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DETERMINATION OF SULFUR SPECIATION IN INDUSTRIAL AEROSOLS IN AN SO_2 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, acidity, 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 and for the speciation of acid components of aerosols. Studies have been conducted to determine the ambient rate of oxidation or formation of metal-sulfite and organic-sulfite complexes in a copper smelter and a steel mill plume. Similar studies in the plume of a coal-fired generating station were inconclusive due to sampling problems. Experiments are planned in the next phase of the project to determine the effects of aerosol trace element content, fuel type, humidity, temperature, SO_2 concentration, and aerosol acidity 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 aerosols 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 determing 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 formation and/or oxidation of potential metal-sulfite complexes in industrially produced aerosols.

3. Correlation of Trace Element Content, Humidity, Acidity, 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 during the period of this report on these objectives is outlined in Section II.

II. RESULTS

A. General

Results which have been obtained to date or projects which are currently in progress are related to a. analytical developments in analysis for S(IV) and in analysis by x-ray fluorescence and photo electron spectroscopy, b. the evaluation of losses of S(IV) from samples due to aerosol acidity, c. the analysis of selected samples from the MAP3S stations and metropolitan areas, and d. the study of S(IV) chemistry in the plume of a coal fired generating station, a copper smelter, and a steel mill. These are briefly summarized in the following sections.

B. Analytical Developments

1. Analysis for S(IV). Work summarized in our previous progress report (COO-2988-1) indicated the presence of both metal-sulfite and organic - sulfite species in environmental samples, with the organic species predominating in samples from areas impacted by the burning of fossil fuels, whether from power plant electric production or automobiles (see Section II.C.). Depending on the source, aerosol acidity, and age of the sample, it appears this organic - S(IV) species may vary from a negligible fraction of the sulfur component of aerosols to over 50% of the sulfate concentration. This result is in direct contradiction with published results from EPA (R. Stevens, Proceedings of the International Symposium on Sulfur in the Atmosphere). Because of the possible implications of our results on health effects as related to the sulfur component of aerosols we have attempted to develop an independent analytical scheme for identi-

fication of these species. We have shown that due to the stability of the organic - SO_2 adducts and metal - sulfite compounds and the catalytic conversion of SO_3^{2-} to SO_4^{2-} in basic solutions containing Fe(III) or Cu(II) that ion exchange chromatography and conventional West-Gaeke analysis techniques are not suitable for analysis of S(IV) species in environmental samples. Results of comparative analysis for samples where S(IV) is shown to be present by ESCA and by calorimetric titration with dichromate are given in Table 1.

TABLE 1. Comparative Analysis of Samples for S(IV) Species by Wet Chemical Techniques, wt % as SO_3^{2-}.

Sample	Calorimetry	Ion Exchange Chromatography	West-Gaeke	Modified West-Gaeke
Copper Smelter Flue Dust-1	1.10 ± 0.15	0.023 ± 0.002	0.00 ± 0.00	0.17 ± 0.05[a] ~ 0.8[b]
Copper Smelter Flue Dust-2	1.9 ± 0.2	n.a.[c]	0.01 ± 0.01	n.a.[c]
Los Angeles Aerosol	2.9 ± 0.6	0.000 ± 0.000	0.00 ± 0.00	0.78 ± 0.05[a]

[a] Modified by addition of 1M NaF

[b] Modified by replacement of $HgCl_2$ with $Hg_3(PO_4)_2$

[c] n.a. = not analyzed

Work is currently underway to modify the West-Gaeke procedure for analysis of stable sulfite species. The problem is basically that $FeSO_3^+$ and the organic - SO_2 adducts are too stable to be analyzed by the conventional procedure. Addition of ligands specific for Fe^{3+}, e.g. F^-, or replacement of the Cl^- anion with an anion which complexes only weakly with Hg^{2+} (e.g. SO_4^{2-}, PO_4^{3-}, ClO_4^-, etc.) should shift equilibria so that stable sulfite species may be analyzed by this procedure. Early results, Table I, are encouraging and this analytical work is continuing. Even if the modifications are successful, the West-Gaeke procedure will not completely replace the present calorimetric procedure since the calorimetric procedure can distinguish between inorganic and organic S(IV) species while the West-Gaeke procedure cannot.

2. X-Ray Fluorescence Analysis. While it has been shown that x-ray flourescence spectroscopy techniques may be a non-destructive, reliable technique for analysis of simple sulfate salts, the possible loss or chemical conversion of volatile or reactive sulfur containing species and the relative sensitivity of the technique to various sulfur oxidation states has not been addressed. That these effects may be important is suggested by analysis of several environmental samples, examples of which are given in Table II.

TABLE II. Comparison of PIXE Results for Total Sulfur with Wet Chemical Results for Total Sulfate

Sample	Pretreatment for PIXE	PIXE Total S as SO_4^{2-}, wt %	Total SO_4^{2-}, wt % by[a] Calorimetry	Total SO_4^{2-}, wt % by[a] Ion Chrom.
Coal power plant fly ash	H_2O or HCl extracts	0.6	1.3	1.0
Oil power plant fly ash-1	HCl extracts	25.	45.	--
Oil power plant fly ash-2	HCl extracts	7.	13.	--
Smelter plume, highly acidic	None	15.	47.	40.
$HOCH_2SO_3Na$	Various	6-17	24.	24.

[a] Includes S(IV) species.

We have completed a series of experiments on proton and x-ray induced x-ray fluorescence analysis of pure samples and environmental samples. The results of these experiments indicate x-ray fluorescence analysis can give erroneous results of the magnitude indicated in Table II due to sensitivity for various oxidation states and loss of some acidic or S(IV) species during analysis.

3. ESCA. During the past year we have developed techniques for quantifying ESCA data. These developments have been published. This development will allow the quantitative comparison of bulk and surface concentrations as is illustrated in Figure 1 for several copper and lead smelter dust samples.

C. Loss of S(IV) Species from Acidic Samples and Implications for Sampling in the MAP3S Region.

Chamber studies completed during this past year in aerosols produced from solutions of $Fe_2(SO_4)_3$ and Na_2SO_3 or $NaHSO_3$ have shown that two different Fe(III) - S(IV) species can be produced as summarized in Table III.

TABLE III. Fe(III) - S(IV) Species Formed in Chamber Experiments

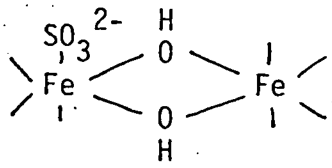
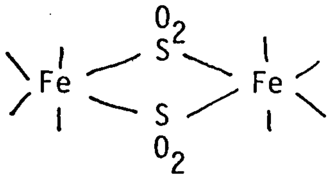
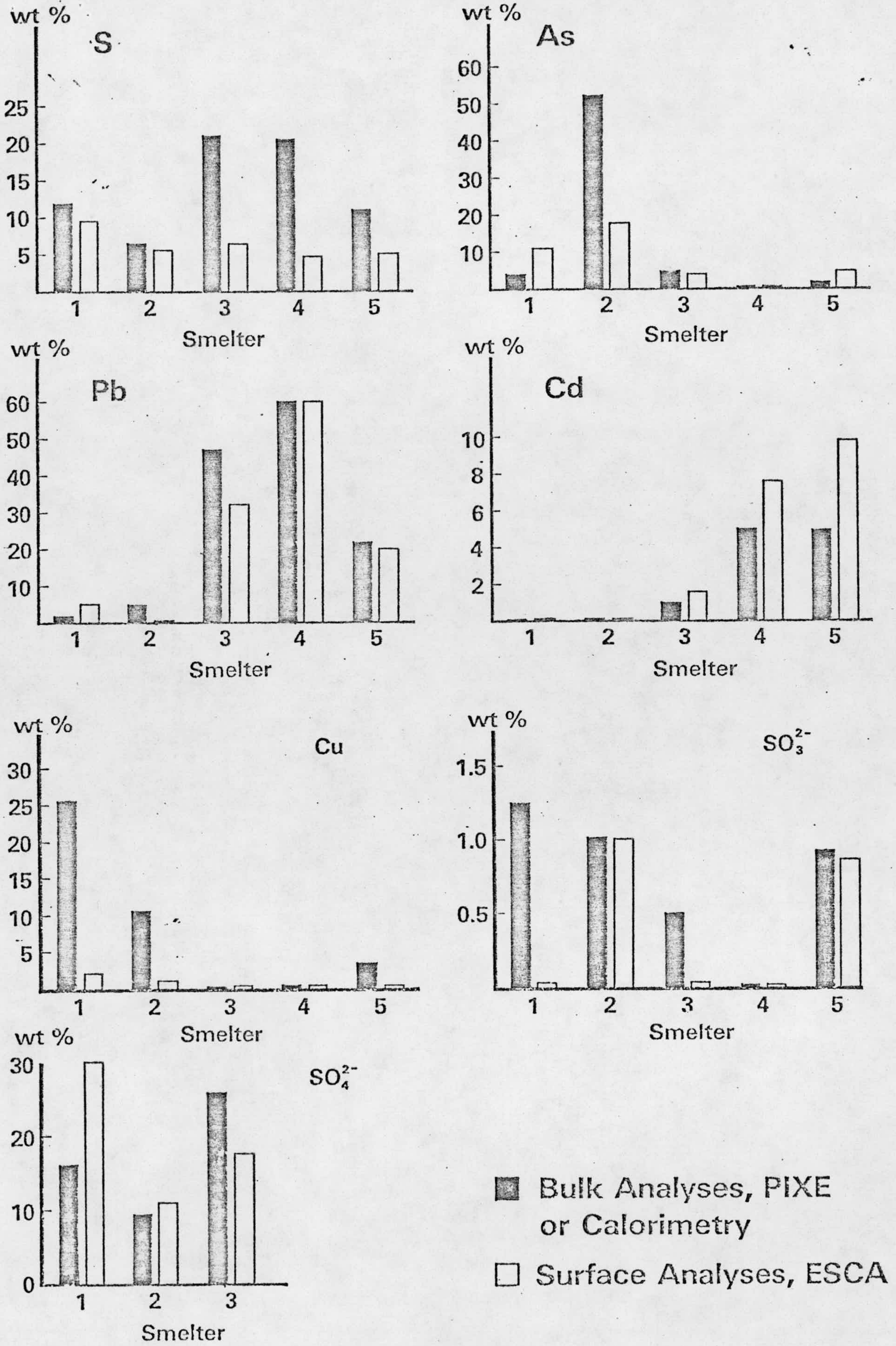
Species	ΔH_{oxid} of S(IV) (kcal/eq)	Fe(III):S(IV) mole ratio	S(IV) bond	Postulated Bonding
1	-24	2:1	labile	
2	-16	1:1	inert	

FIGURE 1. Comparison of bulk and surface analysis for several copper (1 and 2) and lead (3 - 5) smelter flue dusts.



Both species were observed in aerosols from the plume of a copper smelter, with evidence that Species 1 was not stable. To test the postulate that the high acidity in the plume could result in loss of S(IV) as $SO_2(g)$, experiments were performed where the collected sample was chemically "fixed" at the sampling site immediately after collection and where the sample was returned to the lab for normal analysis. Results of these experiments, summarized in Table IV,

TABLE IV. Comparison of On-Site to In-Lab Analysis of Acidic Aerosols from a Copper Smelter Plume.

			μeq of the indicated species/μmole SO_4^{2-}		
Test	SO_2, ppm	Extraction	SO_3^{2-} (ΔH=-23)	SO_3^{2-} (ΔH=-16)	As(III)
1	1.4	On Site	0.31 ± 0.03	0.32 ± 0.02	0.27 ± 0.03
		In Lab	0.00 ± 0.00	0.19 ± 0.01	0.34 ± 0.11
2	0.2	On Site	0.00 ± 0.00	0.21 ± 0.03	---
		In Lab	0.00 ± 0.00	0.28 ± 0.06	---

clearly indicate loss of S(IV) from the acidic samples during storage. It further appears that the S(IV) species which is lost is from the labile $Fe^{3+} - SO_3^{2-}$ bond (ΔH = -23 kcal/eq) and not from the $Fe{\diagup}\overset{O_2}{S}{\diagdown}Fe$ bridge (ΔH = -16 kcal/eq.). From the data obtained in Test 1, and Henry's Law and other literature thermodynamic data the value of log K for the reaction

$$Fe^{3+} + SO_3^{2-} = FeSO_3^{+}$$

is calculated to be 19, in excellent agreement with results from solution thermodynamic data. This would predict SO_2 would be rapidly lost from the aerosol in Test 2 at the observed ambient SO_2 concentration and the high acidity of the aerosol, in agreement with the observation that no labile sulfite was seen in either the on-site or in-lab extraction for Test 2.

Since the equilibrium constant for formation of the $FeSO_3^+$ species is larger than for formation of observed organic adducts, the same losses could occur during storage of aerosols containing the oragnic adduct. That this may be the case is suggested by data obtained to date on aerosols from urban areas and from MAP3S collection sites, summarized in Table V.

TABLE V. Observed Concentrations of Organic - SO_2 Adducts in Collected Samples

Source	Season	Acidity	Organic - SO_2 Adduct, % of SO_4^{2-} Concentration
New York City	Winter	Neutral	17-49
	Summer	Neutral	12-49
Los Angeles	Summer	Neutral	11-45
Charleston	Summer	Neutral	6-23
Argonne	Winter	Neutral	8
Brookhaven	Winter	Acidic - Neutral	5-<2
Penn State	Summer, Winter	Acidic	<2

Samples from the Brookhaven or Penn State sites rarely contain organic - SO_2 adducts. This may reflect absence of these species in aerosols at the site or it may be due solely to loss of SO_2 from the acidic aerosols during storage and transport. On-site chemical analysis needs to be performed to determine which is the case.

D. Plume Studies

Aerosol sulfur chemistry has been studied in the plumes of a coal fired power plant, a copper smelter, and a steel mill. The presence and stability of S(IV) compounds in collected particulate samples have been investigated. An important goal of the project is to examine the apparent kinetics of the following reactions in particulate samples.

$$SO_3^{2-} \xrightarrow{O_2} SO_4^{2-} \tag{1}$$

$$S^{2-} \xrightarrow{O_2} SO_3^{2-} \tag{2}$$

$$SO_2(g) \overset{\text{aerosols}}{\rightleftarrows} SO_3^{2-} \tag{3}$$

Extensive studies on stored samples of particulates collected from the flue lines of copper and lead smelters and the plume of a coal fired station indicated reactions (1) and (2), are extremely slow. Reaction (3) was investigated in the plume studies summarized in this report and is shown to be reversible and rapid.

1. Coal Fired Power Plant. In February 1977, 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 S(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 detected in stack but not in plume samples. Unfortunately the amount of material availalbe for analysis was insufficient to reliably define the plume S(IV) chemistry. Thus, 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.

2. Copper Smelter. Sulfur transformation chemistry was studied in the plume of the Garfield smelter in Utah from April - October, 1977. A series of sampling stations were located on the eastern edge of the Oquirrh

mountains at an elevation about 1700 feet above the smelter such that all stations were in the plume when northerly wind flows off the Salt Lake placed the plume along the mountain. Simultaneous samples were taken at up to four stations to a distance of from 3 km to 50 km from the stacks. Data were collected at each station on SO_2 concentration, lo vol collected total particulates, hi vol collected size fractionated particulates, wind velocity and direction, temperature, and relative humidity. Background data were collected under meteorological conditions where the plume lay to the west of the mountains or north across the lake.

The complete data set is presently being analysed and a detailed report written. However, some preliminary observations may be made about the results.

Collected particulate samples were analyzed for S(IV), sulfate, strong acid, anions, and elemental concentration and also, by ESCA and SEM-EDAX techniques. Concentrations of As and Mo in collected particulates were used as plume tracers. It was found that the ratios Mo/As, Pb/As, and Zn/As were constant in particulates collected at all sampling sites for any particle size and that the $SO_2(g)/As$ ratio was also constant. This is illustrated by data in Figures 2 and 3 for a sampling set where data are now complete. Strong mineral acid was neutralized within 40 km of the smelter, apparently by background metal oxide and/or carbonate particulates. S(IV) species were stable in collected particulates only in the neutralized material, but with proper sampling techniques could be demonstrated to be present even in very acidic particulates at high ambient SO_2 concentrations, see Section C. Two distinct Fe(III) - S(IV) species similar to those observed in laboratory aerosol experiments were found. Conversion of SO_2 tO SO_4^{2-} proceeds at a significant rate only when the plume particulates are

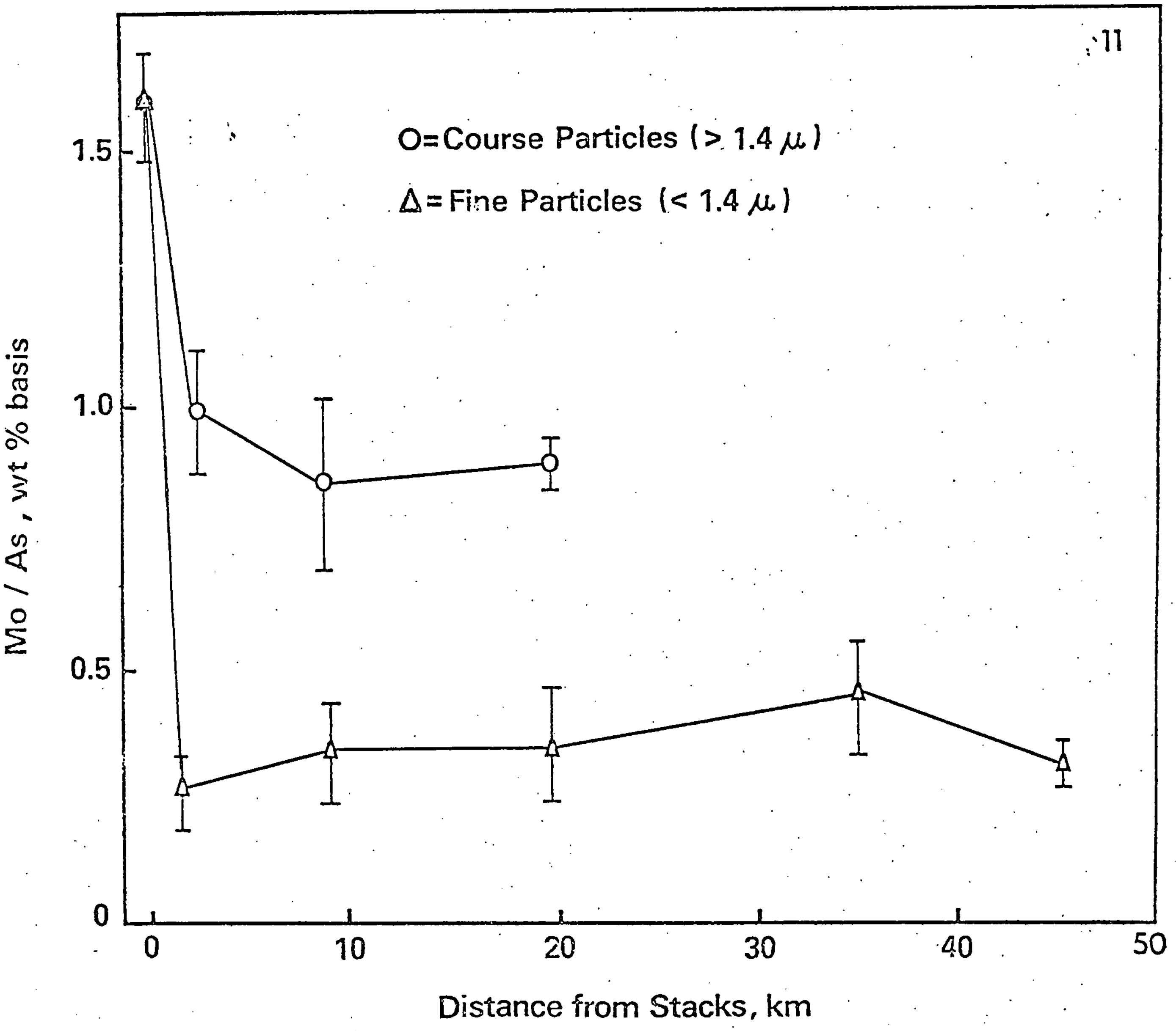


FIGURE 2. Plot of collected particulate of Mo/As ratio vs distance from the stacks.

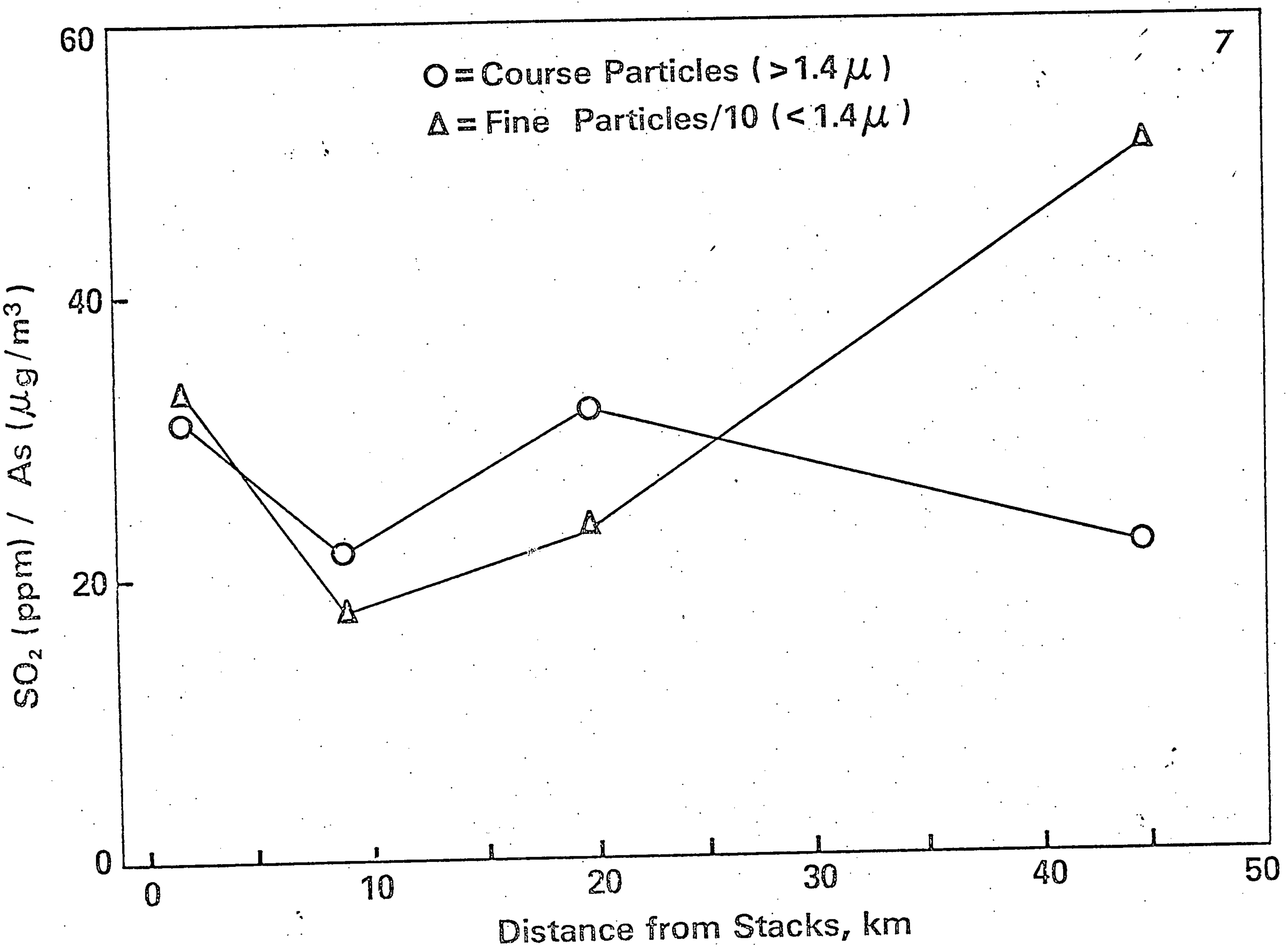


FIGURE 3. Plot of the ratio of $SO_2(g)$:particulate As vs distance from the stacks.

neutralized and labile Fe(III) - S(IV) complexes are present.

The transofrmation of SO_2 to sulfate in a copper smelter plume appears to be characterized by the following sequence of reactions.

a. Production of H_2SO_4 as hot flue gases and particulates are emitted into the atmosphere.

b. Loss of particulate S(IV) species as $SO_2(g)$ in the resulting highly acidic particulate.

c. Neutralization of strong mineral acid content of the particulates during plume transport.

d. Formation of metal - S(IV) complexes in the neutralized particulate.

e. Conversion of SO_2 to SO_4^{2-} via the intermediate metal - S(IV) complexes.

f. Reacidification of the aerosol due to the production of H_2SO_4 in the particulates.

g. Loss of particulate S(IV) species as $SO_2(g)$ in the resulting acidic particulate.

It appears that Fe(III) - S(IV) species control the redox chemistry. Two distinct Fe(III) - S(IV) complexes are formed. One is labile and controls the redox process. One is non-labile and does not lead to the conversion of SO_2 to sulfate.

3. Steel Mill. Sulfur transformation chemistry was studied in the plume of a steel mill from October 1977 - March 1978, using the same equipment and analytical procedures as summarized in 2. Data from that study is still being analyzed. It appears the sulfur chemistry from this source is predominated by the formation of organic - SO_2 adducts. SO_2 concentrations in the plume are extremely low (< 2ppb) and the concentration of organic - SO_2 adducts is frequently higher than the concentration of sulfate. No metal - sulfite complexes appear to form in the dry metal

oxide emitted by the facility.

4. Equipment for Future Studies. It has become apparent from the results obtained this year that rapid changes can occur in collected S(IV) containing acidic aerosols due to the loss of SO_2. It is essential that samples be fixed and analyzed immediately after collection. To accomplish this aim in studies planned for next year we are now assembling a camper - trailer sampling system equipped with a chemical laboratory for on-site analysis.

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

Investigator	Man Months Effort 15 June 1977 - 1 Mar 1978	Projected Man Months Effort. 1 Mar - 15 Jun 78
Delbert J. Eatough	3.0	1.5
Norman L. Eatough	3.0	0
Lee D. Hansen	1.0	1.0
Max Hill	0	0.5
Reed M. Izatt	1.0	0.5
Nolan F. Mangelson	1.0	1.0

V. PUBLICATIONS

A. The following articles have been published or submitted for publication since the last progress report or are presently being prepared for publication. A reprint of 4, is appended.

1. 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," in Methods and Standards for Environmental Measurements, NBS Special Publication 464, November 1977, pp. 637-642.

2. 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," in Methods and Standards for Environmental Measurement, NBS Special Publication 464, November 1977, pp. 643-650.

3. L. D. Hansen, B. E. Richter, and D. J. Eatough, "Determination of Nitrite by Direct Injection Enthalpimetry," Anal. Chem. 49, 1779 (1977).

4. D. J. Eatough, "Recent Progress in Titration Calorimetry," J. Therm. Anal., in press.

5. D. J. Eatough, T. Major, J. Ryder, M. Hill, N. F. Mangelson, N. L. Eatough, and L. D. Hansen, "The Formation and Stability of Sulfite Species in Aerosols," Atmos. Environ., in press.

6. D. J. Eatough, N. L. Eatough, M. W. Hill, N. F. Mangelson, J. Ryder, L. D. Hansen, R. G. Meisenheimer, and J. W. Fischer, "The Chemical Composition of Smelter Flue Dusts," Atmos. Environ., submitted.

7. D. J. Eatough, S. Izatt, J. Ryder, and L. D. Hansen, "The Use of Benzaldehyde as a Selective Solvent for Sulfuric Acid: Interferences by Sulfate and Sulfite Salts," Environ. Sci. Tech., submitted.

8. D. J. Eatough, N. L. Eatough, J. W. Fischer, L. D. Hansen, M. W. Hill, T. D. Major, N. F. Mangelson, R. G. Meisenheimer, M. E. Post, and J. J. Ryder, "Environmental Chemistry in a Copper Smelter Plume," in preparation.

9. L. D. Hansen, N. F. Mangelson, M. L. Lee, J. Ryder, M. Hill, and D. J. Eatough, "Loss of Sulfur Compounds from Samples During Analysis by X-Ray Fluorescence Methods," in preparation.

10. L. D. Hansen, J. Ryder, N. F. Mangelson, M. Hill, B. Richter, and D. J. Eatough, "The Chemical Composition of Fly Ash from a Coal Fired Power Plant," in preparation.

11. L. D. Hansen, J. Ryder, N. F. Mangelson, M. Hill, T. D. Major, and D. J. Eatough, "The Chemical Composition of New York City Airborne Particulates," in preparation.

B. The following communications have been presented at meetings and will be published in the Proceedings of the meetings. Preprints of 2 - 3 are appended.

1. R. M. Izatt, D. J. Eatough, M. L. Lee, T. Major, B. E. Richter, and L. D. Hansen, "The Formation of Inorganic and Organic S(IV) Species in Aerosols," Proceedings, Fourth Joint Conference on Sensing of Environmental Pollutants, New Orleans, November 1977.

2. R. G. Meisenheimer, J. W. Fischer, D. J. Eatough, N. F. Mangelson, and M. Hill, "A Comparison of Bulk and Surface Analysis of Metal Smelter Aerosols," UCRL 79396, Presented to the Federation of Analytical Chemistry and Spectroscopy Societies, Detroit, November 1977.

3. D. J. Eatough, W. P. Green, and L. D. Hansen, "Oxidation of Sulfite by Activated Charcoal," Proceedings, Conference on Carbonaceous Particles in the Atmosphere, Lawrence Berkeley Laboratory, March 1978.