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Calorimetric determination of the interaction of Cu, Fe, and V oxides with SO_2 and measurement of sulfur (IV) and sulfur (VI) in particulate samples from Utah Valley

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CALORIMETRIC DETERMINATION OF THE INTERACTION OF CU, FE, AND V OXIDES WITH SO_2 AND MEASUREMENT OF SULFUR (IV) AND SULFUR(VI) IN PARTICULATE SAMPLES FROM UTAH VALLEY

A Thesis
Presented to the
Department of Chemistry
Brigham Young University

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

by
Douglas F. Cannon
December 1975

This thesis, by Douglas F. Cannon, is accepted in its present form by the Department of Chemistry of Brigham Young University as satisfying the thesis requirement for the degree of Master of Science.

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I. INTRODUCTION AND LITERATURE SURVEY

The purpose of this study is threefold:

1) to determine qualitatively by a calorimetric titration procedure the extent of reaction of SO_2 with metal oxides in decane. The results may have application in understanding the reaction of SO_2 with metal oxide-containing aerosols in the environment. The metal oxides chosen for study (Cu_2O, CuO, Fe_3O_4, $Fe_2O_3 \cdot xH_2O$, V_2O_5) represent the metals commonly found in aerosols in the Utah Valley area.[1]

V_2O_5 was included in the study since vanadium compounds are present in liquid fuels and are released into the atmosphere as V_2O_5. Previous studies show a close correlation between vanadium concentrations from oil combustion products and sulfur dioxide concentrations. The vanadium concentrations show an inverse correlation with temperature in the atmosphere.

2) to obtain samples of Utah Valley aerosols and determine quantitatively the S(IV) and S(VI) concentrations in these particles.

3) to compare the results of purpose 2 with a similar study conducted in the Magna, Utah area for S(IV) and S(VI) concentrations.

There is an apparent synergistic effect between metal containing aerosol and sulfur dioxide so that respiratory impairment is greater than for either sulfur dioxide or particulates alone. Sulfur dioxide alone causes minimal pulmonary damage since the main portion of inhaled sulfur dioxide is absorbed in the upper respiratory tract. But the combination of sulfur dioxide with aerosols results in the development of respiratory problems. The first evidence for toxic synergism between particulate matter and irritant gases in the respiratory system was presented by Dautrebunde in 1939. He suggested that absorption of gas on an inert aerosol particle increased the amount of the gas reaching the lungs.[2] Studies indicate that SO_2 reacts with aerosols and the SO_2 is stabilized in the S(IV) oxidation state. Exposures to combinations of irritant gases and aerosols delays recovery of the irritant response as compared to the recovery from exposures to the gas alone.[3] This stabilization of SO_2 in particulates may occur by formation of transition metal-SO_3^{2-} complexes which could then contact lung membrane tissue during respiration and destroy disulfide and sulphydryl bonds by formation of organothiosulfates resulting in membrane alteration.

Samples were taken by a high-volume air sampler at various places in Utah Valley to determine the extent of metal sulfite and sulfate pollution. Five locations were chosen: (Fig. 1.) 1) in downtown Provo on top of the County Building, 2) in downtown Springville on top of the fire station, 3) at the Lindon Elementary School in Lindon, 4) at the Pleasant Grove High School in Pleasant Grove, and 5) at the Cedar Fort Grocery Store in Cedar Fort. The Department of Health of the State of Utah has anemometers at all locations except Springville and Cedar Fort.

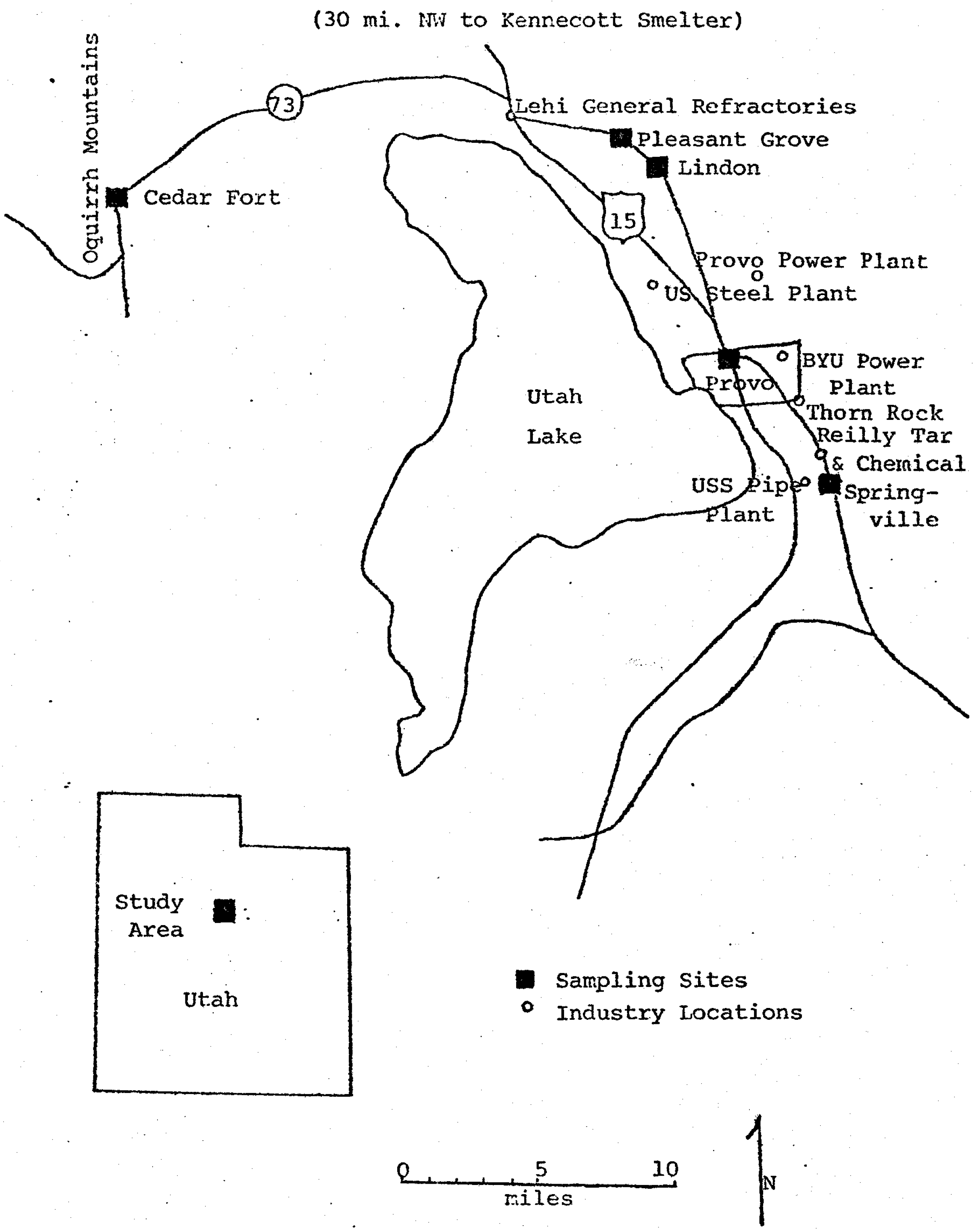

Fig. 1. Location of Sampling Sites.

A. Health Considerations

The basic physiological response to inhalation of pure SO_2 appears to be a mild degree of bronchochonstriction reflected in a measurable increase in flow resistance. The changes produced by pure SO_2 are readily reversible. Although the response is highly vareable, most individuals tested have responded to 5 ppm. and levels of 5 to 10 ppm. have upon occasion produced severe bronchospasm in sensitive individuals. Sulfuric acid and sulfate salts are more potent irritants than sulfur dioxide. The irritant potency of these substances is affected by particle size and by relative humidity. The presence in particulate material of substances capable of oxidiaing sulfur dioxide to sulfuric acid causes a threefold to fourfold potentiation of the irritant response. Among the oxidizing agents which increase the irritant response are those which contain salts of iron (III), manganese (IV) and vanadium (V). Within a range of 0.3 to 2.5μ, the smaller the particle size of sulfuric acid or zinc ammonium sulfate, the greater the irritant potency.[3]

A history of repeated, acute, lower-respiratory illness in childhood may be associated with the development of chronic bronchitis in later life.[4] Studies concucted by investigatorys in Britian and Japan showed an excess number of lower respiratory tract infections in children from the more heavily polluted areas compared to children in a low-exposure area.[4,5,6]

Pollution exposure for three years or longer has been shown to be an important component in increased risk for acute respiratory disease.[7] The Salt Lake Basin area has a single anthropogenic source that produces high sulfur dioxide levels but relatively low levels of total suspended particulates. Laryngotracheobronchitis is the major example of excess, acute, lower-respiratory disease in children in heavily polluted communities in the Salt Lake Basin. This pollution effect is independent of socioecononic status and cigarette smoking.[7]

Studies with radioactively labeled ^{35}S indicate that sulfur is absorbed into the bloodstream from all portions of the respiratory tract and is distributed essentially to all body tissues. S(IV) in mammalian plasma and serum reacts with disulfide bonds present in plasma, largely in the plasma proteins, with the resulting formation of S-sulfonate residues:[8]

$$RSSR + HSO_3^- \longrightarrow RSSO_3^- + RSH$$

This reaction mechansim is used as a gentle method for breaking proteins into fragments (sulfitolysis). Most of the urinary ^{35}S excreted after exposure to high $^{35}SO_2$ levels was in the form of inorganic sulfate.[9] Short term exposure to low concentrations of SO_2 in mice for 135 days caused an unexpected enhancement of antibody production but the activity fades after 192 days.[10]

B. Lung Effects

The human respiratory tract has unique and specific aerodynamic properties which cause patterns of distribution for air-borne particles.[11] See Figure 2. There is a maximum alveolar deposition of particles of 1 μ diameter and a minimum deposition at 0.3 μ. However, particle deposition for the range below 0.1 μ increases again to a posint just slightly lower than values for 1 μ.[3]

Any aerosol sampling device should reproduce to a reasonalbe degree the dust-collectiong characteristics of the human respiratory system so that lung penetration by air-borne particles can be predicted from sampling data. The sampling instrument should classify particles collected according to the aerodynamic dimension which is the true measure of lung penetrability. The fraction of inhaled dust retained in the respiratory system and the site of deposition vary with size, shape, density, and all the physical properties of the particles that constitute the aerodynamic dimension. Methods that employ light scattering or filtration and microscopic sizing of particles do not reckon with density and some other properties that affect the movement of the partilces in air. The combined effect of all the aerodynamic properties of particles determines settling velocities, jet impaction, and lung penetration of airborne particles. The aerodynamic classification of particles can best be done using a series of jets of decreasing size. The smaller the jets (within certain limits), the more efficient and precise they are with respect to impaction and particle size discrimination. In smaller jets the particles flow nearer to the axis of the jets. In the Andersen sampler a cascading series of jets cause a distribution in cutoff with less overlap of particle sizes as the jets get smaller with smaller particles carried further to impact on later stages. Smaller jets are favored but smaller jets cause less volume

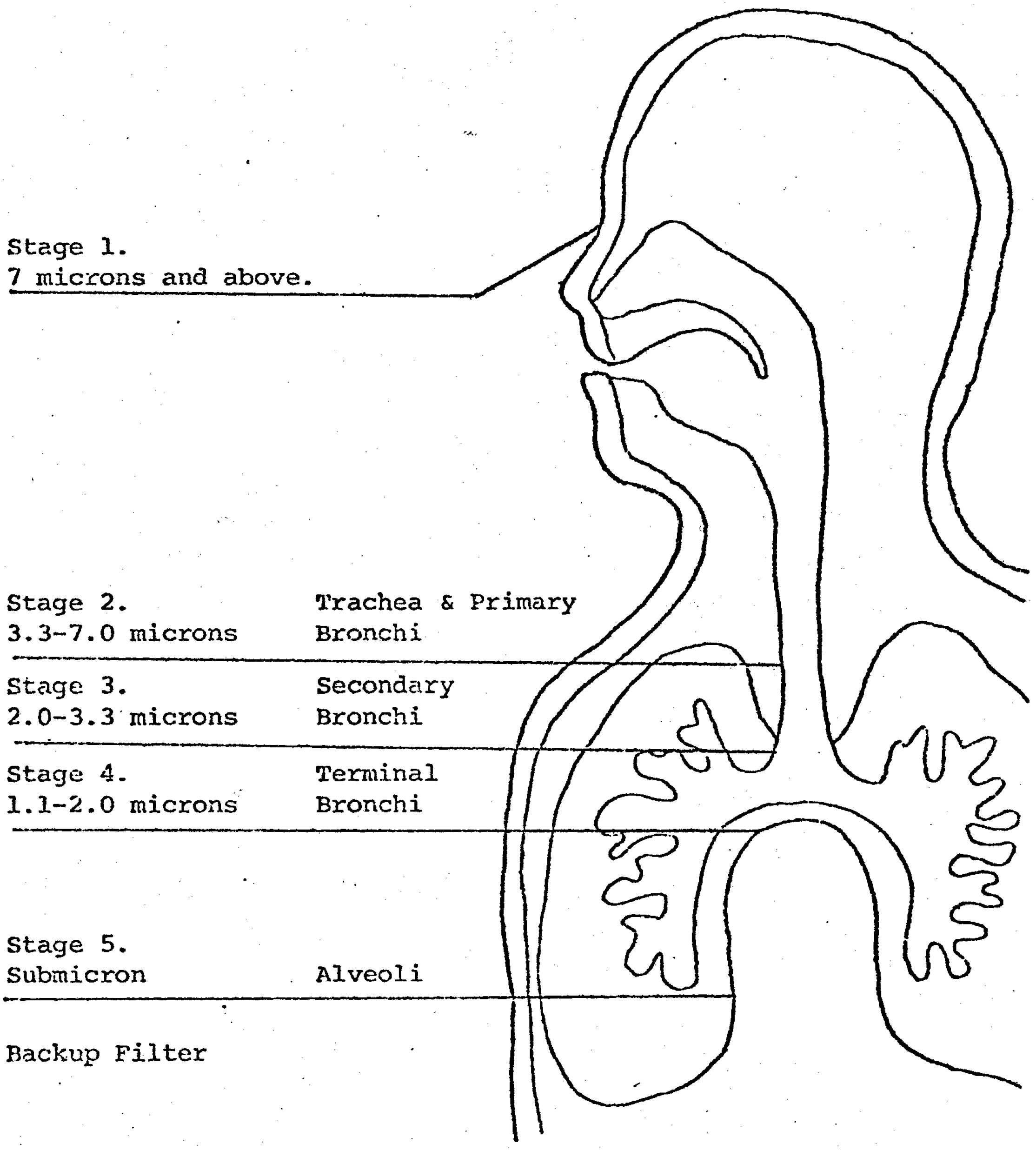

Fig. 2. Andersen Samplers Simulate Human Respiratory System.[11]

for the sample. This disadvantage is overcome by having a multiplicity of jets in each stage. Several stages are necessary for evaluating the sample since penetration of particles into the respiratory tract varies with particle size.[11] For a given volume of air passing through the sampler, its velocity increases as it passes through jets in each succeeding stage.[1]

C. Aerosol Sources

In general the three main classes of airborne particles are wind-erosion products, industrial dusts and combustion products.[12] The most prominent sources of airborne particulates in Utah Valley come from 1) soil and other dusts originating on the farms and roads; 2) fine material (i.e., kish) associated with a) steel processing at the Geneva plant, b) the U.S. Steel pipe plant in Springville, c) the concrete block plant in Lehi, d) Reilly Tar and Chemical Company of Springville, e) Thorn Rock Products Company and f) Kennecott smelter in Salt Lake; and 3) combustion products from automobiles and electrical generating plants at Brigham Young University and Provo Power Company and from the sources listed in number 2, above.

"The highest annual geometric mean particulate concentration in the State of Utah monitored in 1970 was 79 $\mu g/M^3$ at the monitoring station at Provo. The Kennecott smelter in Salt Lake is responsible for 96% of the sulfur oxide emissions in Salt Lake County and 81% of the sulfur oxide emissions in the Wasatch Front. Fuels combustion is the second largest categorical emitter of sulfur oxides. This category accounted for about 9% of the total emissions in the Wasatch

Front. Sulfur oxide emissions from all other point and area sources are less than 1% of total emissions in the Wasatch Front."[13]

Airborne particulate matter ranges in size from less than 0.1 micron to 100 microns.[14] Air particles having a diameter greater than ten microns settle from the atmosphere quickly, and this occurrence is known as dustfall.[15] Of particular interest are the small particles having a diameter less than one micron because they are a health hazard and are not easily removed from industrial emissions by existing control equipment.[16]

Appendix A shows a summary of source emission estimates for Utah for the year 1970.[13] The contribution for each source for both particulates and sulfur oxides is given. The data for Salt Lake County are included for comparison with the data for Utah County.

II. ADSORPTION OF SO_2 ON METAL OXIDES

A. Introduction

There is a marked increase in the irritation produced in human subjects exposed to sulfur dioxide (SO_2) when exposures occur in the presence of various metal oxide aerosols. A special type of synergism may occur as a result of differences in the aerodynamic behavior of gases and particles. A gas such as SO_2 can penetrate more deeply into the lungs when it is adsorbed on particles of respirable size.

Adsorption of Sulfur-35-labelled SO_2 on airborne particles of iron oxide (Fe_3O_4), aluminum oxide (Al_2O_3), lead compounds (PbO, $PbCO_3$ and $PbO{\cdot}H_2O$) and platinum has been studied. At an initial SO_2 concentration of 6.2 ppm., adsorption of SO_2 onto $1.8\mathrm{x}10^5$ Fe_3O_4 particles per $cm.^3$ (initial count) reached about 3%. Adsorption on Al_2O_3 particles was much greater so that adsorption reached 50% with an initial SO_2 concentration of about 1 ppm. The aerosols of lead compounds completely remove SO_2 from the free gaseous state almost immediately (about 5 minutes) after mixing. This is expected because SO_2 reacts readily with lead oxides. An adsorption isotherm for SO_2 on Fe_3O_4 particles shows an increase in specific adsorption with increasing SO_2 concentration over the range from about 1 to 66 ppm. at 24°C. The single monolayer coverage through chemisorption is complete at about 2 ppm. of SO_2; coverage increases to a surprising equivalent of 75 monolayers at 66 ppm. of SO_2 through physical adsorption. The conclusion is that chemisorption on Fe_3O_4 and Al_2O_3 is preferential at low SO_2 concentrations and is followed by multilayered physical adsorption at higher concentrations.[2]

Adsorption of sulfur dioxide with particulates with and without ultraviolet irradiation has been studied by a combination of colorimetric and radio-tracer techniques. Gaseous mixtures of SO_2 kept in the dark for days did not react, whereas sulfur dioxide in the presence of powdered oxides of aluminum, calcium, chromium, iron, lead and vanadium reacted within minutes with or without sunlight or ultraviolet irradiation.[17] The unreacted sulfur dioxide was measured colorimetrically, and a scintillation method was used to account for all of the sulfur dioxide. The values in Table 1 for the amount of loss of sulfur dioxide from the gas phase before rinsings were analyzed are shown in parentheses next to the values for the overall reaction.

Two-liter flasks held the particulate and air mixtures. The results in Table 1 for calcium carbonate, chromium trioxide, and vanadium pentoxide gave reaction rates of approximately 0.2, 0.5, and 0.7% per hour respectively. These rates were surprisingly low, especially for chromium trioxide and vanadium pentoxide, which are known to catalyze the oxidation of sulfur dioxide at higher temperatures. In all reactions a large excess of metal oxide over sulfur dioxide was used. Finely ground powders were placed in a 2-liter flask and SO_2 from a mylar bag was allowed to enter the flask through a stopcock.

Table 1[a]

Summary of SO_2 Reactions in the Presence of Various Particulates

Reactants	Total time in Flasks, Min.	% S^{35} Recovered of total used.	% SO_2 Adsorbed
SO_2 14 ppm. NaCl 21.0 mg.	1000	99	-1.8
SO_2 14 ppm. $CaCO_3$ 30.3 mg.	1100	99	4.2
SO_2 18 ppm. Fe_2O_3 20.0 mg.	22	100	99
SO_2 8 ppm. Fe_3O_4 14.0 mg.	4	102	17
SO_2 14 ppm. Cr_2O_3 11.0 mg.	1030	99	9.0
SO_2 17 ppm. PbO 11.0 mg.	15	101	(26)
SO_2 18 ppm. PbO_2 12 mg.	9	103	(53)
SO_2 8 ppm. V_2O_5 17.2 mg.	800	97	9.3
SO_2 12 ppm. CaO 19.7 mg.	30	92	53
SO_2 14 ppm. Al_2O_3 33.1 mg.	1145	93	46

( ) % SO_2 removed from gas phase before flasks were rinsed.

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[a] See Reference 16.

The surface area of the metal oxide exposed to the sulfur dioxide gas was not determined. The weights of particulates used in the heterogeneous experiments (SO_2 gas with particulates) were from 100 to 200 times the weight of the sulfur dioxide taken. In a polluted atmosphere the total weight of particulates suspended in air is much smaller relative to sulfur dioxide and other gaseous pollutants.[17]

B. Experimental Design for Studying SO_2-Metal Oxide Interaction

When metal oxides are exposed to SO_2 in a container, there is usually no visible reaction. However, any reaction can be determined by calorimetric titration using decane to suspend both the metal oxides and the SO_2.

Two 500 g. bottles of decane (Pract. Grade, J. T. Baker) from the same lot were used. Decane has a boiling point of 172-174°C. Sulfur dioxide was bubbled slowly through one bottle for 15-30 minutes. To determine the SO_2 concentration in the decane, a titration scheme using potassium dichromate was used. The titrant was the decane-SO_2 solution and the titrate was 20 ml. of 0.00300 $\underline{M}$ $K_2Cr_2O_7$ in 0.1 $\underline{M}$ HCl. The reaction was followed on the recorder with the Tronac Model 450 Calorimeter. The following reaction was monitored:

$$11H^+ + 3HSO_3^- + K_2Cr_2O_7 = 3H_2SO_4 + 2Cr(III) + 2K^+ + 4H_2O$$

For each mole of $K_2Cr_2O_7$ three moles of SO_2 were titrated in the decane solution. The concentration of the SO_2 in the decane was 0.102 $\underline{M}$ ±0.006. The metal oxides were all reagent grade chemicals and were prepared by screening so that all passed through a 150 mesh screen. The metal oxide surface areas were determined by BET analysis. BET is an abbreviation for the Brunauer-Emmett-Teller multilayer theory. The surface area determinations are accurate to within 5%. In this case nitrogen gas a liquid-nitrogen temperatures (-195.8°C at 760 torr) was used.[18]

The Tronac thermometric titrator model 450 isoperibol calorimeter was equipped with a 25 ml. Dewar. The termistor bridge on this calorimeter has a sensitivity of 25 mv/°C. The Tronac Model 450 makes possible the collection of calorimetric data having a precision of 0.3% or better.[19] The water bath temperature in all cases was 25°C. A Gilmont 2 ml. capacity buret constructed of glass and teflon was used. The buret delivery rate was 0.00662 ml/min. Delivery from the buret was within ±0.5% accuracy.[20.21]

The number of millimoles of metal oxide was determined by dividing the weight of titrant (grams) in the Dewar by the molecular weight (g./mole). The total milliliters of SO_2 in decane solution delivered can be calculated by multiplying the buret delivery rate by the number of seconds the reaction proceeded until the endpoint. The concentration of SO_2 in decane was 0.102 M. The milliliters of titrate added to the Dewar multiplied by the molarity of the titrate gives the millimole of SO_2 reacted. If there is one adsorption site per metal oxide molecule, the millimole of metal oxide equals the millimole of SO_2. This value, divided by the total millimoles of metal oxide in the Dewar multiplied by 100 yields the percent of the metal oxide that reacted. In the case where there are two "endpoints" in the titration (dashed line in Figure 3), the

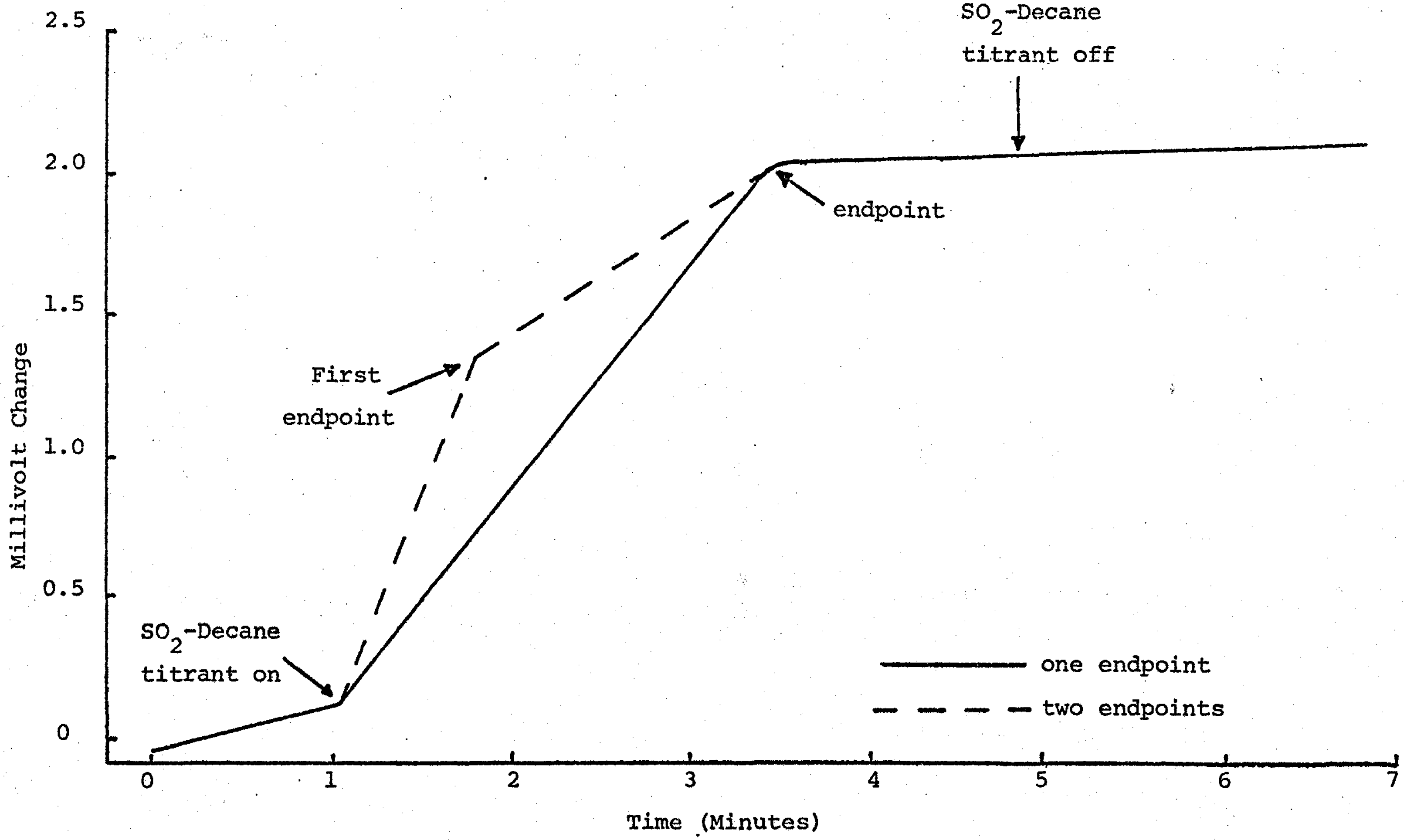


Fig. 3. Idealized Recorder Output of Metal Oxide in Decane Titrant with SO_2 in Decane Titrate.

percentage of metal oxide reacted is the total amount reacted to the respective endpoints. For example, the second percentage given includes the percentage of metal oxide reacted since the reaction started and therefore includes the percentage to the first endpoint.

C. Results

Table 2 summarizes the BET theory determined metal oxide surface areas.

Table 2

BET Determined Metal Oxide Surface Areas

Metal Oxide Sample	BET Surface Areas ($M^2/g.$)
Cu_2O	0.704
CuO	0.526
Fe_3O_4	6.49
Fe_2O_3	11.0

The results showed reaction for every metal oxide tested under these conditions except V_2O_5. A typical output curve is shown in Figure 3. No BET surface areas were determined for $Fe_2O_3 \cdot xH_2O$ so that the results for the reaction of SO_2 with metal oxides which are given in Table 3 in terms of millimoles SO_2 per M^2 surface do not include $Fe_2O_3 \cdot xH_2O$. The slope of the line changed on the strip chart recorder output as the reaction proceeded in the case of cuprous oxide and ferric hydroxide. The results are therefore given for these two metal oxides in terms of "first and second endpoints." The test results are given in Table 3.

Table 3

Metal Oxide in Decane Titrant with SO_2 in Decane Titrate Results

Compound Tested	% of the Compound That Reacted	Millimoles of SO_2 per M^2 of Surface Area
CuO	4	1
Cu_2O	3	0.3
	7	0.8
Fe_2O_3	2	0.01
Fe_3O_4	1.5	0.01
$Fe_2O_3 \cdot xH_2O$	3	----
	10	----
V_2O_5	0	0

In every case the percentage of metal oxide that reacted increased as the weight suspended in decane decreased. This indicates that more surface area was exposed to SO_2 because the amount of clumping of metal oxide particles decreases as the amount in solution decreases. The metal oxide weight used was from 0.1 to 0.3 g. in 20 ml. of decane. Two other compounds were also tried: $Fe_2O_3 \cdot xH_2O$ and V_2O_5. The ferric hydroxide had two endpoints. Two endpoints indicate two different loci of reaction. See Table 3. The reaction of SO_2 with the metal oxide in millimoles of SO_2 per M^2 surface decreases in order $CuO > Cu_2O > Fe_2O_3 > Fe_3O_4 > V_2O_5$. V_2O_5 should oxidize SO_2 to SO_4^{2-} but the results indicate very little reaction.

A second series of experiments was made using decane dehydrated by adding Fisher Scientific Company Type 5A molecular sieves to a bottle of 500 g. M.C.B. decane. SO_2 was next bubbled through a portion of the dehydrated decane. The concentration of SO_2 in the dehydrated decane was determined by titrating the SO_2-decane solution into $K_2Cr_2O_7$ in a dewar.

In every case the metal oxide reacted only slightly or not at all with the SO_2. Moisture, U. V. light and oxygen are factors which enter into the reaction. Therefore, the simple reaction $MO + SO_2 = MSO_3$ is probably not the reaction that ultimately occurs in aerosols in the environment. Kirshman[22] found that when alkalized alumina reacted with SO_2 ". . . as time passed the retardation of the reaction rate became severe unless a trace of water was present." Cheng[23] found that the extent of reaction between SO_2 and particules depended on the % relative humidity. "In the completely dry state the reaction $SO_2 + 1/2\ O_2 \xrightarrow{\text{catalyst}} SO_3$ simply cannot proceed."

A third series of experiments was conducted using decane saturated with distilled water. The results were the same as those obtained using decane from the bottle to prepare the titrate and titrant. Apparently there is sufficient water dissolved in the decane to complete the reaction and the difference is shown only when the decane is dehydrated with molecular sieves.

III. DETERMINATIONS OF S(IV) AND S(VI) IN AIRBORNE PARTICULATES IN UTAH VALLEY

A study of Pasadena aerosols showed that sulfur content was highest at night and consisted of S(IV) and S(VI). The S(IV) predominated at night on the smaller particles and was presumed to be adsorbed SO_2 which was later oxidized to S(VI), (SO_4^{2-}), and predominated in the larger particles during the day. Previously, the chemical states of sulfur had been determined using specific colorimetric reactions in solution for the SO_4^{2-} anion. However, the sample size on a cascade impactor stage approached the lower quantitative limit of the colorimetric method. X-ray photoelectron spectroscopy, ESCA, was used to determine the relative elemental composition and oxidation states in the Pasadena study. The sample took a scanning time of two hours for sulfur. Accretion of SO_3^{2-} proceeded rapidly during the day followed by slower oxidation to SO_4^{2-} at night.[24]

There are several questions about the Pasadena study. Before the sulfur oxidation states were determined, the samples were apparently allowed to stand exposed to air which could cause oxidative processes on sulfur compounds. Also, care must be taken in interpreting the relative concentrations determined by ESCA because of the semisurface nature of the method. The photoelectrons detected by ESCA have an escape depth of only several tens of Ångstroms for solid samples.[25]

Sulfur dioxide is oxidized by oxygen to form sulfur trioxide: $SO_2 + 1/2O_2 = SO_3$.[26] The reaction sequence of SO_2 on the surfaces of metal oxides is 1) chemisorption of oxygen onto the surface sites, 2) diffusion of SO_2 to the surface, 3) reaction between SO_2 and chemisorbed oxygen to form SO_3. The oxidation reaction of sulfur dioxide to form sulfur trioxide does not occur in the dark but an external radiation in the 3000-4000 Å range makes the reaction kinetically possible.[27]

Basset[28] proposed that in the oxidation of sulfurous acid in catalyst solutions, the active catalyst is a transitional metal-sulfite complex. The complex form picks up a molecule of oxygen and rearranges to form either a sulfite or dithionate group.

Spectroscopic evidence indicates that CU^{2+} and SO_3^{2-} form a stable complex in solution. Below pH 6 the complex with a $Cu^{2+}:SO_3^{2-}$ ratio of 1:2 is in equilibrium with a yellow solid whereas the yellow precipitate formed at high total $Cu^{2+} + SO_3^{2-}$ concentrations has a $Cu^{2+}:SO_3^{2-}$ ratio of 1:1. Above pH 7 a completely soluble green complex is formed with a $Cu^{2+}:SO_3^{2-}$ ratio of 2:1. The complex is stable but oxidizes slowly in air over a twelve-hour period.[29]

In solution the reaction $2Fe^{3+} + H_2SO_3 + H_2O = 2Fe^{2+} + SO_4^{2-} + 4H^+$ has a log K value of 20 based on half cell potentials. Results of thermometric titrations with 0.002 M SO_3^{2-} solution in 0.1 M $HClO_4$ and 0.002 M SO_4^{2-} with $FeCl_3$ in 0.1 M $HClO_4$ show that Fe^{3+} does not oxidize SO_3^{2-} to SO_4^{2-} in solution but forms stable $Fe^{3+} - SO_3^{2-}$ complexes.[28] See Figure 4. In 0.1 M acid solution containing some sulfate the reaction:

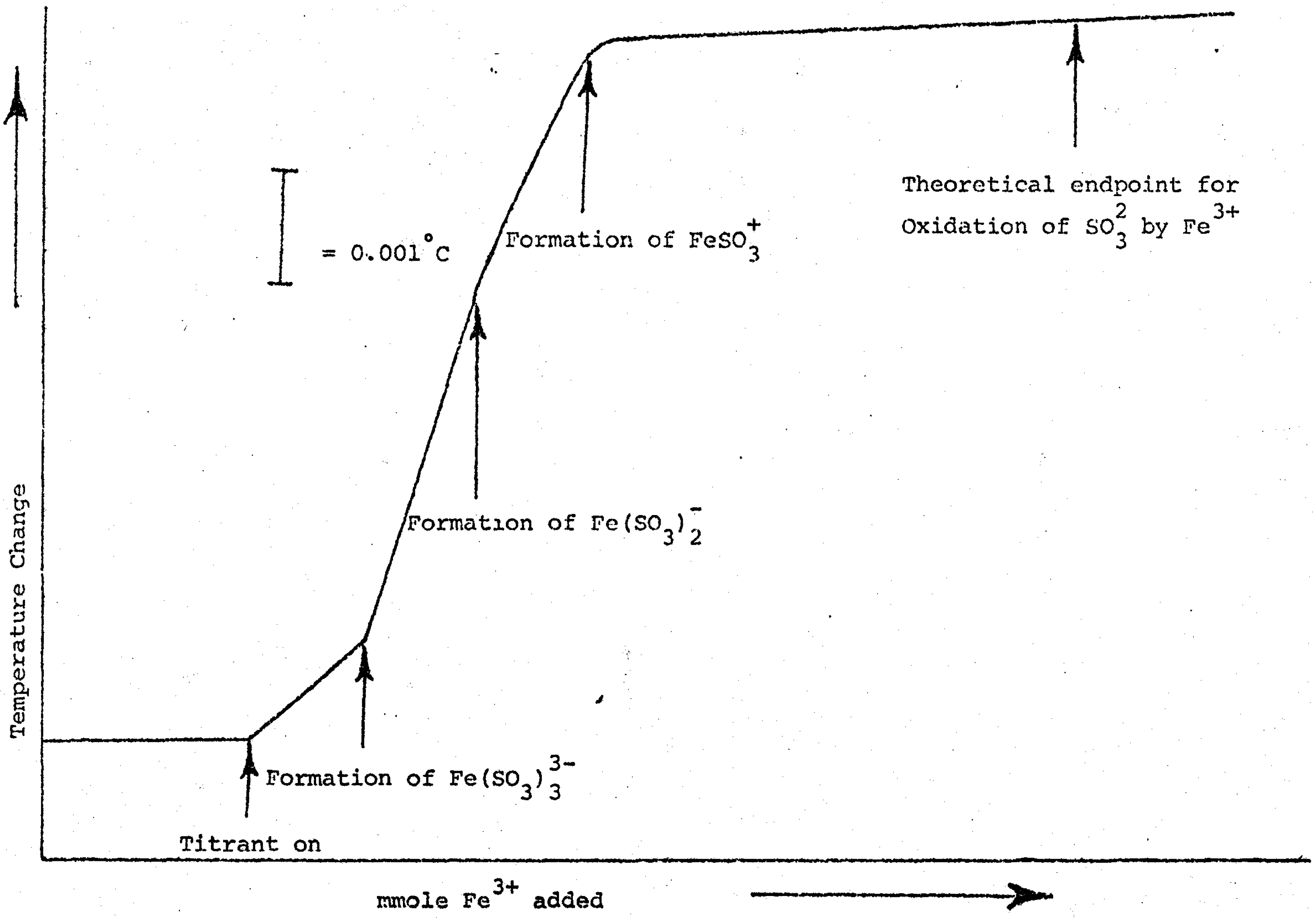


Fig. 4. Thermometric Titration of Fe^{3+} by SO_3^{2-} from Hansen, L., et.al.[29]

$$Fe(SO_3)_{n-1}^{5-2n} + HSO_3^- = Fe(SO_3)_n^{3-2n} + H^+ \quad (n=1,2,3) \ \log K=17 \quad (1)$$

occurs in preference to:

$$2Fe^{3+} + HSO_3^- + H_2O = 2Fe^{2+} + SO_4^{2-} + 3H^+ \quad \log K = 22.1 \quad (2)$$

If the reaction is carried out at higher pH or with solutions containing no initial SO_4^{2-}, then the two reactions, (1) and (2) occur in the same solution. Thermometric titration data indicate that various complexes are stoichiometrically formed, i.e. the $Fe(SO_3)_3^{3-}$ species has been reported but thermometric titration data for the first time show stepwise formation of $Fe(SO_3)_n^{3-2n}$ (n=1,2,3) complexes and show their high stability.[29]

To quantitatively determine the S(IV) and S(VI) concentrations in particulate samples, a relatively simple and inexpensive method was used, based on a thermometric titration of sulfur (IV) with $K_2Cr_2O_7$ solution followed by a direct injection enthalpimetric determination of total sulfate using $BaCl_2$.

The thermometric method for measuring S(IV) has a sensitivity range of 10^{-5} to 10^{-6} M corresponding to approximately 1 to 0.1 ppm. of the unknown present in the analyzed solution with a precision of 1%. The reaction occurring is

$$3FeSO_3^+ + Cr_2O_7^{2-} + 8H^+ = 3SO_4^{2-} + 4H_2O + 2Cr^{3+} + 3Fe^{3+}$$

The sensitivity of the instrument used is 2×10^{-5} °C. The level of SO_3^{2-} expected from solution of 0.1 gram of total particulate containing 0.5% SO_2 dissolved in 100 ml. of solution is a concentration of about 10^{-5} M.[29]

Using this thermometric method Eatough, et.al.[30] determined that the ratio of S(IV) to S(VI) in particulates collected from the Kennecott smelter in Salt Lake is greater than 4. Hansen, et.al.[29] postulated that stabilization of SO_2 in particulates occurs by formation of transition metal-SO_3^{2-} complexes in which the SO_3^{2-} is resistant to oxidation. ESCA Spectra were run on two of the aerosol samples. The spectra verified the presence of S(IV) and S(VI) in the samples. The ESCA Spectra show that the S(IV) was present either as a sulfite compound or as adsorbed SO_2.[30]

A. Sample Collection

The Sampler head is used to support the filters and funnel the air through jets onto the filters. It consists of the Interface Plate and gaskets and plates 1-5. See Figure 5. The Sampler head used was manufactured by Andersen Air Samplers, Inc. The Sampler head is a high-volume sampler (Model 65-000). It is designed to operate with various Hi-volume Air Samplers but the High Volume Sampler made by General Metal Works, Inc., Model GMWL2000H was used in this study. The suspended particulate matter is sized aerodynamically into four fractionations in the head: 1.1, 2.0, 3.3, and 7.0 microns, with submicron material being trapped on the backup filter (stage 5) located below the filter holder on the interface plate. There are aluminum plates located one above the other ranging in thickness from 0.25 to 0.05 inches. The plates have holes through them (air jets)

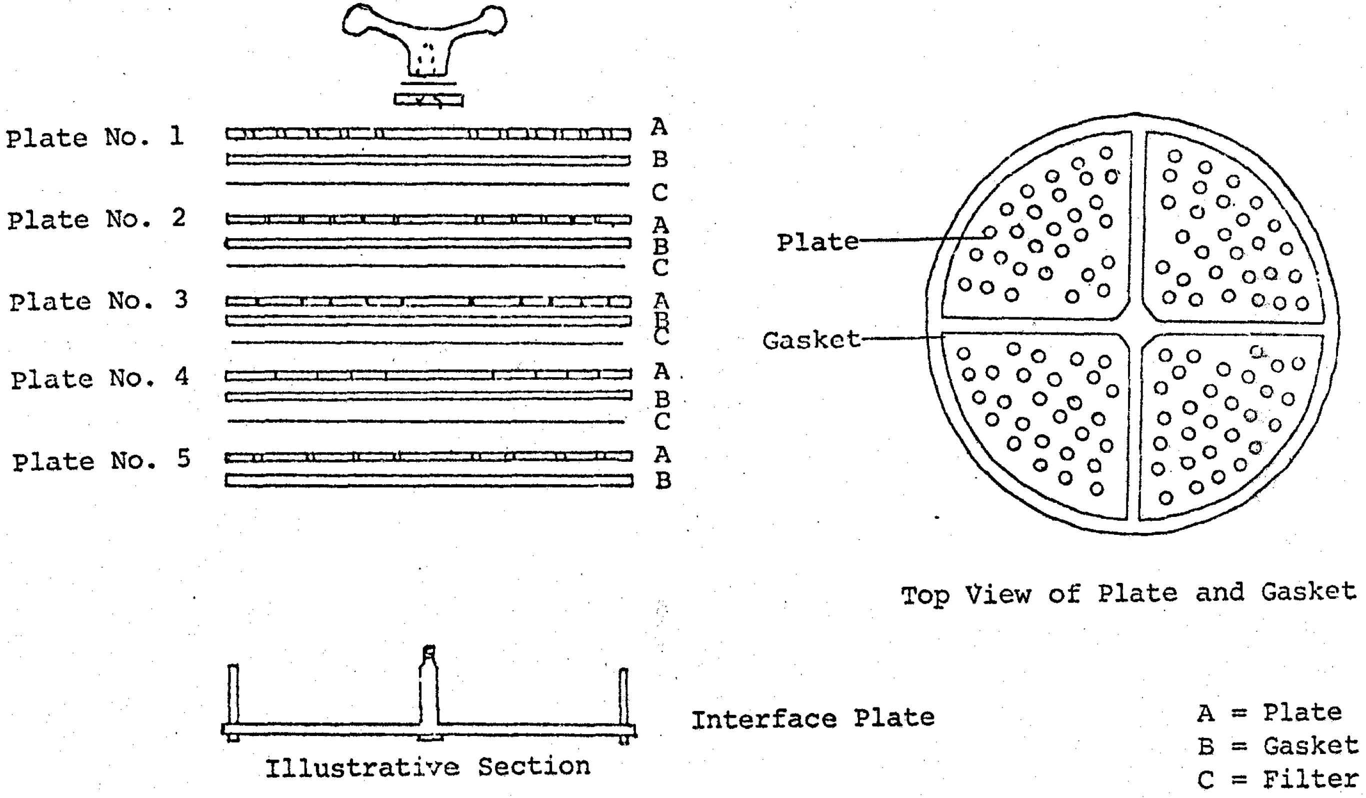


Fig. 5. Schematic of the Andersen Head Sampler.[31]

through which the air passes and impacts on the filter below. An interface adapter plate hooks the Sampler head onto the Sampler. There are five 0.25 inch thick neoprene gasket/spacers to separate the plates. A speedball handle is used to tighten down the head by hand and also to carry the head from the field to the laboratory. There are two configurations of specially designed and cut perforated collection paper. The holes in the paper line up with the holes cut in the collection plates and allow the air to pass through. Each collection plate is offset from the one above or below so that the air won't pass straight through but impacts on each plate. Paper configuration I. (Collection paper #1 and #3) holes correspond to the jets of plates #2 and #4; configuration II. (Collection paper #2 and #4) holes correspond to the jets of plates #3 and #5. The paper used is Type "A" non-hygroscopic fiber glass and is placed on the plates with rough side up. See Figure 5. Below the round plates is an interface gasket which acts as a seal between the interface plate as well as to hold down the 8x10 backup filter paper. This 8x10 backup filter is located below the interface plate on the filter holder and provides the fifth and final stage to collect particles in the submicron range. The 8x10 inch fiberglass filter is placed on the stainless steel wire screen mesh support with the rough side up. A manometer is used to accurately set the unit for a pressure drop which corresponds to 20 cfm. flowing air. The scale is calibrated with red gage oil to correspond with inches of water. The unit was calibrated at the University of Utah Mecical School by Dr. Tom Smith so that a separation of 5.2 inches on the manometer corresponds to

20 cfm. The flow rate was adjusted by a variable voltage transformer.[31]

General Metal Works Sampler Housing

The sampler housing consists of a motor-driven blower and a supporting screen for the filter ahead of the blower unit. The sampler is supported in a protective housing so that the sampler head surface of the filter is in a horizontal position. Flow rate readings are adjusted before each sampling period. The shelter is fabricated from 0.08 inch aluminum sheet metal with 0.125 inch aluminum angle braces and lips. When assembled for field use the shelter is 15x15x52 inches and weighs apporximately 70 pounds. At an average mass concentration of 128 $\mu g/M^3$ (corresponding to a relative standard deviation of 4%).[32]

Calorimeter

A Tronac Model 450 calorimeter was used to determine air particulate sulfite and sulfate levels. The calorimeter was equipped with a 3 ml. Dewar and two extra 0.015 inch teflon tubes in the insert, and a 1 ml. Gilmont precision buret. Three teflon tubes inserted into the Dewar delivered respectively 1) $BaCl_2$, 2) $K_2Cr_2O_7$ and 3) the sample and argon. The bridge output was amplified by a Kiethley Model 150B amplifier. The output was recorded on a HP 1700B recorder with a 17505A plug-in module.[32]

B. Sulfur (IV) and Sulfur(VI) Analyses

The filters were weighed on a Mettler Balance Model H20T and placed in the sampler prior to field use. In all cases the sampler was run for about 48 hours at 20 cfm. Days with clear weather and little or no wind were chosen on which to sample. The weather varied somewhat over the sampling period and between different stations. After air sampling the Andersen Head was disassembled and each filter was reweighed to determine particulate levels. Each filter in succession was cut into four equal parts so that two samples consisting of 2 to 25 milligrams of particulates could be analyzed. The filter was carefully folded into a large test tube and securely sealed with a rubber stopper. Two Monojet 200 stainless steel needles with aluminum hubs were used to puncture the stopper to provide openings so that one needle could be attached to a cylinder of argon to flush the tube and filter with argon (which is heavier than air) to purge any oxygen which could oxidize sulfite to sulfate. The tube was purged for five minutes with a slow stream of argon. The needles were removed from the stopper and the tubes were refrigerated until analysis time.

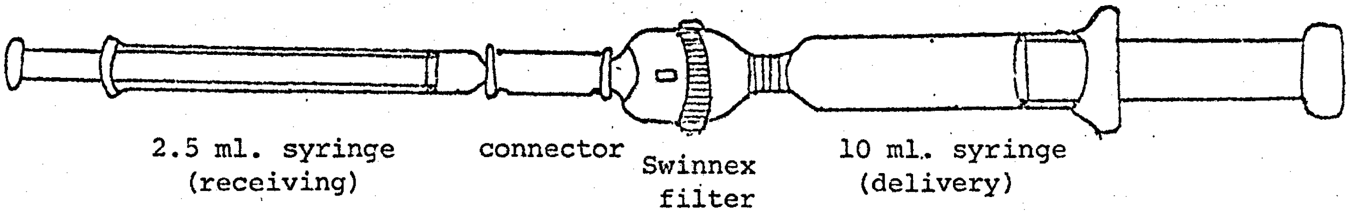
In designing a procedure to analyze for sulfite in the presence of ferric ion and cupric copper the solution should have an H^+ concentration of 0.1 M to prevent sulfur (IV) oxidation but should also not exceed 1 M to prevent reduction of sulfur (IV) which takes place more easily in strong acid. HCl was chosen since the anion of the acid does not interfere with the precipitation reaction for sulfate using $BaCl_2$ and also Cl^- does not interfere with redox reactions by $Cr_2O_7^{2-}$. SO_2 gas is lost from the system if the Fe^{3+} concentration is not at least 0.005 M in the acid solution. 0.1 M Hcl solution containing 0.005 M $FeCl_3$ was chosen since the sulfite and sulfate salts of most elements expected to be present in airborne particulates are readily soluble except for Ca, Sr, Ba, and Pb. The SO_3^{2-} is oxidized by oxygen-free $Cr_2O_7^{2-}$ to SO_4^{2-} and the resulting ΔT obtained by thermometric titration gives the amount of sulfite in the sample. Next, a solution of $BaCl_2$ is added and the amount of SO_4^{2-} is determined from the precipitation and corresponding exothermic reaction to form $BaSO_4$. The amount of sulfate represented by the ΔT value is found by comparison to the output from a standard solution. The amount of sulfate in the sample is the total sulfate (including the sulfite previously oxidized to sulfate) minus the previously determined sulfite concentration.[29]

In the procedure errors are introduced unless the system is purged with argon. S(IV) in particulate samples is oxidized by oxygen in the air unless an inert gas such as argon is used. Because of the errors introduced in the analysis, the concentration of S(IV) by this procedure represents the minimum concentration of S(IV) present.

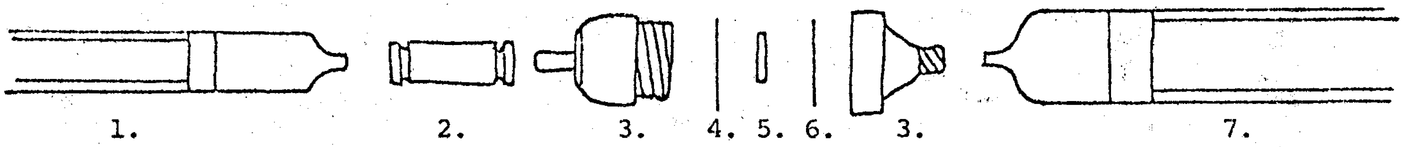
A liter of 0.10 M $BaCl_2$ was prepared using $BaCl_2 \cdot 2H_2O$ (Reagent, B&A). A 50 ml. solution of 0.005032 M $K_2Cr_2O_7$ in 0.1 M HCl was made using NBS standard $K_2Cr_2O_7$ and analytical reagent, MCB HCl. The extractor solution was made 0.00251 M. Fe^{3+} in 0.1 M HCl using $FeCl_3 \cdot 6H_2O$ (analytical reagent, MCB) and HCl (analytical reagent, MCB). All the solutions were stored under an argon atmosphere. The samples to be analyzed were removed from the refrigerator and 15 ml. (18 ml. for backup pad, Stage 5) of the extraction solution was injected through the rubber septum after first purging the syringe and needle with argon. The extraction lasted at least 3 hours while refrigerated at 5°C and rotating in a plate at 6 rpm. The tubes were tilted about 20° to the vertical to allow the solution to contact the entire filter but still prevent any solution from touching the rubber stopper. A 10 ml. Hamilton gas tight syringe fitted with a Monoject 200 stainless steel needle with an aluminum hub was purged with argon for about 10 to 15 seconds and then used to withdraw the solution from the tube. The solution was next injected through a filter assembly (described below) into two 2.5 ml. Hamilton gas tight syringes. The two 2.5 ml. syringes and filter assembly were first purged with argon.

The filter assembly used was a Swinnex-13 which contains a silicone gasket between two halves which screw together (Millipore). In preparing the filter apparatus, the filter (Millipore GSTF01300) was centered on the holder support screen using unserrated-tip forceps. Next the prefilter (AP2001000) was placed on top with the grid surface facing away from the filter. Next a silicone gasket was placed on top of the prefilter and the two polypropylene Swinnex holder halves (Millipore SX0001300) were screwed together. See Fig. 6. The two 2.5 ml. syringes were filled with solution to 2.25 ml.

Instrumentation is shown in Fig. 7. The Dewar was attached to the calorimeter and purged with argon for 5 minutes. The solution was injected from the syringe into the Dewar reaction vessel and the argon was again left on to clear any solution from the injection line into the Dewar. The argon was turned off before titration



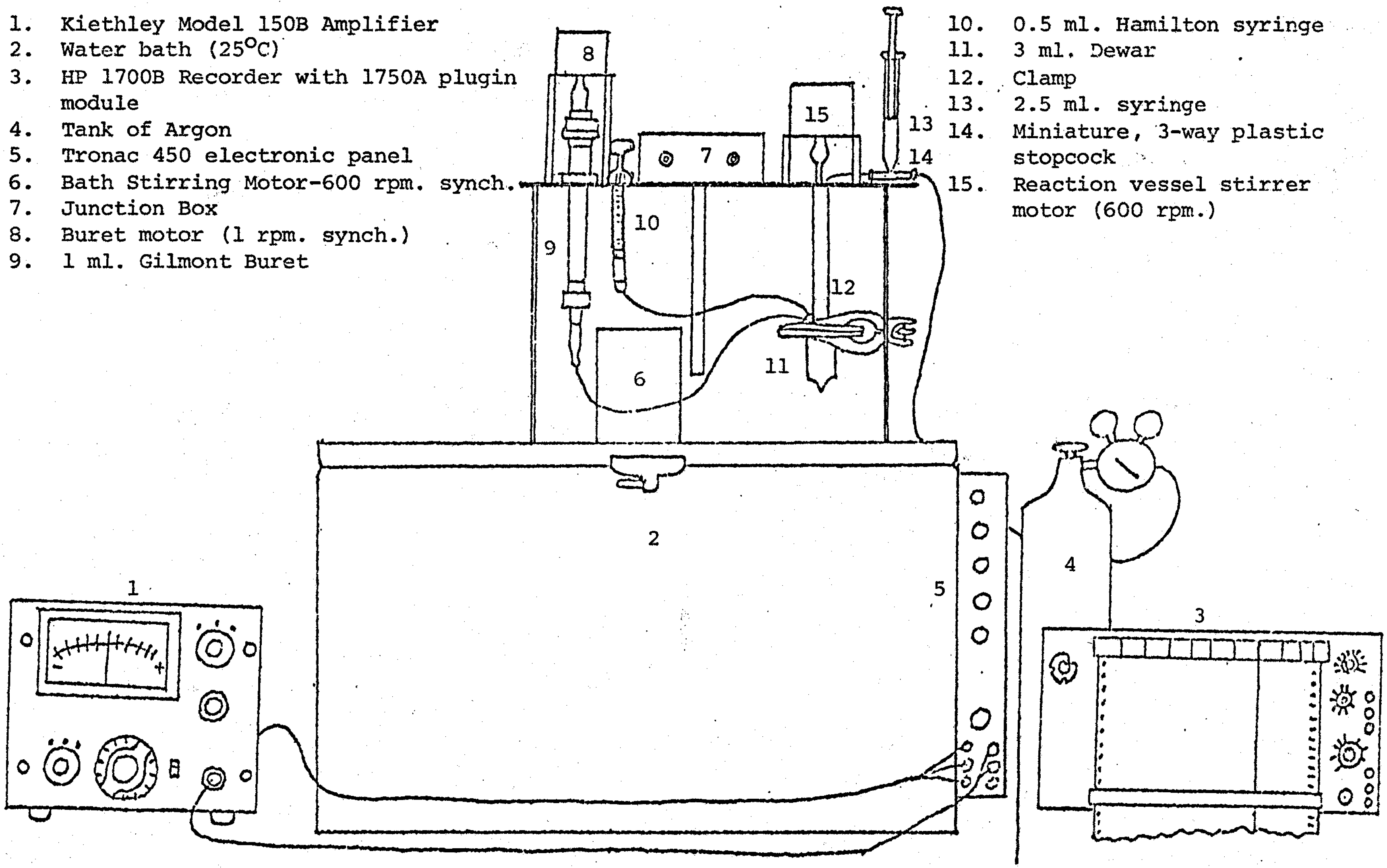
Assembled view.



Illustrative Section

1. 2.5 ml. syringe (receiving)
2. Hamilton connector
3. Swinnex filter holder (2 Parts)
4. Millipore filter
5. Depth filter
6. Silicone rubber gasket
7. 10 ml. syringe (delivery)

Fig. 6. Filtration Assembly



1. Kiethley Model 150B Amplifier
2. Water bath (25°C)
3. HP 1700B Recorder with 1750A plugin module
4. Tank of Argon
5. Tronac 450 electronic panel
6. Bath Stirring Motor-600 rpm. synch.
7. Junction Box
8. Buret motor (1 rpm. synch.)
9. 1 ml. Gilmont Buret
10. 0.5 ml. Hamilton syringe
11. 3 ml. Dewar
12. Clamp
13. 2.5 ml. syringe
14. Miniature, 3-way plastic stopcock
15. Reaction vessel stirrer motor (600 rpm.)

Fig. 7. S(IV) and S(VI) Analytical Instrumentation

began. The reaction vessel temperature was 0.08°C below bath temperature when the titration began. The buret runs 4 minutes at 0.0987 cc./min. and the thermogram was recorded at 0.2 inches per second. The recorder range was at 10 μV/inch. The Kiethley bridge output amplifier model 150B was set for 1 mv. input and 1 volt output. The buret was turned off after 4 minutes and the recorder chart speed was changed to 2 inches per minute but the recorder range was not changed. The heater was turned on until the reaction vessel temperature was equal to bath temperature. The calorimeter was calibrated electronically. A set point was taken at the start of the day to determine where the bath temperature registers on the recorder. 0.25 ml. of $BaCl_2$ solution at the same temperature as the bath was added at a constant rate for 1 minute by means of a syringe with a threaded plunger (to minimize extraneous heat production). The Dewar used was previously coated with $BaSO_4$ and after every run was rinsed with only deionized water since the $BaSO_4$ coating promotes the rapid precipitation of $BaSO_4$. An idealized recorder output is shown in Fig. 8. Blank determinations were made by using the same procedure.

The amount of S(IV) in the sample was determined from the endpoint in the redox region of the thermogram. The sulfite oxidation reaction gives a very characteristic slope which differs from other reducing agents which may be present [Fe(II), As(III) and organics.]. The sulfate concentration was determined by comparison of the sample output with the temperature rise attained by injecting the $BaCl_2$ solution into a known amount of SO_4^{2-} in 0.1 $\underline{M}$ HCl and 0.005 $\underline{M}$ $FeCl_3$. Blank corrections from analyses of unused filters

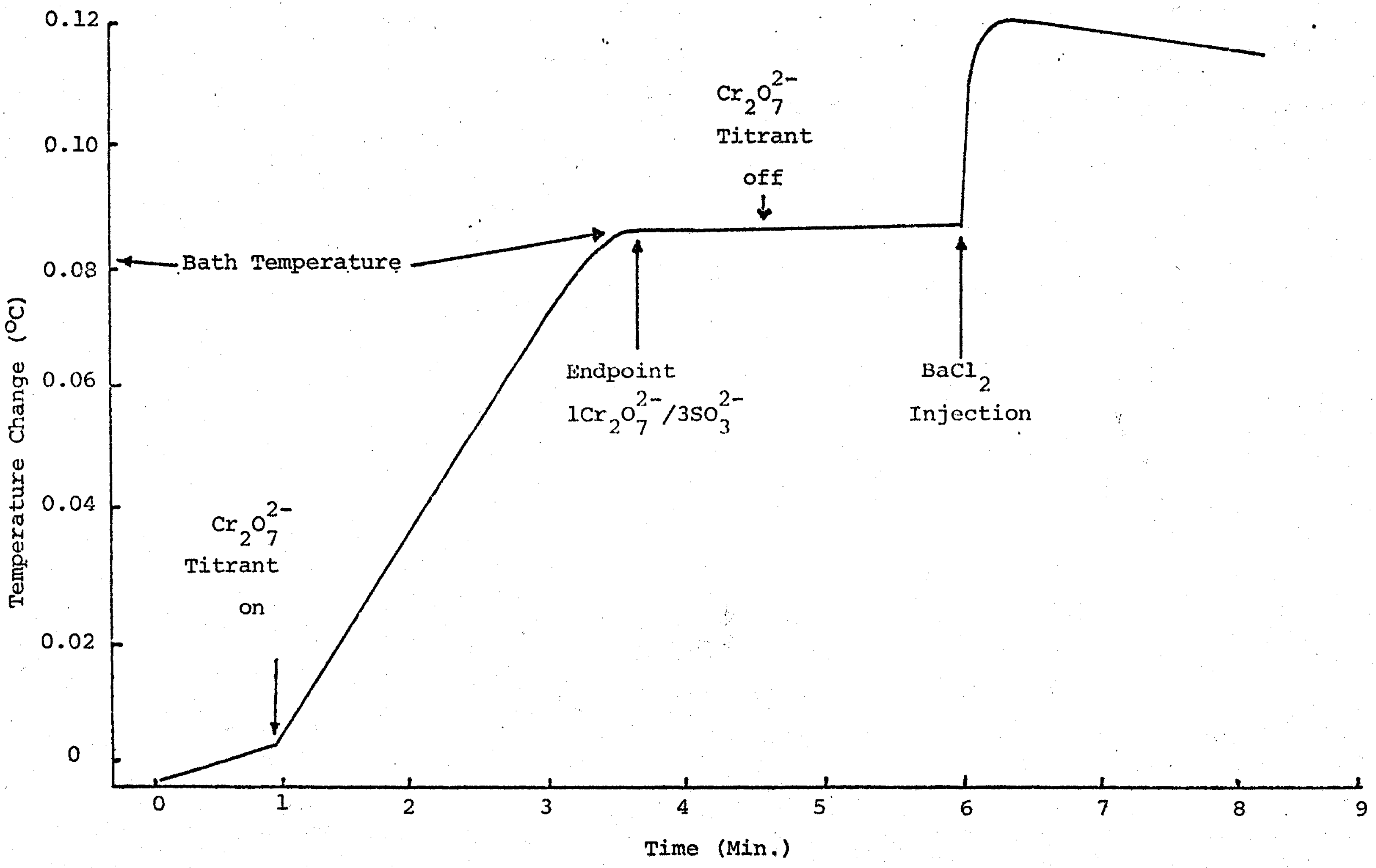


Fig. 8. Idealized Thermometric Titration for S(IV) and S(VI) Concentrations from Hansen, L., et. al.[29]

were used to make corrections. Previous determinations show that the precision of the method is ± (5% of the total sulfur (IV) + 3 nanomoles) and ± (10% of the total sulfate + 30 nanomoles) in 2.25 ml. of extractant solution.

C. Air Sampling Results

The results of the particulate S(IV) and S(VI) concentrations are shown in the following tables for each of the five sampling stations. In each case the S(IV) and S(VI) levels are reported in terms of millimoles per gram of particulate. The total sulfur is the sum of S(IV) and S(VI) in millimoles/g. The percent S(IV) is the result of dividing S(IV) (in mmoles/g.) by total sulfur (in mmoles/g. and multiplying by 100. The sampling period was 48 hours in each case, which is a rather limited time period from which to draw any general conclusions concerning yearly concentrations at the various sampling stations. Also, the samples were taken in winter or early spring when particulate concentrations are highest. Therefore, data from the Utah Division of Health were included to show that the particulate concentrations on the days samples were taken are representative of particulate concentrations of other days in the month and to show how this compares with other days in the year. Those data give only rough comparisons however, since the State takes the raw data values and changes them to reflect levels comparable at standard temperature and pressure (STP) from values at ambient temperatures and pressure. In each case where the total particulate in grams and particulate concentration in $\mu g/m^3$ are given, no correction to STP has been made on the samples taken at the five sampling stations.

Dustfall measurements are available for 1969 and 1970. The average two year measurements are shown in Table 4.[33]

Table 4

Dustfall Concentrations in Utah Valley[a]

Location	Tons per square mile per month
Lindon	9.4
Provo	9.3
Springville	18.0
Richfield (located 100 miles south of Provo)	6.8

[a] See Ref. 33.

The particulate concentrations shown in Table 4 show that the data collected in this present study are also representative for yearly averages. The sampling sites in this present study also included Lindon, Provo and Springville. The total particulates collected (See Tables 5, 6, and 7) compare favorably with results in Table 4. For example, the Springville sample (Table 8) is about twice as large as the Provo (Table 5) and Lindon (Table 7) samples. The Lindon and Provo samples have about the same concentration (Tables 5 and 7); however, Table 4 shows the Lindon sample slightly more concentrated, whereas Table 5 shows the particulate concentration of the Provo sample slightly more concentrated on the days the samples were taken than the Lindon sample (Table 11).

Tables 5, 6, 7, 8 and 9 show the S(IV) and S(VI) concentrations whereas Tables 16, 17, 18, and 19 show statistical data gathered from the Air Quality Section of the Utah Division of Health. Tables 20, 21, 22, 23, and 24 show the speed of wind blowing (MPH) and direction (azimuth). The data for Lehi are given since the State has no sampling station at Cedar Fort and Lehi is the closest station but is 15 miles east of Cedar Fort. Also, the wind data for Mapleton, which is 3 miles south of Springville, are given instead of Springville, since the State has no sampling station in Springville either.

The data from the Air Quality Section of the Utah Division of Health is in appendix B. The data indicate that the days on which samples were taken were close to the particulate concentration geometric mean for other days in the month. However, the Springville samples had the higher particulate levels for the days on which samples were taken than for any other days in the month by a factor of 2.

The uncertainty in Tables 5, 6, 7, 8, and 9 is the standard deviation. The abreviations used on data from the Air Quality Control Section of the Utah Division of Health are TM = this month, YD = year to date, RY = running year. All entries are referred to STP (standard temperature and pressure) except those labelled 'actual.' 'Actual' refers to annual station pressure and average daily temperature. Particulates are measured in ambient air and 24 hour average in micrograms per cubic meter.

The Provo station samples were taken on days in which the particulate levels were lower by about 10 μg/M^3 than the geometric mean levels for the rest of the month but were very near the geometric mean particulate values for the running year. (Table 16.) The wind blew from the northwest or west during most of the sampling period and was less than 5 miles per hour during most of the time.

The Mapleton data show that the samples in Springville were taken on days in which the particulate levels were higher by about 40 μg/M^3 than the geometric mean levels for the rest of the month. One day on which I sampled had the maximum particulate level for the month. However, no day during the month had a level greater than 150 μg/M^3 (Table 17). For the data given, the wind came mainly from the southeast at less than 5 mph. during the whole sampling time.

The Lindon station samples were taken on days in which the particulate levels were higher by about 30 μg/M^3 than the geometric mean levels for the rest of the month (Table 7). However, the particulate level for the sampling period is very close to the particulate level for the geometric mean running year. The wind blew mainly from the northeast and northwest for most of the sampling period and was mostly under 5 mph. (Table 18.)

The leasant Grove samples were taken on days in which the particulate levels were slightly higher by about 10 μg/M^3 than the geometric mean levels for the rest of the month. However, only 2 of the 3 days sampled were available from the State data. Also, the particulate level for those days were highly variable by a factor of about 7. No day during the month had particulate levels greater than

150 μg/M^3 (Table 19). The wind during the sampling period came mainly from the southeast at between 5 and 10 mph. during most of the sampling time.

No statistical data are available from the State Air Quality Section for the Lehi station. However, the wind data (Table 24) indicate that the wind was quite variable in both speed and direction for the sampling period.

Table 5

Results from Provo in mmole/g. Particulate[a,b]

Stage	S(IV) millimole/g	S(VI) millimole/g	Total S millimole/g	mole %S(IV)
S#5 B.U.	0.075 ± 0.007	1.84 ± 0.02	1.92	3.91
S#4	0.162 ± 0.009	7.76 ± 0.17	7.92	2.04
S#3	0.095 ± 0.005	6.72 ± 0.26	6.81	1.40
S#2	0.282 ± 0.049	3.11 ± 0.08	3.39	8.32
S#1	0.083 ± 0.010	1.09 ± 0.02	1.17	7.09

[a] Total particulate = 0.135060 g.

[b] Particulate concentration = 82.6 μg/M^3

Table 6

Results from Springville in mmole/g. Particulate[a,b]

Stage	S(IV) millimole/g	S(VI) millimole/g	Total S millimole/g	mole %S(IV)
S#5 B.U.	0.048 ± 0.006	2.06 ± 0.01	2.11	2.27
S#4	0.028 ± 0.007	4.14 ± 0.02	4.17	0.671
S#3	0.065 ± 0.042	4.38 ± 0.08	4.45	1.46
S#2	0.073 ± 0.012	2.55 ± 0.25	2.62	2.79
S#1	0.052 ± 0.004	0.836 ± 0.034	0.888	5.86

[a] Total particulate = 0.25198 g.

[b] Particulate concentration = 154.5 μg/M^3.

Table 7

Results from Lindon in mmole/g. Particulate[a,b]

Stage	S(IV) millimole/g	S(VI) millimole/g	Total S millimole/g	mole %S(IV)
S#5	0.076 ± 0.005	1.53 ± 0.34	1.61	4.72
S#4	0.161 ± 0.080	7.15 ± 0.43	7.31	2.20
S#3	0.276 ± 0.088	3.96 ± 0.01	4.24	6.51
S#2	0.000 ± 0.029	2.69 ± 0.14	2.69	0
S#1	0.108 ± 0.045	1.41 ± 0.05	1.52	7.11

[a] Total particulate = 0.114370 g.

[b] Particulate level 70.1 μg/M^3

Table 8

Results from Pleasant Grove in mmole/g. Particulate.[a,b]

Stage	S(IV) millimole/g	S(VI) millimole/g	Total S millimole/g	mole %S(IV)
S#5 B.U.	0.005 ± 0.003	2.17 ± 0.19	2.18	0.236
S#4	0.178 ± 0.046	5.33 ± 0.03	5.51	3.46
S#3	0.342 ± 0.017	4.27 ± 0.30	4.61	7.42
S#2	0.000 ± 0.003	3.80 ± 0.42	3.80	0
S#1	0.157 ± 0.002	1.60 ± 0.04	1.76	8.92

[a] Total particulate = 0.09009 g.

[b] Particulate concentration = 56.4 μg/M^3.

Table 9

Results from Cedar Fort in mmole/g. Particulate[a,b]

Stage	S(IV) millimole/g	S(VI) millimole/g	Total S millimole/g	mole %S(IV)
S#5 B.U.	0.217 ± 0.031	1.99 ± 0.03	2.21	9.82
S#4	0.364 ± 0.051	7.04 ± 0.26	7.40	5.17
S#3	0.354 ± 0.011	5.22 ± 0.66	5.57	6.78
S#2	0.271 ± 0.026	3.42 ± 0.16	3.69	7.34
S#1	0.162 ± 0.016	2.08 ± 0.05	2.24	7.23

[a] Total particulate = 0.10276 g.

[b] Particulate level = 64.0 μg/M^3.

To give a better idea of the effect on health and to compare with sulfur oxide data in the literature, the data from Tables 5-9 for S(IV) have been converted to $\mu g/M^3$ of S(IV) collected on the various stages of the Andersen Sampler.

Fig. 9 shows the S(IV) in $\mu g/M^3 x10$ from both Springville and Provo since these two sampling sites give rather similar trends. The hypothesis to explain this similarity is that both samples have a similar source of S(IV). The main source in both cases is probably from combustion of fossil fuels. Both the samplers in Provo and Springville were taken in areas close to heavily travelled roads. Both samplers show their highest concentrations of S(IV) on stages one or two and then decrease on stages three and four. S(IV) concentrations increase again on stage 5 but don't increase to the concentrations of the highest (stage one or two).

Fig. 10 shows the S(IV) in $\mu g/M^3 x10$ from both Lindon and Pleasant Grove since these two sampling sites also have similar trends. In this case both samples have a sawtooth pattern on the plot. Stage one has the greatest concentration of $S(IV)/M^3$ and stage two is zero. Stage three shows an increase in concentration again but still is below the concentration on stage one. The concentration of S(IV) on stage 5 increases over the concentration of $S(IV)/M^3$ on stage 4 in the Lindon sample but decreases on stage 5 on the Pleasant Grove sample. An explanation for this might be that the Lindon sample was taken close to a highway (See map Fig. 2.) and the increase of μg $S(IV)/M^3$ for stage 5 may reflect the source of S(IV) from the burning of fossil fuels in automobile exhaust.

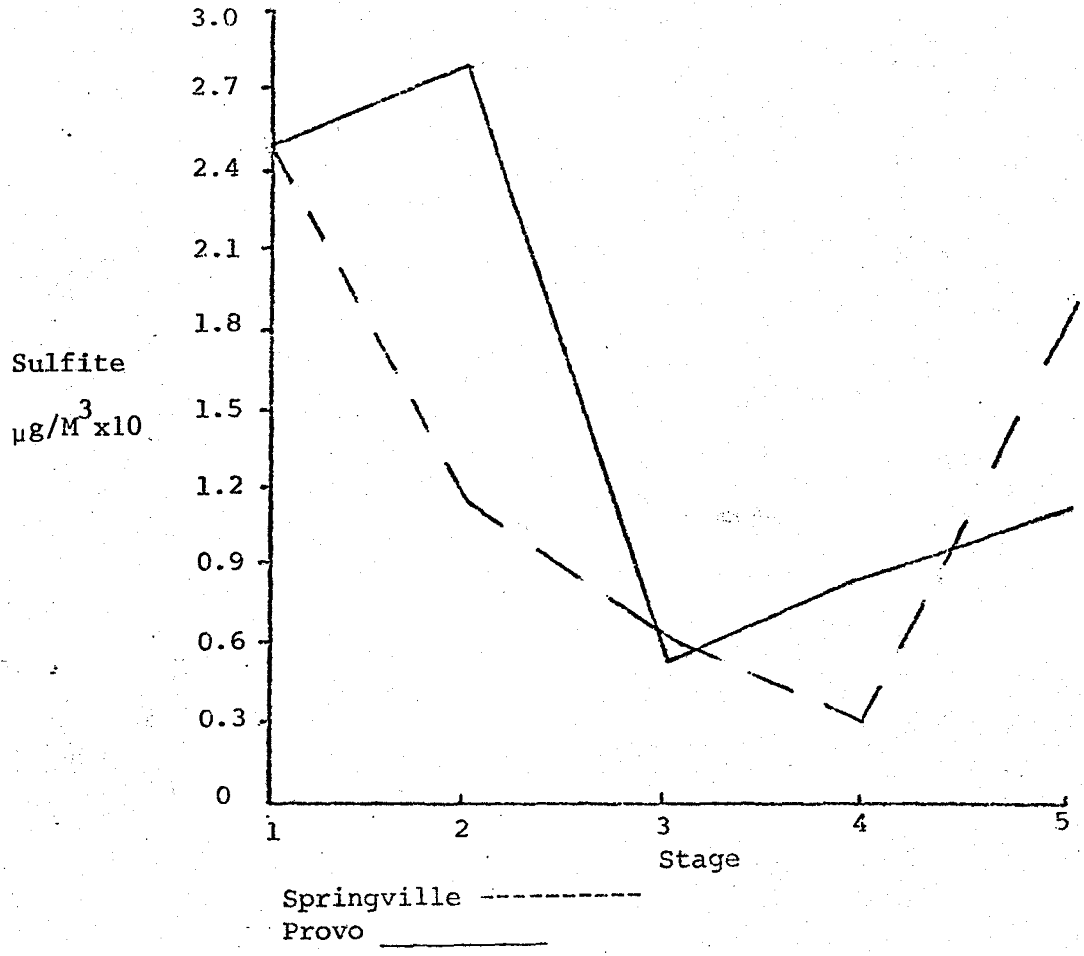


Fig. 9. Plot of S(IV) in µg/M^{3}x10 for each stage of the Andersen Sampler for Provo and Springville.

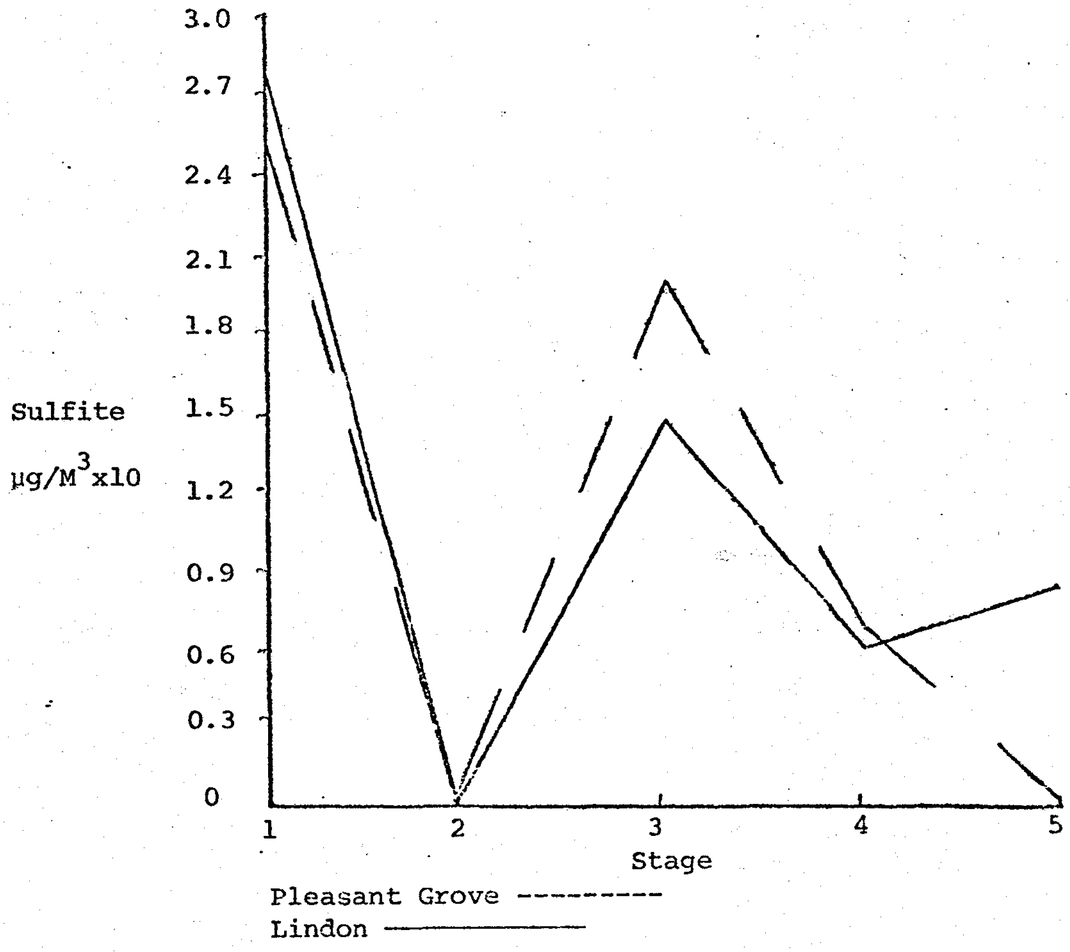


Fig. 10. Plot of S(IV) in µg/M^{3}x10 for each stage of the Andersen Sampler for Lindon and Pleasant Grove.

Table 10

$\mu g/M^3$ Sulfite on each Stage of the Andersen Sampler for Provo and Springville

Provo Sulfite in $\mu g/M^3$		Springville Sulfite in $\mu g/M^3$	
Stage 1	0.250	Stage 1	0.247
Stage 2	0.280	Stage 2	0.115
Stage 3	0.0562	Stage 3	0.0613
Stage 4	0.0825	Stage 4	0.0332
Stage 5	0.114	Stage 5	0.188

Table 11

$\mu g/M^3$ Sulfite on each Stage of the Andersen Sampler for Pleasant Grove and Lindon

Pleasant Grove Sulfite in $\mu g/M^3$		Lindon Sulfite in $\mu g/M^3$	
Stage 1	0.2544	Stage 1	0.2709
Stage 2	0.0000	Stage 2	0.0000
Stage 3	0.2071	Stage 3	0.1524
Stage 4	0.0726	Stage 4	0.0632
Stage 5	0.0047	Stage 5	0.0894

Figure 11 shows the S(IV) concentrations in $\mu g/M^3$x10 for Cedar Fort for the five different stages of the Andersen Sampler. The plot shows the unique trend of this sample in comparison to the other

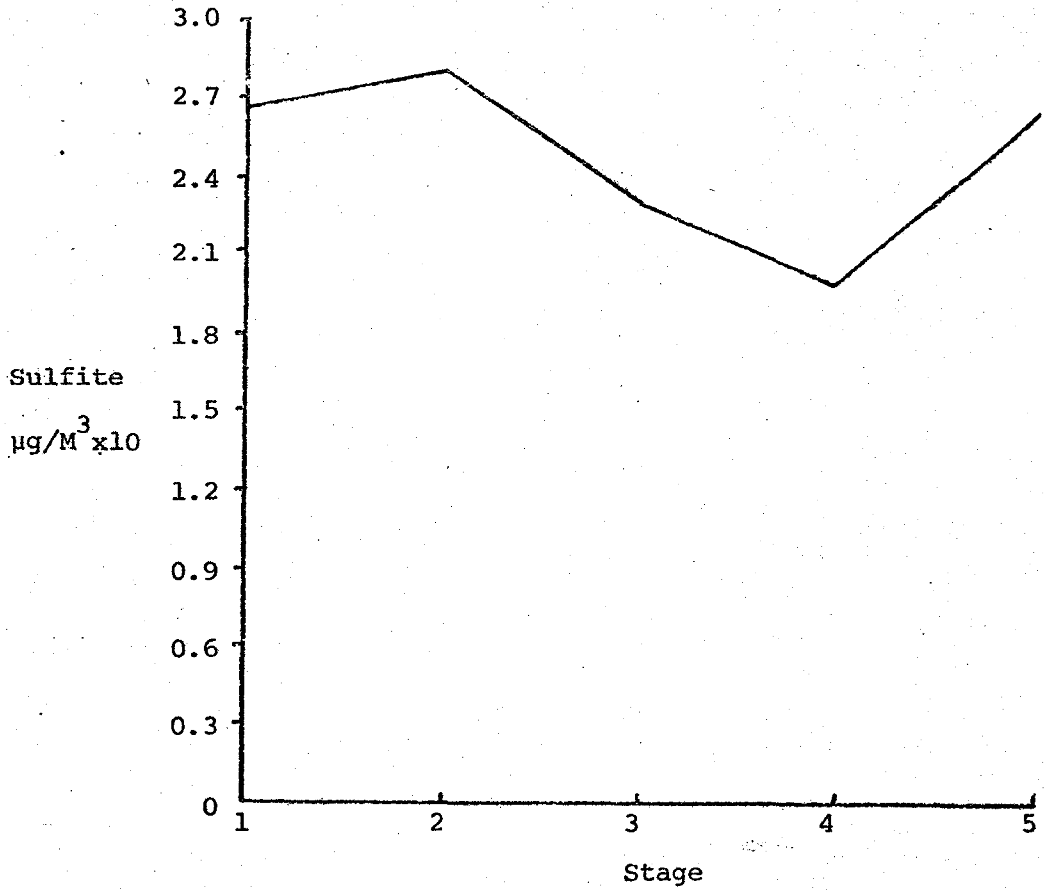


Fig. 11. Plot of S(IV) in µg/M^{3}x10 for Each Stage of the Andersen Sampler for Cedar Fort.

Table 12

µg/M^3 Sulfite on Each Stage of the Andersen Sampler for Cedar Fort

Stage	µg/M^3
1	0.267
2	0.277
3	0.231
4	0.206
5	0.266

samples from Utah Valley sites. In this case the probable source for most of the sulfur oxides in the sample was the Kennecott smelter.

The data in Table 13 show the results of this study in addition to a similar study conducted around Magna and Ogden.

Table 13

Weight Percent Suspended Particulates[34]

Location	Distance from Smelter	No. Samp.	Part Size	SP[a] $\mu g/M^3$	S(IV) SO^{2-}	S(VI) SO_4^{2-}
Smelter	0	7	>7.0	1450±690	2.1±0.4	2.0±1.1
			1.1-7.0	680±750	1.9±0.5	6.6±4.2
			<1.1	500±630	1.5±0.4	16.0±15.8
			TSP	2630±2000	1.9±0.4	5.9±4.2
Magna	4	3	>7.0	31±9	1.2±1.0	17.7±1.8
			1.1-7.0	47±11	2.8±1.0	30.7±5.2
			<1.1	29±4	2.1±0.9	28.9±9.8
			TSP	107±22	2.3±1.0	26.2±4.1
Kearns	15	2	>7.0	22±1	1.1±0.3	16.7±0.5
			1.1-7.0	34±8	2.7±0.3	19.5±15.1
			<1.1	24±3	1.1±0.6	22.5±12.2
			TSP	80±12	1.8±0.1	19.9±9.9
Salt Lake City	26	2	>7.0	21±2	1.9±0.1	16.7±9.7
			1.1-7.0	33±1	2.8±0.1	21.5±1.3
			<1.1	24±5	1.7±1.2	17.4±0.4
			TSP	78±8	2.2±0.4	18.9±3.0
Cedar Fort	44	1	>7.0	21	1.3	19.9
			1.1-7.0	28	2.5	46.5
			<1.1	15	1.7	18.4
			TSP	64	1.9	31.4
Ogden	62	2	>7.0	43±11	0.5±0.1	5.4±2.7
			1.1-7.0	67±30	0.5±0.4	8.0±0.7
			<1.1	49±18	0.2±0.2	10.7±4.2
			TSP	159±59	0.4±0.2	8.2±1.7
Geneva Area[b]	7[c]	3	>7.0	30±9	0.9±0.3	12.9±2.8
			1.1-7.0	25±1	1.2±0.3	43.1±6.6
			<1.1	15±4	0.9±0.2	17.5±2.8
			TSP	70±13	1.0±0.2	24.8±2.6
Springville	20[c]	1	>7.0	59	0.42	6.6
			1.1-7.0	46	0.48	35.8
			<1.1	49	0.39	19.8
			TSP	159	0.43	19.5

[a] SP is suspended particulates, either total, TSP or indicated size fraction.

[b] Geneva Area includes Provo, Lindon and Pleasant Grove.

[c] Kilometers from the steel mill.

IV. CONCLUSION

Except for the Cedar Fort sample, in which stage five also had a high concentration of S(IV), the larger particle sizes have the highest concentration of S(IV) in $\mu g/M^3$. Cedar Fort had the highest overall concentration in terms of μg S(IV) per cubic meter of air (Table 21). If the data for S(IV) and total particulate weight are calculated to reflect weight percentage S(IV), some trends appear. In all cases the highest percentage of S(IV) was formed on the first stage except for Cedar Fort where the second stage had the highest percentage of S(IV) and the Provo sample where the second stage was slightly higher than Stage 1.

It is significant that the Cedar Fort sampling site had the highest overall concentrations of S(IV). This particular location is downwind from the Kennecott Smelter at Magna. The plume can often be seen drifting south over the Oquirrh Mountains (see Figure 2.)

Salt Lake has high SO_2 concentrations whereas Utah Valley has high particulate concentrations. The average of all stages for S(IV) concentration in airborne particulates at the Kennecott smelter in Salt Lake is 1.8±0.4 weight percent in suspended particulate, whereas the S(VI) weight percent is variable by a factor of eight but averages 7.6±6.3 weight percent. The S(IV):S(VI) ratio at the smelter is 1:4.2. The average of all stages for S(IV) is 2.1±1.0 weight percent at Magna (the closest city to the smelter), whereas the S(IV) average for all stages is 25.9 5.2 weight percent. The S(IV):S(VI) ratio is 1:12.3. At Cedar Fort the average of all stages for S(IV) is 1.8 whereas the average for all stages for S(VI) is 29.0. Therefore the S(IV):S(VI) ratio is 1:16.1.[34]

These data support the conclusion that the S(VI) concentration increases rapidly in the smelter stack. Only a slight amount of oxidation occurs from S(IV) to S(VI) as the plume travels 44 kilometers south to Cedar Fort compared to the amount of oxidation in the stack. This also testifies to the fact that the metal sulfites formed in the particulates are stable to oxidation for relatively long periods of time in the plume from the Magna smelter. The Kennecott smelter sample consists of particulates directly from the furnace and not discharged from the smoke stack. The Magna and Cedar Fort samples, on the other hand, consist of plume particulates from the smoke stack.

V. SUMMARY

The first purpose of this study was to determine qualitatively the extent of adsorption of SO_2 in decane with metal oxides in decane in order to simulate in the laboratory the reactions which occur in the environment between SO_2 and particulates. Surface areas of metal oxides commonly found in Utah Valley aerosols were determined by BET analysis. The reaction order of SO_2 with the metal oxides decreases in order $CuO > Cu_2O > Fe_2O_3 > Fe_3O_4 > V_2O_5$. Under anhydrous conditions the adsorption of SO_2 on metal oxide occurred only slightly or not at all. There is no difference in adsorption of SO_2 on the metal oxides between the SO_2 dissolved in Decane and the SO_2 dissolved in hydrous Decane. Apparently there is enough moisture in Reagent Grade Decane to allow the adsorption reaction to preceed.

The second purpose of this study was to obtain samples of Utah Valley aerosols and to determine quantitatively the S(IV) and S(VI) levels. This part of the study showed that the highest sulfur level in Utah Valley occurred at the sampling site closest to the Kennecott smelter located at Magna. Other sources of sulfur oxides occur in Utah Valley such as various coal burning operations and automobile exhaust; however, these operations have a negligible effect on the sulfur oxide level compared to the Kennecott smelter smoke.

The third purpose of this study was to compare the results for S(IV) and S(VI) to a similar S(IV) and S(VI) study[34] conducted around the Magna, Utah area (Table 13). The S(IV), S(VI) and total sulfur levels in the Magna area range up to 100 times the amount found in Utah Valley around Provo. The Cedar Fort sample indicates that once the particulates are released from the stack the S(IV):S(VI) ratio stays fairly constant during the time it takes the plume to travel the 40 kilometers to Cedar Fort from Magna.

Recommendations for Further Study

This study is valuable because it gives S(IV) and S(VI) values for Provo and the surrounding communities in Utah Valley. These values are particularly valuable since Kennecott, whose smelter at Magna is the highest source of SO_2 in Salt Lake Valley, is now building a new smoke stack at the smelter. This smoke stack will have the effect of spreading the smoke plume over a greater area. Further studies will determine whether the stack is beneficial as officials of Kennecott maintain.

Another interesting study could be made by sampling the Kennecott plume as it travels south along the Oquirrh Mountains (see Figure 2) to show the transition of SO_2 and the interaction of SO_2 with particulates to form metal sulfites and sulfates.

A study of S(IV) and S(VI) concentrations over the course of a full year would be helpful since change of concentrations from month to month is unknown.

APPENDIX A

Appendix A is a summary of source emission estimates for Utah for the year 1970[13] for the Wasatch Front--particulates (pages 52-54) and sulfur oxides (pages 55-57).

Table 14

Particulate Emissions Inventory Summary in Tons Per Year
Wasatch Front Air Quality Control Region

	Salt Lake County	Utah County
Source Category	1970	1970
I. Fuel Combustion Stationary Sources		
A. Residential and Commercial (Area Sources)		
1. Bituminous Coal	65	143
2. Distillate Oil	55	174
3. Residual Oil	N	N
4. Natural Gas	344	76
Total	464	393
B. Institutional (Point Sources)		
1. Bituminous Coal	336	287
2. Distillate Oil	1	N
3. Residual Oil	N	-
4. Natural Gas	15	N
Total	352	287
C. Industrial (Point Sources)		
1. Bituminous Coal	395	676
2. Distillate Oil	N	3
3. Residual Oil	97	113
4. Natural Gas	43	13
5. Process Gas	63	142
6. Wood	2	-
Total	600	947

Table 14--Continued

Source Category	Salt Lake County	Utah County
	1970	1970
D. Electric Power Generation (Point Sources)		
1. Bituminous Coal	1031	841
2. Distillate Oil	2	-
3. Residual Oil	74	-
4. Natural Gas	120	30
5. Process Gas	-	6
Total	1227	866
E. Total Fuel Stationary Sources	2643	2513
II. Process Losses (Point Sources)		
A. Chemical Process Industries	511	5
B. Food and Agricul. Industries	6	123
C. Metallurgical Industries	3206	4068
D. Mineral Product Industries	297	2539
E. Petroleum and Petrochem. Indus.	149	-
F. Wood Process	69	-
G. Others	-	-
H. Total Process Loss	4238	6735
III. Solid Waste		
A. Incineration		
1. Area Sources	125	34
2. Municipal--Point Sources	6(*)	-
B. Open Burning		
1. Area Sources	67	52
2. Point Sources	-	-
C. Agric. Burning (Area)	50	38
D. Total Solid Waste	248	124

Table 14--Continued

Source Category	Salt Lake County 1970	Utah County 1970
IV. Transportation (Area Sources)		
A. Autos and Light Trucks	699	239
B. Diesel-On Hiway	115	69
C. Diesel-Off Hiway	153	51
D. Aircraft	492	10
E. Railroads	84	90
F. Gasoline Handling Losses	-	-
G. Total Transportation	1543	459
V. Grand Totals	8672	9831

(N) = Negligible

(*) Auto Body Incineration, Salt Lake County Only

Note: 8% ash for Utah coal used where not specifically given.

Table 15

Sulfur Oxides Emissions Inventory Summary in Tons Per Year
Wasatch Front Air Quality Control Region

Source Category	Salt Lake County 1970	Utah County 1970
I. Fuel Combustion Stationary Sources		
A. Residential and Commercial (Area Sources)		
1. Bituminous Coal	92	204
2. Distillate Oil	233	743
3. Residual Oil	N	N
4. Natural Gas	11	2
Total	336	949
B. Institutional (Point Sources)		
1. Bituminous Coal	321	299
2. Distillate Oil	8	N
3. Residual Oil	N	-
4. Natural Gas	N	N
Total	329	299
C. Industrial (Point Sources)		
1. Bituminous Coal	121	80
2. Distillate Oil	6	18
3. Residual Oil	2021	252
4. Natural Gas	11	1
5. Process Gas	2330	7341
6. Wood	N	-
Total	4489	7692
D. Electric Power Gen. (Point Sources Only)		
1. Bituminous Coal	706	372
2. Distillate Oil	4	-
3. Residual Oil	4654	-
4. Natural Gas	5	1030
5. Process Gas	-	2
Total	5369	1404

Table 15--Continued

Source Category	Salt Lake County 1970	Utah County 1970
E. Total Fuel Stationary Sources	10532	10344
II. Process Losses (Point Sources Only)		
A. Chemical Process Industries	-	-
B. Food & Agricultural Industries	-	-
C. Metallurgical Industries	280171	136
D. Mineral Product Industries	-	-
E. Petroleum & Petrochem. Indus.	1521	-
F. Wood Process	-	-
G. Others	-	-
H. Total Process Losses	281692	136
III. Solid Waste		
A. Incineration		
1. Area Sources	12	3
2. Municipal--Pt. Sources	N	N
B. Open Burning		
1. Area Sources	4	3
2. Point Sources	-	-
C. Agricultural Burning (Area)	N	N
D. Total Solid Waste	16	6

Table 15--Continued

Source Category	Salt Lake County 1970	Utah County 1970
IV. Transportation (Area Sources)		
A. Autos and Light Trucks	419	144
B. Diesel--On Hiway	207	124
C. Diesel--Off Hiway	276	91
D. Aircraft	244	41
E. Railroads	218	233
F. Gasoline Handling Losses	-	-
G. Total Transportation	1364	633
V. Grand Totals	293595	11119

(N) = Negligible

Notes: (1) 0.6% sulfur in Utah coal used where not specifically given.

(2) 0.4% sulfur in light fuel oil used where not specifically given.

(3) 0.9% sulfur in heavy fuel oil used where not specifically given.

APPENDIX B

Appendix B is a series of statistical results compiled by the Air Quality Section, Utah Division of Health.

Table 16[a]

Provo Data for February 17 to February 19, 1975 and Statistical Comparisons

Date	STP $\mu g/M^3$	Actual $\mu g/M^3$
February 17	100	92
18	90	84
19	78	72

	TM	YD	RY
Geometric mean $\mu g/M^3$	98	96	88
Geometric Standard Deviation	1.55	1.74	1.70
Geometric Mean Actual Temp. and Press. ($\mu g/M^3$)	91	90	78
Maximum 24-hr. average ($\mu g/M^3$)	206	226	727
Arithmetic mean ($\mu g/M^3$)	108	110	102
Number of days over 150 $\mu g/M^3$	6	14	38
200 $\mu g/M^3$	1	3	13
260 $\mu g/M^3$	0	0	5

[a] From Air Quality Section, Utah Division of Health

Table 17[a]

Mapleton Data for February 24 to February 26, 1975
and Statistical Comparisons[b]

Date	STP μg/M^3	Actual μg/M^3
February 24	---	---
25	123	111
26	98	89

	TM	YD	RY
Geometric mean (μg/M^3)	38	49	51
Geometric Standard Deviation	1.79	1.96	1.93
Geometric Mean Actual Temp. and Press. (μg/M^3)	35	45	45
Maximum 24-hr. average (μg/M^3)	123	154	490
Arithmetic mean (μg/M^3)	45	60	63
Number of days over 150 μg/M^3	0	2	9
200 μg/M^3	0	0	4
260 μg/M^3	0	0	2

[a] From Air Quality Section, Utah Division of Health

[b] The State has no monitoring station in Springville and this station is the closest to the Springville location.

Table 18[a]

Lindon Data for March 3 to March 5, 1975 and Statistical Comparisons

Date	STP $\mu g/M^3$	Actual $\mu g/M^3$
March 3	66	58
4	82	73
5	70	61

	TM	YD	RY
Geometric mean ($\mu g/M^3$)	40	64	75
Geometric Standard Deviation	1.75	2.23	1.89
Geometric Mean Actual Temp. and Press. ($\mu g/M^3$)	36	58	66
Maximum 24-hr. average ($\mu g/M^3$)	91	359	566
Arithmetic mean ($\mu g/M^3$)	46	88	91
Number of days over 150 $\mu g/M^3$	0	12	26
200 $\mu g/M^3$	0	8	13
260 $\mu g/M^3$	0	3	7

[a] From Air Quality Section, Utah Division of Health

Table 19[a]

Pleasant Grove Data for March 18 to March 20, 1975 and Comparisons with Data for the Month with Previous Data for Running Year

Date	STP $\mu g/M^3$	Actual $\mu g/M^3$
March 18	11	10
19	71	62
20	--	--

	TM	YD	RY
Geometric mean ($\mu g/M^3$)	34	62	68
Geometric Standard Deviation	1.88	2.40	1.96
Geometric Mean Actual Temp. and Pressure ($\mu g/M^3$)	31	57	60
Maximum 24-hour average ($\mu g/M^3$)	90	859	859
Arithmetic mean ($\mu g/M^3$)	41	94	86
No. days over 150 μg/cm.	0	15	25
200 μg/cm.	0	8	11
260 μg/cm.	0	3	6

[a] From Air Quality Section, Utah Division of Health

No data are available from the Air Quality Section, Utah Division of Health concerning particulate levels in Cedar Fort or comparisons for the running year, etc.

Table 20[a,b]

Provo Wind Data for Sampling Period from Monday, February 17 at 2:28 p.m. to Wednesday, February 19 at 2:33 p.m.

	Monday		Tuesday		Wednesday	
Hours	azimuth	wind speed	azimuth	wind speed	azimuth	wind speed
0-1			220	2	330	3
1-2			10	2	290	4
2-3			360	3	270	3
3-4			310	3	280	2
4-5			210	2	200	2
5-6			210	2	290	2
6-7			200	2	290	3
7-8			230	1	270	3
8-9			340	1	340	2
9-10			200	4	20	2
10-11			170	3	280	2
11-12			250	4	310	3
12-13			250	6	70	3
13-14			270	7	130	4
14-15	310	12	290	7	180	4
15-16	290	13	300	6		
16-17	290	13	300	6		
17-18	300	12	290	4		
18-19	300	11	280	3		
19-20	310	7	100	2		
20-21	310	4	250	2		
21-22	270	3	170	3		
22-23	270	3	160	3		
23-24	230	2	320	2		

[a] From Air Quality Section, Utah Division of Health.

[b] Wind speed given in miles per hour and azimuth in degrees (0 is north and 90 is east, etc.)

Table 21[a,b]

Mapleton Wind Data for Sampling Period from Monday, February 24 at 3:10 p.m. to Wednesday, February 26 at 3:10 p.m.

	Monday		Tuesday		Wednesday	
Hours	azimuth	wind speed	azimuth	wind speed	azimuth	wind speed
0-1			203	1		
1-2			45	3		
2-3			158	2		
3-4			135	1		
4-5			45	2		
5-6			113	1		
6-7			68	1		
7-8			45	2		
8-9			158	1		
9-10			158	2		
10-11			180	2		
11-12			293	1		
12-13			No data available for rest of sampling period.			
13-14	180	3				
14-15	158	4				
15-16	180	2				
16-17	180	3				
17-18	158	2				
18-19	270	1				
19-20	90	3				
20-21	180	2				
21-22	90	2				
22-23	180	1				
23-24	338	3				

[a] From Air Quality Section, Utah Division of Health.

[b] Wind speed given in miles per hour and azimuth in degrees (0 is north and 90 is east, etc.)

Table 22[a,b]

Lindon Wind Data for Sampling Period from Monday, March 3 at 3:30 p.m. to Wednesday, March 5 at 3:30 p.m.

Hours	Monday azimuth	 wind speed	Tuesday azimuth	 wind speed	Wednesday azimuth	 wind speed
0-1			-	0	90	5
1-2			-	0	90	5
2-3			-	0	90	3
3-4			90	3	90	4
4-5			-	0	68	3
5-6			225	1	68	2
6-7			68	2	68	3
7-8			23	1	68	2
8-9			225	1	270	1
9-10			315	2	248	1
10-11			248	1	113	3
11-12			293	1	113	7
12-13			135	2	113	6
13-14			225	1	203	5
14-15	225	6	203	1	90	3
15-16	270	7	135	3		
16-17	270	8	90	1		
17-18	270	4	113	4		
18-19	225	5	68	1		
19-20	23	1	68	3		
20-21	68	1	68	5		
21-22	113	1	68	5		
22-23	90	2	293	2		
23-24	113	4	45	2		

[a] From Air Quality Section, Utah Division of Health.

[b] Wind speed given in miles per hour and azimuth in degrees (0 is north and 90 is east, etc.)

Table 23[a,b]

Pleasant Grove Wind Data for Sampling Period from Tuesday, March 18 at 2:42 p.m. to Thursday, March 20 at 2:30 p.m.

Hours	Tuesday		Wednesday		Thursday	
	azimuth	wind speed	azimuth	wind speed	azimuth	wind speed
0-1			113	5	113	9
1-2			90	8	113	8
2-3			90	7	90	5
3-4			90	6	135	3
4-5			68	6	90	4
5-6			90	6	90	7
6-7			90	5	113	7
7-8			90	4	113	7
8-9			135	3	113	6
9-10			113	3	113	6
10-11			135	6	113	4
11-12			135	5	135	4
12-13			135	5	100	6
13-14			135	6	203	6
14-15	135	7	180	7	113	7
15-16	158	8	158	8		
16-17	158	6	130	7		
17-18	135	8	203	7		
18-19	113	7	180	7		
19-20	90	8	203	6		
20-21	90	8	135	8		
21-22	90	8	180	11		
22-23	90	8	158	8		
23-24	113	5	135	7		

[a] From Air Quality Section, Utah Division of Health.

[b] Wind speed given in miles per hour and azimuth in degrees (0 is north and 90 is east, etc.)

Table 24[a,b]

Lehi Wind Data for Sampling Period from Monday, April 21 at 2:18 p.m. to Wednesday, April 23 at 1:34 p.m.

Hours	Monday		Tuesday		Wednesday	
	azimuth	wind speed	azimuth	wind speed	azimuth	wind speed
0-1			68	1	0	3
1-2			338	4	135	2
2-3			315	3	68	4
3-4			315	9	23	5
4-5			338	7	90	1
5-6			0	4	23	1
6-7			45	4	68	2
7-8			45	3	68	1
8-9			90	2	45	1
9-10			135	5	135	5
10-11			113	6	180	6
11-12			203	5	180	4
12-13			135	8	315	6
13-14			0	12	338	16
14-15	180	9	338	13		
15-16	158	13	338	13		
16-17	158	12	23	13		
17-18	158	8	23	10		
18-19	180	3	23	13		
19-20	0	2	0	11		
20-21	45	4	0	7		
21-22	338	6	293	12		
22-23	0	5	68	7		
23-24	68	1	135	3		

[a] From Air Quality Section, Utah Division of Health

[b] Wind speed given in miles per hour and azimuth in degrees (0 is north and 90 is east, etc.)

APPENDIX C

Appendix C contains the particulate weight on each stage of the Andersen Sampler for all sampling locations.

Table 25

Particulate Weights for all Sampling Stations

Location	Stage	Weight Milligrams
Provo	1	61.43
	2	20.26
	3	12.07
	4	10.38
	5	30.92
Springville	1	96.85
	2	32.02
	3	19.24
	4	24.18
	5	79.69
Lindon	1	51.14
	2	19.98
	3	11.26
	4	8.01
	5	23.98

Table 25--Continued

Location	Stage	Weight Milligrams
Pleasant Grove	1	32.35
	2	18.64
	3	12.10
	4	8.14
	5	18.86
Cedar Fort	1	33.10
	2	20.54
	3	13.11
	4	11.35
	5	24.63

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CALORIMETRIC DETERMINATION OF THE INTERACTION OF CU, FE, AND V OXIDES WITH SO_2 AND MEASUREMENT OF SULFUR (IV) AND SULFUR (VI) IN PARTICULATE SAMPLES FROM UTAH VALLEY

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ABSTRACT

The adsorption of SO_2 by metal oxides suspended in decane were studied by calorimetric titration. The adsorption per surface area decreases in order $CuO > Cu_2O > Fe_2O_3 > V_2O_5$. An Andersen High Volume sampler was used to obtain particulate samples from five sites in Utah County. Particulate sulfur (IV) and sulfur (VI) was analyzed by thermometric titration with $K_2Cr_2O_7$ and by a direct injection enthalpimetric determination using $BaCl_2$. Results show that little oxidation of the S(IV) occurs after it is released from the Kennecott smelter stack.