DETERMINATION OF SULFUR SPECIATION IN
INDUSTRIAL AEROSOLS IN AN SO₂ RICH ENVIRONMENT

Progress Report

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Abstract

Recent epidemiological and toxicological studies have suggested that sulfur components of aerosols may present a serious health hazard. The chemistry, transformation, and stability of various sulfur oxidation states in aerosols produced by point sources emitting SO_2 and aerosols is presently not well understood. The research being conducted under this contract is designed to identify concentrations of sulfite, sulfate, trace metals, and nitrite species in particulates produced by smelting and fossil fuel industries, establish the conditions (metal content, fuel type, SO_2 levels, temperature, humidity) and mechanism(s) of sulfite formation and study the stability of the various sulfur species in the ambient atmosphere.

Research completed to date has resulted in the development of techniques for the above listed speciation problems. Additional work is presently underway on speciation of acid components of aerosols. Studies are now being conducted to determine the ambient rate of oxidation or formation of metal-sulfite and organic-sulfite complexes in a coal-fired generating station, a copper smelter and a steel mill plume. Experiments are planned in the last phase of the project to determine the effects of aerosol trace element content, fuel type, humidity, temperature, and SO_2 concentration on the formation and stability of S(IV) constituents in aerosols.

I. Scope of Investigations

The observed synergistic effects of SO_2 and aerosols may be in part due to the formation of stable aerosol sulfite complexes which serve to "store" the sulfite reducing agent in aerosols permitting long range transport of these potentially biologically harmful species. Three research tasks which would establish the conditions under which such complexes may be formed and determine the levels and stability of S(IV) produced in particulates formed in an SO_2 , trace metal rich environment were originally proposed, as follows.

1. Development of Analytical Technique.

Objective: Develop and test calorimetric and ESCA techniques for determining the oxidation states of S, Fe, Cu, and N and the trace metal concentrations in ambient particulate samples.

2. Determination of Stability of Aerosol S(IV) Species with Time.

Objective: To determine the ambient rate of oxidation of potential metal-sulfite complexes in industrially produced aerosols.

3. Correlation of Trace Element Content, Humidity, and Temperature with S(IV) Concentration in Aerosols and Determination of the Mechanism of Aerosol Formation.

Objective: To determine the conditions under which SO_3^{2-} may be formed and stabilized in industrially produced aerosols and establish the relative importance of SO_3^{2-} and SO_4^{2-} species in such aerosols.

~~Work completed to date on these objectives is outlined in Section II.~~

II. Results.

A. General

Results which have been obtained to date on projects which are currently in progress are related to 1. analytical developments in calorimetry, PIXE, and ESCA, 2. the evaluation of sampler efficiency and artifact formation, 3. the analysis of selected samples from fossil fuel burning facilities and New York City, and 4. the study of S(IV) chemistry in the plume of a coal fired generating station and a copper smelter. These are briefly summarized in the following sections.

B. Analytical Developments

1. Calorimetry. Titration calorimetry is the principal tool being used for the analysis of sulfur oxidation states (sulfite, sulfate), reduced nitrogen species (nitrite), and acidic species. Our analytical technique for analysis of sulfite and sulfate was described in the literature before the initiation of the contract (Anal. Chem., 48, 634 (1976)) but had been tested only on collected samples associated with a copper smelter. We have now examined samples from several coal fired and oil fired generating stations, from a number of lead and copper smelters, and from New York City and have demonstrated that no interferences exist in any of these samples with the determination of inorganic sulfite or sulfate by the calorimetric procedure. We have identified what appears to be an organic-SO₂ adduct in samples from a coal fired station flue line and plume and in samples from New York City. Confirmation of this species by ESCA, by IR spectroscopy and by GC-mass spectroscopy is presently under investigation. Inorganic and organic sulfite species may be specific tags to plume transport from smelter and fossil fuel sources, respectively.

A calorimetric procedure for the determination of nitrite based on the reaction of sulfamic acid with nitrite in an acid solution to give N₂(g) and sulfate has been developed. The technique has been tested on particulate samples from fossil fuel sources and New York City and appears to be free of interferences. Nitrite levels from 0 - 1400 ppm have been seen in these samples. Nitrite does not appear to correlate with sulfite levels, nor to interfere with the analysis for sulfite. Development of a calorimetric procedure for nitrate is still underway. Confirmation of the calorimetric techniques for nitrite and nitrate by ESCA analysis will be investigated in the near future.

A calorimetric titration instrument incorporating a miniature glass electrode system has been built, tested, and used for the analysis of acid species in several environmental samples. With this instrument both ΔH and pH data can be simultaneously obtained allowing better identification of strong and weak acid species in sample extractions. We have investigated a procedure which uses benzaldehyde as a selective extraction solvent for H₂SO₄, and is followed by counter extraction into water and quantitative

analysis for H_2SO_4 . These studies have shown transition metal bisulfate salts and some sulfite salts (from basic aerosols only) as well as H_2SO_4 are readily extracted by this solvent. If the benzaldehyde contains over 500 ppm of the oxidation impurity, benzoic acid, non-acidic sulfate salts of transition metal ions are also extracted. We are currently investigating the possible direct calorimetric titration of acidic species in propylene glycol solvent.

2. PIXE. Proton Induced X-ray Emission (PIXE) analysis is the principal tool being used for trace element analysis. During the current period we have improved our quality control procedures generally and have developed improved calculation techniques for analysis of sulfur. Analysis of standard samples (SRM bovine liver and orchard leaves) and prepared sulfate standards indicate we can now expect an accuracy of $\pm 10\%$. A program developed at Florida State University which makes possible the improved determination of spectrum background, peak areas, and peak identification is now being incorporated into our data analysis procedures.

3. ESCA. ESCA analysis for the project are being obtained under a subcontract with Lawrence Livermore Laboratory. Robert G. Meisenheimer, LLL, is responsible for this effort. The subcontract was initiated in December, 1976 and work to date has included studies on instrument calibration, argon etching techniques and analysis of flue dust samples from copper and lead smelters.

The chemical shift positions expected for S 2p and 1s electrons have been investigated using several pure compounds with sulfur in the -2, 0, +4, and +6 oxidation state to give a data bank for comparison with spectra obtained with environmental samples. One objective of the ESCA work will be to study sulfur species as a function of depth through the particle. The validity of using argon etch techniques to study sulfur speciation has been investigated using sulfate salts. It was found that etching induced chemical changes in the salt studied. For example, etching of a CaSO_4 sample results in the appearance of peaks in the spectra corresponding to CaSO_3 and CaS . Evidently oxygen is removed faster than sulfur by the etch, resulting in an alteration in the chemical structure of the analyzed sample. Other techniques are now being explored in an effort to develop a reliable scheme for depth analysis of particulates by ESCA.

Intercomparison of the calorimetric and ESCA speciation techniques has been completed for five flue dust samples with qualitative results given in Table 1. As can be seen, no samples have been analyzed where S(IV) species detected by ESCA were not found calorimetrically. The calorimetric analysis has detected S(IV) in two samples where no corresponding peak was present in the ESCA spectra. It is possible all the sulfite in these samples is present as a non-surface component. When a suitable depth analysis technique is available for ESCA this possibility can be studied further.

C. Sampler Studies

The principal sampler to be used in the study is the Sierra Hi Vol cascade impactor. In addition, low volume total suspended particulate samplers and to a limited extent, a virtual impactor will also be used for collection of particulate samples. Separate portions of the cascade impactor stage collection media will be used for various analyses. We have, therefore, extensively characterized the collection consistency across the impactor head. These studies have included specific chemical analysis, total weight determination, and some scanning electron microscope examination on each strip. The results (see Figure 1, for example) indicate the collection will be sufficiently uniform for the requirements of the study. As shown in Figure 1, a consistent end effect is seen which can be explained by the sampler aerodynamics.

Based on the results of recent studies at Battelle Columbus Laboratories and Radian Corporation on artifact sulfite and sulfate formation, we have chosen acid washed quartz fiber filters for the backup filter and stages and also double stick scotch tape for some work on the stages. We have examined possible SO_2 adsorption and/or conversion to sulfate on these filters and found artifact formation to be negligible below 2 ppm SO_2 . Data on collection of aerosols by various filters indicate some adhesives on the mylar tapes may oxidize sulfite. This is presently being further investigated.

D. Sulfur(IV) Chemistry in Selected Samples

The presence and stability of sulfur(IV) compounds in smelter and fossil fuel associated particulate samples have been investigated. An important goal of the project is to examine the apparent kinetics of the following reactions in particulate samples.

Table I. Sulfur Species Identified by Calorimetric and
ESCA Analysis of Smelter Flue Dust Samples

<u>Sample</u>	<u>Calorimetry</u>	<u>ESCA</u>
Copper Smelter-1	S(IV), S(VI)	S(VI)
Copper Smelter-2	S(IV), S(VI)	S(-II), S(IV), S(VI)
Copper Smelter-3	S(IV), S(VI)	S(-II), S(IV), S(VI)
Lead Smelter-1	S(IV), S(VI)	S°, S(VI)
Lead Smelter-2	S(VI)	S(-II), S(VI)
Lead Smelter-3	S(IV), S(VI)	S(-II), S(IV), S(VI)

Figure 1. Analysis for all S(IV) compounds on individual strips of the fine particle stage of a Sierra Hi Vol Cascade impactor.

Extensive studies on stored samples of particulates collected from the flue lines of copper and lead smelters and a coal fired station indicated reactions (1) and (2), are extremely slow. This is well illustrated by the data summarized in Figure 2, giving the change in sulfite in lead and copper smelter flue dust samples over a period of twelve months. Reaction (3) is being investigated in plume studies which are summarized in Section E.

Inorganic sulfite complexes, stabilized as complexes of Fe(III), Cu(II), and Zn(II) have been seen with one exception in all samples associated with smelters. In contrast, no comparable sulfite species have been identified in samples collected from the flue lines of four oil fired generating stations. Nitrite has been seen in these samples. All the samples from oil fired generating stations were several months old before receipt for analysis so it is possible transient sulfite species may be formed by these sources. We have analyzed samples from three different coal fired sources for sulfite species and have noted that the levels of sulfite vary greatly as summarized in Table II. Of greatest interest is the presence of large levels of sulfite species in the heating plant sample compared to the two stacks of a different power station. It is possible that the difference in observed chemical species may be related to fire box conditions such as temperature and water content. Such influences are to be studied in part in Phase III of our proposed program.

Table II. Concentrations of S(IV), and sulfate in particulates from coal-fired stations, given as relative mole basis values.

Sample	Inorganic S(IV), as SO_3^{2-}	Organic S(IV), as SO_3^{2-}	S(VI), as SO_4^{2-}
Heating Plant	0.84	0.28	1.00
Electrostatic Precipitator Stack	0.00	0.00	1.00
Scrubber Stack	0.06	0.00	1.00

Figure 2. Levels of sulfite determined in two copper (○, △), and two lead (◇, □) smelter flue dust samples over an extended time period.

E. Plume Studies

Phase II of our proposed project will be concerned mainly with the study of reaction (3) in plumes from copper smelter and coal fired station plumes. We have some preliminary results in both these areas now.

In February, in cooperation with the research group of Dr. Clyde Hill, University of Utah, we collected total aerosol samples by aircraft in the plume of a coal fired station. The only sulfur(IV) species seen in this source were apparently sluff off products from the wet scrubber which presumably existed as CaSO_3 species. These labile sulfite complexes were oxidized in the plume with $t_{1/2}$ values on the order of minutes. No data are yet available on the transformation of more stable sulfite species which we have shown to exist in the plume of the other coal-fired station studied.

Our most extensive data, from in-plant and in-plume environments of a single copper smelter, allow some conclusions to be made about the chemistry of sulfite species in aerosols. The concentrations of sulfite in the aerosols are significantly ($P < 0.01$) correlated with Fe in the in-plant samples and the sum of Fe and Cu in the in-plume samples. Mossbauer and photoelectron spectra of an in-plant sample are both consistent with the formation of $\text{Fe(III)} - \text{S(IV)}$ bonds. Analysis of samples by photoelectron spectroscopy indicated the level of sulfite increased as the metal sulfide species in the ore were oxidized during storage. These data, together with the observation that Cu(II) and Fe(III) form strong complexes with SO_3^{2-} in solution suggest that the S(IV) observed in aerosols is due to the formation of stable Cu(II) and/or Fe(III) complexes.

Exposure in experimental chambers of fresh CuSO_4 or FeSO_4 aerosols to SO_2 results in the formation of sulfite containing aerosols. The formation in the lab of sulfite containing aerosols suggests similar chemistry may occur in the ambient environment. Our present ambient samples in the vicinity (and presumably representative of the plume) of a copper smelter may give an indication of such chemistry. The present data may be tested for this hypothesis in two ways. If it is assumed that the arsenic content of aerosols produced by the smelter is constant and much higher than background arsenic levels, a comparison of the S(IV):As ratio found in the plume to that found

in the smelter should show if the particulate sulfite concentrations change as aerosols are emitted from the source and age in the plume. This comparison is plotted vs plume residence time (time elapsed between emission from the smelter and collection at some point removed from the smelter) in Figure 3. Since the existence of sulfite species in these samples is dependent on the presence of copper and iron in the aerosols which are capable of stabilizing the S(IV) oxidation state by formation of complexes, we may also compare the in-smelter to in-plume chemistry by comparing the S(IV):(Fe + Cu) ratios for the ambient and smelter aerosols. This comparison is given in Figure 4. In both cases the results indicate increased levels of sulfite in ambient compared to smelter collected samples. Further there may be an indication that the relative concentrations of sulfite are increasing in the $<7\mu$ particle size range as residence time in the plume increases. It should be stressed that these ambient samples were all collected on different days and do not represent monitoring of samples from a single stable. Nonetheless, the results do suggest that increases in aerosol sulfite levels may be occurring with time. We are now conducting more detailed plume transformation studies to determine if this is the case.

We are in the final stages of setting up four stations for the detailed study of S(IV) formation in the copper smelter plume. Each station will monitor particulates by size fraction for chemical study, total particulates for metal and SEM-EDAX analysis, SO_2 , temperature, relative humidity, and wind speed and direction. The stations will allow the simultaneous measurement of plume material at four sites over a distance of fifty miles.

III. Compliance with Contract Requirements

No significant changes in project objectives or scope have been made during the period of this report and we are presently in compliance with all contract requirements.

IV. Time and Effort

<u>Investigator</u>	<u>Man Months Effort. to 1 Mar 77</u>	<u>Projected Man Months Effort. 1 Mar - 15 Jun 77</u>
Delbert J. Eatough	2.0	1.0
Norman L. Eatough	1.5	3.5
Lee D. Hansen	1.5	1.8
Max Hill	0	1.0
Reed M. Izatt	1.5	1.0
Nolan F. Mangelson	0	1.0

Figure 3. Plot of the ratio of SO_3^{2-}/As in plume collected samples to SO_3^{2-}/As in the smelter collected samples as a function of residence time in the plume.

Figure 4. Plot of the ratio of $\text{SO}_3^{2-}/(\text{Fe} + \text{Cu})$ in plume collected samples to $\text{SO}_3^{2-}/(\text{Fe} + \text{Cu})$ in the smelter collected samples as a function of residence time in the plume.

V. Publications

A. The following articles have been published or are being presently prepared for publication in referred journals. A reprint of 1. is appended.

1. T. J. Smith, D. J. Eatough, L. D. Hansen, and N. F. Mangelson, "The Chemistry of Sulfur and Arsenic in Airborne Smelter Particulates," Bull. Environ. Contamination and Tox., 15, 651 (1976).

2. D. J. Eatough, N. L. Eatough, L. D. Hansen, M. W. Hill, N. F. Mangelson, and R. G. Meisenheimer, "The Chemical Composition of Smelter Flue Dust," in preparation.

3. L. D. Hansen, B. R. Richter, and D. J. Eatough, "A Direct Injection Enthalpimetric Method for the Analysis of Nitrite," in preparation.

4. L. D. Hansen, T. E. Jensen, and D. J. Eatough, "A Micro Combined pH-Calorimetric Titration Instrument," in preparation.

5. D. J. Eatough, S. Izatt, and L. D. Hansen, "On the Use of Benzaldehyde as a Selective Extractant for Acid Sulfates," in preparation.

B. The following communications have been or are scheduled for presentation at meetings and will be published in the Proceedings of the meetings. Preprints of 1-3 are appended.

1. D. J. Eatough, L. D. Hansen, R. M. Izatt, and N. F. Mangelson, "Determination of Acidic and Basic Species in Particulates by Thermometric Titration Calorimetry," Proceedings, Methods and Standards for Environmental Measurements, National Bureau of Standards, September, 1976, in press.

2. L. D. Hansen, D. J. Eatough, N. F. Mangelson, and R. M. Izatt, "Determination of Reducing Agents and Sulfate in Airborne Particulates by Thermometric Titration Calorimetry," Proceedings, Methods and Standards for Environmental Measurements, National Bureau of Standards, September 1976 in press.

3. D. J. Eatough, L. D. Hansen, R. M. Izatt, and N. F. Mangelson, "Analysis of Sulfite Species in Aerosols," to be presented at the Division of Environmental Chemistry, American Chemical Society, New Orleans, March, 1977.

4. L. D. Hansen, T. Major, J. Ryder, B. Richter, M. Hill, N. F. Mangelson, and D. J. Eatough, "Reduced Species and Acid-Base Compounds of the New York City Aerosols," to be presented at the American Industrial Hygiene Conference, New Orleans, May, 1977.

C. The following presentations are scheduled.

1. D. J. Eatough, "The study of Aerosol Sulfur Chemistry by PIXE, ESCA, and Thermometric Methods," to be presented at the Nuclear Applications Award Symposium, American Chemical Society, New Orleans, March, 1977.

2. T. Major, D. J. Eatough, L. D. Hansen, and R. M. Izatt, "Sulfur(IV) Chemistry in Smelter and Fossil Fuel Plumes," for presentation in the Symposium "Chemical Reactions in the Atmosphere," 32nd ACS Northwest Regional Meeting, June 1977.

3. B. Richter, D. J. Eatough, and L. D. Hansen, "A Calorimetric Procedure for the Determination of Nitrite in Aerosol Samples," for presentation in the Environmental Division, 32nd ACS Northwest Regional Meeting, June, 1977.