ANALYTICAL REAGENTS AND ADSORBENTS FOR SULFUR DIOXIDE

by

LARRY D. VAN ARENDONK

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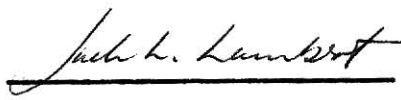
Approved by:



Major Professor

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CHAPTER I

INTRODUCTION

The emission of sulfur dioxide into the atmosphere has become of great concern in recent years, and undoubtedly will continue to be a serious problem for the foreseeable future. The increased reliance on coal as a major source of energy will place even more importance on the monitoring and control of SO_2 concentrations in the atmosphere. Harmful effects of SO_2 include irritation of the respiratory system at 1-5 ppm, chronic plant injury at concentrations as low as 0.03 ppm, and acceleration of metal corrosion rates.[1]

A multitude of continuous-monitoring commercial instruments for ambient SO_2 are currently available. The principles employed include conductivity, coulometry, colorimetry, flame photometry, non-dispersive IR, and condensation nuclei.[2,3] Generally these instruments are expensive and lack the portability desired for use in ambient monitoring.

Manual periodic sampling methods most commonly used for the determination of SO_2 include the hydrogen peroxide method, the conductometric method, and the fuchsin-formaldehyde technique and its West-Gaeke modification.[2,4] Each of these methods involve bubbling air through solution bottles which are subsequently analyzed by wet chemistry in the laboratory. Although these methods feature a relatively small initial capital outlay, the laboratory analysis is time-consuming and subject to errors caused by impure reagents, etc.

Very few solid phase reagents have been developed for the determination of SO_2. Probably the most well-known method involving a solid reagent is the Stratman method in which SO_2 is adsorbed on silica gel. Subsequent

analysis is accomplished by reduction to H_2S which forms a blue complex with ammonium molybdate. A platinum catalyst and high temperatures (700-900 °C.) are required in the reduction step. Other materials which have received attention as total adsorbents include molecular sieves,[5] zeolites,[6] activated charcoal,[7] manganese dioxide,[8] limestone,[8] alumina,[9] Cu/CuO,[9] PbO_2 (lead candle method)[10] and ion exchange resins.[11] The use of such adsorbents to determine the concentration of SO_2 is limited by their poor desorption properties.

Several methods for the analysis or collection of SO_2 have been studied. A brief investigation of a piezoelectric quartz crystal sensor is described. Two compounds found by Hamlin[12] to react reversibly with SO_2 were studied as adsorbents on the crystal surface. Other coatings were also examined. A brief study of the decolorizing action of SO_2 on triphenylmethane dyes adsorbed on alumina was also made. An examination of the adsorption and desorption properties of various compounds coated on inert porous glass was undertaken. Finally, a detailed examination of the adsorption-desorption properties of a porous glass containing chemically attached amine groups was made. Effects of sample storage time, storage atmosphere, and common atmospheric pollutant gases were included.

CHAPTER II

DETECTION OF SO_2 WITH A PIEZOELECTRIC CRYSTAL

Piezoelectric quartz crystals have been shown to be very sensitive sensors in air pollution analysis. The pioneering work by Sauerbrey[13,14] on the theoretical aspects and the work by King[15] on the practical applications of the vibrating quartz crystal as a mass detector have led to the further study of this device. The basic principle behind the use of the crystal detector is that an increase in mass on the surface of the crystal will result in a decrease in the resonant frequency of the oscillating crystal. For the common AT-cut crystal, the equations derived by Sauerbrey[13] for the sensitivity of a crystal detector reduce to:

$$\Delta F = -2.3 \times 10^6 F^2 \times \frac{\Delta W}{A}$$

where ΔF = change in frequency, Hz
ΔW = mass added to the surface of the crystal, grams
F = frequency of the crystal, MHz
A = area of the electrode, cm^2

The use of the piezoelectric detector in air pollution monitoring depends on the adsorption of the pollutant gas in question onto a coating which has been placed on the surface of the crystal. Obviously, this substrate coating should adsorb the desired gas while being only minimally reactive toward other gases which may be present. Additionally, the coating must be stable and relatively non-volatile. These requirements have proven to be very difficult problems which must be solved before general use can be made of this detector.

Recent workers in the field have used a variety of materials as substrate coatings. Frechette, et al.[16,17] have investigated a number of

possible coatings for SO_2 adsorption, and found several possibilities, the most promising of which is a styrene-dimethylaminopropyl maleimide 1:1 copolymer. Guibault and Lopez-Roman[18] have studied the use of sodium tetrachloromercuriate as a substrate coating; Guibault and Karmarkar[19] have studied the use of triethanolamine. Cheney and Homolya[20] also investigated triethanolamine, extending the study to temperature effects. All of the investigations except the latter used a piezoelectric detector in a static system--a small quantity of SO_2 was injected into a closed system and the resulting frequency changes were monitored. It was felt, however, that a dynamic system in which an air stream containing SO_2 is continually moving past the crystal would be more applicable for actual use in the determination of pollutant concentrations.

As mentioned in the Introduction, Hamlin[12] has found a class of compounds not previously known to be reactive with sulfur dioxide. The parent compound is the 2,5-dimercapto-1,3,4-thiadiazole anion (Bismuthiol I), which can be used as the dipotassium salt, or 3-substituted anions such as 5-mercapto-3-phenyl-1,3,4-thiadiazole-2-thione anion (Bismuththiol II). These compounds were found to react specifically with SO_2 to form a deep yellow compound of unknown structure. The reaction appeared to be reversible in that if the SO_2 source was removed, the color returned to the original very light yellow. Hence it was considered feasible to use these compounds as substrate coatings in a piezoelectric detector.

A diagram of the dilution system used is shown in Figure 1. The entire apparatus was constructed from Pyrex glass with Teflon joints except for the air-only lines between the air inlet and the permeation tube which were tygon or polyethelene tubing. Incoming dilution air was

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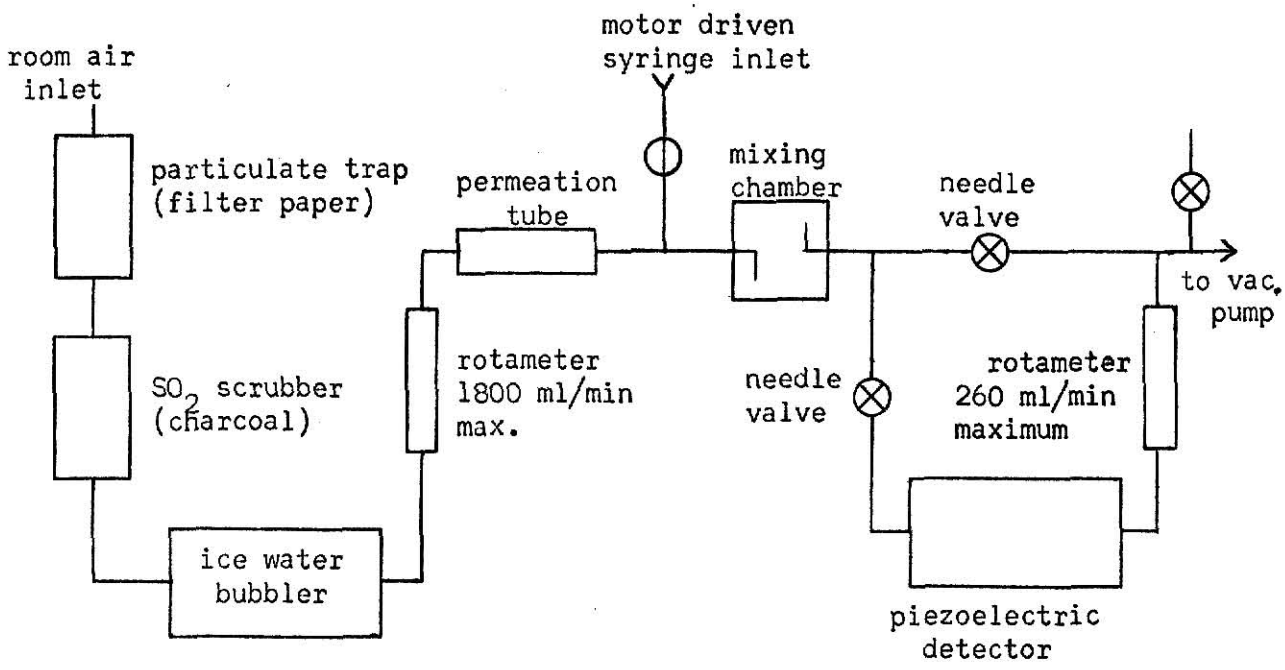


Figure 1. Gas Dilution System

dehumidified with an ice water bubbler, as shown. Two methods of sulfur dioxide introduction were possible: 1) A National Bureau of Standards Certified permeation tube was generally used to produce relatively low concentrations of SO_2 (0.1-2.0 ppm), or 2) A motor driven syringe, filled with either pure SO_2 or a mixture with air, was used for higher SO_2 concentrations. Since the permeation rate from a permeation tube is highly temperature dependent, it was held at a constant temperature by a water jacket through which water from a temperature stabilized water bath was circulated.

The piezoelectric detector consisted of two crystal-controlled oscillators each producing an output frequency of approximately 10 MHz. These two signals were then heterodyned to produce a difference frequency which was monitored with a digital frequency meter as illustrated in Figure 2. Using this method one can eliminate or at least reduce output

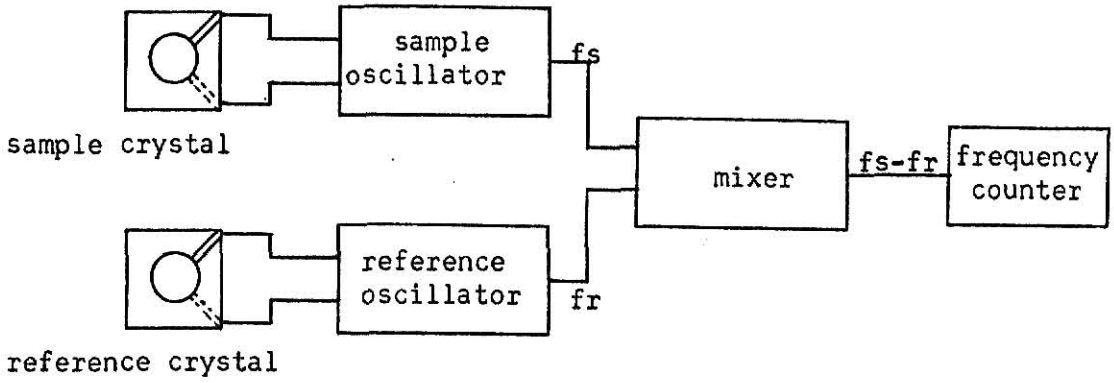
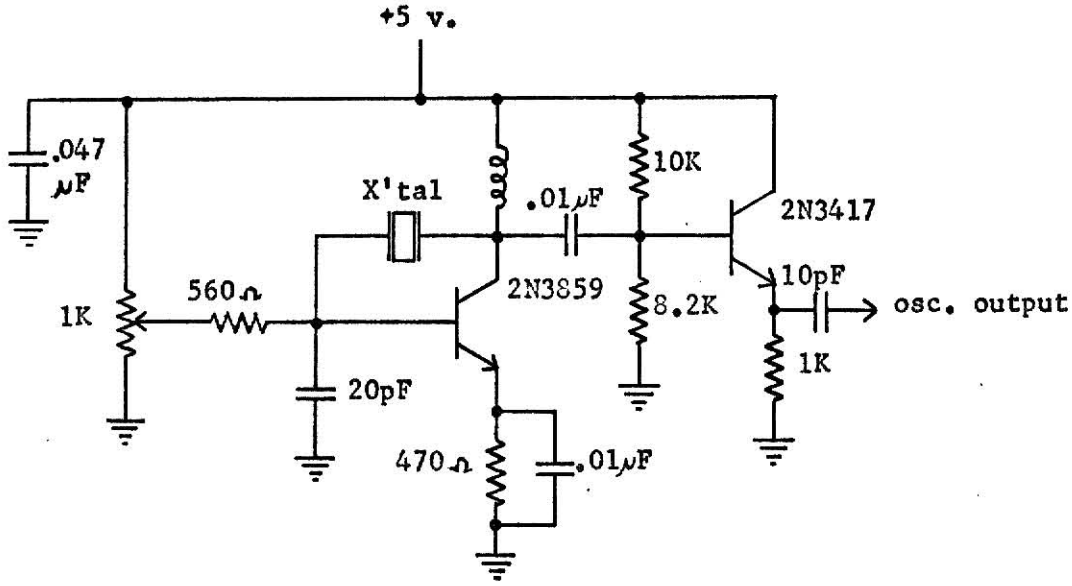


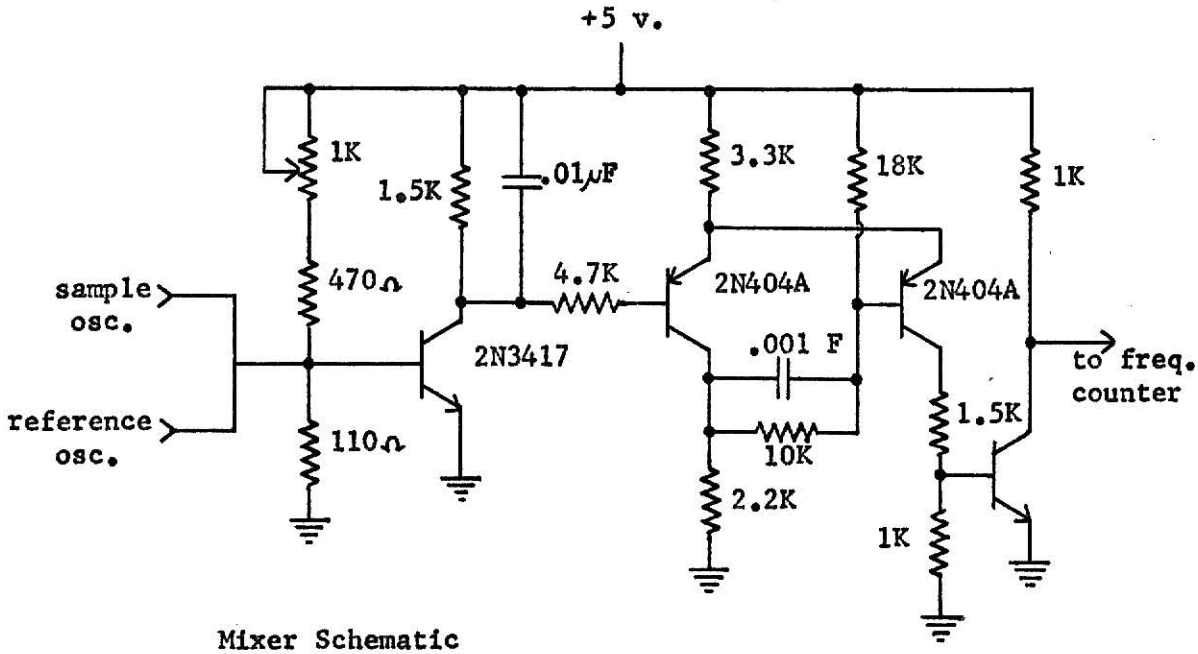
Figure 2. Piezoelectric Detector Block Diagram

frequency variations caused by power supply voltage changes, temperature effects, etc. (AT-cut crystals are characterized by a very small temperature coefficient, however). The crystals used were 10.0000 MHz crystals measuring 0.500 inch square with 0.250 inch diameter gold plate electrodes, as obtained from Piezo Crystal Co., Carisle, Pa. Each crystal was mounted on the end of a Teflon block which was machined to fit inside a female 29/42 ground glass joint. Two small holes were bored through the Teflon blocks through which the leads for the crystal holder were passed, which were then soldered to a printed circuit board. The air stream entered the crystal chambers via small glass tubes on opposite sides of a dome on the end of each 29/42 joint.

Schematic diagrams of the oscillator and mixer circuitry are given in Figure 3. Each oscillator was constructed on a separate printed circuit board, as was the mixer. The frequency counter used was constructed in our lab and was capable of counting and displaying frequencies of at least 10 MHz (up to 25 MHz with the use of the internal X10 or X100 prescaler). The time base was derived from an internal crystal oscillator controlled by a 100 KHz frequency standard crystal. Time base selections were 0.01, 0.1, 1.0, and 10.0 seconds.



Oscillator Schematic



Mixer Schematic

Figure 3. Piezoelectric Detector Circuitry

The substrate coating material was dissolved in a suitable solveht, and the solution thus obtained was applied to the entire electrode surface dropwise with an eyedropper, allowing time between successive drops for the solvent to evaporate, or by means of a 10 μl syringe.

Only limited results were obtained with the 2,5-dimercapto-1,3,4-thiadiazole dipotassium salt. The response observed for concentrations on the order of 1 ppm SO_2 was generally small (only a few Hz change in frequency) and was buried in the frequency drift of the oscillators. A strong response was obtained with a high concentration of SO_2--8 KHz frequency shift when the crystals were exposed to 100% SO_2 from a lecture sphere.

A poor response was also found for the 5-mercapto-3-phenyl-1,3,4-thiadiazole-2-thione monopotassium salt. Although the sensitivity of the crystal being used was 725-750 Hz/μg (frequency shifts of 1446 Hz for 2 μg, 3805 Hz for 5 μg of the potassium salt substrate placed on the electrode surface), virtually no response could be obtained with 200 ppm SO_2.

A check was made on visual response of the mono- and di-potassium salts on anionotropic alumina. The color of each changed from a light pale yellow in the absence of SO_2 to a dark yellow in the presence of pure SO_2. When a mixture of 0.55% SO_2 in air (V/V) was passed over the alumina samples, a very faint darkening was just detectable. When the salts were coated on a filter paper, however, only a faint color change was observed for even pure SO_2. This indicates that perhaps the adsorption sites in the alumina are playing an active role in the adsorption of SO_2 and perhaps the salts are merely indicators for the presence of SO_2 in these sites. In any event, these compounds are apparently too unreactive toward SO_2 to be used as quartz crystal coatings in a piezoelectric detector.

Triethanolamine was also examined as a possible substrate coating. A solution of 0.112 g triethanolamine in 100 ml water was made. Using a 10 μl syringe, 5 μl of this solution was carefully placed on the electrode surface of the sample crystal and allowed to air dry. The beat frequency changed by 7460 Hz when the 5.6 μg amine coating was applied, indicating an apparent sensitivity of 1332 Hz/μg. However it should be noted that since triethanolamine is hygroscopic, there would also be an increase in weight due to the water present, and hence a much lower actual sensitivity.

Sulfur dioxide dilution was accomplished with the motor driven syringe at a rate of 0.194 ml/min into an air stream of 825 ml/min to produce an SO_2 concentration of 235 ppm. The flow rate through the crystal chambers was 74 ml/min. When the SO_2 was switched on, the beat frequency increased rapidly--from 19550 Hz to 20344 Hz in 1 minute time, after which it increased at a nearly linear rate. When the SO_2 was switched off, the frequency decreased rapidly at first, then more and more slowly. This sequence was repeated several times as shown in Figure 4. This was repeated for an SO_2 concentration of 121 ppm (syringe flow rate of 0.097 ml/min), as is shown in Figure 5.

The piezoelectric crystal was also coated with an identical amount of tris(hydroxymethyl)aminomethane, commonly known as THAM. Figure 6 shows the resulting adsorption curve for an SO_2 concentration of 456 ppm. It is apparent that the response time to equilibrium is quite large (>22 minutes for a concentration of 456 ppm at a flow rate of 74 ml/min). None of the runs were permitted to proceed to the equilibrium point since it was felt that substrate materials exhibiting such a marked affinity for SO_2 would be of little value in determining the SO_2 concentration in a dynamic system.

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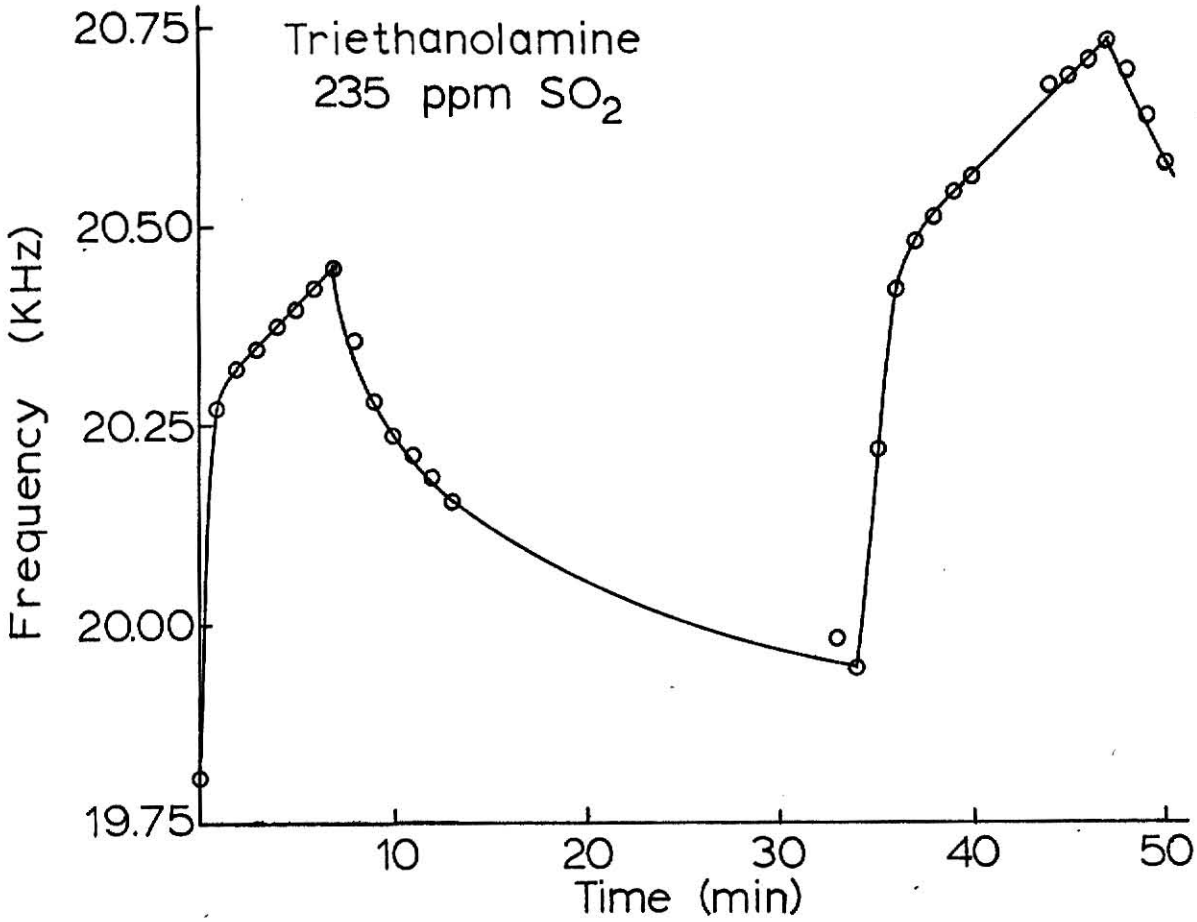


Figure 4. Response to 235 ppm SO_2 With a Triethanolamine Substrate

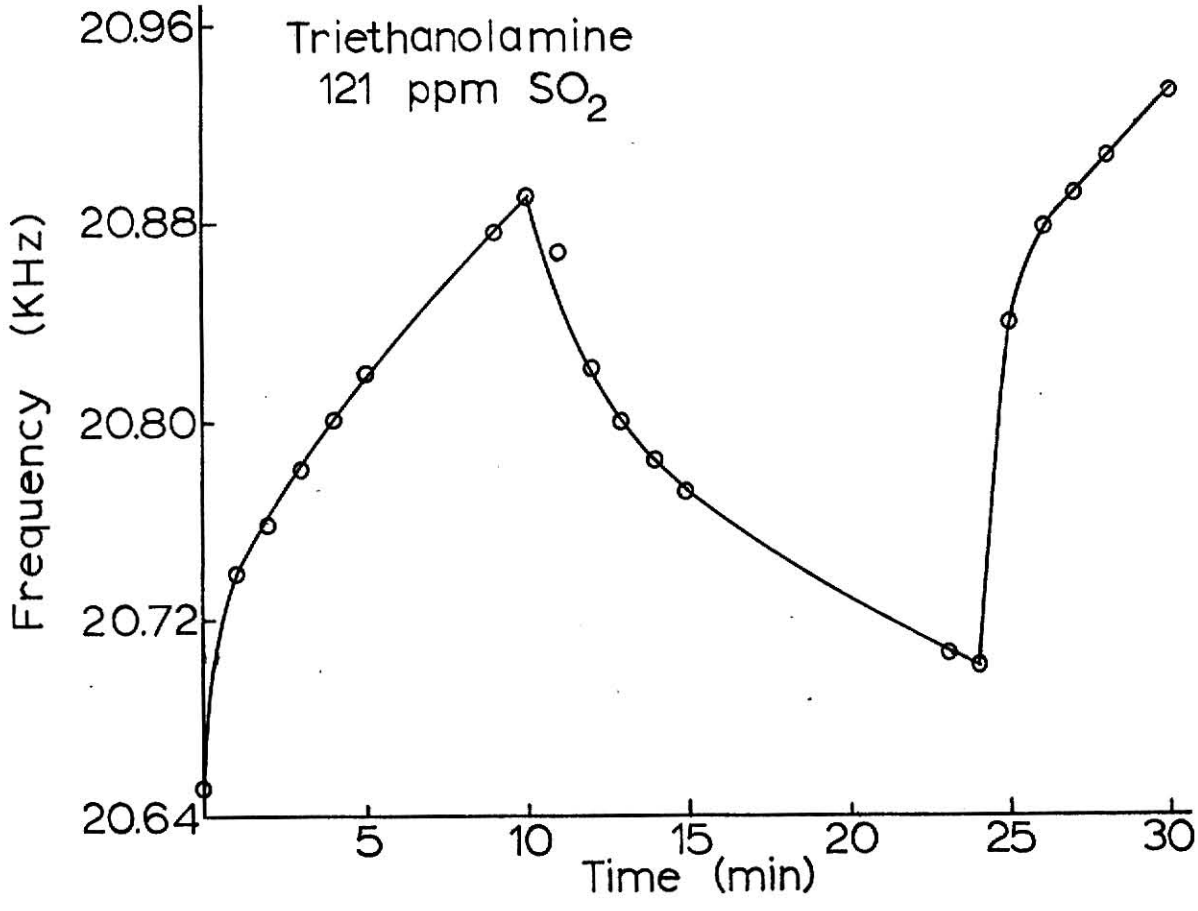


Figure 5. Response to 121 ppm SO_2 With a Triethanolamine Substrate

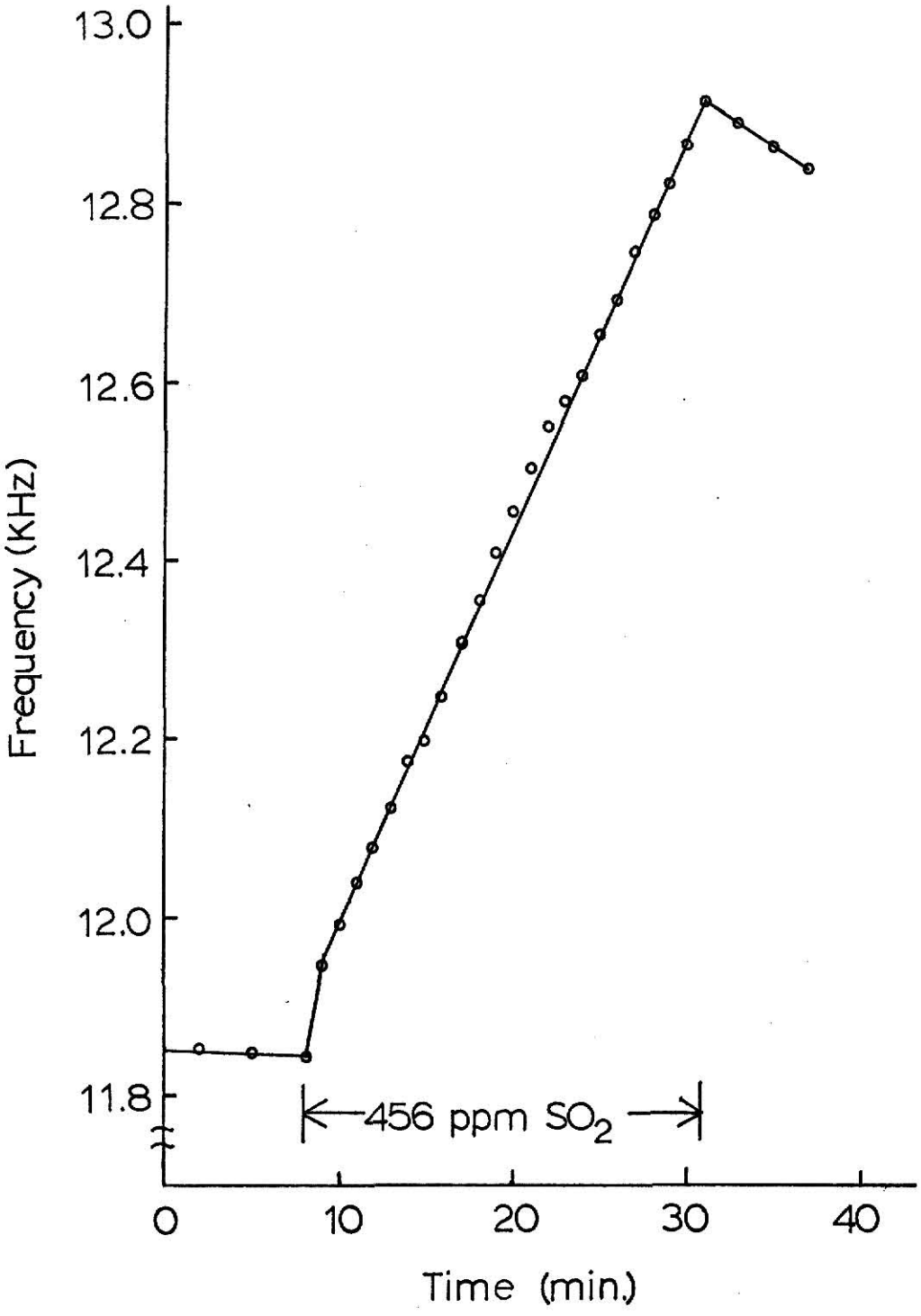


Figure 6. Response to 456 ppm SO_2 With a THAM Substrate

The reason for the rapid increase in frequency when the SO_2 was started is uncertain. It is thought to have arisen from a sudden equalization of pressures in the motor driven syringe and the dilution system (which is somewhat reduced from atmospheric pressure due to the air drag of the ice water bubbler, etc.; P≈630 torr), which allowed a "slug" of SO_2 to enter the crystal chambers. In addition, it is likely that the substrate surface was relatively free of SO_2 when the valve was initially opened, allowing a more rapid adsorption.

It is interesting to note that although these amines appear unsuitable for use in determining the concentration of SO_2 in a dynamic system by observing the equilibrium frequency, the slope of the change in frequency vs. time yields a value closely proportional to the SO_2 concentration. This would be expected to be the case for any substrate coating which exhibits a large adsorption power for SO_2, with only limited desorption potential. No references could be found in the literature in which this technique was investigated. Results for our limited amount of work in this area are shown below:

substrate	SO_2 conc.	$\frac{\Delta F}{\text{time}}$, Hz min^{-1}	$\frac{\text{slope}}{\text{conc}}$, Hz min^{-1} ppm^{-1}
TEA	121 ppm	14.3	0.118
TEA	235 ppm	24.75	0.105
THAM	456 ppm	43.64	0.096

The slight decrease in expected slope for higher concentrations may be caused by diffusion limitations of the SO_2 through the layer of amine molecules, and for the 456 ppm run, it could be due to different characteristics of the new substrate coating. Although these data appear promising, no additional investigations of this method were carried out.

CHAPTER III

RESPONSE OF SOME TRIPHENYLMETHANE DYES TO SULFUR DIOXIDE

Previous workers in this laboratory have observed that the dyes Crystal Violet and Brilliant Green, when adsorbed on alumina, exhibit a color change in response to SO_2.[21,22] The color change with the Brilliant Green dye was relatively permanent while that with Crystal Violet was reversible in a short time (<1 minute). A study was therefore made of other dyes with similar structures in the hope that they could be used as a visual indicator for sulfur dioxide.

One percent water solutions of each of the dyes in Table 1 were made. Each dye was then applied to Woelm Activity Grade I cationotropic alumina according to the following procedure: The alumina was first washed three times with distilled water to remove some of the fine particles. A small amount of the wet alumina was then placed in a No. 3 casserole. An excess of dye solution was then poured over the alumina. After swirling for about 5 minutes, the dye solution was poured off and the alumina was washed three times with 25 ml distilled water. Most of the dyes continued to leach off the alumina. The sample was divided into two parts: one was dried at room temperature on the lab bench and the other in a vacuum oven at 80° C. Each sample was then exposed to 100% SO_2 from a Lif-O-Gen Chemisphere. No differences were noted in the results for the different drying methods. The results are tabulated in Table 1. All indicated color changes appeared to be permanent, except for that of Crystal Violet.

Brilliant Green was also adsorbed on silica gel (Woelm, 0.05-0.20 mm), porous glass beads, and filter paper. No visual response was detectable for any of these materials when subjected to 100% sulfur dioxide. Therefore

Table 1. Response Of Dyes On Alumina To SO_2

dye	color change*
Crystal Violet	violet ⟶ white
Guinea Green B (C.I. 42085)	light blue-green ⟶ white
Light Green SF Yellowish (C.I. 42095)	light blue-green ⟶ N.C.
Fast Green FCF (C.I. 42054)	blue ⟶ green
Brilliant Blue FCF (FD&C Blue #1)	blue ⟶ N.C.
Brilliant Green (C.I. 42040)	blue-green ⟶ white
Malachite Green (C.I. 42000)	green ⟶ white
Patent Blue A (C.I. 42080)	blue ⟶ N.C.
Patent Blue VF (C.I. 42045)	blue ⟶ N.C.
Victoria Blue B (C.I. 44045)	blue ⟶ N.C.
Victoria Blue R (C.I. 44040)	purple ⟶ N.C.

* N.C. = no change

it is apparent that the alumina support is necessary for the color change to occur, although its role is not understood.

The most promising dyes appeared to be Brilliant Green and Malachite Green. Attempts were made to reduce the leaching of the dyes from the alumina during washing by the use of ion association compounds[23] in which three layers of dye were used as diagrammed below (the first and third layer being the same dye):

where + = Brilliant Green or Malachite Green
- = Fast Red S, Orange II, or Buffalo Black

Each of the above six combinations of dyes were tried on each of the following types of alumina:

cationotropic	anionotropic
Woelm Activity Grade I	Woelm Activity Grade I
Woelm Activity Grade Super I	Woelm Activity Grade Super I
Matheson, Coleman, & Bell, Type F-1	Matheson, Coleman, & Bell, Type H-151

The samples were made using the method described above. After drying at room temperature on the lab bench, the samples were placed in 1 dram vials for later analysis. The samples were all black in color. It was discovered that many of the samples (all those on the cationotropic aluminas and over half of those on the anionotropic aluminas) changed color after several days even without exposure to SO_2 (except that which was present in the room air during drying). The final colors were typically red (Fast Red S), orange (Orange II), or bluish-black (Buffalo Black).

An attempt was made to determine if the color changes described above were caused by SO_2 (or other gases) present in the lab atmosphere or if they were caused by light. A new sample was made by placing Brilliant Green, then Fast Red S, then another layer of Brilliant Green on cationotropic alumina (Woelm Activity Grade I). The wet sample was immediately divided into three parts, each in a separate casserole:

A. allowed to stand uncovered on a lab bench
B. placed in the dark in a lab drawer
C. placed in a dessicator with $CaCl_2$ as a drying agent and activated cocoanut charcoal to remove any SO_2 present

The results obtained are as follows:

	after 1 day	after 3 days
A.	starting to turn slightly red	red
B.	black	red
C.	black	black

Decreased air circulation over the sample in the lab drawer could have caused the slower change in color of sample B. Since sample C did not change color in the absence of SO_2 and water, it was split into two parts:

C_1. placed in a dessicator containing $CaCl_2$; 0.9 μl SO_2 added to make a dry atmosphere containing SO_2

C_2. placed in a dessicator containing activated charcoal; also present was a small beaker of water to ensure a humid SO_2-free atmosphere

Three days later sample C_1 was still black while sample C_2 had changed to red. Three weeks later the sample in the dry dessicator was still black. Thus it is seen that the SO_2 is not necessary for the color change to occur. Therefore further studies of the dyes were discontinued.

CHAPTER IV

SOLID PHASE ADSORBENTS FOR SULFUR DIOXIDE

The research described in this and the subsequent chapter deals with the development and testing of solid phase adsorbents that will quantitatively trap SO_2 in concentrations normally encountered in the environment and which will quantitatively release it by gentle heating. The released SO_2 can then be easily determined by any of the instrumental or manual methods currently in use. The present chapter deals with adsorbents made by coating various aldehydes, dienes, and amines on porous glass beads. Tests with various polymers are also described. Chapter V describes adsorbents of amine groups chemically attached to the porous glass support.

Dilute SO_2 concentrations were generated with the dilution apparatus shown in the Appendix. The SO_2 source in all runs was a sulfur dioxide permeation tube, No. 14-24, obtained from the National Bureau of Standards. Permeation rates as a function of temperature for this tube are given in the Appendix. The permeation tube was maintained at a constant temperature by storing it in a water-jacketed tube between runs. The permeation tube holder in the dilution system was also water-jacketed. Both were fed with water pumped from a constant temperature water bath. Slight temperature variations from the normal 25.0 °C. were accounted for by use of a water bath thermometer reading in the determination of the permeation rate.

Air flow rates were determined with Gilmont gas flowmeters, which were calibrated with a Precision Scientific Model 63115 Wet Test Meter, which had an accuracy of ±½% by volume.

Sulfur dioxide concentrations were monitored with a Meloy Laboratories, Inc. Model SA 185-2 FPD Sulfur Analyzer on loan from the Environmental Protection Agency. This instrument uses a flame photometric detector in which the sulfur species, passing through a hydrogen flame, emits a band of light radiation with a maximum intensity at 394 nm which is monitored with a photomultiplier tube. Since the emission intensity is proportional to a power slightly less than the square of the sulfur concentration, the instrument was equipped with a linearizer option (S-1) to convert to a linear output voltage signal in the range of 0 to 1 volt for a maximum SO_2 concentration of 1.0 ppm. The instrument specifications, as provided by Meloy Laboratories, are given below:

Range	0-1 ppm
Mimimum Detectable Sensitivity	0.005 ppm
Precision	±1% F.S.
Accuracy	±1% F.S.
Zero Drift	±0.01 ppm/day
Span Drift	±0.01 ppm/day
Linearity	±1% F.S.

Other options included in the instrument were a reignition timer circuit (Option S-6A) to provide for automatic relight of the hydrogen flame, a thermoelectric PM tube temperature controller (Option S-9), a "manual calibrate" option (S-11A) which provided a front panel mode toggle switch to select one of three air inlet ports--sample, calibrate, or zero air. In the zero air position, air was drawn through an internal charcoal filter. The calibrate mode position was not used since the instrument was calibrated with the same SO_2 source and the same dilution system as was

used for sample loading. Also included in the instrument was Option S-12 which provided for automatic hydrogen shut-off in the event of either power failure or flame-out.

The output signal from the sulfur analyzer was recorded on a Heath Model EU-20B stripchart recorder. Peak area was integrated with a planimeter.

Adsorbent samples were held in a 5 mm inside diameter Pyrex glass tube approximately 18 cm in length, which was placed in a micro tube furnace (Arthur H. Thomas catalog no. 5304-B10). Small indentations were made on opposite sides of the glass tube approximately 8 cm from one end to provide support for a glass or quartz wool plug which held the sample to be analyzed. It was found that the Pyrex wool plug (source and brand unknown) initially examined for use as a plug to support the glass beads, adsorbed and desorbed a small amount of SO_2. At a concentration of 0.6 ppm a small plug (~0.05 g) adsorbed 0.4 μg SO_2 at breakthrough. Several other types of glass wool were examined including one type, also of unknown origin, which adsorbed somewhat less than the first glass. Also examined was another Pyrex wool sample (Corning #3950 Pyrex obtained from Fisher Scientific Co.) which adsorbed somewhat more than the original sample, and a soft glass wool (also from Fisher--Cat. No. 11-390) which adsorbed so much SO_2 as to render it useless for this application. It was found that a plug of quartz wool (obtained from Amersil, Inc.) was ideal in that it adsorbed virtually no SO_2. It was later discovered that Pyrex wool, when treated with dilute HCl followed by washing with acetone and then water, would no longer adsorb SO_2.

Various compounds were to be tested for SO_2 adsorption-desorption properties. Corning Controlled Pore Glass CPG-10-550 was initially used

as an inert support. It is described by the manufacturer as follows:

Pore volume	1.7 ml/g
Particle size	40/60 mesh
Pore diameter	525 ±6% Å
Lot no.	0048

Although this glass itself adsorbed a small amount of SO_2, it was believed to be satisfactory for preliminary qualitative testing.

Each compound listed in Table 2 was dissolved in a suitable solvent (ethanol or acetone). After the compound was completely dissolved, a small amount (~.15 g) of the glass beads was added and the beaker was swirled for a few minutes. The solution was then poured off and the wet glass was dried between two pieces of filter paper. After thorough drying, the sample was subjected to 1.0 ppm SO_2 at a flow rate of 600 ml/min for 2 minutes. If the compound exhibited no SO_2 adsorption properties, it was discarded and no further work was done with it. If the compound adsorbed part or all of the SO_2 load, the tube oven through which the sample tube had been placed was heated to determine if the SO_2 could be driven off. Also, the air flow rate through the sample tube was reduced to the 195-200 ml/min required by the sulfur analyzer in order to provide maximum sensitivity for analysis.

Clearly, only the 2-carboxyhenzaldehyde shows any promise for use as an SO_2 adsorbent. However, its capacity is very low and its melting point (95-98 °C.) is too low to permit complete SO_2 release. Exposure to SO_2 after heating to 90 °C. and cooling showed no adsorption taking place. No further work was done with aldehyde compounds because of the poor adsorption.

Table 2. Adsorption of sulfur dioxide on aldehydes

compound	response to sulfur dioxide
m-nitrobenzaldehyde	only trace adsorbed; no SO_2 released by heating
4-cyanobenzaldehyde	slow rise in effluent conc. while loading (to 0.9 ppm in 2 minutes) and slow fall of effluent conc. when permeation tube was removed (to 0.1 ppm in 3 minutes); no SO_2 released by heating
2-carboxybenzaldehyde	some adsorption; conc. to 0.6 ppm in 2 min; small SO_2 peak obtained when heated, with max. conc. at 87 °C.
1-naphthaldehyde	inconclusive results; however this compound is a lachrymator and irritant so it was not investigated further
2-naphthaldehyde	no adsorption

Table 3. Adsorption of sulfur dioxide on dienes

compound	response to sulfur dioxide
2,4-pentadienoic acid	partial adsorption; poor release on heating*
2,4-hexadienoic acid	partial adsorption; poor release on heating*
2,4-hexadienoic acid NH_4^+ salt‡	complete adsorption; no SO_2 released*
1,4-diphenyl-1,3-butadiene	only slight adsorption; no SO_2 released by heating

‡ formed by passing NH_3 from a lecture bottle through a sample tube containing glass with a coating of the 2,4-hexadienoic acid

* a white cloudy film was observed to collect on the bottom of the sample tube, indicating sublimation of the compound

Sulfur dioxide is known to react with conjugated dienes to yield a 1,4 addition product, a cyclic sulfone, which can decompose to the original reactants on heating.[24] Consequently several diene compounds were coated on controlled pore glass beads and analyzed in the same manner as were the aldehydes. The results are given in Table 3.

As noted in Table 3, the major problem encountered with the dienes was poor SO_2 release, presumably at least partly because of the tendency toward sublimation. Even the 2,4-hexadienoic acid ammonium salt, which had been expected to be much more resistant to sublimation, formed a white layer in the bottom of the sample tube. It is not known whether this was due to decomposition of the salt or merely sublimation.

As noted earlier, the glass support alone exhibited slight adsorption-desorption properties. Although the SO_2 release occurred at quite high temperatures (peak at 240 °C.) so that, once saturated with SO_2, it could be used at lower temperatures without interference, it was felt that a more suitable support should be found. Consequently, porcelain chips were analyzed with the surprising finding that they were not inert toward SO_2. In fact, the porcelain adsorbed and desorbed SO_2 quite well, although the capacity was quite low. Approximately 0.30 g of the porcelain chips were placed in a new sample tube and subjected to 0.95 ppm SO_2 at a flow rate of 430 ml/min for 2 minutes. No SO_2 was detected in the air exiting the sample tube. The sample was then heated slowly to 400 °C. releasing 1.97 μg (95% recovery) of the SO_2 with a peak maximum at 210 °C. A new sample of porcelain chips was then examined for several consecutive runs, as shown in Table 4. It is seen that the capacity of the porcelain is quite small (initially about 7.0 μg SO_2/g) and that the capacity decreases on succeeding runs.

Table 4. SO_2 Adsorption on Porcelain

SO_2 conc. (ppm)	flow rate (ml/min)	SO_2 loaded (μg)	SO_2 recovered (μg)	percent recovery
0.65	550	1.82	1.62	89
0.66	550	2.77	2.59	93
0.66	550	1.86	1.66	89
0.65	550	1.83	1.44	79
0.19	550	1.04	0.80	77
0.62	550	1.90*		
0.60	195	2.60*		

* capacity to breakthrough

Since compounds containing amine groups are also known to adsorb SO_2 (note the triethanolamine and THAM used in the piezoelectric detector), several amine compounds were tested for adsorption-desorption properties. An effort was made to select compounds having a large molecular weight and high melting point to minimize sublimation during heating. The amines listed in Table 5 were coated on the Dow Corning Controlled Pore glass described below, which was used as received from Pierce Chemical Company.

glass code number GZO-7900

pore diameter . . . . . 1350 A°

pore volume . . . . . 1.45 cm^3/g

particle diameter . . . . . 177-840 μm

surface area . . . . . 34 m^3/g

lot no. 2G02

This glass was found to be considerably more inert than the glass used previously. The uncoated glass adsorbed no SO_2 from an air stream. The amines shown in Table 5 were coated on the glass using the technique described for the aldehydes and dienes. Analysis was carried out with an SO_2 concentration of 0.4-0.5 ppm, a flow rate of 550 ml/min, and a 3 minute load time.

The n-octadecylamine sample exhibited complete adsorption and released the SO_2 in a sharp peak at 70-90° with a maximum at 78° C. Recovery was initially rather low (40%), but subsequent runs with the same sample showed better release (80% on the 4th run). The di-N-octalamine and tri-N-octalamine also completely adsorbed the SO_2 load. Sulfur dioxide recovery from the di-N-octalamine was only 13% on the first run but increased to 57% on the second and to 69% on the 6th run. Release from the tri-N-octalamine ranged from 69 to 83%. The pararosaniline sample exhibited a relatively small adsorption capacity for SO_2 (1.3 μg), although it gave a good recovery of 87%. The THAM sample showed complete adsorption for the SO_2 load, but recoveries were a rather low 65-75%. Quinuclidine, prepared by adding NaOH to a quinuclidine hydrochloride solution, followed by extraction into benzene, proved to be extremely volatile.

It is apparent that some of the amines give much better adsorption and release of SO_2 than the dienes and aldehydes previously examined. It appears that primary amines give better results than either secondary or tertiary amines. Of the compounds examined, the only secondary or tertiary amines which adsorbed were the di-N-octalanine, tri-N-octalanine, and triethanolamine. The triethanolamine sample would not readily release the SO_2 (~10% recovery) and the di-N-octalamine SO_2 release exhibited

Table 5. Adsorption of SO_2 on Amines

compound	response to sulfur dioxide
n-octadecylamine	good adsorption; fair recovery
di-N-octalamine	good adsorption; fair recovery with much tailing
tri-N-octalamine	good adsorption; fair recovery
tri-N-hexadecylamine practical grade as received from Pfaltz and Bauer, M.P. 35-52 °C.	good adsorption; fair recovery-2 peaks: sharp peak at 68° and broader peak with maximum at 85 °C.
recrystalized from $CHCl_3$ and EtOH (1:1), M.P. 39-43 °C.	immediate breakthrough with slow rise on loading; slow fall of effluent conc. when the permeation tube was removed; no SO_2 released by heating
1,6-diaminohexane	good adsorption; no SO_2 released by heating (coating melted and collected on bottom of sample tube)
N,N-diethylcyclohexylamine	poor adsorption capacity; SO_2 released at room temperature
diphenylamine	no adsorption
dibenzylamine	poor adsorption; SO_2 released at room temperature
tribenzylamine	poor adsorption; SO_2 released at room temperature
tris(4-aminophenyl)methane (pararosaniline)	good adsorption capacity; fair recovery
EDTA disodium salt	essentially no adsorption
triethanolamine	good adsorption; poor release (note: compound is hygroscopic)
tris(hydroxymethyl)aminomethane (THAM)	good adsorption; fair recovery
quinuclidine hydrochloride	no adsorption
quinuclidine	(too volatile to be of use)
1-adamantanamine	good adsorption; poor release
2-adamantanamine	good adsorption; poor release

extensive tailing, perhaps indicating impurities in the amine. However, the tri-N-octalamine did produce sharp peaks with little tailing. All of the primary amines exhibited good adsorption properties. The 1,6-diaminohexane and the two adamantanamine compounds released only a trace of the SO_2, presumably because of sublimation problems.

The type of reaction between SO_2 and an amine is not understood. One possibility is the formation of a sulfite or bisulfite ion as shown below:

$$R\text{-}NH_2 + H_2O + SO_2 \longrightarrow R\text{-}NH_3^+ HSO_3^-$$

$$2R\text{-}NH_2 + H_2O + SO_2 \longrightarrow (R\text{-}NH_3^+)_2 SO_3^{-2}$$

Theoretically this could be tested by merely excluding the water from the air stream. It would probably be necessary to use a static system for such an analysis, however, because of the difficulty of eliminating microgram quantities of water. Another possible reaction mechanism is the formation of a charge transfer complex in which electrons are presumably transferred from the nitrogen to the sulfur atom.[25] This type of reaction is known to occur between SO_2 and several amine compounds. Examples include p-toluidine[25] and trimethylamine.[26,27,28,29] It also seems plausible that an actual reaction does not occur but the SO_2 is merely held on the surface of the glass, for example, between two amine groups.

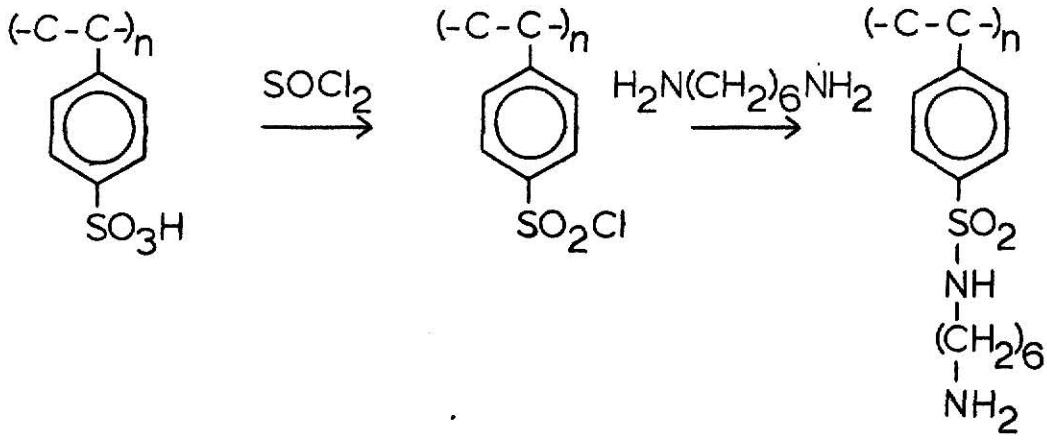
Also examined was a sample of porous glass with propylamine groups chemically attached through silyl bonds. The glass, described in detail in Chapter V, was found to have good adsorption and release properties. Recovery percentages in excess of 90% were routinely obtained, and problems due to sublimation of a coated compound were completely eliminated. Since the alkylamine glasses were investigated quite extensively, the last chapter is devoted entirely to them.

Several polymers containing amine groups were also investigated since these materials would undergo no sublimation. The first one described below was coated on a glass bead support, while the others were used without a support since they were insoluble resinous polymers.

Poly(ethylenimine) was obtained from Aldrich Chemical Co. as a viscous 30% solution in water. Approximately 5 ml distilled water was added to 0.012 g of the 30% solution. After gently heating (40-60 °C.) for 3 hours with stirring to ensure complete dissolution, 0.201 g of the Dow Corning GZO-7900 glass was added. The mixture was then allowed to stand for ~½ hour, after which the solution was poured off and the glass was blotted dry on a filter paper. The glass was then allowed to air dry. Analysis with sulfur dioxide at 0.4 ppm yielded recoveries in the range of 30-40% with no apparent improvement on succeeding runs.

Poor results were also obtained with the other polymers, one of which was Duolite ES-15 aliphatic tertiary amine weak base anion exchanger resin. No SO_2 could be recovered by heating to a temperature of 130 °C.

A strong acid cation exchanger, Rexyn RG 50 (H^+) obtained from Fisher (Cat. No. R-203), was modified by the attachment of an alkylamine group to the sulfonate group. This was accomplished by refluxing the resin (acid form) with thionyl chloride, followed by addition of 1,6-diaminohexane:



The resulting product showed only limited adsorption for SO_2. No SO_2 could be recovered by heating. At temperatures in excess of 100 °C. the resin apparently began to decompose, resulting in a response on the sulfur analyzer even when no SO_2 had been loaded on the sample.

The above reaction was also carried out with PCl_5 instead of $SOCl_2$ in the chlorination step. The product thus obtained showed no affinity for sulfur dioxide.

The same modifications (with $SOCl_2$) were also made on two other sulfonic acid resins--Bio-Rad AG50W-X4 and Dowex 50W-X1. It was hoped that the lower degree of crosslinking with the resulting more porous polymer would permit better entry into the resin. The resins were swelled in $CHCl_3$ prior to modification as above. Both resins adsorbed small amounts of SO_2 but problems with resin decomposition (at temperatures as low as 70 °C. for the X1) resulted in discontinuation of their study.

CHAPTER V

ADSORPTION OF SO_2 ON ALKYLAMINE CONTROLLED PORE GLASS

As briefly discussed in the previous chapter, alkylamine glasses were found to adsorb SO_2 at room temperature and desorb it at 50-100 °C. In this chapter further experiments with both commercial and lab-prepared alkylamine glasses will be described.

The sulfur analyzer and dilution system described in Chapter IV were used in the research to be described. The controlled-pore glass sample (typically 0.05-0.10 g) was supported in a 5 mm inside diameter Pyrex glass sample tube (~18 cm in length) by a small plug of quartz wool. The sample tube was inserted through the cooled tube furnace and was connected into the dilution system by means of a short piece of Tygon tubing. Care was taken to ensure a tight glass to glass butt seal to minimize exposure of the Tygon section to sulfur dioxide.

The sulfur analyzer was calibrated with the permeation tube used as a source of SO_2 for sample loading. Permeation rates for the tubes used in the research described in this chapter are given in the Appendix. A typical analysis procedure is as follows. The air flow through the permeation tube holder was adjusted to produce the desired SO_2 concentration (which depends on the leakage rate of SO_2 from the permeation tube being used). Simultaneously the flow rate through the sample tube was adjusted to a predetermined value (usually 550 ml/min). The permeation tube was then quickly inserted into the water-jacketed holder through the ball-joint on top, and a timer was started. At the end of the desired time interval the permeation tube was removed and the sample flow rate was reduced to 195-200 ml/min as required by the analyzer. This was done merely to

increase the sensitivity in the subsequent desorption process. The valve between the output of the sample tube and the vent to the atmosphere was closed to prevent any SO_2 escape. The sample was then heated by means of the tube furnace which was powered with a Variac. The amount of SO_2 recovered from the sample was determined by integrating the peak area on the stripchart recording with a planimeter.

The two commercial alkylamine glasses, used as received from Pierce Chemical Company, are described by the manufacturer (Dow Corning) as follows:

	Alkylamine/CPG-550	Alkylamine/CPG-1350
pore diameter	550 Å	1350 Å
particle diameter	125-177 μm	177-840 μm
surface area	70 m^2/gram	34 m^2/gram
meq. amine/g	0.1	0.06
lot number	#05144-8	#08204-6

These glasses are the same type glass, except for the alkylamine groups, as those used in the previous chapter as supports for coating with various other materials.

An attempt was made to select either the large pore (1350 Å) or the small pore (550 Å) alkylamine glass to be used in further study. A series of runs was made for each glass as shown in Table 6. No humidity control was used (relative humidity was 40-50%). Each sample was heated for analysis immediately after loading. Sulfur dioxide recovery typically occurred over a temperature range of 40 to 100° C.

The differences in sulfur dioxide recoveries for the two glasses are not great, although the large pore glass gave somewhat more consistent

Table 6. Comparison of Glass Pore Size on SO_2 Recovery

glass pore size (A°)	SO_2 conc. (ppm)	air flow (ml/min)	loading time (min)	SO_2 loaded (μg)	SO_2 recovered (μg)	percent recovery
1350	0.40	550	3	1.67	1.59	96
1350	0.39	550	3	1.66	1.59	96
1350	0.40	550	3	1.69	1.66	98
1350	0.40	550	3	1.69	1.65	98
1350	0.40	550	3	1.68	1.61	96
1350	0.28	430	3	1.55	1.50	97
1350	0.081	550	15	1.70	0.95	56
1350	0.38	600	3	1.75	1.74	99
550	0.40	550	3	1.67	1.56	93
550	0.39	620	3	1.85	1.65	89
550	0.41	550	3	1.72	1.74	101
550	0.40	550	3	1.68	1.60	95
550	0.39	620	3	1.85	1.94	104
550	0.076	550	16	1.71	1.60	94
550	0.067	550	15	1.41	1.08	76

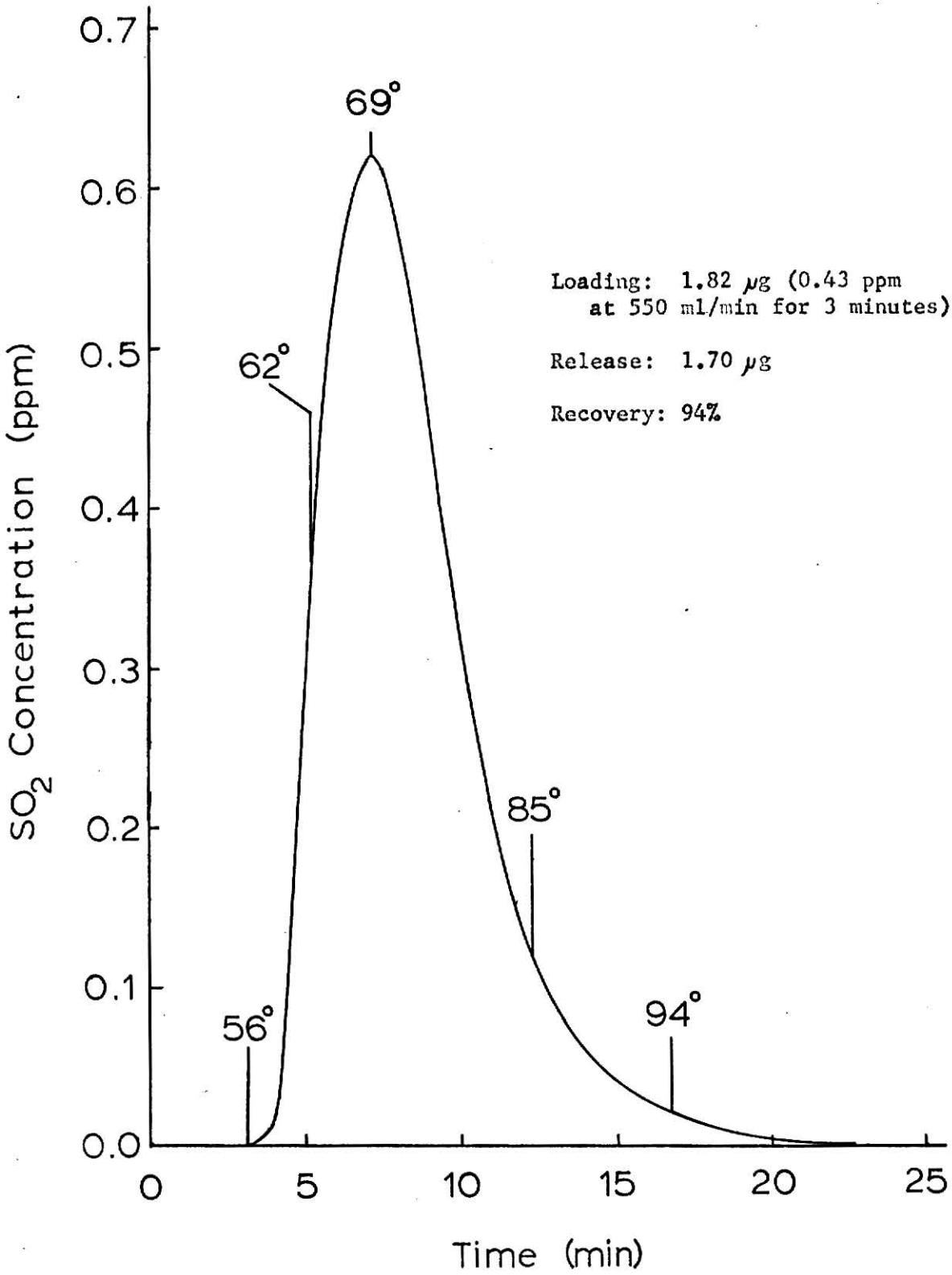


Figure 7. SO_2 Release From Alkylamine/CPG-1350 glass

results. This and the fact that the large pore glass had a larger particle diameter, which would permit less air flow resistance, led to the use of the large pore glass in further studies. A representative SO_2 release curve for this glass is shown in Figure 7.

It should be mentioned that the four zirconium clad (Zir-Clad) glasses (both 550 and 1350 A°, with and without aminopropyl groups, were analyzed. All types strongly adsorbed sulfur dioxide but would not desorb even at temperatures as high as 200 °C.

Studies were made on the effects of relative humidity on the recovery of SO_2 from the large pore propylamine glass. No changes in recovery percentages could be detected when the inlet air was changed from room air (40-50% relative humidity) to air from an ice water bubbler (~19% relative humidity) or to a condenser in dry ice/acetone (~0% relative humidity). Therefore, it can be concluded that control or removal of water would be unnecessary in the collection of SO_2 from ambient air. It should not be assumed, however, that water is not necessary for the adsorption to occur, since even with the dry ice/acetone trap a substantial amount of water is still present compared to the amount of SO_2.

The recovery of SO_2 from the Alkylamine/CPG-1350 glass was also studied with respect to SO_2 loading concentrations. The results obtained are shown in Table 7. Good recoveries were obtained for concentrations above 46 ppb, while lower concentrations gave somewhat lower recoveries. No explanation is given for this behavior. Additional study is needed at even lower concentrations than those listed in Table 7 if this sample collection method is to be used in ambient air having such concentrations. Lower concentration studies were not made because this would have necessitated re-design of the dilution system.

Table 7. Effect of SO_2 Concentration on SO_2 Recovery

SO_2 conc. (ppm)	air flow (ml/min)	loading time (min)	SO_2 loaded (μg)	SO_2 recovered (μg)	percent recovery
0.027	550	52.6	2.01	1.58	79
0.046	550	30.0	1.95	1.87	96
0.118	550	11.9	1.97	1.78	91
0.194	550	7.3	1.98	1.83	93
0.282	430	5.0	1.55	1.50	97
0.478	550	3.0	2.02	1.96	97

Tests were made on the SO_2 losses during storage since it could sometimes be necessary to store the samples for several days before analysis in actual use of this method. In each of the runs shown in Table 8 (Part A) approximately 0.07 g Alkylamine/CPG-1350 glass was used. Approximately 1.7 μg SO_2 was loaded onto the sample at a concentration of 0.4 ppm. The sample tube was then removed from the dilution system and, for the room air storage runs, it was stoppered and stored on a lab bench. The results indicate a recovery of only about 50% for 1 week of storage. Because of these low results, other storage atmospheres were examined. For the runs labeled H_2, O_2, and H_2O (100% relative humidity), the samples were loaded as explained above. Immediately after loading, the sample was removed from the dilution system and H_2, O_2, or air saturated with water at room temperature was passed through it for several minutes. It is seen that the effect of H_2 and O_2 is rather small, but high concentrations of water vapor cause substantial reductions in recoveries.

Because of the degradation of recoveries caused by water vapor, more runs were made with air dehumidified by the ice water bubbler (19% relative humidity). These results, also shown in Table 8 (Part A), indicate about the same losses as with room air humidity.

Table 8. Effects of Storage on Recovery Percentages

	Storage time			
	1 day	3 days	7 days	14 days
A. Stored on lab bench				
room air (40-50% relative humidity)	81	-	49	43
room air, with air flow at 550 ml/min	79 (10 hrs)		-	-
H_2	83	79	57	36
O_2	-	71	63	-
air (100% relative humidity at 25° C.)	54	39	23	-
air (19% relative humidity at 25° C.)	90	78	52	37
B. Stored in the dark				
room air	-	-	-	58
air (19% relative humidity at 25° C.)	-	-	78	-
air (19% relative humidity, glass sample size = 0.15 g)	-	-	73	-
air (dehumidified with dry ice/acetone trap, store at 0° C.)	-	-	77	-
C. Stored in sunlight				
air (19% relative humidity)	-	-	14	-

Effects of incident light intensity on sample storage were also examined. As shown in Table 8 (Part B), samples stored in a dark desk drawer produced significantly better recoveries than those stored on a lab bench, and a sample stored in strong light gave a dramatically lower recovery. This sensitivity to light probably accounts for some of the irregularities encountered in storage under different atmospheres as shown in Table 8 (Part A).

In conclusion of the study of storage properties, it can be said that protection of the sample from light is essential. High concentrations of water vapor during storage have a detrimental effect, although a relative humidity up to at least 20% can be permitted.

The possible interference of various common atmospheric pollutants was also studied. Dilute NO_2 concentrations were generated with an NBS certified NO_2 permeation tube with a permeation rate of $1.10 \pm .01$ μg/min at 25° C. NO_2 was found to drastically reduce the amount of recoverable SO_2. When both the SO_2 and NO_2 permeation tubes were placed in the dilution system simultaneously, producing 0.47 ppm SO_2 and 1.06 ppm NO_2, no SO_2 could be recovered by heating. Several runs were then made, loading various amounts of NO_2 onto the sample, either before or after the SO_2 as shown in Table 9. It is seen that for the SO_2 loading used (~2.0 μg), less than about 1 μg NO_2 has little effect on SO_2 recovery, while more NO_2 inhibits SO_2 release, if the NO_2 is loaded first. When the SO_2 was loaded first, however, a much larger effect of the NO_2 is observed. No attempts were made to analyze for NO_2 or NO_2 reaction products in the air stream out of the sample tube.

Attempts were made to remove the NO_2 from the air stream with sulfamic acid (used in water solution for NO_2 removal in the West-Gaeke method for SO_2[30]). It was found that sulfamic acid (crystals) does not adsorb

Table 9. NO_2 Interference Studies

A. NO_2 loaded first

SO_2 conc. (ppm)	SO_2 loaded (μg)	SO_2 recovered (μg)	percent recovery	NO_2 conc. (ppm)	NO_2 "loaded" (μg)
0.47	2.00	1.77	89	0	none
0.47	2.00	1.66	83	1.07	1.08
0.48	2.01	1.72	86	0	none
0.48	2.01	1.32	66	1.08	2.18
0.47	2.00	1.13	57	1.07	5.41
0.47	1.98	0.92	46	1.06	10.7
0.47	1.98	0.74	38	1.06	21.5
0.47	2.00	1.62	81	0	none
0.47	2.00	1.65	83	0	none

B. SO_2 loaded first

SO_2 conc. (ppm)	SO_2 loaded (μg)	SO_2 recovered (μg)	percent recovery	NO_2 conc. (ppm)	NO_2 "loaded" (μg)
0.47	1.98	1.82	92	0	none
0.47	1.98	none	0	1.06	3.22
0.47	1.98	1.70	86	0	none
0.47	1.98	none	0	1.06	1.07
0.47	2.20	1.84	83	0	none
0.47	1.64	0.13	8	1.06	0.36
0.47	1.65	1.48	89	0	none

SO_2 but neither does it adsorb NO_2, therefore rendering it useless for this purpose. No additional attempts have been made to remove the NO_2 interference.

Low concentration hydrogen sulfide dilutions for interference tests were made as follows: A 1.0 ml gastight syringe was filled with 0.5 ml H_2S from a lecturesphere. This 0.5 ml H_2S was then injected into a 20 ml syringe mounted on the motor drive, and the plunger of the 20 ml syringe was then drawn back to the 20 ml mark with air. After several minutes time to allow for diffusion, all but 6.0 ml was exhausted into the hood and the syringe was again filled with air to the 20 ml mark. This was repeated one more time, saving 5.0 ml and diluting to 20 ml. Then with the motor drive set at 0.388 ml/min and an air flow rate of 1.33 l/min, 0.55 ppm H_2S was produced. A similar method was used for other concentrations.

Hydrogen sulfide was not adsorbed by the propylamine glass (Alkylamine/CPG-1350). Although H_2S produced a response in the sulfur analyzer, no interference in SO_2 recovery was found as long as the air stream was free of H_2S during the heating and SO_2 recovery part of the analysis. Hydrogen sulfide concentrations up to 17.6 ppm which were applied to a sample before, during, and after loading with SO_2 at 0.56 ppm produced no interferences.

Dilutions of carbon monoxide were made using the technique described above for hydrogen sulfide. No interference was found for CO. Concentrations of CO up to 17.6 ppm loaded before, during, and after loading with 0.48 ppm SO_2 produced no reduction in SO_2 recoveries.

Dilute ozone concentrations were generated with a McMillan Electronics Corp., Model 1000 ozone generator, which had a range of 0-1000 ppb with a

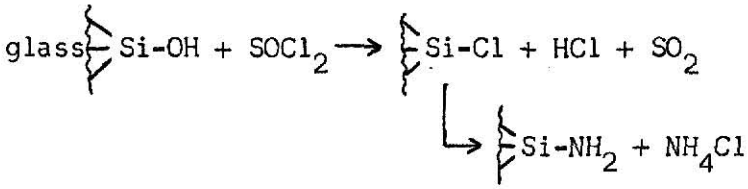
resolution of 1 ppb. During O_3 interference studies, care was taken to ensure that no oxidizable materials were on the sample tube walls, etc. For this reason, an empty sample tube with a quartz wool plug was initially treated with 1.0 ppm O_3 for several hours. Due to the dilution system configuration, ozone could not be loaded simultaneously with SO_2.

Ozone was found to reduce SO_2 recovery from an alkylamine sample even when loaded before SO_2. In addition, ozone substantially decreased the SO_2 adsorbing capacity of the alkylamine glass. An ozone concentration of 1.0 ppm flowing through 0.07 g glass at a flow rate of 550 ml/min for 5 minutes caused a reduction in holding capacity to about 1/6 the original capacity, along with a reduction in SO_2 recovery to about 60%. An ozone concentration of 0.40 ppm reduced the recovery to 84%. The treatment with ozone also caused a change in the rate of SO_2 release resulting in much broader, more shallow peaks.

Removal of ozone with a plug of cotton in the top of the sample tube was attempted since it is known that cotton adsorbs O_3. It was found that the cotton itself initially adsorbed a small amount of SO_2, but that in succeeding runs the same cotton plug did not adsorb. No improvement in SO_2 recovery was found using the cotton for O_3 removal--0.40 ppm ozone for 5 minutes reduced the recovery to 77%. No attempt was made to determine whether this behavior was due to incomplete elimination of ozone by the cotton or entrapment of the SO_2 in the ozonized cotton.

No additional work has been done to remove the ozone from the air sample. According to McGee, et al.,[31] alkylthiol mercury chloride, dialkylthio mercury, alkylthio lead chloride or dialkylthio lead, or a mixture thereof will selectively remove the ozone from an air stream without affecting the SO_2 concentration.

In addition to the use of the alkylamine glasses purchased from Dow Corning which were previously described, alkylamine glasses were also made by silanizing a 1350 Å controlled pore glass. The glass used was Dow Corning #GZO-7900 CPG, purchased from Pierce Chemical Company. The two silanes used were γ-aminopropyltriethoxysilane, also purchased from Pierce, and N-(β-aminoethyl)-γ-aminopropyltrimethoxysilane, obtained from PCR Inc. Also, an attempt was made to attach amine groups directly to the silicon atoms of the glass:[32,33]



This reaction was carried out as described below. Into a 50 ml round bottom flask was placed 1.11 g of the 1350 Å CPG and an excess of thionyl chloride (~15 ml). This was then refluxed for 18 days. Since exposure of the chlorided surface to water vapor rapidly replaces the -Cl groups with -OH groups,[34] the remaining steps were performed in a glove bag under dry N_2 (dried in succession through silica gel, $CaCl_2$, and P_2O_5). The thionyl chloride was then drawn off with a hypodermic syringe. Most of the remaining $SOCl_2$ was then allowed to evaporate. Gaseous ammonia was then introduced into the flask from a lecture cylinder via a polyethylene tube equipped with a long syringe needle. The resulting reaction changed the color of the glass from white to a light pink.

The product glass retained a considerable amount of a volatile sulfur containing species as evidenced by a strong response (>1.0 ppm) on the sulfur gas analyzer. It was found that this could be eliminated by gentle heating (~60°C.) with air flow through the sample over a period of

several hours. The resulting glass was found to be totally inert toward SO_2. Another sample from the same batch was washed briefly in distilled water. It too exhibited no adsorption properties for SO_2.

Silanization of the glass beads with N-(β-aminoethyl)-γ-aminopropyltriethoxysilane (Dow Corning Z-6020) initially produced little success. The silanization was carried out as follows. While vigorously stirring 0.2 g of the 1350 Å controlled pore glass (GZO-7900) in 100 ml distilled water, 3.5 ml of the silane was added. The solution remained colorless and no visible gelling of the silane occurred. After 5 minutes, the solution was poured off the glass and the product glass, which remained colorless, was dried in a dessicator over $CaCl_2$. The reaction is believed to be similar to that shown below.[35] Initial hydrolysis of the methoxy portion of the silane molecule enables it to attach to the glass substrate.

$$\text{glass}\begin{cases}\text{OH}\\ \text{OH}\\ \text{OH}\end{cases} + (CH_3O)_3Si\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}NH\text{-}CH_2\text{-}CH_2\text{-}NH_2 \longrightarrow$$

$$\text{glass}\begin{cases}\text{O}\\ \text{O}\\ \text{O}\end{cases}\!\!>\!\!Si\text{-}CH_2\text{-}CH_2CH_2NHCH_2CH_2NH_2 + 3CH_3OH$$

The dried product was found to be a good adsorbent for SO_2. However, small quantities (1-2 μg) of SO_2 could not be recovered by heating the glass sample. Even after saturating a 0.07 g sample of glass with SO_2 (~50 μg), followed by heat to remove the recoverable SO_2, a 1.7 μg loading could not be recovered.

Similar results were obtained with a quartz wool sample silanized as above, except 1.0 ml silane was used in 100 ml H_2O.

Since the samples made as described above would not release small loadings of SO_2, it was assumed that perhaps the glass was being coated

with a substantial layer of silane rather than a mono-molecular layer as desired. This was considered plausible when it was noted that the silane in water solution is capable of undergoing a self-catalyzed condensation reaction which transforms the silane into an insoluble polymer.[36]

Another silanization was therefore performed with a dilute solution of the silane in water. One drop of the Z-6020 silane was placed in 25 ml distilled water in a 50 ml beaker, and 0.25 g of the 1350 Å glass was added. After swirling for 5 minutes, the solution was poured off, and the glass rinsed with H_2O, then EtOH, and finally $CHCl_3$. After drying, the product was analyzed as before. Typical conditions used were: 0.48 ppm SO_2, 550 ml/min sample flow rate, and 3 minutes SO_2 loading time. It was immediately apparent that the SO_2 release was completed over a smaller temperature range than that which was observed with the Alkylamine/CPG-1350 glass purchased, producing a noticeably sharper peak for the same heating rate. Recovery was somewhat less than with the Alkylamine/CPG-1350, averaging 85.4% with a standard deviation of 4.0 for a series of 6 runs. A typical SO_2 release curve for this glass is shown in Figure 8.

Another amine sample glass was made as above, except that a 5 hour reaction time was used. No significant differences in SO_2 release were found as compared to the amine glass above.

The Z-6020 silane was also applied to a glass substrate in a toluene reaction medium. It was expected that a lack of water would prevent the rapid hydrolysis of the silane and therefore either prevent the silanization of the glass or produce a silane coating with substantially different properties than that of a water solution. The toluene used was initially dried over $CaCl_2$ for several hours. One drop of the Z-6020 silane was added to 25 ml toluene in a 100 ml round bottom flask, to

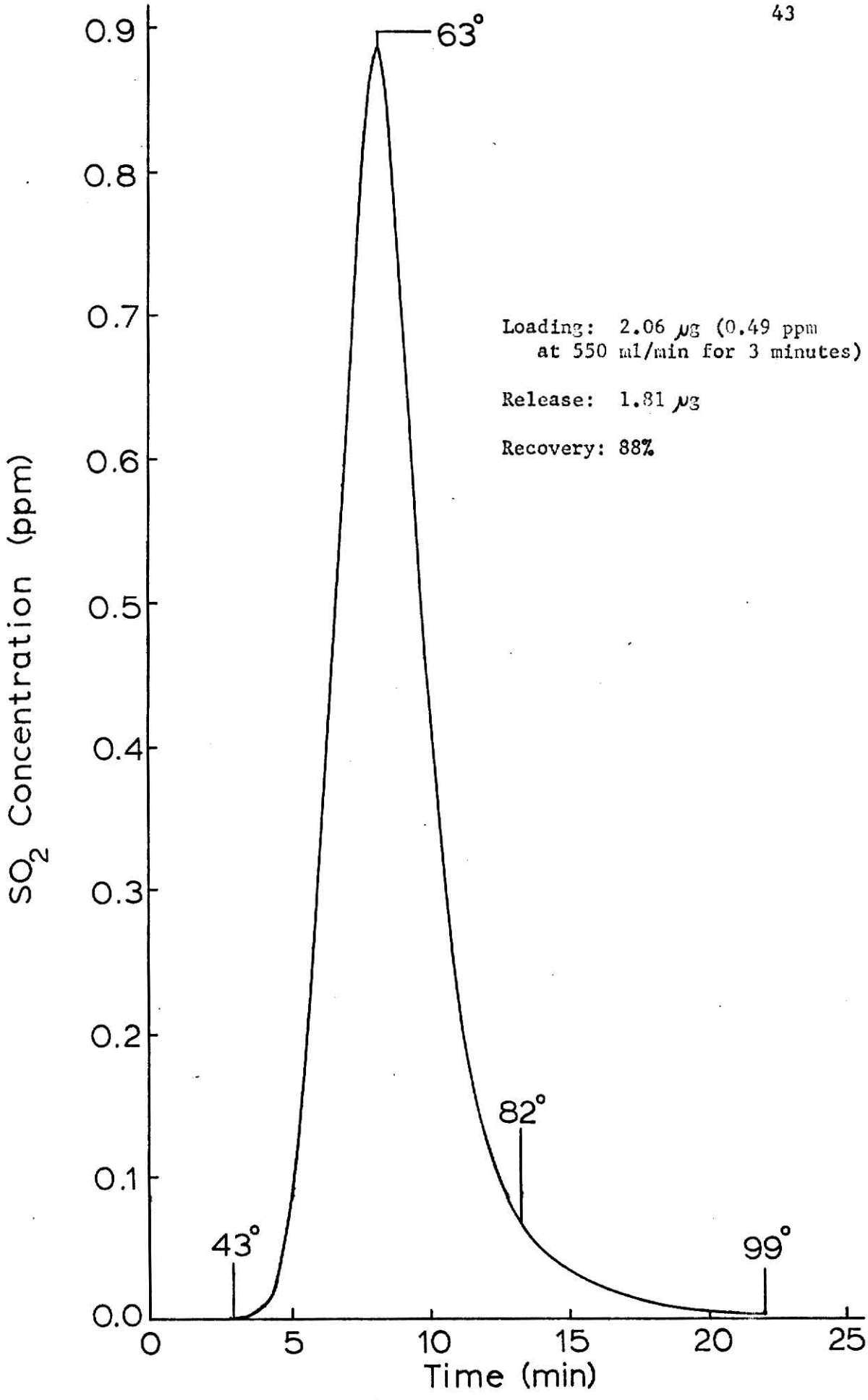
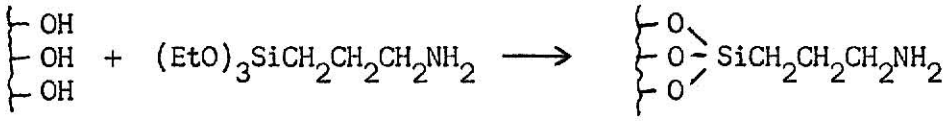


Figure 8. SO_2 Release From Glass Treated With Z-6020 Reagent

which was added 0.25 g GZO-7900 glass. The flask, fitted with a reflux condenser with a silica gel water vapor trap, was then heated. A steady reflux was then maintained for 10 hours. After cooling, the toluene solution was poured off and the glass was washed with dry toluene, then with EtOH, and finally with distilled water. After drying, the glass was analyzed as before. The initial loading and recovery cycle generally produced very poor results (40-50% recovery), with subsequent runs on the same sample yielding somewhat better results (~75% recovery on the 5th run). SO_2 release began at ~65°C. and reached a maximum at ~79°C. for a 5°C/minute rate of temperature increase, as compared to 45°C. and 60°C. respectively, for the Alkylamine/CPG-1350 purchased and for the Z-6020 water solution product. Also, it was noted that this product produced less peak tailing than the other amine glasses.

A propylamine glass was made by treating the 1350 Å glass (GZO-7900) with γ-aminopropyltriethoxysilane.



The reaction was carried out by the addition of 0.25 g glass to a solution consisting of one drop of the silane in 25 ml distilled H_2O. After allowing the silanization to proceed 5 minutes (at room temperature), the solution was poured off and the product glass was washed twice with water and then with EtOH. After drying, the glass was analyzed as before. Extremely sharp peaks were obtained although some tailing was observed. Sulfur dioxide release began at a markedly lower temperature (~29°) than the other samples previously described, and reached a peak at ~44°C. On successive runs with the same glass sample (0.06 g), its capacity became

a little smaller each time, eventually reaching a point (after only 3 or 4 runs) where the load (~2 μg) would exceed the capacity and SO_2 would start coming through at room temperature. Although this degradation of capacity with each loading had also been observed for the Z-6020 silanized glass, it was more noticeable in this case because of its lower initial capacity of only slightly over 2 μg.

Since the capacity for the sample described above was quite small, another amine glass sample was made according to the procedure described above, with the exception that 0.25 ml of the silane was used. This glass had a much larger capacity--over 25 μg SO_2 for a 0.07 g sample. The SO_2 recovery peaks were much broader--more like those from the Alkylamine/CPG-1350 glass purchased. SO_2 release began at about 68°and reached a maximum at 85-90 °C. for a temperature increase of 5°C/minute. Thus it can be seen that heavier amine coatings produce increased capacity, cause release at higher temperatures, but somewhat degrade SO_2 release properties.

CHAPTER VI

EXTENSIONS AND CONTINUATIONS

Additional work needs to be done with the piezoelectric detector. The use of a strongly adsorbing substrate coating should result in a very sensitive air pollutant detector, provided concentrations are determined by calculation of the frequency change per unit time. An inexpensive microprocessor could readily be used to periodically open air intake solenoid valves for different time lengths depending on the concentration so as not to quickly overload the crystal.

Further studies of the adsorption of SO_2 on alkylamine glass should be undertaken. Other common atmospheric gases should be analyzed to identify those which reduce SO_2 release. Studies should also be conducted with the aim of further reducing SO_2 losses during storage. An examination of the type of interaction of SO_2 with the amine group may provide insight into the fate of the unrecoverable SO_2. Finally, additional studies of the adsorption of SO_2 in the ppb range should be made.

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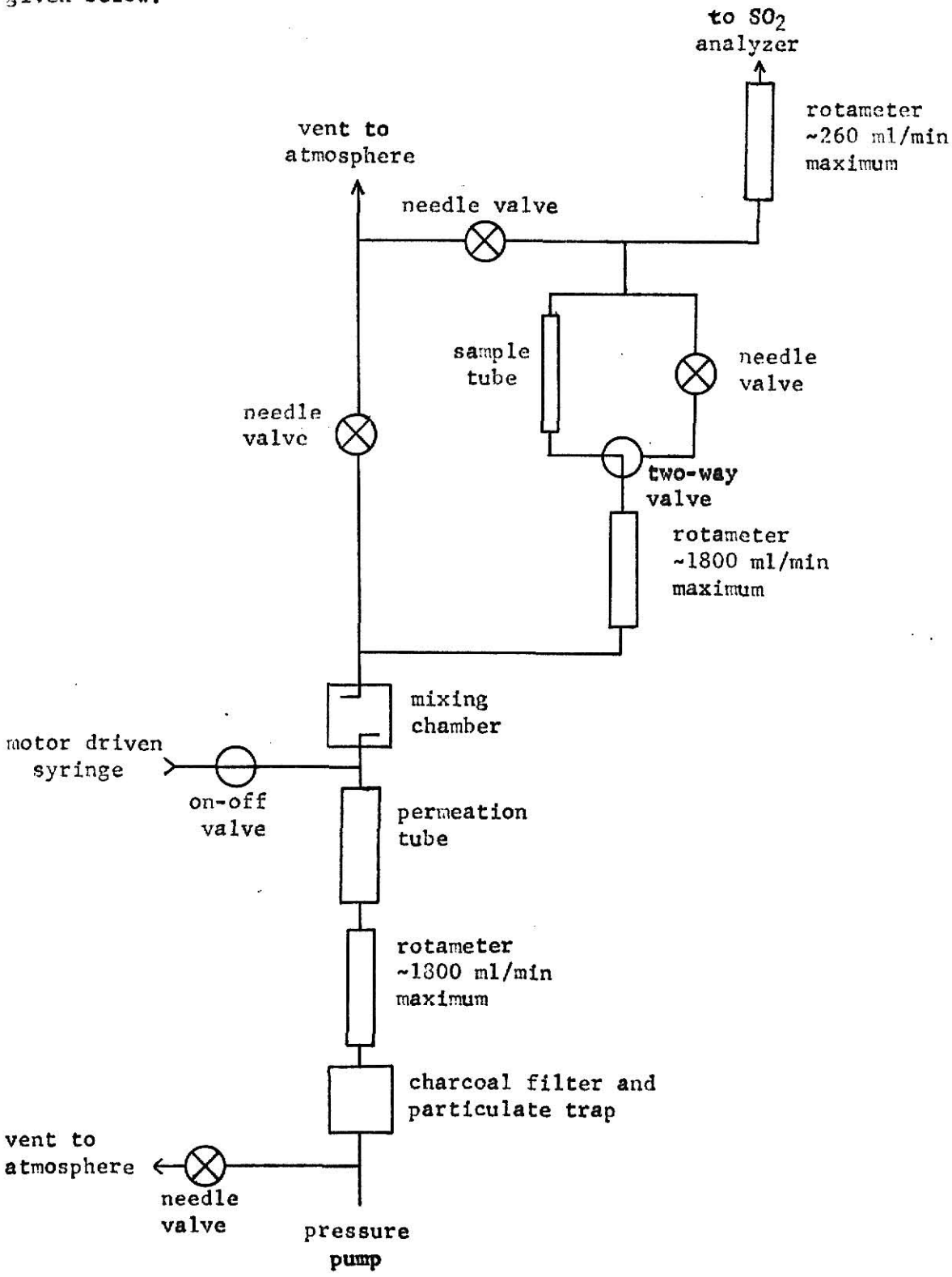
APPENDIX

A diagram of the dilution system used in Chapters IV and V is given below:



The permeation tubes used in Chapters IV and V were purchased from the National Bureau of Standards. Each tube was individually calibrated by NBS. The permeation rate uncertainty depended on the size of the tube as follows (values given are for 25°C.; uncertainty doubles at 20° and 30°C.):

2 cm tube	1.0%
5 cm tube	0.5%
10 cm tube	0.5%

The permeation rates in μg/min for the tubes are given below:

	Permeation Tube Number			
temp. (°C)	14-24 (10 cm.)	17-24 (5 cm.)	21-61 (2 cm.)	26-10 (2 cm.)
20.00	2.124	0.969	0.462	0.418
21.00	2.295	1.046	0.499	0.453
22.00	2.479	1.130	0.538	0.490
23.00	2.679	1.220	0.581	0.530
24.00	2.895	1.318	0.626	0.574
25.00	3.128	1.423	0.676	0.621
26.00	3.380	1.537	0.729	0.672
27.00	3.652	1.660	0.787	0.728
28.00	3.946	1.792	0.849	0.788
29.00	4.264	1.936	0.916	0.853
30.00	4.607	2.091	0.988	0.923

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VITA

Larry D. Van Arendonk was born on July 19, 1949 in Oskaloosa, Iowa. He was the eldest of four sons born to Hubert and Betty Van Arendonk. He lived on a farm near Oskaloosa until 1959 when he moved with his parents to another farm near Prairie City, Iowa. He graduated from Pella Christian High School in 1967 and continued his education at Dordt College, Sioux Center, Iowa. Dordt College awarded him an A. B. degree in Chemistry/Physics/Mathematics in May of 1971. In September of 1971 he began his studies as a full time graduate student in chemistry at Kansas State University. He married Mary M. Hendrikse on December 22, 1971.

ANALYTICAL REAGENTS AND ADSORBENTS FOR SULFUR DIOXIDE

by

LARRY D. VAN ARENDONK

A. B., Dordt College, 1971

AN ABSTRACT OF A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Chemistry

KANSAS STATE UNIVERSITY

Manhattan, Kansas

1975

The determination of sulfur dioxide concentrations in air using a piezoelectric micro-balance was attempted. Two compounds previously shown to give a reversible color change in the presence of SO_2 were examined as piezoelectric crystal coatings: 2,5-dimercapto-1,3,4-thiadiazole dipotassium salt and 5-mercapto-3-phenyl-1,3,4-thiadiazole-2-thione potassium salt. Normal ambient SO_2 concentrations could not be detected using these compounds. Also examined were coatings of triethanolamine and tris(hydroxymethyl)aminomethane.

Color changes resulting from exposure to SO_2 of some triphenylmethane dyes on a cationotropic alumina support were studied. Some ion association compounds incorporating triphenylmethane dyes were also examined.

Further investigations involved the development of solid reagents which will quantitatively adsorb SO_2 from an air stream at ambient temperatures, and which will release it by heating for determination by a currently accepted analytical method. Three classes of compounds were examined as coatings on controlled pore glass: aldehydes, dienes, and amines. Only the amines exhibited the necessary adsorption-desorption properties, with the primary amines generally yielding the best results. The major problem associated with such adsorbents was the tendency of the coating to sublime when heated to desorb the SO_2.

Attempts to use polymers containing amine groups as adsorbents were unsuccessful. Problems encountered were poor adsorption or desorption of SO_2 and, with some of the polymers studied, thermal decomposition.

Finally, controlled pore glasses containing chemically attached alkylamine groups were studied. These materials were found to consistently give recoveries in excess of 90%. The glasses studied included two commercial propylamine glasses (Dow Corning Alkylamine/CPG-550 and Alkylamine/CPG-1350)

and amine glasses prepared by silanizing Dow Corning CPG-1350 with γ-aminopropyltriethoxysilane and N-(β-aminoethyl)-γ-aminopropyltrimethoxysilane. Investigations included effects of relative humidity, SO_2 concentration, and storage conditions on SO_2 recovery. Several common atmospheric gases were checked as possible interferences. H_2S and CO caused no reduction in SO_2 recovery, while NO_2 and O_3 interfered. Removal of these and other possible interferences would make the adsorption method practicable.