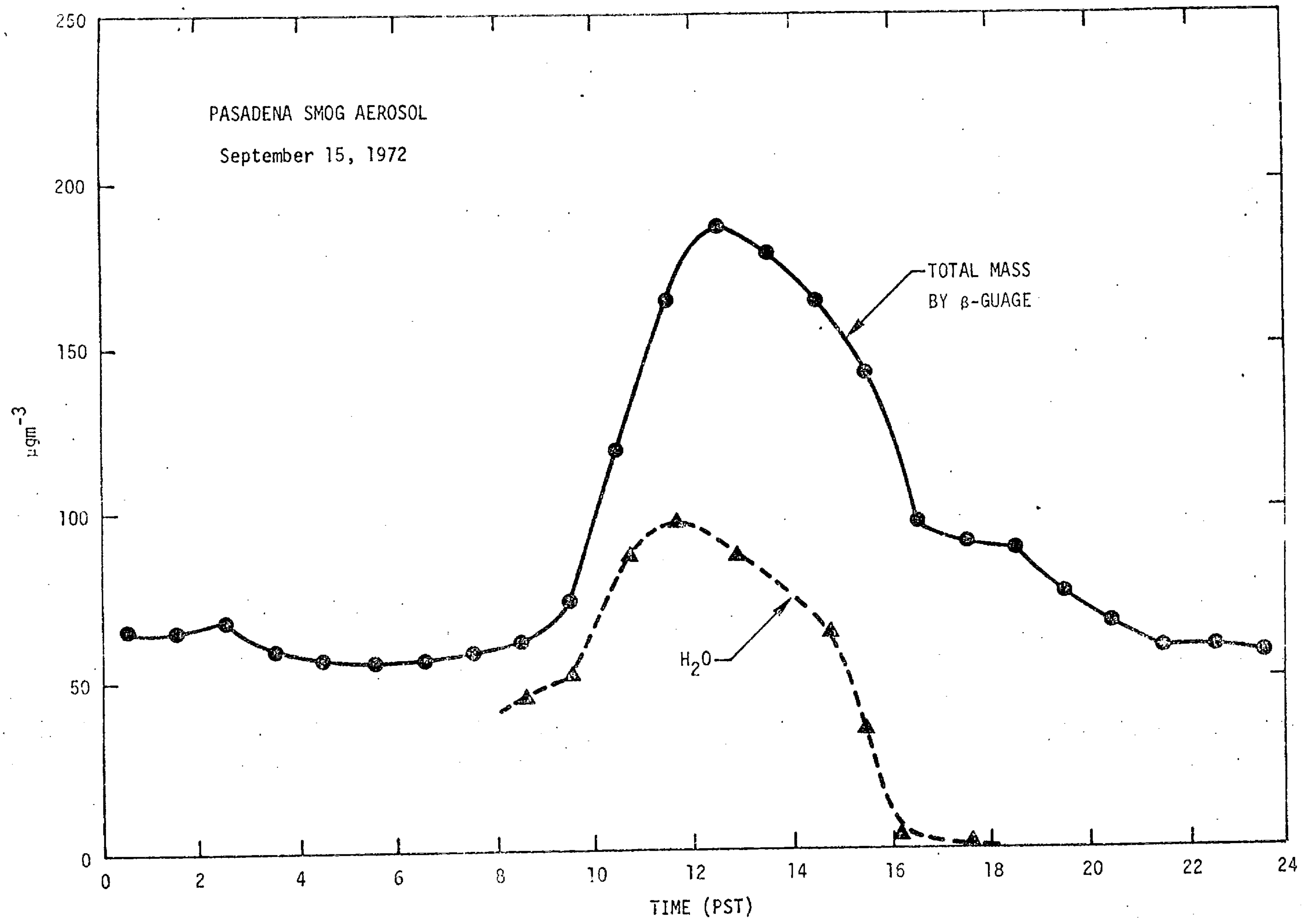

PASADENA SMOG AEROSOL
September 15, 1972
TOTAL MASS BY β-GUAGE
H_2O
μgm^{-3}
0
50
100
150
200
250
TIME (PST)
0
2
4
6
8
10
12
14
16
18
20
22
24

Fig 16

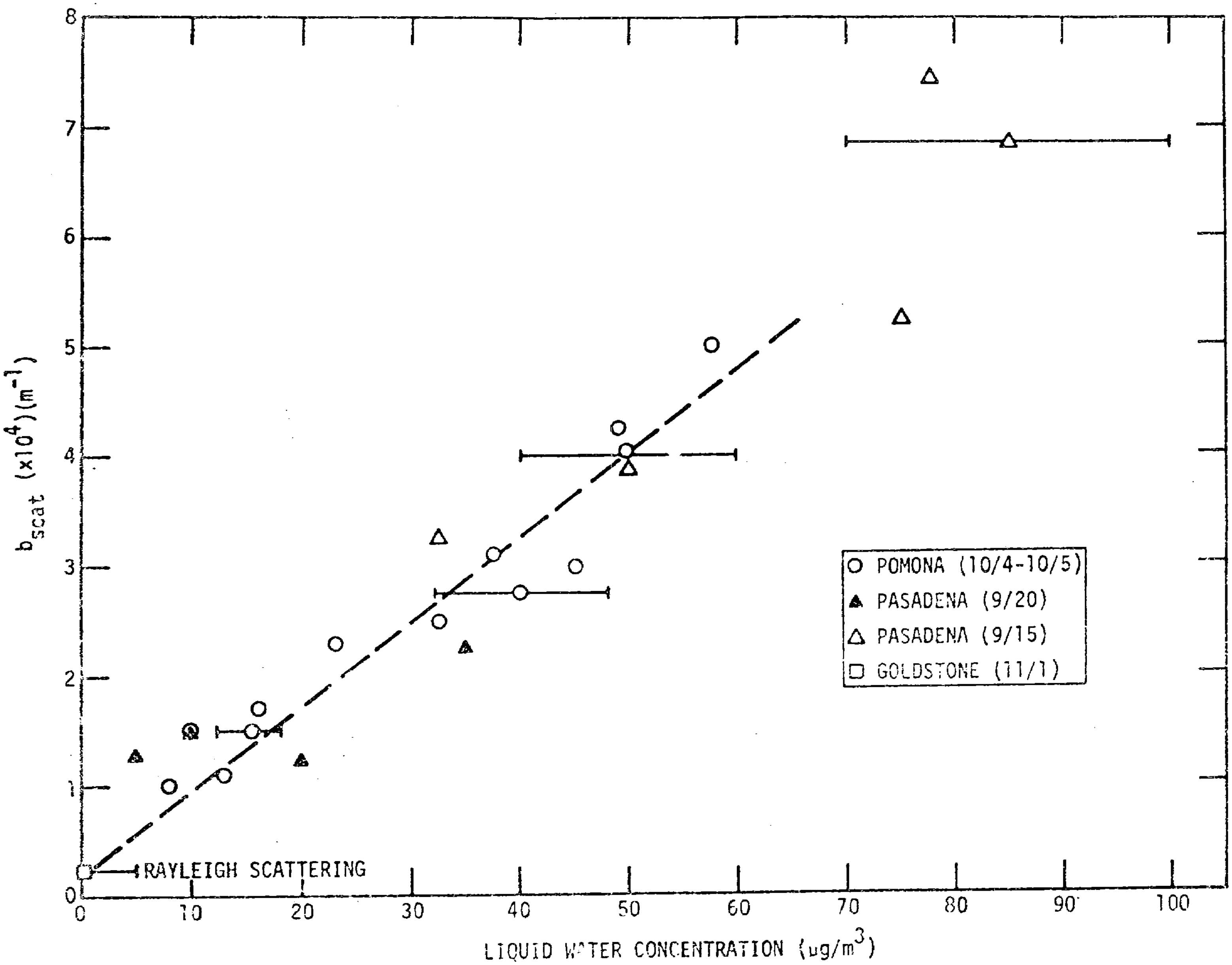


Figure 17 Comparison of Light Scattering Coefficient with Liquid Water Content

3. Summary of Observations

With the variety of information cited briefly during this discussion, one can draw some tentative conclusions and construct some hypotheses about the nature of photochemical aerosols in polluted air. A set of such conclusions is listed in Table 5. In some respects these may seem highly non-definitive, based on the information gained after years of study of atmospheric processes. However, one should bear in mind that even with modern techniques, the time resolution of chemical changes in aerosols for ingredients suspected to be related to photochemistry is limited, and insufficient data are available to follow changes with time in great detail, as yet. This is complicated by the problems of interpreting data describing the chemistry in an air mass traveling over a single or a few stations fixed in space.

4. Mechanisms of Formation of Aerosols

Having outlined the atmospheric observations available within whose framework the theories must stand or fall, let us pass on to considering the implications of these data to photochemical aerosol formation.

To construct realistic models for aerosol formation and growth in the atmosphere, consideration has to be given to certain physical constraints. These cover the requirements for thermodynamic stability of condensed material and for particle nucleation and condensation processes, as presently understood.

Physical Constraints. From our knowledge of aerosol behavior, it is known that particles must be close to or at equilibrium with respect to the vapor phase to exist in air for any length of time. Thus, the vapor pressure of the condensed species on the particle must be essentially equal to the saturation vapor pressure at atmospheric temperature. This poses no basic problem for inorganic salts, or sulphuric acid, even at the ppb concentration in the vapor phase. However, it places severe constraints on the ability of HNO_3 to condense as a pure compound or as an acid diluted in water. Vapor pressure data of Toon and Pollack (1973), for example, indicate that concentrated HNO_3 has a vapor pressure more than 100 times higher than concentrated H_2SO_4, making the possibility of finding nitric acid in aerosols

Table 5

SUMMARY OF ATMOSPHERIC OBSERVATIONS OF PHOTOCHEMICAL AEROSOLS

1. Formation of new particles very limited.

2. Growth on existing nuclei strong in 0.1 μm - 1.0 μm range, but filtered, polluted air a good nuclei producer when irradiated.

3. Key Components: > 80% of mass
   -- Carbon - oxygenated species
   -- Sulfur - sulfate
   -- Nitrogen - Ammonium & nitrate
   -- Water (despite R.H. < 100%)

   Confined to submicron range

4. Chemistry
   -- mostly $(NH_4)_2SO_4$; higher R.H. more $SO_4^=$ production.
   -- $S^+/S \gtrsim 0.1$, $N^+/N \sim 0.01$, $C/C_g \sim 0.01$.
   -- NO_3^- formed in night and winter as well as summer days; NO_2 less reactive than SO_2(?)
   -- $SO_4^=$, NO_3^-, $C_xO_yH_z$ formation appears correlated and may correlate with changes in light scattering.

5. Rapid diurnal changes in haze, with variations most strong after daylight -- conversion must be on "hours" time scale.

6. No well defined correlation of aerosol behavior with photochemical pollutants like O_3 and NO_2; however, sometimes b_{scat} vs. O_3 correlation appears.

7. "Guess" -- water plays a crucial role in aerosol chemistry.

much slimmer than sulfuric acid.

The requirements of low vapor pressure are particularly important to the question of stable organic materials in aerosols. To illustrate this point, consider a list of low molecular weight hydrocarbons found in polluted air (Table 6). These data taken from Stephens and Burleson (1969), for example, indicate the olefins, or the "reactive" species are in the ppb concentration above molecular weight equivalent to C_3. Assuming, as we shall see later, that organic reactions of interest lead to oxygenated materials as a major product, we can estimate the requirements for molecular weight for condensation of organics. A typical list of vapor pressures for oxygenated materials through C_{12} is shown in Table 7. Clearly, up to the C_{12} range, the equilibrium vapor will lie at an equivalent gas concentration in the ppm level. Thus, for thermodynamic stability, organic materials must be largely of molecular weight equivalent to C_{12} or larger. This appears to be borne out by the data of Schuetzle shown earlier.

Particles may be formed in the atmosphere by two basic processes - first by condensation of supersaturated vapor or by chemical reaction leading to spontaneous formation of condensed material either as new particles, or second as material accumulating on existing particles. In the latter case, the chemical reactions actually could take place within or on the existing particles.

For spontaneous formation of condensable material, the rate of formation can take place by homogeneous nucleation, or by heterogeneous nucleation. The rate equations are shown in Table 8. Here nucleation in all cases is seen to depend on the supersaturation ratio, S, temperature, T, the molecular volume in the liquid phase, V_L, a surface energy parameter, and a "critical" volume of nuclei v or v*, and N* is the number concentration of critical nuclei. It can be shown that H_2SO_4 could nucleate homogeneously in the atmosphere, yet it is very unlikely that HNO_3 could undergo such a transition because of its relatively high vapor pressure. So little is known about the products of organic reactions that nothing can be said about the importance of homogeneous nucleation in this case. However, the fact that few new particles are seen to be produced in a highly reactive atmosphere like that of L.A. during the day, makes it unlikely that homogeneous nucleation is a widely important formation process in the urban atmosphere.

Table 6

SOME HYDROCARBON VAPORS IN SOUTHERN CALIFORNIA AIR

(After Stephens & Burleson, 1969)

Species	(ppb)
Methane	2355
Ethane	63.6
Acetylene	77.0
Ethylene	65.6
Propene	19.2
1,3 Butadiene	3.6
1 Butene	2.6
Isobutene	5.2
Cyclopentene	4.4
Trans-2-Butene	1.4
Trans-2-Pentene	2.4
2-Methyl Butene 2	2.6

Table 7

CANDIDATE PRODUCTS FOR OZONE 1-BUTENE REACTION

Species	C_x	B.P. (°C)	Vapor Pressure (mm Hg)
Propionic Acid	3	141.1	1 (4.6°C)
butyl ester	-	145.4	
Propionaldehyde	3	48.8	10 mm (19.4°C)
1-Propanol	3	165	40 (23.8°C)
Butyraldehyde	4	75.7	-
Bytyric Acid	4	163.5	1 (25.5°C)
propyl ester	-	143	-
Caproic Acid	6	205	1 (71.4°C)
Caprylic Acid	8	237.5	-
Caprylaldehyde	8	163.4	1 (73.4°C)
*Lauric Acid	12	225 (100 mm)	1 (121°C) ~ .005 (20°C)

* or $\frac{.005}{760} \approx 6\times10^{-6} \rightarrow > 1$ ppm

Table 8

PARTICLE NUCLEATION PROCESSES

1. Homogeneous

$$\text{Rate} \sim v^{*\frac{2}{3}} N^* \exp\left[\frac{16\pi\sigma^3 V_L{}^2}{3(kT\ell nS)^2}\right]$$

2. On Ions of Concentration N_c

$$\text{Rate} \sim v^{*\frac{2}{3}} \cdot N_c \exp\left[\frac{16\pi\sigma^3 V_L{}^2}{3(kT\ell nS)^2}\right]$$

3. On Insoluble Particles

$$\text{Rate} \sim v^{\frac{2}{3}} n_{ads} \exp\left[\frac{16\pi\sigma^3_{LG} V_L{}^2}{3[kT\ell nS]^2} f\,(\cos\phi)\right]$$

ϕ = wetting angle

n_{ads} = number of adsorbed molecules/area

4. On Soluble Particles

$$\text{Rate} \sim v^{\frac{2}{3}} \cdot N_c \exp\left[\frac{16\pi\sigma^3 V_L{}^2}{3(kT\ell nS)^2}\right]$$

S affected by salt solution.

For the purposes of this discussion, we will consider heterogeneous nucleation essentially as vapor diffusion controlled particle growth beyond an initiation stage given by the rates in Table 8.

The growth of particles can be classed as two broad processes, shown in Fig. 18. If the vapor is supersaturated, growth can take place at a rate controlled by S and the particle volume, as well as the accommodation coefficient α_c. The rate law changes in terms of volume depending on particle size, for a given mean free path λ of suspending gas. If the vapor is unsaturated, growth may still take place by reactions in the particle. Here, the rate law should be proportional to the existing particle volume if the reaction is uniform in rate throughout the particle. There is insufficient data available to determine the rate law or reaction mechanism most likely to predominate in urban aerosol growth.

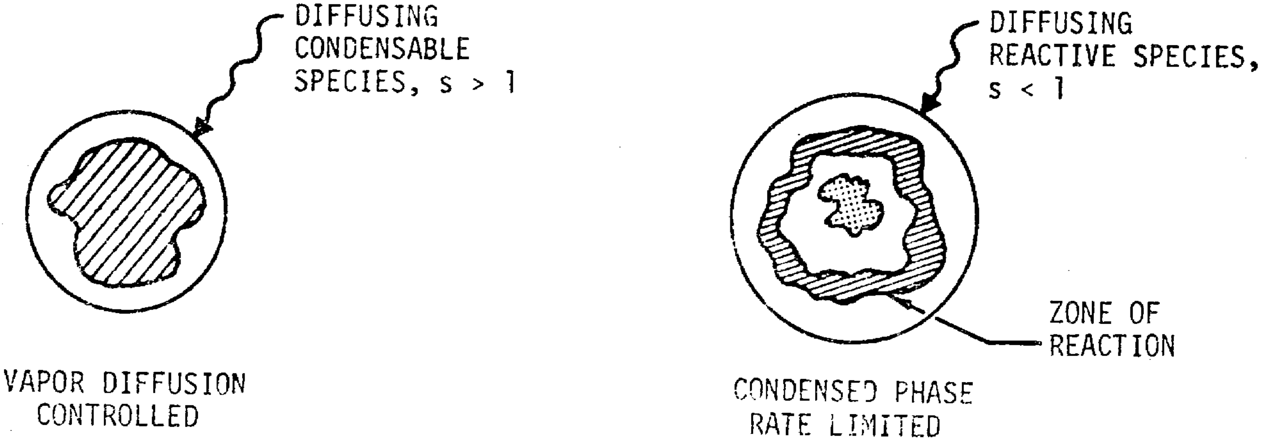
It is interesting, however, that the observations in Los Angeles indicate that vapor diffusion control cannot fully explain aerosol growth, for the rate equations would predict growth primarily on particles < 0.1 µm (largest number and highest rate, see Hidy, 1972a). The influence of thermodynamic equilibrium again enters here. If the radius of particles is too small, the vapor pressure of condensable species can increase significantly by the curvature influence (Fig. 18). From Kelvin's equation, the surface tension of a range of materials would suggest that this influence would constrain growth to particles greater than 0.05 µm diameter, as found in the observations.

Chemical Reactions Leading to Aerosol Precursors. The physical processes of phase change and stabilization restrict the maximum rate of formation and the classes of materials expected in aerosols of chemical origin. In many instances, the rate controlling step in the formation mechanism may be the precursor formation. To complete our discussion, let us now review briefly some mechanisms of potential importance for photochemical (and related) production of particles.

The precursor of principal interest for sulfate aerosol is believed to be SO_3. Several photochemical mechanisms have been proposed for SO_3 formation. These are summarized in increasing degrees of complexity in Table 9. Without the presence of NO_2 and reactive hydrocarbons, the

PARTICLE GROWTH PROCESSES

v = PARTICLE VOLUME



VAPOR DIFFUSION CONTROLLED

CONDENSED PHASE RATE LIMITED

$\frac{\lambda}{v^{\frac{1}{3}}} \gtrsim 1$ Rate $\sim \alpha c\, v^{\frac{2}{3}}(S-1)(1-c(v^{\frac{1}{3}}/\lambda)^2+\cdots)$

$\frac{\lambda}{v^{\frac{1}{3}}} < 0.1$ Rate $\sim v^{\frac{1}{3}}(S-1)$

Supersaturation $S = p/p_\infty(T)$

Rate $\sim v$

Equilibrium $\ln S = \frac{2\sigma V_L}{kTv^{\frac{1}{3}}}$

Fig. 18

Table 9

SOME OXIDATION REACTIONS OF SO_2

(After Bufalini, 1971)

Key: $SO_3 + H_2O \rightarrow H_2SO_4$ (collision dominated) then SO_3 formation rate determining.

1. The SO_2 system

$$SO_2 + h\nu \rightarrow {}^1SO_2$$

$${}^1SO_2 + SO_2 \rightarrow {}^3SO_2 + SO_2$$

$${}^1SO_2 \rightarrow {}^3SO_2$$

$${}^3SO_2 + SO_2 \rightarrow \underline{\underline{SO_3}} + SO({}^3\Sigma^-)$$

2. The $SO_2 - O_2$ system

$$SO_2 + h\nu \rightarrow SO_2^*$$

$$SO_2^* + SO_2 \rightarrow \underline{\underline{SO_3}} + SO \xrightarrow{O_2} \underline{\underline{SO_3}}$$

$$SO_2 + O_2 \rightarrow \underline{\underline{SO_3}} + O \; \lfloor \xrightarrow{O_2} O_3$$

$$\rightarrow SO_4 + O_2 \rightarrow \underline{\underline{SO_3}} + O_3$$

$$SO_2 + O \rightarrow \underline{\underline{SO_3}}$$

3. The $SO_2 - NO_x$ system

$$SO_2 + NO \rightarrow SO + NO_2$$

$$SO_2 + NO_2 \rightarrow \underline{\underline{SO_3}} + NO$$

$$SO_2 + O + M \rightarrow \underline{\underline{SO_3}} + M$$

$$SO_2 + O_3 \rightarrow \underline{\underline{SO_3}} + O_2$$

$$SO_4 + NO \rightarrow \underline{\underline{SO_3}} + NO_2$$

$$SO_4 + NO_2 \rightarrow \underline{\underline{SO_3}} + O_2$$

$$SO_4 + O \rightarrow \underline{\underline{SO_3}} + O_2$$

4. The $SO_2 - NO_x - HC$ system

$$R\cdot\ (RO\cdot, RO_2\cdot) + SO_2 \rightarrow RSO_2(ROSO_2, RO_2SO_2)$$

$$RO\cdot(RO_2\cdot) + SO_2 \rightarrow R\cdot\ (RO\cdot) + \underline{\underline{SO_3}}$$

photooxidation of SO_2 appears to be relatively slow (Table 10) and are unlikely to play a role in the urban atmosphere. If NO_2 and hydrocarbons are present in irradiated gas mixtures containing SO_2, the disappearance of SO_2 is increased significantly, as suggested by experimental data in Table 11. Unfortunately, the mechanism for SO_2 oxidation is not well understood in this system and the observations were taken at reactant concentrations considerably higher than encountered in the atmosphere. This makes it difficult to extrapolate the rate data to atmospheric conditions.

Cox and Penkett (1972) published an important paper recently on the SO_2 oxidation mechanism in the presence of ozone and hydrocarbons. Even in the dark, this system of reactants will produce sulfate aerosol at a significant rate (Table 12). This may be the major mechanism for aerosol formation in irradiated SO_2-NO_2-hydrocarbon mixtures. Cox and Penkett have proposed an oxidation through an intermediate of an ozonide or a zwitterion (Table 12).

In the presence of sufficient quantities of liquid water, sulfate can be formed by a heterogeneous mechanism at a rate faster than accounted for by other known mechanisms relying on SO_3 production. The aqueous reaction relies on NH_4^+ as a buffer (Scott and Hobbs, 1967; de Pena and Miller, 1972) and is controlled by $SO_3^=$ formation and a set equilibria shown in Table 13. Though this process was confined to fogs or to rain by the original proponents, it would seem that the recent measurements of aerosol liquid content at $40\% \leq$ R.H. $\leq 80\%$ should be sufficient to provide a medium for this mechanism to take place effectively. Thus, we conclude, at this point, that the most likely sulfate producing mechanism in urban air stem from the heterogeneous, aqueous process, or the ozone-olefin-SO_2 system.

The nitrate reaction is likely to be very complicated in its chemistry as the reviews like that of Gray and Yoffe might suggest.

The nitrate forming mechanism has been studied primarily as a subcategory of the photochemical smog process. Laboratory studies in chambers have not produced nitrate aerosols in significant quantities. However, nitrate has been found mainly in the walls of the chambers. On the other hand, the nitric acid step plays a potentially important role, as shown in Table 14.

Table 10

COMPARISON OF SOME SO_2 PHOTOCHEMICAL REACTION RATE STUDIES

Reference	Initial (SO_2)	Percent Relative Humidity	Rate of SO_2 consumption[a] % min^{-1}
Gerhard & Johnstone (1955)	5-30 ppm	32-91	$(1.7\text{-}3.3) \times 10^{-3}$
Renzetti & Doyle (1960)	0.2-0.6 ppm	50	0.11
Urone *et al.* (1968)	10-20 ppm	50	1.4×10^{-3}
Hall (1953)	SO_2 = 56-230 mm Hg O_2 = 5-200 mm Hg	0	8×10^{-4}
Urone *et al.* (1972)	1000 ppm	0	3.9×10^{-4}
		50	4.6×10^{-4}
Sidebottom *et al.* (1972)	-	50	3.5×10^{-2} (maximum calculated)
Katz & Gale (1972)	3.2 - 6.6 ppm	0-50	$4.7\times10^{-4}\text{-}1.67\times10^{-3}$ (fn of R.H.)

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[a] Values adjusted to noonday sunlight.

Table 11

PHOTOCHEMICAL REACTION RATES OF SO_2 IN THE PRESENCE OF NO_2 AND HYDROCARBONS

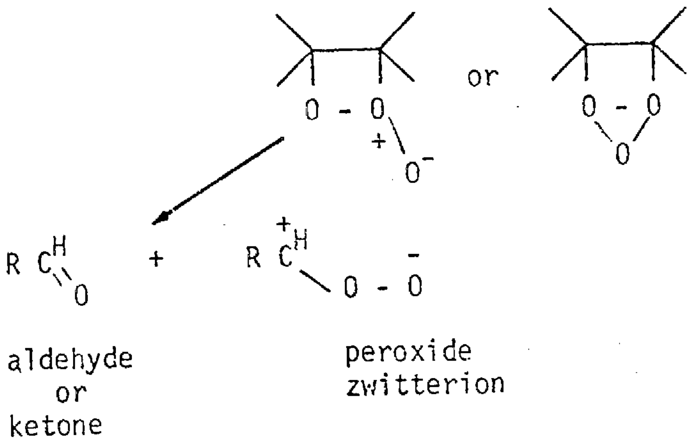
REFERENCE	CONDITIONS	RATE OF SO_2 CONSUMPTION ($\% \min^{-1}$)
A. IRRADIATED CHAMBER STUDIES		
Renzetti & Doyle (1960)	Stirred - flow pyrex reactor	0.8 - 4.9
Urone *et al*. (1968)	Static two-liter pyrex flasks	0.03 - 0.2
Katz (1950)	Ambient air	0.035
Wilson & Levy (1970)	Dynamic-flow pyrex reactor	0.25 - 0.50
Katz & Gale (1972)	Stirred boro-silicate glass reactor	reaction inhibited by olefin complex formation
B. DARK REACTION (O_3 + OLEFIN + SO_2)		
Cox & Penkett (1972)	aluminum chamber	0.05 (calculated for $0.05 < [O_3] < 0.10$ ppm $0.05 < [HC] < 0.10$ ppm $[SO_2] = 0.10$ ppm RH = 40%)

Table 12

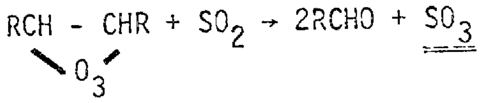
THE OZONE - SO_2 - HC SYSTEM

(After Cox & Penkett)

$O_3 + R\ CH = CH\ R \rightarrow$ initial complex (like)



Addition Complex



$$RCH - CHR(O_3) + SO_2 \rightarrow 2RCHO + \underline{\underline{SO_3}}$$

Zwitterion

$$\overset{+}{RCH} \cdot O - \overset{-}{O} + SO_2 \rightarrow RCHO + \underline{\underline{SO_3}}$$

Table 13

OXIDATION OF SO_2 ABSORBED IN LIQUID WATER DROPLETS

Rate Determining Step $SO_3^{=} + O_2 \xrightarrow{K} SO_4^{=}$

$K \approx 10^{-3} sec^{-1}$

In aqueous medium - complex equilibria important

$H_2O \rightleftharpoons H^+ + OH^-$

$(SO_2)_g + H_2O \rightleftharpoons SO_2 \cdot H_2O$

$SO_2 \cdot H_2O \rightleftharpoons HSO_3^- + H^+$

$SO_2 \cdot H_2O + OH^- \rightleftharpoons HSO_3^-$

$HSO_3^- \rightleftharpoons SO_3^{=} + H^+$

$(NH_3)_g + H_2O \rightleftharpoons NH_3 \cdot H_2O$

$NH_3 \cdot H_2O \rightleftharpoons NH_4^+ + OH^-$

$(CO_2)_g + H_2O \rightleftharpoons H^+ + HCO_3^-$

$CO_2 \cdot H_2O \rightleftharpoons H^+ + HCO_3^-$

$HCO_3^- \rightleftharpoons H^+ + CO_3^{=}$

Table 14

Generalized Mechanism for Photochemical Smog (from Lamb & Seinfeld (1973))

Reactions	Rate constants, ppm, min
1. $NO_2 + h\nu \rightarrow NO + O$	$0.355\ min^{-1}$
2. $O + O_2 + M \rightarrow O_3 + M$	$2.76 \times 10^6\ min^{-1a}$
3. $O_3 + NO \rightarrow NO_2 + O_2$	$21.8\ ppm^{-1}\ min^{-1}$
4a. $O_3 + NO_2 \rightarrow NO_3 + O_2$	$6 \times 10^{-3}\ ppm^{-1}\ min^{-1}$
4b. $NO_3 + NO_2 \rightleftharpoons N_2O_5$	
4c. $N_2O_5 + H_2O \rightarrow 2HNO_3$	
5. $NO + NO_2 + H_2O \rightarrow 2HNO_2$	$2.5 \times 10^{-3}\ ppm^{-1}\ min^{-1b}$
6. $HNO_2 + h\nu \rightarrow NO + OH\cdot$	$5 \times 10^{-3}\ min^{-1}$
7. $CO + OH\cdot \xrightarrow{O_2} CO_2 + HO_2\cdot$	$2 \times 10^2\ ppm^{-1}\ min^{-1}$
8. $HO_2\cdot + NO_2 \rightarrow HNO_2 + O_2$	$1 \times 10^1\ ppm^{-1}\ min^{-1}$
9. $HC + O \rightarrow \alpha\ RO_2\cdot$	$3.1 \times 10^4\ ppm^{-1}\ min$ $(\alpha = 5)$
10. $HC + O_3 \rightarrow \beta RO_2\cdot + \gamma\ RCHO$	$1.7 \times 10^{-2}\ ppm^{-1}\ min^{-1}$ $(\beta = 1.9)$
11. $HC + OH\cdot \rightarrow \delta\ RO_2\cdot + \epsilon\ RCHO$	$1 \times 10^4\ ppm^{-1}\ min^{-1}$ $(\delta = 0.2;\ \epsilon = 0.22)$
12. $RO_2\cdot + NO \rightarrow NO_2 + \theta\ OH\cdot$	$1.8 \times 10^3\ ppm^{-1}\ min^{-1}$
13. $RO_2\cdot + NO_2 \rightarrow$ PRODUCTS	$10.\ ppm^{-1}\ min^{-1}$
14. $HO_2\cdot + NO \rightarrow NO_2 + OH\cdot$	$1.8 \times 10^3\ ppm^{-1}\ min^{-1}$

NOTE: It is possible to combine Reactions 4a–4c as

$$O_3 + NO_2 \xrightarrow[\substack{NO_2\\H_2O}]{4} 2HNO_3$$

in which the overall rate is that of Reaction 4a, the rate-controlling step.

[a] Pseudofirst order.

[b] Pseudosecond order.

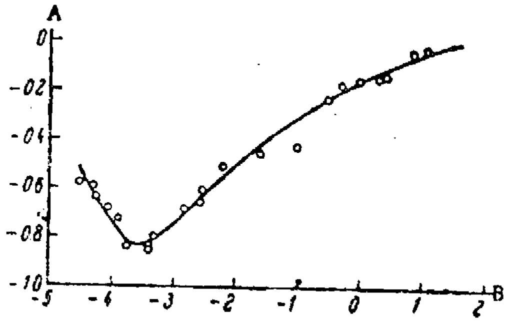
taken from Lamb and Seinfeld (1973). The rate of formation is very slow compared with generation of NO_2 in polluted air. Furthermore, the vapor pressure of HNO_3 precludes spontaneous nucleation (though absorption of HNO_3 vapor on aerosols is highly probable). It is interesting, however, that there may be sufficient absorption of NO_2 in the moisture on aerosols to provide for the nitrate observed. The data for NO_2 chemisorption in aqueous media is very scarce, but results of Nash (1970) suggest that the fraction of conversion ranges from 1-10% for acid to slightly basic solutions. The data of Borok (1960) for the degree of absorption of NO_2 in water shown in Fig. 19 suggests a similar conversion. Thus a simple absorption of NO_2 into moist aerosols during the haze formation process could account for the nitrate concentrations observed. To verify this, work on absorption rates by concentrated salt solutions containing $(NH_4)_2SO_4$ and NH_4NO_3 should be undertaken

Although the reactions responsible for production of atmospheric organic aerosols are not known, circumstantial evidence points to the importance of the ozone-olefin reactions, or oxygen atom-olefin reactions as prime candidates. Just as the attack of ozone on olefins has been found to be crucial to SO_2 oxidation, this class of reaction can produce polymerized, oxygenated species that would condense out in the ppb vapor concentration range. It also is likely that such reactions could be promoted on particle surfaces, where the aerosol could act as a preconcentrator for the olefin or an intermediate species.

Water appears to play a ubiquitous role in aerosol formation. For example, recent experiments in our laboratory have suggested that the addition of water vapor to a 1-butene-ozone system can strikingly quench aerosol formation. However, the work of Ripperton _et al_. (1972) suggests that aerosol formation takes place in the presence of water vapor, though relative humidity was observed to influence the quantity of aerosol produced.

The ozone-olefin reaction mechanism is still being resolved in organic chemistry. However, one approach that can serve as a framework for discussion is Story's mechanism, shown in Fig. 20. Here the intermediates alluded to by Cox and Penkett again appear, but the complexity of the reaction steps is more clear. The importance of aldehydes and water are indicated schematically, with the suggestion of polymerization of some material. Formation of polymerized constituents up to 1% of the product yield is well known in liquid phase ozonolysis of olefins. One can readily see that the breakdown of the intermediates in the ozonolysis could produce acids and aldehydes found, for example, by Schuetzle in urban aerosol samples.

The ozonolysis process and subsequent degradation of products may be of interest in relation to the liquid water observed. An example of a water producing reaction is indicated in Fig. 21. It is known that olefin-ozone reactions involving ethylene and propylene in the gas phase produce water, but this product has not been found for a liquid medium.



Variation of the degree of absorption of nitrogen dioxide with its initial concentration C_i in the gas mixture. A) Log α; B) log C_i (C_i in vol.%). Absorbent–distilled water; temperature 17-20°; gas rate in absorber 0.5 liter/min.

Fig. 19

(From Borok, 1960)

$$\alpha = \frac{C_i - C_D}{C_i}$$

, C_i is the volume concentration in the gas,

C_D is the volume concentration in the liquid.

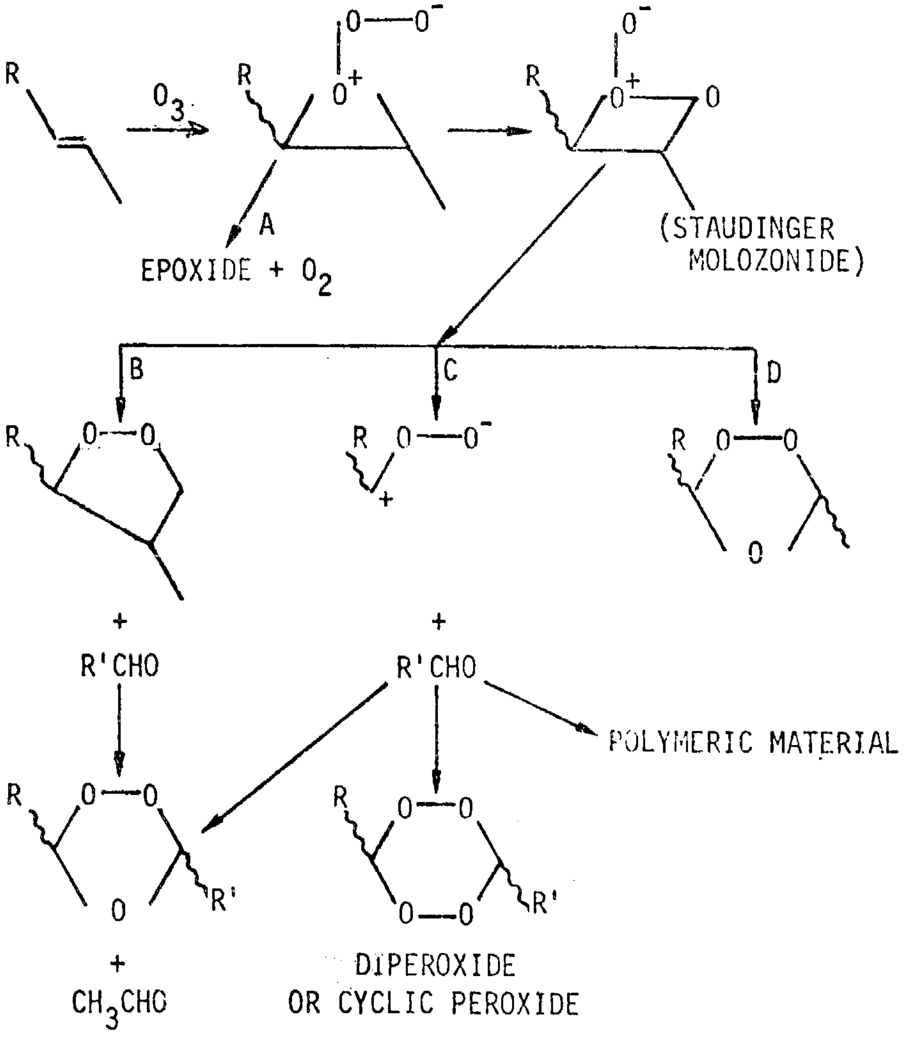

R
O_3
R
O^+
$O—O^-$
A
EPOXIDE + O_2
R
O^-
O^+
O
(STAUDINGER MOLOZONIDE)
B
C
D
R
O—O
R
O—O^-
+
R
O—O
O
+
R'CHO
+
R'CHO
POLYMERIC MATERIAL
R
O—O
O
R'
R
O—O
O—O
R'
+
CH_3CHO
DIPEROXIDE OR CYCLIC PEROXIDE

Fig. 20

A WATER PRODUCING SMOG REACTION

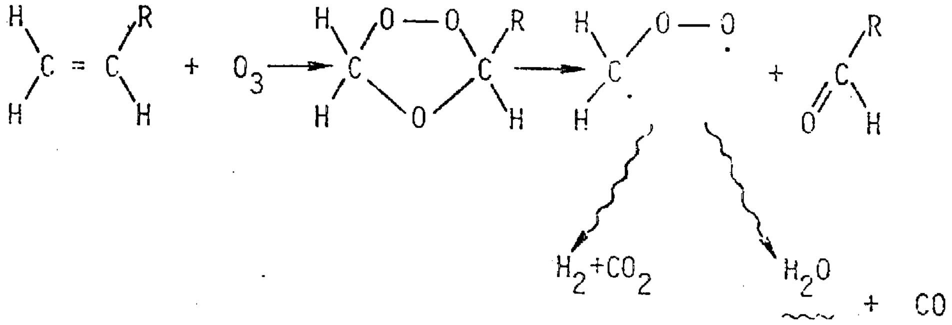


Fig. 21

Since the end products of these reactions are poorly characterized, it is impossible to detail the mechanism of particle formation and growth at this time. The question is open as to whether reactions take place by homogeneous gas phase reaction followed by condensation or by heterogeneous reactions on existing particles. However, from the proposed mechanism, it is clear that the ozone attack on olefins provides for fragmentation of the olefin. Thus, terminal olefins on cyclic compounds of high molecular weight should be the better candidate as aerosol formers.

Early experiments reviewed by Leighton (1961) and later smog chamber work of Groblicki and Nebel (1969) and of Ripperton et al. (1972) suggest that condensation of organic material is most likely from atmospheric reactions of olefins exceeding C_6 in equivalent molecular weight. This conclusion is borne out from other studies of Burton et al. (1973) in a steady flow reactor. An example of the difference in aerosol produce rate from different species is taken from Groblicki and Nebel's work and is shown in Table 15.

The question of aerosol formation and growth mechanisms may be resolved for smog chambers in the near future. In interesting studies of Husar et al. (1973) and later Clark (1973) the evolution of photochemically generated aerosol can be correlated in a uniform way in terms of an equilibrium surface area and the volume production rate. Clark's (1973) results are shown in Fig. 22. Here the lower part below the dividing line will give homogeneous nucleation. Aerosol formation with equilibrium surface above the line will take place by heterogeneous processes. The range of the 1969 Pasadena smog data are indicated in the hatched rectangle. According to this criterion, the evolution of Los Angeles aerosol is in the regime that may involve mixed nucleation to form new particles and heterogeneous growth. Other previous data cited indicate a dominance of heterogeneous processes on existing particles.

5. Tentative Conclusions About Atmospheric Photochemical Aerosols

The information gained from laboratory experiments can be used to clarify reactions of potential interest in the urban atmosphere. Some deductions from the laboratory studies are listed in Table 16. These results represent

Table 15

Aerosol Formed by the Dark Reaction
of Various Hydrocarbons and Ozone[a]

Hydrocarbon	Smokemeter Reading[b]
α-Pinene	3.0, 3.2
Cyclohexene	2.2, 2.6
Cyclopentene	1.4
Propylene	0.25
1-Heptene	0.25
Benzene	0.25
Isooctene	0.20
Isooctane	0.15
3-Heptene	0
Styrene	0

[a] HC 4 ppm, ozone 0.6 ppm.

[b] Corrected for initial values.

From Groblicki & Nebel (1969)

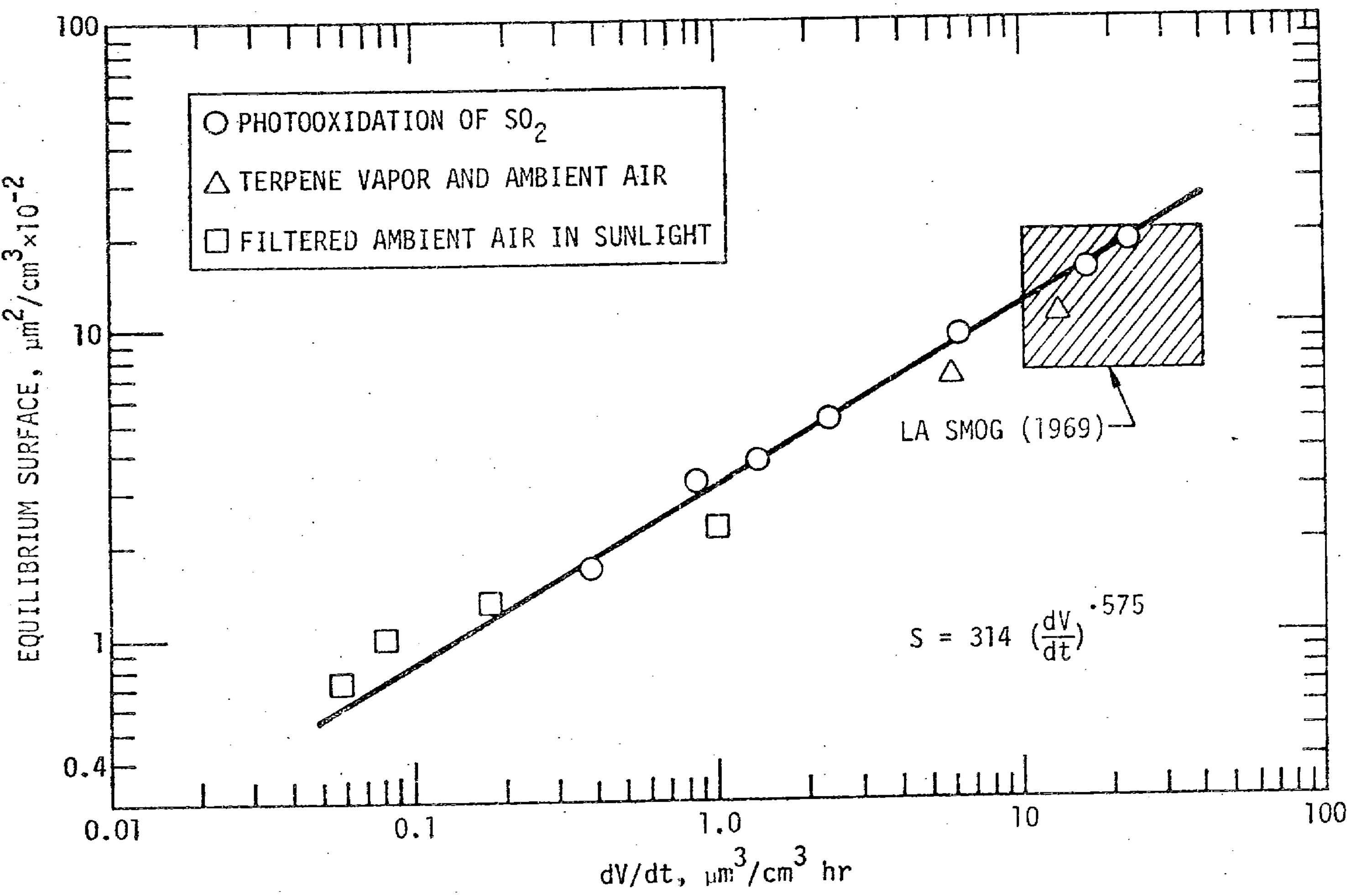


Figure 22. Variation of the apparent equilibrium surface area with volumetric conversion rate (After Clark, 1973).

Table 16

SUMMARY OF LABORATORY & "BASIC" OBSERVATIONS

1. Homogeneous SO_2 oxidation reactions too slow.
   -- also R.H. dependence appears to be incorrect.
2. Heterogeneous oxidation of SO_2 via $SO_3^=$ formation in aqueous, NH_4^+ buffered medium is promising explanation for atmospheric sulfate formation.
3. Vapor pressure of HNO_3 >> Vapor pressure of H_2SO_4.
4. NO_2 readily absorbs in water.
5. $(HNO_3)_g$ production appears to be slow compared with other products.
6. Nitrate difficult to generate as aerosol in smog chamber experiments.
7. Olefin-Ozone reactions excellent aerosol producers for $C_n > 6\text{-}8$ and low < ppm concentration in the absence of water vapor. Water vapor plays a ubiquitous role.
8. Formation and growth behavior in smog chambers appears to be similar regardless of initial reactant materials.

a capsule summary of information gained in the laboratory that helps interpret the behavior of the atmosphere.

Based on the results listed in Table 16, and their relation to the summary of "facts" about atmospheric photochemical aerosols, several tentative conclusions can be drawn. These are listed in Table 17. Such conclusions can be considered mainly hypotheses about photochemical aerosols in polluted air. They undoubtedly will shift as new experiments in the field and in the laboratory improve the picture of the formation and growth of the particles. Despite this prospect, it is hoped that this summary will orient you towards the complexities of the problem of interpreting atmospheric data in the light of laboratory chemistry with a limited sprinkling of theory.

Acknowledgements:

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Table 17

PHOTOCHEMICAL AEROSOLS IN A POLLUTED ATMOSPHERE

(Some Tentative Conclusions - Summer 1973)

1. Most likely candidate for SO_2 oxidation to $SO_4^=$
   -- quasi-aqueous reaction of $SO_3^=$ in the presence of Ammonia
   -- however, ozone-olefin - SO_2 reaction also may be important with moderate to heavy photochemical smog
2. A possible candidate for NO_3^- formation is the absorption and aqueous reaction of NO_2 in "moist" aerosols.
3. Olefin ($> C_6$) - Ozone reactions are likely to be dominant in the formation of organic aerosols, but the olefin-oxygen atom reactions may give similar products and cannot be ruled out. Evidence for organic aerosol forming reactions in an urban atmosphere is not definitive because of similarities in auto exhaust aerosols.
4. Liquid water/water vapor is an important and perhaps critical factor in urban aerosol formation.
5. Heterogeneous nucleation and growth on existing particles is the preferred mechanism for atmospheric transformations.
6. The thermodynamics of vapor pressure around droplets forces the stable aerosol growth to take place on particles $\gtrsim 0.05$ μm diameter.
7. Form of growth rate model unknown.

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CHAPTER VIII

MODES OF FORMATION OF THE SALTS OF SULFUR AND NITROGEN IN AN NO_x-SO_2-HYDROCARBON POLLUTED ATMOSPHERE

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CHAPTER VIII

Table of Contents

MODES OF FORMATION OF THE SALTS OF SULFUR AND NITROGEN IN AN NO_x-SO_2-HYDROCARBON-POLLUTED ATMOSPHERE

Available quantitative information related to the chemistry of sulfate and nitrate salt formation leaves many unanswered questions. However, important features can be discerned from the present data related to these systems, and reasonable speculation can be made concerning other potentially important features which require further study.

One route to future understanding of these extremely complex systems is through the computer simulation of the changes which are expected to occur in simpler analogues to the very complex mixtures which are characteristic of our urban atmospheres. Several groups have chosen this course in their research on atmospheric chemistry, and there have been a variety of attempts at computer modeling of the chemical changes which occur in smog chamber studies (6-15). In this section, the rather detailed chemical mechanisms developed by Demerjian, Kerr, and Calvert (4) and later expended in studies of McQuigg and Calvert (5) are used for computer simulation of atmospheric reactions. Further detail concerning this method of study of atmospheric chemistry can be found in the more detailed accounts of these calculations in Calvert's paper (16) presented at the National Academy of Sciences Conference on Health Effects of Air Pollutants, Ocotober 3-5, 1973.

1. Paths for Sulfate Salt Formation in the Urban Atmosphere

Assume that the conversion of SO_2 to sulfur trioxide, SO_3, in the atmosphere will be equivalent to the formation of a molecule of H_2SO_4. In other words, assume that the homogeneous reaction of SO_3 with water, $SO_3 + H_2O \rightarrow H_2SO_4$, is fast. This assumption may oversimplify the SO_2-sulfate salt conversion process, since the O-atom attack on SO_3 and possibly other processes may reconvert SO_3 to SO_2 (75). Having made this simplifying assumption, any processes which make either SO_3 or H_2SO_4 as products will be considered as equivalent.

a. Homogeneous reactions leading to SO_3 or H_2SO_4

The relatively slow rates of photooxidation of SO_2 in air exposed to sunlight (17-19) and the demonstrated catalytic influence of certain solids and moisture on the rate of SO_2 oxidation (20-26) have led to the common belief that heterogeneous paths for SO_2 oxidation probably outweigh the homogeneous modes. The most compelling argument which has favored the importance of the heterogenous removal processes has been the apparent lack of alternative homogeneous reaction paths of sufficient rate which might be invoked. Many research groups have suggested some possible homogeneous reaction paths. These are summarized in Table I (from Calvert {16}with minor changes to update the data) including the approximate enthalpy changes for the reactions and the theoretical rates of SO_2 removal in the specific reactions which would occur in a sunlight irradiated ($z = 40^o$), simulated polluted atmosphere as estimated by McQuigg and Calvert (5). The initial concentrations of impurities (ppm) selected for computer simulation were as follows: $\{NO_2\}^o = 0.025$; $\{NO\}^o = 0.075$; $\{\text{trans-2-butene}\}^o = 0.10$; $\{CH_2O\}^o = 0.10$; $\{CH_3CHO\}^o = 0.06$; $\{CO\}^o = 10$; $\{CH_4\} = 1.5$; $\{SO_2\}^o = 0.05\text{-}1$; relative humidity = 50%. The rates shown are those expected 30 min into the simulated run and typical of those throughout the first two hours of the run.

1) Oxidative reactions

All the reactions shown are rather exothermic and are favored from the viewpoint of thermodynamics. However the rates of reactions 50-56 (Table 1) including the photooxidation and attack by $O(^3P)$, O_3, NO_2, NO_3 and N_2O_5, appear to be severely rate limited; the most reliable kinetic data available to us suggests that all of these reactions are too slow to account for the observed rates of SO_2 removal in smog chamber experiments, in the urban atmospheres, and in stack plumes, where rates of 2% per hour and higher are not uncommon (27-32).

The reactions 56 and 57 of Table 1 have been suggested recently by Cox and Penkett (32) from kinetic studies of synthetic olefin-ozone-SO_2 mixtures at low concentrations. They found that SO_2 is oxidized at an appreciable rate by some reactive species formed in the dark on reaction between ozone and olefinic hydrocarbons. The higher rate of 3% per hour noted in Table 1 was observed when the olefinic hydrocarbon was *cis*-2-pentene, while with propylene a rate of 0.4% per hour was seen.

Radical reactions such as 58-61 in Table 1 do seem to occur, and analogous steps may account for the oxidation of SO_2 in the O_3-olefinic hydrocarbon mixtures. For this reason a less-than-or-equal-to sign has been placed in front of the estimated rate for reactions 56 and 57. Whatever the real oxidizing agent for SO_2 might be, it is very clear from the important experiments of Cox and Penkett that the homogenous oxidation of SO_2 can be stimulated in the dark at a significant rate when olefinic hydrocarbons and ozone react.

Very little is known about the rate of peroxyradical addition reactions to unsaturated molecules. However, estimates for the olefinic systems based largely on the considerations of Lloyd (39) suggest that these reactions are considerably slower than the corresponding HO-radical reactions (10^{-4} times slower). If this relationship is maintained for the SO_2 system then the rate of 58b will be <0.1% per hour. The rate of 59b is probably also of this order of magnitude.

2) Hydroxyl radical reactions

Measurements of the rate constant for the potentially important reaction 60 of Table 1, $HO + SO_2 \rightarrow HOSO_2$, are now being attempted in several laboratories.

Gordon (38) reported results obtained in pulse radiolysis experiments at 162°C in 1 atmosphere of water vapor giving $k_{60} \cong 1.08 \times 10^9$ $\ell.mole^{-1}sec^{-1}$. These preliminary results seem to confirm the previous expectations of the probable importance of reaction 60 in SO_2 removal mechanisms operative in the urban atmosphere. It is not now known what is the temperature coefficient for this reaction, so a realistic extimate for k_{60} at 25°C. is not possible. However, if the reaction 60 follows the usual kinetic behavior observed for HO radical addition to carbon-carbon π-systems, then it should have a fairly small positive activation energy. In this case the estimate of $k_{60} \cong 1.08 \times 10^9$ $\ell.mole^{-1}$ sec^{-1} must represent a maximum possible value for 25°C. With this assumption and the HO radical concentration predicted by the simulations employed in calculating the data of Table 1, the maximum rate of SO_2 conversion from reaction 60 is estimated as 1.4% per hour. The true rate of this reaction probably lies between the two extremes, 0.23-1.4% per hour. Thus it seems highly likely that the HO-addition reaction 60, and similarly the alkoxy radical additions to SO_2 represented by the reaction 61 of Table 1, are important steps involved in the conversion of SO_2 to its salts in the urban atmosphere.

Presumably the radical addition to SO_2 in reactions 60 and 61 would be followed by subsequent steps which will lead to sulfuric acid, peroxysulfuric acid, alkysulfates and various other theoretically possible precursors to sulfuric acid, nitric acid, and the salts of these acids. All of the compounds should ultimately give sulfuric acid, sulfate, peroxysulfate, nitrate or nitrite salts as a further chemical modification of the primary products would occur, probably in a dynamic liquid phase on an aerosol particle. One such reaction sequence which may be important in urban atmospheres and which will illustrate the possible mechanisms for HO attack on SO_2 is the following:

$$\mathrm{HO} + \mathrm{SO_2}\ (+\underline{\mathrm{M}}) \rightarrow \mathrm{HOSO_2.}\ (+\underline{\mathrm{M}}) \tag{60}$$

$$\mathrm{HOSO_2.} + \mathrm{O_2} \rightarrow \mathrm{HOSO_2O_2.} \tag{62}$$

$$\mathrm{HOSO_2O_2.} + \mathrm{NO} \rightarrow \mathrm{HOSO_2O.} + \mathrm{NO_2} \tag{63}$$

$$\mathrm{HOSO_2O.} + \mathrm{HO_2} \rightarrow \mathrm{HOSO_2OH} + \mathrm{O_2} \tag{64}$$

$$\mathrm{HOSO_2O.} + \mathrm{NO} \rightarrow \mathrm{HOSO_2ONO} \tag{65}$$

$$\mathrm{HOSO_2O.} + \mathrm{NO_2} \rightarrow \mathrm{HOSO_2ONO_2} \tag{66}$$

$$\mathrm{HOSO_2O.} + \mathrm{RH} \rightarrow \mathrm{HOSO_2OH} + \mathrm{R} \tag{67}$$

$$\mathrm{H_2SO_4} + \mathrm{H_2O}\ (\mathrm{NH_3}, \mathrm{CH_2O}, \mathrm{C_nH_{2n}}, \text{etc.}) \rightarrow \text{growing aerosol} \tag{68}$$

$$\mathrm{HOSO_2ONO_2} + \mathrm{H_2O} \rightarrow \mathrm{H_2SO_4} + \mathrm{HONO_2} \xrightarrow{(\mathrm{nH_2O})} \text{growing aerosol} \tag{69}$$

$$\mathrm{HOSO_2ONO} + \text{sunlight} \rightarrow \mathrm{HOSO_2O.} + \mathrm{NO} \tag{70}$$

$$\mathrm{HOSO_2ONO} + \mathrm{H_2O} \rightarrow \mathrm{H_2SO_4} + \mathrm{HONO} \xrightarrow{(\mathrm{nH_2O})} \text{growing aerosol} \tag{71}$$

Any mechanism which deserves serious consideration should satisfy the few requirements which seem to evolve from the limited chamber data from NO_x-hydrocarbon-SO_2 mixtures in air (40-44). These results suggest: (1) the presence of SO_2 does not alter significantly the ultimate ozone level reached in the system; and (2) the SO_2 removal rate shows an induction period characteristic of the time delay expected for the build-up of the reactive radical species (HO, HO_2, etc.) which are generated in the chain reactions involving the olefinic hydrocarbons (4,16).

By proper choice of rate constants for the reaction sequence 60-67, one can satisfy these limited requirements. At this point in time the complete simulation of the rates of formation of H_2SO_4 and the theoretically proposed intermediates such as $HOSO_2ONO_2$, etc., is premature, since the computer-derived mechanism, although reasonable, is highly speculative and must be tested properly by experiment before its true utility can be assessed.

3) Summary, homogeneous formation of SO_3 or H_2SO_4

If the various estimates of the SO_2 homogenous removal rates for each of the possible reactions are added the total potential rate of conversion of SO_2 to SO_3, H_2SO_4, or sulfates is about 2-5% per hour. This is the order of magnitude of the observed rate of SO_2 removal in NO_2-NO-hydrocarbon irradiations in smog chamber experiments (40-44). Therefore, certain homogenous removal paths of SO_2 are probably significant in the polluted atmospheres of our cities. However, quantitative rate data related to reactions 56-61 must be had before truly meaningful estimates of these rates can be derived.

b. Heterogeneous oxidation of SO_2

Whether SO_3 or H_2SO_4 are formed homogeneously or heterogeneously on particulate matter, the reactions which follow and lead to aerosol growth become heterogeneous quickly. The rapid rates of oxidation of SO_2 observed in stack plumes have been rationalized well in theory by Foster (20) using reasonable models for the catalytic processes. The detailed experimental work of Matteson, et al. (24), van den Neuval and Mason (25), and Corn and Cheng (26) all suggest that the SO_2 oxidation can be accelerated at room temperature by purely thermally induced, catalytic processes, particularly at high humidities. It is possible that the heterogeneous thermal conversion of SO_2 to sulfate occurs in a growing aerosol particle in the photochemical smog mixture. One such possible route is through the reactions involving ozone in the aqueous aerosol phase.

$$SO_2 + H_2O \text{ (in aerosol) } \rightleftarrows H_2SO_3$$

$$H_2SO_3 \rightleftarrows H^+ + HSO_3^-$$

$$HSO_3^- \rightleftarrows H^+ + SO_3^=$$

$$SO_3^= + O_3 \rightleftarrows SO_4^= + O_2$$

Penkett (61) and Cox and Penkett (62) have observed significant rates of conversion of SO_2 to sulfate using dilute ozone solutions in the laboratory. It is not possible to evaluate the relative importance of such heterogeneous paths at this time, but some scientists have favored such reactions in rationalizing sulfate formation; for examples, see Hidy (49) and Castleman (63).

The hygroscopic nature of the photochemical aerosols and their high sulfate, nitrate and organic matter ($C_xH_yO_z$) composition suggests that these materials contain a grand sample of the almost limitless number of compounds found in photochemical smog. The simplest interpretation of the origin of these photochemical aerosols is through initial sulfuric acid formation. The photochemical aerosol studies from several groups (40-44,50-54, 56,59) are consistent with this view.

c. Acidic aerosols

The observations of Charlson and co-workers show that relatively pure H_2SO_4 aerosol forms under certain conditions which prevail in regions of St. Louis (57). Whether SO_3 is formed as the first product of SO_2 oxidation (as required by reactions 56, 57, 58a and 59a) and H_2SO_4 subsequently appears as the reaction of SO_3 with water occurs, or whether H_2SO_4, $HOSO_2O_2H$, $HOSO_2ONO_2$, CH_3OSO_2OH, and $CH_3OSO_2O_2H$, are formed directly (following reactions 58b, 59b, 60, and 61), the net result should be a highly hygroscopic product molecule which may accumulate water even at the relatively low atmospheric humidities characteristic of Los Angeles (49). Into this highly acid solution will diffuse a variety of reactants which can build the bulk and alter the chemical composition of the original acid droplet.

The capture of normally volatile molecular species and the subsequent chemical conversion of these compounds to new non-volatile products must occur also. For example, formaldehyde, acetaldehyde, and the olefins diffusing to the aerosol surface may be captured and then polymerized to higher molecular weight species in this acid medium. The epoxides of the olefins are apparently formed a large fraction of the time following O-atom addition to the olefinic hydrocarbon even in air (54). These compounds when captured by the acid solution of the aerosol should hydrolyze to generate the non-volatile, hydroscopic glycols, $R_2C(OH)C(OH)R_2$. The dibasic acids which will result ultimately from the attack of O_3 or free radicals on the cyclic olefins in the atmosphere should be good contributors to aerosol formation as well.

2. The Modes of Formation of Nitrate Salts in the Atmosphere

The formation of nitrate salts in the atmosphere may occur by a variety of reaction paths. One such theoretically possible mode was described in the preceeding section: that of the hydration and neutralization of the hypothetical mixed anhydride of sulfuric and nitric acid, $HOSO_2ONO_2$. More conventional modes of nitrate salt formation are considered in this section.

a. Homogeneous formation of HNO_3 by hydroxyl radical reaction with NO_2

Computer analysis of the reaction systems points to two major homogenous sources of nitric acid in photochemical smog mixtures; these are reactions 14 and 8 (see ref. 16):

$$HO + NO_2 + M \rightarrow HONO_2 + M \qquad (14)^{a}$$

$$N_2O_5 + H_2O \rightarrow 2HONO_2 \qquad (8)^{b}$$

([a]The best current estimates of the homogeneous rate constant for reaction 14 vary within the range 1.5×10^4 to 0.46×10^4 $ppm^{-1} min^{-1}$ (expressed as apparent second order reactions with M=1 atm of nitrogen gas). These values have been estimated in the reviews of Demerjian, Kerr, and Calvert (4) and Tsang (64), respectively.)

([b]The best current kinetic data for the homogeneous reaction 8 of which we are aware are those of Morris and Niki (74) which give $k_8 \le 1.9 \times 10^{-5}$ ppm^{-1} min^{-1}.)

The rate of nitric acid formation through the hydrogen abstraction from H-atom containing molecules and radicals by the intermediate NO_3 species present in the photochemical smog is much less important than reactions 14 and 8 for the usual atmospheric conditions encountered; more detailed rate comparisons are possible (Table II, ref. 16). Using these rate data and concentrations of the intermediates and reactants for a simulated, typical NO_x-hydrocarbon-polluted atmosphere (see Table I, ref. 16) the following rates of $HONO_2$ formation are estimated:

$$R_{14} \cong 2.0 \times 10^{-5} \text{ ppm min}^{-1} \text{ (reference 66)}$$

$$R_{14} \cong 6.6 \times 10^{-5} \text{ ppm min}^{-1} \text{ (reference 4)}$$

$$R_8 \le 1.6 \times 10^{-5} \text{ ppm min}^{-1}$$

It appears probable that the nitric acid formed homogeneously in the smoggy atmosphere results largely from reaction 14. The rate of NO_2 conversion to $HONO_2$ in this reaction amounts to about 2.4-7.9% per hour at the 30 minute irradiation point picked for the simulation. This range is somewhat higher but not out of line with the rates of formation of NO_3-containing aerosol observed in Los Angeles smog (73).

In smog simulations which neglect the heterogenous removal processes, $HONO_2$, peroxyacetylnitrate (PAN) and methyl nitrate are the major sumps for the nitrogen oxides in smog (16). The conversion of NO to NO_2 is followed by a continuing transformation of the NO and NO_2 into two major products, nitric acid and PAN. A much smaller quantity of methyl nitrate builds up as the reactions continue. Nitrous acid and methyl nitrite are formed but their concentrations do not climb appreciably since both compounds are rapidly dissociated by sunlight. The nitric acid, PAN, and methyl nitrate absorb sunlight only weakly, and other homogeneous reactions included in this mechanism which remove them are not fast; hence they do accumulate with time in the synthetic polluted atmospheric reactions described elsewhere (Fig. II, ref. 16).

In the real urban atmosphere nitric acid does not seem to build up as expected from the foregoing reaction scheme, but presumably the nitric acid formed reacts in the real world with certain basic impurities in the atmosphere: ammonia, the oxides of the metals, etc. The quantitative treatment of such heterogenous reactions is not possible at this time.

b. Homogeneous nucleation of HNO_3

One path analogous to that present in the H_2SO_4-sulfate salt-forming mechanisms is unimportant for nitric acid and nitrate salt formation. In the former case the low vapor pressure of pure sulfuric acid results in a rapid homogeneous nucleation at partial pressures of H_2SO_4 in the range 10^{-8} to 10^{-10} Torr, according to Doyle (69) and Kiang, et al. (70). The hydration of sulfuric acid droplets is thermodynamically favorable over a wide range of relative humidities, and the aerosol particles of H_2SO_4 solution grow as they take on water. On the other hand the vapor pressure of nitric acid is very high, and homogeneous nucleation of nitric acid aerosol formation in a moist atmosphere is not expected to occur for normal atmospheric conditions (70). However, nitric acid does form some mixed compounds or complexes of considerable stability in sulfuric acid solutions (71). It has been suggested that nitric acid may become incorporated within sulfuric acid droplets at the lower temperatures of the upper atmosphere (72,63). Presumably such a chemical entrapment of nitric acid would be followed by neutralization of the aerosol with atmospheric ammonia, and NH_4NO_3 and $(NH_4)_2SO_4$ would be the ultimate products.

c. Homogeneous reactions of HNO_3 with NH_3

The direct homogeneous capture of gaseous nitric acid by gaseous ammonia, $NH_3 + HONO_2 \rightarrow NH_4NO_3$, may be a significant source of NH_4NO_3 salt in the atmosphere if the ammonia levels in the polluted atmosphere are sufficiently high. Countess and Heicklen (67) have found that the analogous homogeneous reaction between NH_3 and HCl gases occurs with a rate constant of 2.8×10^{-2} $ppm^{-1}min^{-1}$. Assuming the NH_3-$HONO_2$ reaction to have a rate constant of this magnitude and ammonia and nitric acid concentrations of 1 pphm the homogeneous rate of NH_4NO_3 formation would be 2.8×10^{-6} ppm min^{-1}. Note in the foregoing discussion that this rate is a significant fraction of the theoretical rate of $HONO_2$ formation (reactions 14 and 8 given above). This $HONO_2$ removal path appears to be worthy of further quantitative consideration and study. Certainly the rate constant of the $HONO_2$-NH_3 reaction must be measured and the ambient levels and the diurnal pattern of gaseous NH_3 which is present in the urban atmosphere must be known before any realistic modeling of this reaction can be made.

d. Heterogeneous reactions of HNO_3

Quantitative treatment of heterogeneous reactions leading to formation of nitrate salts is not possible at present and is therefore not included in computer simulations of atmospheric reactions. However, they must occur in the real atmosphere, and nitric acid may be converted efficiently to ammonium nitrate if the concentration of ammonia impurity is sufficiently high. Ammonium nitrate comprises approximately 10-15% of the total airborne particles in composite samples collected in the Los Angeles area over the year 1971-72 (65).

It is probably significant that the simulation (16) predicts that a large fraction of the NO_x ultimately ends up as PAN. It is known that PAN hydrolyzes in solution to form nitrite ion (69). Thus one might expect that the heterogeneous removal of PAN may occur following encounters with and absorption by the aerosol droplet, and nitrite salts may be formed from the PAN provided that the pH of the solution is kept sufficiently high through NH_3 molecule capture by the aerosol.

The extent to which NO_3^- and NO_2^- salts form as a result of gaseous NO_2 and NO absorption into aerosol droplets is not now known. But the following reactions can lead to nitrate in principle, provided that sufficient NH_3 or other basic compounds neutralize the acids formed upon formation of the solution:

$$2NO_2 + H_2O \rightleftarrows H^+ + NO_3^- + HONO$$

$$NO + NO_2 + H_2O \rightleftarrows 2HONO$$

$$HONO + OH^- \rightarrow H_2O + NO_2^-$$

$$2NO_2^- + O_2 \text{(in aerosol soln.)} \rightarrow 2NO_3^-$$

$$NO_2^- + O_3 \text{ (in aerosol soln.)} \rightarrow NO_3^- + O_2$$

These potential heterogeneous reactions forming nitrate may be sufficiently rapid to account for all of the observed nitrate formation according to Hidy (44).

However, the reliability of this conclusion must be questioned at this incomplete stage in the development of our knowledge concerning these mechanisms. A major problem with the former "standard" method for NO_2 analysis in the atmosphere (Jacobs-Hochheiser method) is the inefficiency in the collection of the NO_2 by the basic solution employed in the bubblers in the collection train. Since the reaction of NO_2 with the large volume of very basic bubbler solution is slow for these very favorable conditions of capture, then it would not be surprising if it is slow and not very important in the acidic or near neutral aerosol droplets finely dispersed in the atmosphere. Obviously further study of this system will be necessary to evaluate its significance in nitrate salt formation in smog.

3. Conclusions

There are many uncertainties which remain concerning the mechanism of generation of sulfate and nitrate salts in the sunlight-irradiated, NO_x-SO_2-hydrocarbon polluted atmosphere. However, theoretical homogeneous rates of transformation of NO_x to nitric acid and SO_2 to SO_3 and H_2SO_4 are not insignificant. Free radicals generated in the smog reactions probably are the important reactants which promote these changes in the real atmosphere.

Several heterogeneous paths may act independently to effect these transformations, although their importance is also uncertain at this time. Of course the heterogeneous reactions which lead to the accumulation of the acids in the aerosol particles and the subsequent neutralization reactions must be significant in the overall conversion of these acids to the salts.

Extensive fundamental research related to these processes will be necessary to establish the relative importance of the different possible mechanisms for the atmospheric conversion of SO_2 and NO_x to the sulfate and nitrate salts and to allow realistic control procedures to be developed.

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CHAPTER IX.

$H_2SO_4/(NH_4)\ SO_4$ BACKGROUND AEROSOL: OPTICAL DETECTION IN ST. LOUIS REGION

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in Association with Photochemical Oxidant

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Abstract

Atmospheric H_2SO_4 present as droplets of the free acid and the half neutralized acid, NH_4HSO_4 mixed with other substances have proved to be extremely difficult to measure with traditional air sampling methods. Knowledge of their existence as a major or minor fraction of atmospheric aerosol is important to studies of health effects of air pollution, atmospheric optics, acid rain and to understanding the global sulfur cycle. The in situ method reported here utilizes a light scattering/humidity relation to detect reaction of the aerosol with NH_3 to form the deliquescent salt $(NH_4)_2SO_4$. Field measurements in and near St. Louis, Missouri, confirm that H_2SO_4 and/or NH_4HSO_4 are frequently present as a major fraction (ca. 1/2 or more) of the submicrometer particles, and that $(NH_4)_2SO_4$ also is frequently found. At one site 35km WSW of the Arch, over 98% of the measurements were dominated by H_2SO_4 or its neutralization products and showed no dependence on wind direction or synoptic condition, thus indicating a regional as opposed to urban behavior. While the results to date are qualitative and semi-quantitative in nature, it appears possible to utilize gas phase titration with NH_3 to quantify the method.

Atmospheric chemists have suspected for a long time that H_2SO_4 aerosol and its neutralization products with NH_3 exist in air as oxidation products of SO_2. But while H_2SO_4 mists have been located and quantified by traditional methods in some industrial settings where concentrations are high, these same procedures have failed to provide convincing evidence of the presence or absence of the free or partially neutralized acid in ordinary urban or rural air (1). The difficulty in this chemical analysis can be attributed largely to the presence of many other substances in the collected particulate matter and to low atmospheric concentrations, usually less than 100μg/m^3 for the concentration of total filterable particulate matter. Less traditional methods utilizing electron microscope identification of characteristic patterns on sensitized surfaces have been used by Lodge (2) who concluded that H_2SO_4 and its products of neutralization with NH_3 (i.e., NH_4HSO_4 and $(NH_4)_2SO_4$) are often the predominant material in submicrometer atmospheric particles in rural air. However, this and similar microscopic methods are tedious and are difficult to interpret or quantify. The volatility of H_2SO_4 , NH_4HSO_4 and $(NH_4)_2SO_4$ in the high vacuum and electron beam of the electron microscope is another limitation. The possibility of chemical modification during the sampling process raises additional questions regarding the actual molecular state in the atmosphere. Forrest and Newman (3) reviewed the large number of methods available for sulfates and for H_2SO_4 and emphasized the difficulties and ambiguities of methods for H_2SO_4. One particular problem -- the reaction of sampled H_2SO_4 with other particles, collection surfaces of NH_3 gas during the sampling period or with NH_3 after sampling -- can be singled out as a serious limitation to many methods, especially those which involve the handling of filters or impactor slides while exposed to air containing NH_3. Human beings emit NH_3 gas, and laboratory air is normally contaminated with NH_3, a condition that would consistently yield low results for H_2SO_4. As a result of these considerations, it appears desirable to consider methods for sensing H_2SO_4 and other sulfates _in situ_.

Dzubay et al. (4) utilized the _in situ_ reaction of H_2SO_4 with NH_3 by measuring the decrease in NH_3 after conversion to NO with a chemiluminescent sensor, but found a detection limit of ca. 20 $\mu g/m^3$ which is about a factor of ten to 100 too high for resolving expected H_2SO_4 levels based on total sulfate information.

We want to emphasize the point that by far most of the atmospheric data in existence today are for total sulfate ion, regardless of the cation with which it was associated in the atmosphere. Atmospheric sulfate may be expected to have a number of molecular forms: H_2SO_4, NH_4HSO_4, $(NH_4)_2SO_4$, $MgSO_4$ (from sea salt), $CaSO_4$ (gypsum dust), Na_2SO_4 (from paper mills), etc. Important properties of sulfates (e.g. toxicity, water solubility, refractive index and acidity) depend on their molecular nature rather than on the properties of the anion alone. Besides this ambiguity, much of the existing sulfate concentration data may be influenced by the oxidation of SO_2 to SO_4 on the filter used for sampling (5).

Knowledge of the presence of free H_2SO_4 or NH_4HSO_4 is critically important for understanding the chemical processes that occur in the atmospheric portion of the sulfur cycle, particularly the oxidation of SO_2 to some form of sulfate ($SO_4^=$) prior to removal by fallout or rainout. This knowledge is also important for studies of health effects, where $SO_4^=$ has recently been implicated via epidemiological studies (6).

Both H_2SO_4 and NH_4HSO_4 aerosols react in situ with NH_3 gas to form $(NH_4)_2SO_4$. The former two are hygroscopic substances which are aqueous solution droplets at all humidities from 30 (7) to 100%. In contrast, the latter is a deliquescent salt which undergoes a transition from the dry crystal to a solution droplet at the relative humidity corresponding to that over the saturated solution of the salt (∿80%). Thus reaction with NH_3 serves to provide considerable information if the product of the reaction undergoes a clearcut phase transition at this particular relative humidity.

This reaction can be followed with an integrating nephelometer and appropriate humidity control apparatus (humidograph) as shown in Fig. 1 (8). Briefly, the light scattering coefficient, b_{sp}, is measured as a function of relative humidity in a flow system in which the humidity is varied from ca. 20 to 90%. The air is heated 10-20°C to lower the humidity to 20-30% and then water vapor is added at an increasing flow rate up to ca. 90% in a period of 2 to 3 minutes. A curve of scattering versus hummidity (humidogram) is recorded for the aerosol without NH_3 addition. Subsequently, a small amount of NH_3 (a few ppm) is added to the incoming air prior to humidification. The NH_3 flow was generated by passing air at ca. 1 L/min over the surface of a 0.7 N solution of NH_3 without bubbling, then passing this flow through an absolute filter to assure that no aerosol was generated by the NH_3 source itself. The flow rate through the rest of the system was ca. 100 L/min and nearly constant so that dilution effects were minimized.

If H_2SO_4 or NH_4HSO_4 are present as the dominant substances in the light scattering aerosol, the humidogram is monotonic and has no inflection points (Fig. 2, upper curve). Of course, many substances ($NaNO_3$, polar organic compounds, etc.) have such a response (8). Following the addition of NH_3, however, the acid sulfates react to yield $(NH_4)_2SO_4$ with its specific deliquescent response at ca. 80%, confirming the presence of H_2SO_4 or NH_4HSO_4 in the air flow (Fig. 2, lower curve). To our knowledge, no substances other than these two acid sulfates could (a) form an aerosol at normal conditions and (b) be found in normal air as a major fraction of the submicron particles and (c) have a monotonic humidogram before addition of NH_3 and (d) also have a deliquescent salt humidogram with an inflection point at 80% after reaction with NH_3 gas at ppm concentration.

It is important to recognize that this light scattering technique does not sense all particle sizes equally, since the range of sizes most effective in scattering light lies between 0.1 and 1.0 µm (9). This size range is not only important to the problem of visibility degradation, but also to health effects (since submicrometer particles can be inhaled into the lower airways of man). The discoveries by Whitby et al (10) of a bimodal aerosol volume distribution and by Husar et al. (11) that the volume mode between 0.1 and 1.0 µm consisted largely of products of gas to particle conversion suggest that optical methods such as the one reported here are likely to be relevant for studies of the process of conversion of SO_2 to sulfate.

If the aerosol being studied is not a pure substance the response of the system if modified by the other substances that are present in the submicrometer particles. Depending on whether the substances are mixed within each particle or whether the particles of different substances are separated, differences in response are noted, and depend strongly on the nature of the substances present. In general, in order to have a plainly visible inflection point for $(NH_4)_2SO_4$ in the case where substances are mixed within individual particles, we estimate that it is necessary for the soluble aerosol to be at least 30 to 50 mole percent of the salt. The requirements in the case of physically separated compounds are less stringent, but may never occur in air due to Brownian coagulation. Of course, it is necessary for a substantive fraction of the submicrometer particles to be hygroscopic, or no significant increase in light scattering can be observed.

This apparatus was automated for field use to produce a humidogram at preselected intervals (usually 30 minutes), with extra runs being performed as desired by the operator. NH_3 addition was performed in most measurements by manually opening a valve admitting the gas to the sample flow; however, a small amount of data was obtained in which the NH_3 addition was also automated. At preselected times during field experiments (usually midnight) a standard aerosol (e.g. H_2SO_4 or $(NH_4)_2SO_4$) was injected into a filtered air stream for the generation of one humidogram, and in the case of H_2SO_4 a second humidogram was generated after the addition of NH_3 in order to check the system response and hygrometer calibration. All dilution air (when needed) was passed through an NH_3 trap of H_2SO_4 on a fibrous glass filter, and then passed through an absolute filter to assure no effects due to locally derived aerosol or NH_3 (e.g. from the operator). Tests were also run to establish that NH_3 addition did not create new particles but only reacted with existing ones. The data were examined for increases in b_{sp} due to NH_3 and none was found. In fact, if NH_3 is added at a RH $\sim$ 60%, a decrease in b_{sp} is easily observed when H_2SO_4 or NH_4HSO_4 are present.

The apparatus was installed in a mobile laboratory (truck) which was operated at three sites in St. Louis, Missouri, from 20 August until 5 October, 1973. The first site was on the campus of Washington University at the edge of a soccer field ca. 50 meters from a residential street and ca. 12 km west of the Arch. The second site was near Tyson Hollow, 35 km WSW of the Arch on a hill at ca. 200 m altitude. This is a distinctly rural location in the center of a 2,500 acre, limited access preserve. West and south winds provide air from sparsely populated areas while north and east winds provide city air. The third site was on the campus of St. Louis University ca. 3 km west of the Arch. Air was sampled with a vertical 10 cm ID aluminum pipe at a height of 8 m. During the experiment at Washington University other groups were measuring aerosol composition by other means which allows comparison to our results.

The results of these experiments are summarized in Tables 1 and 2 and in Figure 3. Due to the fact that the NH_3 addition was initially programmed as an occasional test, only one such run was made at the Washington University site. The basis for such low priority was our experience in a similar series of experiments in California and Washington State in 1972, in which NH_3 was added and no change was observed in the humidograms. Even in the heaviest smogs in the south coast basin of California in August and September of 1972, there was no evidence of reactivity with NH_3.

Table 1 summarizes the results where no NH_3 was added, and serves as a description of the interaction of water vapor with the ambient aerosol at the three sites. It is evident that the aerosol contained a significant fraction of a deliquescent salt with properties like $(NH_4)_2SO_4$ at all the sites for a substantial fraction of the runs (ranging from 34% at St. Louis University to 41% at Tyson). The remainder of the cases in Table 1 fall into two classes: (a) hygroscopic, implying a monotonic humidogram and (b) deliquescent at a humidity of ca. 65%. This latter case is particularly interesting since the evidence for an inflection point at this humidity was occasionally well defined. It is possible that this substance is the mixed salt $(NH_4)_3H(SO_4)_2$; however, we can offer no further explanation at this time (12).

Table 2 summarizes the number of cases where NH_3 was added. The run made at Washington University was not definitive, i.e. category D. After the discovery at Tyson on 21 September that the aerosol was reactive with respect to NH_3, runs were made regularly -- usually every hour for ca. 12 hours per day. Ambient runs without NH_3 were continued on an automatic basis every half hour. On the last day at Tyson and for the duration of the period at St. Louis University, the NH_3 addition was carried out automatically every half hour, with a non-NH_3 run preceding it by 15 minutes.

As can be seen in Table 2, the aerosol at Tyson was totally dominated by sulfate behavior with over 98% of the cases either reacting with NH_3 to yield a deliquescent compound like $(NH_4)_2SO_4$ or already having its characteristics prior to NH_3 addition. About half the time, the substance was not deliquescent until NH_3 was added , indicating a substantial fraction present as H_2SO_4 or NH_4HSO_4.

The results at St. Louis University are not quite as definitive as those from Tyson, with a substantial percentage (59%) showing hygroscopic behavior and no change with NH_3. This is reasonable in view of the proximity of this site to a large variety of urban and industrial sources.

It is possible to estimate the mass concentration of submicrometer particulate matter from the light scattering coefficient (9) and to estimate the fraction of it that is sulfate from the humidogram. During a 23-hour period when $(NH_4)_2SO_4$ was evident, Dzubay and Stevens (13) provide mass concentrations and an extensive elemental analysis of two particle classes; those above and those below 2 μm. Thus it is possible to compare the quantities obtained by sampling by sampling with those estimated in situ from light scattering. Between 1015 on 30 August and 0915 on 31 August (CDT) the average light scattering coefficient at 525 nm was $1.2 \times 10^{-4} m^{-1}$ corresponding to a submicrometer mass concentration (9) of ca. 40 $\mu g/m^3$. The measured mass concentration of particles below 2 μm (13) was 26 $\mu g/m^3$ for comparison. We previously estimated that 30-50 mole % of the submicron particles must be a pure salt if deliquescence at a certain humidity is to dominate the humidogram, so that we would guess at ca. 10 to 20 $\mu g/m^3$ of $(NH_4)_2SO_4$ for this 23 hour sample. The concentration of S (as the element) was 3.1 ± 3 $\mu g/m^3$ from x-ray flourescence analysis (13) which would correspond to 13 ± 3 $\mu g/m^3$ if all the sulfur were $(NH_4)_2SO_4$. By comparison, the mass concentration of particles of between 2 and 10 μm was only 19 $\mu g/m^3$ and consisted mainly of Si and Ca compounds with only 1.5 $\mu g/m^3$ as S.

The consistency of these two very different approaches lends credence to the in situ method described above for identifying submicrometer sulfate aerosols. While the results to date do not differentiate between the two acid sulfates, it appears possible to do so by carefully titrating with a known concentration of NH_3 (e.g. from a permeation tube) with carefully controlled flowrates of both the titrant and humidograph. The humidograph, operated repetitively, would be used to sense the end points. A preliminary uncalibrated experiment showed that a small NH_3 flow could be added without causing an inflection to appear in the humidogram. Succeedingly larger NH_3 flows caused the curve to first develop an inflection point at 80% RH (indicating the generation of some $(NH_4)_2SO_4$) and then to enhance it to a final curve beyond which additional NH_3 caused no further change. From the amounts of NH_3 added at the two "end points" (i.e. where the inflection point first appeared and where increased NH_3 caused no further change) the concentration of H_2SO_4 and NH_4HSO_4 can be separately and absolutely determined. It is important to recognize that this aerosol phase titration depends only on the accuracy of flow rates of air and NH_3, and the ability to detect an inflection point in the humidogram and not on the magnitude of light scattering coefficient.

The data in Tables 1 and 2 and the consistency of the humidograms with direct sampling methods provide a strong argument for the existence of H_2SO_4, NH_4HSO_4 and $(NH_4)_2SO_4$ aerosol as normal intermediate substances in the sulfur cycle and as regional pollutants as opposed to urban entities. The bases for this hypothesis follow:

a) There is clearly no dependence of the chemical composition of submicrometer, light scattering particles on wind direction. During the experiments at Tyson virtually all wind directions occurred including wind from and wind toward the city. No contrast of urban versus rural air could be immediately noted.

b) Similarly there is no dependence on synoptic conditions since this period at Tyson exhibited both fair weather and frontal activity, winds ranging from 0 to perhaps 10 m sec^{-1}, clouds, frontal rain, cumulous activity and thunderstorms. No clearcut variation in composition could be observed in any single weather situation.

c) The fraction of the runs at each location in which the aerosol exhibited deliquescence at 80% without the addition of NH_3 was fairly constant, and large. Typically 30-40% of the runs exhibited the $(NH_4)_2SO_4$ character.

d) Samples of particulate matter were taken simultaneously at the Washington University site with a sequential sampler and were analyzed for sulfur and a number of other elements, also by Dzubay and Stevens (13). In analyzing the results from their two-hour samples taken regularly for five days, they noted that the sulfur concentration(14) exhibited much smaller variation than Ti of Pb, indicating local sources for the latter and a lack of a local discrete source for the former.

e) St. Louis is located in a region of the country in which large SO_2 sources (mainly power plants, some non-ferrous metal smelters and oil refineries) are spaced from a few tens to a few hundreds of kilometers apart in virtually all directions extending for several hundred kilometers. Since the typical removal distance for SO_2 and its oxidation products is probably of the order of 1000 km or more (15), any site in the region will constantly be under the influence of a large number and variety of SO_2 sources.

Studies of the global sulfur cycle by Friend (16) indicate that in some populated areas of the continents the sulfur containing aerosol may be dominated by human production of SO_2, even though man produces only about a third of the sulfur containing material injected into the air globally. We cannot now state quantitatively how much of the aerosol is natural; however, it is likely that the human sources dominate in this region based on consideration of the global cycle.

f) The light scattering coefficients at Tyson and the two urban sites (when acid sulfate or $(NH_4)_2SO_4$ aerosols were evident from the humidogram) varied over the same relatively narrow range, from approximately 2×10^{-5}m to about $2 \times 10^{-4}m^{-1}$. No large increase could be noted going from the rural area into the city itself.

g) Simultaneous measurements were made of the imaginary part of the particle refractive index (i.e. light absorption property) by the method of Lin et al. (17). No difference could be noted in this quantity from one site to another or with meteorological conditions. The value of the imaginary part of refractive index (0.05 ± 0.03) corresponds to approximately 10 mole % carbon as soot and is somewhat larger than expected (17), but could be due to the same sources as the sulfate aerosol. The lack of spatial or temporal variability in this quantity indicates that it too has a regional and not urban behavior.

h) Altshuller (18) has noted that sulfate aerosol in non-urban sites likely is due to long distance transport of the products of oxidation of SO_2, and that there is an average background level of $SO_4^=$ of ca. 5 $\mu g/m^3$ in cities due to non-urban sulfate. These points agree conceptually and quantitatively with our results.

If this hypothesis is correct, control of SO_2 or particulate emissions in the city of St. Louis (or other comparable cities) will do little to control urban levels of $SO_4^=$. Perhaps more important is the possibility of increasing the level of $SO_4^=$ in cities by increasing SO_2 emissions in rural areas (e.g. due to using fuels with higher sulfur content or due to development of new fossil fuel power plants).

Perhaps the most important result is the simple observation that the inorganic sulfates dominate the submicron, light scattering aerosol on a regional (100-1000km) scale. Since health effects are presumed largely to be due to submicron particles, it may be possible to utilize these results and methods in health related studies. It is intriguing to speculate that the hazes which one views from aircraft over the vast middle and Eastern parts of the United States may be dominated by hydrated H_2SO_4 and its products of neutralization with NH_3. These hazes which reduce visibility and sunshine at the ground and may have climatic effects seem to be practically permanent features of the country except during rapid intrusions of clean air, e.g. in winter from Canada. Such visible aerosol is noted generally from ca. Colorado to the East Coast and from Minneapolis in the North to Jackson or Little Rock in the South (perhaps clear into Florida), particularly in summer (19). Until more studies of these acid aerosols are available, their real and potential effects can only be matters for speculation and the utility of sulfate control strategies, costing perhaps billions of dollars, will be even less certain than the preliminary results in this paper.

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(14) Dzubay and Stevens (13) showed that two hour averages of sulfur (expressed as the element but understood likely to be $SO_4^{=}$) ranged from 2 to 12 $\mu g/m^3$ while Ti ranged from 0.02 to 2 $\mu g/m^3$ and Pb from 0.1 to 2.5 $\mu g/m^3$.

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Table 1. Ambient Air Humidograms (No NH_3)

Location (Dates) Number of Runs / Category	Washington University (22-31 August 1973) 339 runs		Tyson, First Period (3-21 September 1973) 726 runs		Tyson, Second Period (21-27 September 1973) 224 runs		St. Louis University (27 September - 4 October 1973) 288 runs	
	Number	%	Number	%	Number	%	Number	%
Hygroscopic	212	63	383	50	89	40	190	66
Deliquescent at ca. 80% RH	127	37	295	41	121	54	97	34
Suspected Deliquescence at 60-65% RH	0	0	48	6	14	6	1	0

Table 2. Effect of NH_3 Addition on Ambient Air Humidogram

Location (Date) Number of Runs / Category	Tyson Hollow (21-27 September 1973) 88 pairs of runs*		St. Louis University (27 September - 2 October 1973) 258 pairs of runs*	
	Number	%	Number	%
A. Hygroscopic before addition of NH_3 and NH_3 caused deliquescence at ca. 80% RH	46	52	22	8.5
B. Deliquescent at ca. 80% prior to NH_3 addition and NH_3 enhanced the deliquescence	22	25	5	1.9
C. Deliquescent at ca. 80% and No change with NH_3	19	22	64	24.8
D. Hygroscopic (monotonic) curve and no effect with NH_3	1	1	167	64.8

*Note: Not all runs in Table 1 appear in Table 2 due to the fact that an NH_3 addition run was not performed after each ambient run.

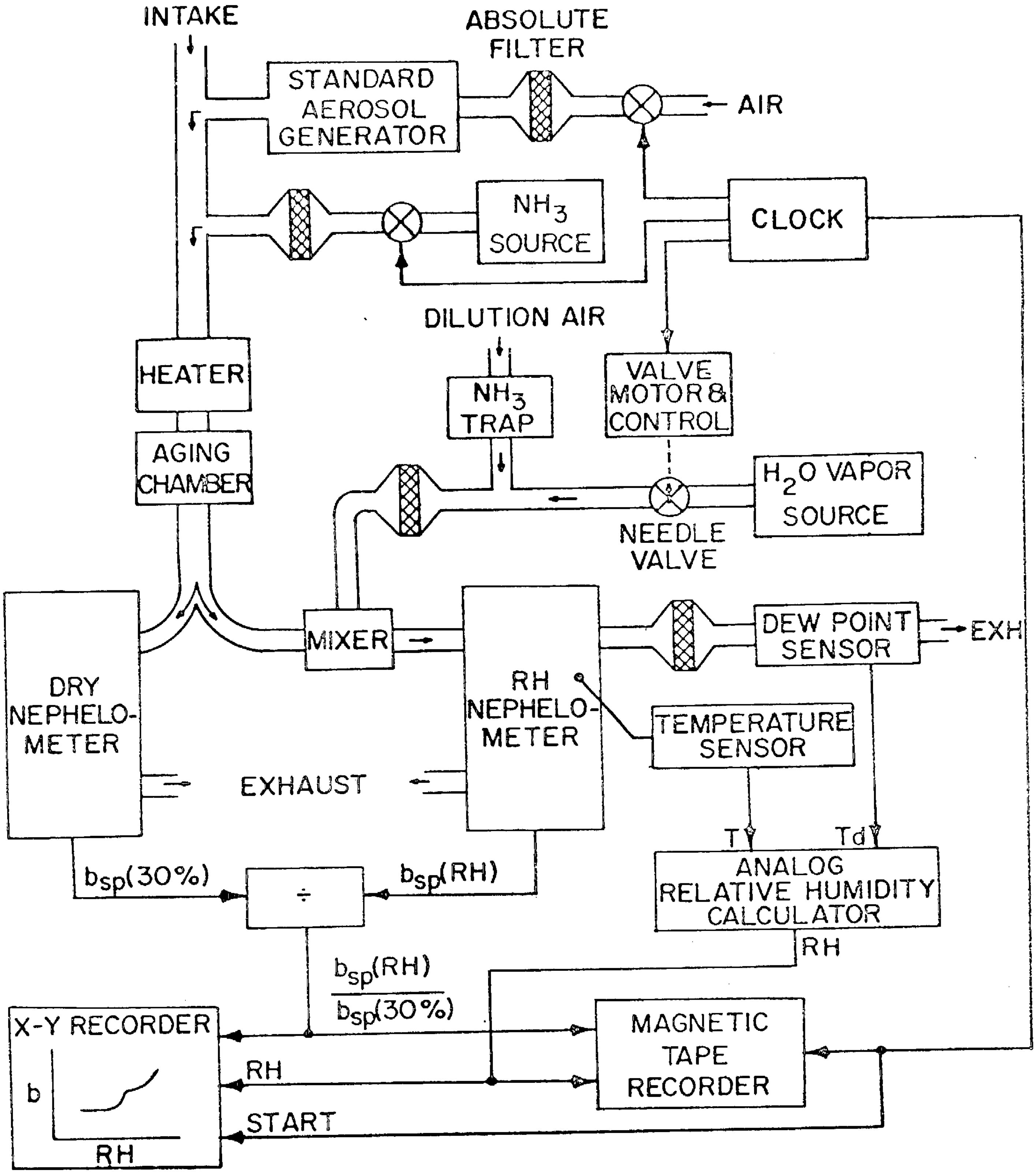


Figure 1. Humidograph with NH_3 pretreatment.

Figure 2. Humidogram for laboratory H_2SO_4 aerosol (dashed) and for the reaction product of this H_2SO_4 and NH_3 (solid). The ordinate is the ratio of light scattering coefficient due to particulate matter at the given relative humidity (b_{sp}(RH)) to the light scattering coefficient at 30%. The abscissa is relative humidity in percent. The inflection point in the $(NH_4)_2SO_4$ curve (arrow) corresponds to the humidity at which all the particles have been converted to droplets. The increase starting at ca. 72% is due to the presence of submicron particles which have a higher than bulk solubility due to curvature or is due to mixing characteristics of the flow system (7).

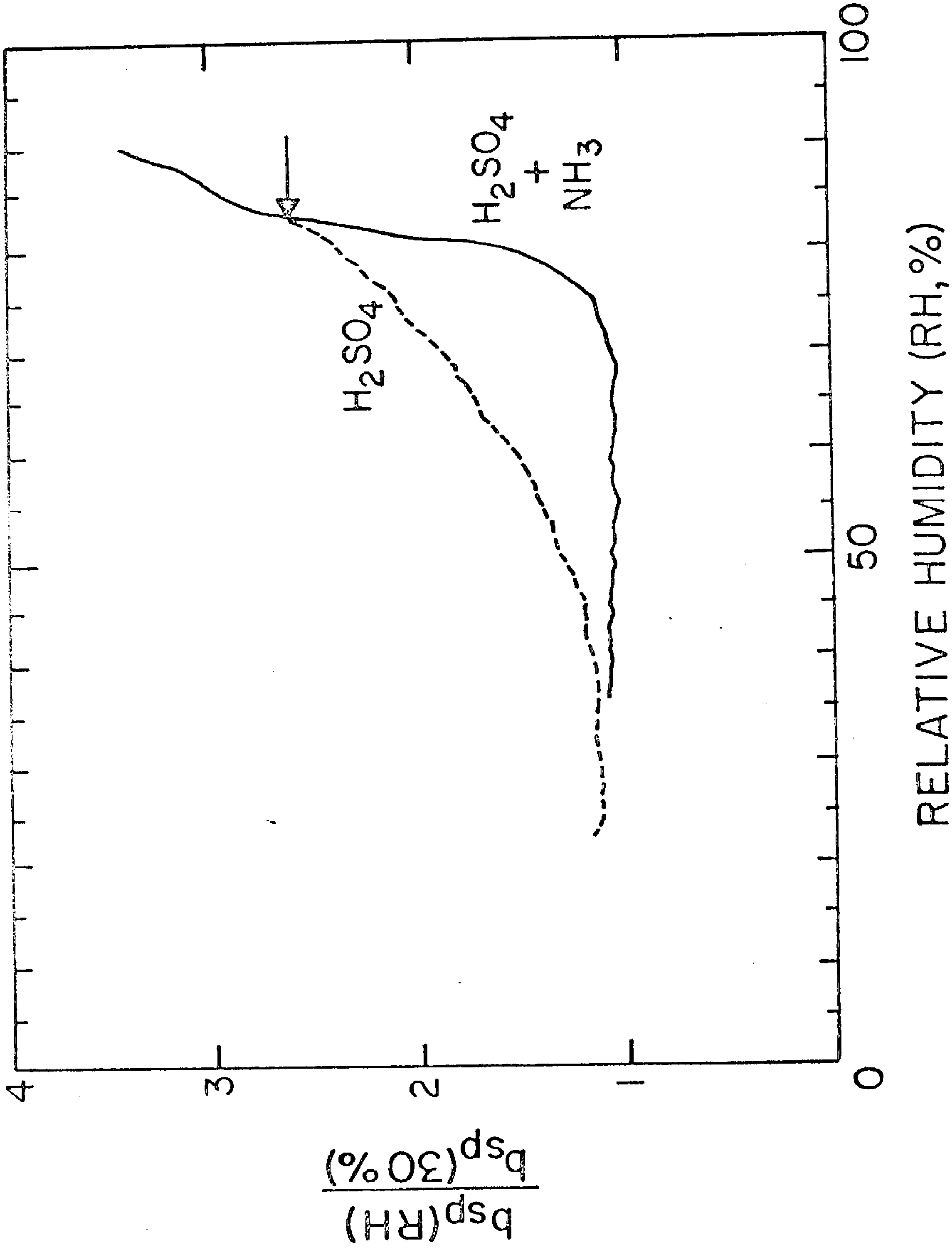

$\frac{b_{sp}(RH)}{b_{sp}(30\%)}$
4
3
2
1
0
50
100
RELATIVE HUMIDITY (RH,%)
H_2SO_4
H_2SO_4 + NH_3

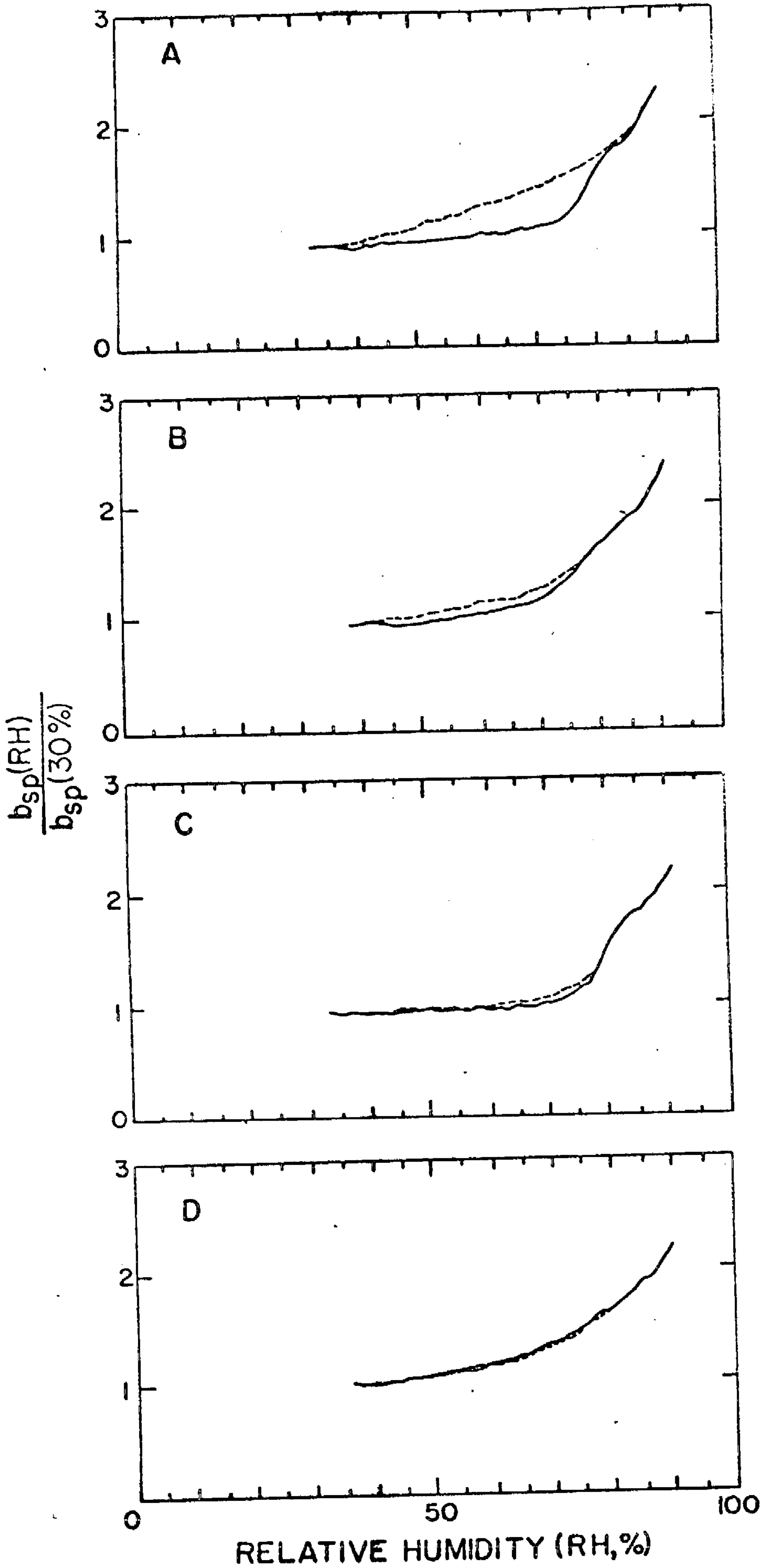
Figure 3. Four classes of humidograms from Table 2.

A. Monotonic (hygroscopic) curve; NH_3 caused inflection point at 80% (deliquescence); 23 September 1973 1208 - 1219 CDT, Tyson.

B. Inflection point at 80% enhanced by NH_3; 21 September, 2030 - 2047, Tyson.

C. Inflection point and no or little enhancement by NH_3; 24 September, 2245 - 2303, Tyson.

D. Monotonic curve unaffected by NH_3; 28 September, 0500 - 0518, St. Louis University.


A
B
C
D
0
1
2
3
$\frac{b_{sp}(RH)}{b_{sp}(30\%)}$
0
50
100
RELATIVE HUMIDITY (RH,%)