

STUDIES OF SOME LEAD AND VANADIUM COMPOUNDS
FOR USE AS ANALYTICAL REAGENTS

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by 349 5839

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CHAPTER I
DETERMINATION OF MANGANESE IN WATER
BY OXIDATION USING LEAD PARAPERIODATE

The awareness of man to all forms of pollution has led to a search for means of detecting and controlling such pollution. A part of that search has been directed towards the detection of metal ion concentration in water. Among those metals, manganese is probably one of the least harmful. A low concentration requirement of manganese recommended by the EPA stems not from its possible toxicological effects but rather from the nuisance it causes.

The methods used to detect manganese in water are many and varied. Instrumental means of detecting manganese include neutron activation analysis,¹ X-ray fluorescence analysis,² and atomic absorption.^{3,4,5,6} The current use of such means is fostered by the advantages in instrumental analysis. These advantages include precision of measurement, low detection limits, and little or no necessity for sample pretreatment. The main deterrent to the use of instrumental means of detection manganese is the initial cost of acquiring the needed instruments.

Less expensive colorimetric methods involve the oxidation of Mn^{+2} by either persulfate⁷ or periodate⁸ to the permanganate ion. The oxidation by periodate or persulfate lacks specificity for manganese and presents problems associated with interferences. In order to utilize the oxidation method, sample pretreatment usually is necessary. Such pretreatment includes the removal of metal ions and organic substances that interfere with the detection of manganese. The oxidation of manganese by persulfate and periodate are used as standard methods.⁹

The use of lead paraperiodate, $\text{Pb}_3(\text{IO}_5)_2$, as an oxidizing agent for the detection of manganese compounds in water had not been attempted previously. Because of its insolubility, $\text{Pb}_3(\text{IO}_5)_2$ was selected for studies described in this chapter. The purpose was to form a column of $\text{Pb}_3(\text{IO}_5)_2$ through which a sample of water containing manganese would be passed. The water sample collected at the bottom of the column would be colored by the presence of permanganate ion. The absorption spectra of the solution would yield information as to the concentration of manganese in the original sample.

Factors that were studied included the conditions necessary to ensure a quick oxidation of the manganese compounds to the permanganate ion and the supports available for use with lead paraperiodate. Lead paraperiodate, a fine crystalline substance, could not be used as a column packing because it would not allow for a suitable flow rate of water through the column.

Experimental:

Reagents used were reagent grade. The deionized water was distilled water which had been passed through a column of deionizing resin and prewashed 6-14 mesh activated coconut charcoal (Fisher-Scientific Co.).

The apparatus used to measure the absorption spectra was a Coleman 124 spectrophotometer. Standard glass 1 cm cells were used. A Beckman Zeromatic pH meter with glass versus calomel electrodes was used for pH measurements.

The preparation of $\text{Pb}_3(\text{IO}_5)_2$ was patterned after the procedure described by Willard and Thompson.¹⁰ Twenty-five g (0.076 moles) of $\text{Pb}(\text{NO}_3)_2$ were dissolved in 100 ml of 0.88 N. acetic acid solution.

Seventeen g (0.079 moles) of NaIO_4 were dissolved in 100 ml of deionized water. The formation of $\text{Pb}_3(\text{IO}_5)_2$ involved the slow addition of the solution of NaIO_4 to the $\text{Pb}(\text{NO}_3)_2$ solution. The solution was stirred continuously via a magnetic stir bar. The crystals of $\text{Pb}_3(\text{IO}_5)_2$ were collected via suction filtration on Whatman No. 40 filter paper. Several portions of cold water were used to wash the crystalline mass. Excess water was removed from the $\text{Pb}_3(\text{IO}_5)_2$ by continuing the aspiration for several minutes. The sample was dried by using a vacuum oven at room temperature. The initial attempt to make $\text{Pb}_3(\text{IO}_5)_2$ used an oven with a temperature of 105°C to dry the product. Contamination due to decomposition of $\text{Pb}_3(\text{IO}_5)_2$ was found to be present. Thus on all subsequent preparations of $\text{Pb}_3(\text{IO}_5)_2$, a vacuum oven was utilized. The dried $\text{Pb}_3(\text{IO}_5)_2$ was stored in a glass vial until used.

The formation of $\text{Pb}_3(\text{IO}_5)_2$ on solid supports was attempted. Solutions of $\text{Pb}(\text{NO}_3)_2$ and NaIO_4 were prepared in the manner described previously. The solid support selected was washed with distilled water. The wet support then was exposed to the appropriate solution and stirred via a magnetic stir bar for 30 min. If a cationotropic support was used, the support was treated initially with $\text{Pb}(\text{NO}_3)_2$. If an anionotropic support was used, the support was treated initially with NaIO_4 . After 30 min, the solution was decanted. The support was rinsed several times with distilled water. The second solution then was added (i.e., if $\text{Pb}(\text{NO}_3)_2$ was initially used, then the second solution used would be NaIO_4). The mixture was stirred for 30 min. The solution was decanted and the support washed and placed in a vacuum oven to dry at room temperature. The treated supports were stored in glass vials.

Preparation of acid solutions necessary to carry out the evaluation of the effects of acidity on the oxidation of Mn^{+2} was done by diluting concentrated acid solutions until the appropriate pH was obtained.

A series of pH determinations was made for each of the following acids: HCl , HClO_3 , HNO_3 , and H_2SO_4 . The range was from a pH of 5 to a pH of less than zero, in increments of 0.5 pH units. To each of the acidic solutions two drops of saturated MnSO_4 solution were added. Approximately 0.10 g of $\text{Pb}_3(\text{IO}_5)_2$ then was added. The solutions were stirred and allowed to react for approximately 30 min. This allowed sufficient time for a reaction to occur and made a visual comparison of color intensity possible.

The Mn^{+2} solutions used for the experiment were prepared from a stock solution of 166 ppm Mn^{+2} . The stock solution was prepared by dissolving 0.5024 g of MnSO_4 in 1 liter of a sulfuric acid solution (pH = 1.0). Volumetric dilutions were made using a sulfuric acid solution (pH = 1.0) to obtain a series of concentrations: 16.6 ppm, 8.3 ppm, 6.7 ppm, 3.3 ppm, and 1.66 ppm. A 125 ml sample of each was prepared.

The procedure involved placing 0.10 g of $\text{Pb}_3(\text{IO}_5)_2$ in each of five 50 ml beakers. To each of the beakers, 25 ml of the Mn^{+2} solutions were added. The mixtures were stirred for 30 min and the unreacted $\text{Pb}_3(\text{IO}_5)_2$ was allowed to settle. A portion of the solution from each of the five beakers was poured into five test tubes. The test tubes were placed in a Sargent Model S-15700 centrifuge to remove any suspended solids. To measure the absorbance the clear solutions were individually poured into 1 cm glass cells. A wavelength of 525 nm was employed in all measurements. The peak at 525 nm is

the most intense peak in a cluster of four peaks in the visible absorption spectra of MnO_4^- .

Results and discussion:

The initial evaluation of acidity revealed that the oxidation of Mn^{+2} was enhanced by increased acidity. Through a quick series of tests, it was found that the oxidation was very slow above a pH of 5. Thus, when investigating pH and the acid to be used, no measurements of a pH greater than 5 were made. It was found that HCl , HNO_3 , and HClO_3 were unacceptable for use in this experimentation. The use of three acids resulted in either the oxidation of the acid itself (HCl), the formation of MnO_2 and no MnO_4^- (HNO_3), or the acid itself acting as an oxidizing agent (HClO_3). Sulfuric acid was not oxidized, did not oxidize Mn^{+2} , and did not promote the formation of MnO_2 . The optimum pH range for sulfuric acid was from pH = 1.0 to pH = 0.80. It should be noted that sulfuric acid was used in the preparation of the stock solutions which were tested.

The results obtained are listed in Table I. It should be noted that only one set of solutions were tested in obtaining the results listed in Table I. It had been hoped that the oxidation of Mn^{+2} by $\text{Pb}_3(\text{IO}_5)_2$ would be clean and efficient enough to allow for detection down to the 100 ppb range. Using 1 cm cells the limit of detectability was 3.3 ppm. If longer path lengths had been employed, the detection limit may have been lowered correspondingly.

An additional cause for our discontinuing to work with this system was the formation of MnO_2 which, even in 1.66 ppm concentration, visibly coated the inside of the beaker. MnO_2 , which is soluble in HCl solutions, is not soluble in H_2SO_4 solutions. The oxidation of Mn^{+2} to MnO_4^- results in the production of compounds that will reduce MnO_4^- to MnO_2 .

Table I

Absorbance Measurements of MnO_4^- Solutions
 Prepared by Oxidation of Mn^{+2} by $\text{Pb}_3(\text{IO}_5)_2$

Concentration of Mn^{+2} in ppm	Absorbance
16.6	0.440
8.3	0.243
6.7	--- <u>a</u>
3.3	0.095
1.6	--- <u>b</u>

(a) not run

(b) not detectable above background

Attempts to form $\text{Pb}_3(\text{IO}_5)_2$ on solid supports were also unsuccessful. The supports used included molecular sieves, anionotropic and cationotropic alumina, strong base resin, zeolites, and silica gel. Of those tested partial success was obtained with anionotropic alumina. The initial screening of the supports was carried out by adding a 166 ppm stock solution to the treated and washed support. It was found that only anionotropic alumina so treated and washed had adsorbed enough $\text{Pb}_3(\text{IO}_5)_2$ to form a significant amount of MnO_4^- by oxidation of Mn^{+2} . Upon drying the support in a vacuum oven, the support became unusable. The addition of water to the dried support washed the adsorbed material completely off of the support. No explanation is made for this type of action.

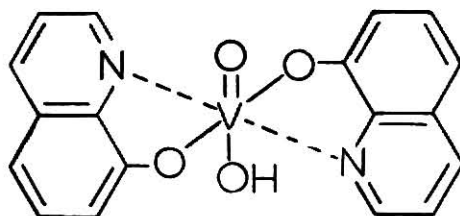
CHAPTER II

INVESTIGATION OF REACTIONS OF OXOHYDROXYBIS(8-HYDROXYQUINOLINO-)VANADIUM(V) AND METAL IONS

Previous investigation of the chemistry of oxohydroxybis(8-hydroxyquinolino-)vanadium(V) have concentrated on three aspects: (a) the formation of oxohydroxybis(8-hydroxyquinolino-)vanadium(V), (b) the structure of the complex, and (c) the reaction of the complex with various organic compounds.

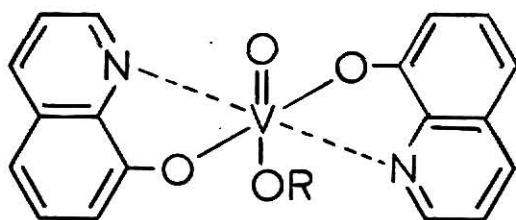
The formation of oxohydroxybis(8-hydroxyquinolino-)vanadium(V), referred to as the black acid, was reported by R. Montequi in 1932.¹¹ He stated that the black acid was a result of the oxidation of a yellow complex by vanadium(V). Later investigation by Montequi¹² indicated that the black acid was the result of a complex formed between 8-hydroxyquinoline and VO_2^+ . The black acid is quite insoluble in water. By the addition of 8-hydroxyquinoline to an aqueous solution containing vanadium(V), vanadium can be extracted from the solution into CHCl_3 , benzene, or other organic solvents.^{13,14,15,16,17} The extracted vanadium is in the form of the black acid.

The structure of the black acid is



Infrared studies, as well as other means of structural determination, are documented in the literature.^{18,19,20}

The reaction of the black acid with various organic compounds is reviewed by Blair and Pantony.^{20,21} Additional investigations of such reactions have been carried out.²² The most significant result of these investigations is the reaction between simple alcohols and the black acid to form a red complex. This complex has an absorption peak at 480 nm. The structure of the compound is



No investigations into the reactions of the black acid and metal cations were found in the literature. The research which is described in this chapter deals with investigations into the possible reactions between metal cations and the black acid. If such reactions exist, information as to the relative stability of the black acid could be ascertained. Also, if only a few metal cations were able to displace the vanadium from the black acid, the black acid could be used as a means of determining the amount of those metals in an aqueous solution. The fact that the black acid is insoluble in water was an additional reason for conducting this type of research. If the black acid reacted with a select group of metal cations, a column packed with a support containing the black acid could be constructed for use.

The chapter contains three sections. The first two sections deal with the preparation of the yellow sodium salt of oxohydroxybis (8-hydroxyquinolino-)vanadium(V) and the conversion of this yellow sodium salt to the black acid. The final section contains information regarding experimentation.

A. Preparation of the Yellow Sodium Salt of Oxohydroxybis (8-hydroxy-quinolino-)vanadium(V)

Twenty-one and one tenth g (0.174 moles) of NaVO_3 , reagent grade, were dissolved in 200 ml of deionized water. The solution was heated and stirred continuously until the NaVO_3 had completely dissolved. Fifty and four tenth g (0.348 moles) of 8-hydroxyquinoline was added slowly. The heated solution was stirred for 15 to 20 minutes to ensure complete reaction. The hot solution then was suction filtered using water aspiration and a Büchner funnel set up. Whatman No. 41 filter paper was used. The filtration served to remove any unreacted solids. The aqueous solution was placed in an ice bath and the yellow sodium salt was allowed to crystallize. The yellow sodium salt was recovered from the solution via suction filtration with Whatman No. 40 filter paper. The yellow sodium salt then was recrystallized in 95% ethanol. The recrystallization yielded two fractions: an alcohol-soluble and an alcohol-insoluble fraction. It should be noted that continued heating of the alcohol-soluble fraction in 95% ethanol will yield consistantly greater quantities of the alcohol-insoluble fraction. Both of the fractions obtained were recrystallized in absolute ethanol and then in acetone. The yellow sodium salt was dried in a vacuum oven at room temperature and stored in a brown glass container.

B. Conversion of Yellow Sodium Salt of Oxohydroxybis(8-hydroxyquinolino-)vanadium(V) to Oxohydroxybis(8-hydroxyquinolino-)vanadium(V)

A saturated solution of the yellow sodium salt was prepared. While stirring the solution, glacial acetic acid was added in a

dropwise manner. The addition of acetic acid was continued until no more black acid precipitated. The resulting slurry was suction filtered using a Büchner funnel and Whatman No. 40 filter paper. The black acid was washed with several portions of deionized water to remove any yellow sodium salt or excess acetic acid from the black solid. The solid was rinsed with acetone to remove excess water and was dried in a vacuum oven. The dried acid was stored in a glass vial.

C. Action of Metal Cations on Oxohydroxybis(8-hydroxyquinolino-) vanadium(V)

The methods used in this work were a sequence of refinements of procedure, the second method being a refinement of the first, etc. A color change, black to any other color, was taken as positive evidence of a reaction taking place.

Method 1:

The black acid was applied to the gummed side of cellophane tape and the excess was shaken off. The blackened strips of tape were attached to a piece of plywood which had been covered by sheets of white paper. Two drops of the solution of metal cation were applied to the tape. Two inch intervals separated the different metal cations being tested and designations as to the metal content were placed on the white sheet of paper next to the point of application.

The solutions were made by adding approximately 0.1 g of a metal salt to 50 ml of deionized water. To insure that the solutions were not basic, two drops of the appropriate concentrated acid were added (e.g., if nitrate salt was employed, nitric acid was added).

The results obtained were inconclusive. Complications arose from the fact that the amount of oxohydroxybis(8-hydroxyquinolino-)vanadium(V) available was much greater than the metal ion available to displace the vanadium. Thus the possibility of observing a color change was minimal due to the black background. Also, the black background created difficulties in distinguishing between wetting effects and legitimate color changes.

Method 2:

The black acid was powdered in a mortar and pestle, and it was added to acetone to form a slurry. Using an eye dropper, two drops of the slurry were placed in the center of a piece of Whatman No. 1 4.25 cm filter paper. The acetone was allowed to evaporate and the excess black acid was shaken off.

The spotted filter paper was placed on a Weisz Ring Oven. This oven was used in conjunction with a Powerstat Type 216 variac that was set at 42 V. The resulting temperature of the ring oven was $110 \pm 20^{\circ}$ C. At this temperature, the water evaporated and facilitated the formation of a thin ring.

After the paper had reached equilibrium temperature of the ring oven, four drops of a solution of the metal to be tested were added dropwise at one minute intervals. Four drops of deionized water then were added dropwise at one minute intervals to concentrate the reacted or unreacted water-soluble compounds in the thin ring that was formed.

The solutions of metals tested were 0.5 M in metal ion concentration. The appropriate amount of metal salt was weighed and dissolved in 125 ml of deionized water. To insure an acidic solution, five drops of the appropriate concentrated acid were added. If some of the solid failed to dissolve in the 125 ml of water, the solution was filtered before use.

The results obtained using this method were superior to those obtained using Method 1. The elimination of the black background served to give clearer indications of reactions. The concentration of the water soluble compounds in a ring further elucidated the presence of a reaction. The temperature of the ring also served to enhance endothermic reactions.

Although superior to Method 1, this method had several problems associated with the procedure both in the spotting of the filter paper and in the testing of metals. Using an eye dropper, problems associated with concentration and drop size of the slurry arose. The addition of both the cation-containing solution and the deionized water was done manually. To prevent the destruction of the original ring by the addition of a drop of solution, a uniform drop size and drop rate were needed. Also, more than four drops of the metal solution were needed to adequately determine if a reaction was taking place.

Method 3:

To insure a uniform spotting of the filter paper, the black acid was powdered as in the previous procedure. The amount of acetone used to make the spotting mixture was doubled. This allowed the apparatus shown in Figure 1 to be used. The apparatus consisted of two pieces of thick walled 2 mm (i.d.) glass tubing. By carefully heating a small section of the tubing, the marias were made. To obtain flat surfaces between which to clamp the filter paper, the glass tubing was momentarily held against the side of rotating glass saw blade. A plastic funnel was attached to the short top section with a piece of tygon tubing. The bottom section was attached via rubber tubing to a water aspirator fitted with a flask to trap the excess acetone.

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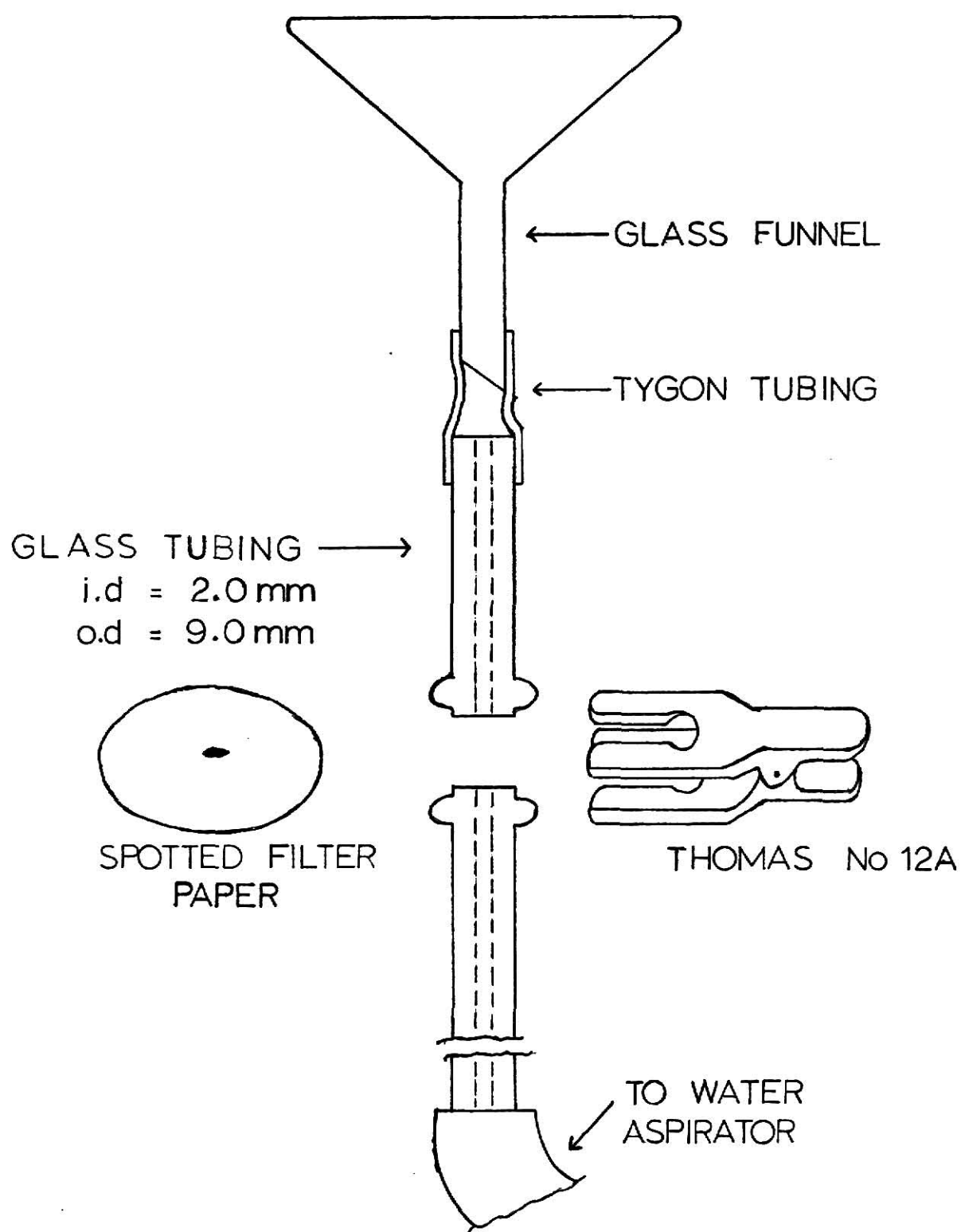


Figure 1 Spotting Apparatus

A piece of Whatman No. 1, 4.25 cm filter paper was placed between the two sections of the apparatus. A Thomas No. 12A clamp was used. Fifteen drops of the acetone-black acid solution was added to the funnel. The aspiration removed the excess acetone, depositing the black acid on the paper. The paper remained in the apparatus for several minutes after the excess acetone had been removed to allow the evaporation of the acetone from the deposited black acid.

The Weisz Ring Oven was used in the same manner as described in Method 2. The solutions used in Method 2, 0.5 M in metal ion concentration, were also used in this method.

Figure 2 shows the apparatus which was constructed to allow a uniform drop rate and drop size. The wash water reservoir consisted of a 10 ml Kimax-95 burette equipped with a refilling reservoir. The sample reservoir consisted of a Kimax A-123, 5 ml microburette. A glass funnel was attached to the top of the microburette, via a section of tygon tubing, to give added capacity to the burette. Sections of tygon tubing attached both reservoirs to the glass Y-tube. A piece of capillary tygon tubing was fastened with epoxy glue to the stem of the Y-tube. The section of capillary tubing was cut at an angle to facilitate the formation of a small uniform drop.

The Y-tube was specifically constructed to counteract the problems associated with the fact that the sample was more dense than the wash solution. Before testing metal-ion samples, several designs of the Y-tube had been tested. Colored solutions, such as KMnO_4 , were used to detect how much unwanted seepage of the sample solution occurred when running the wash solution. At flow rates of less than 1 drop per min, the amount of seepage was considerable. The use of straight armed

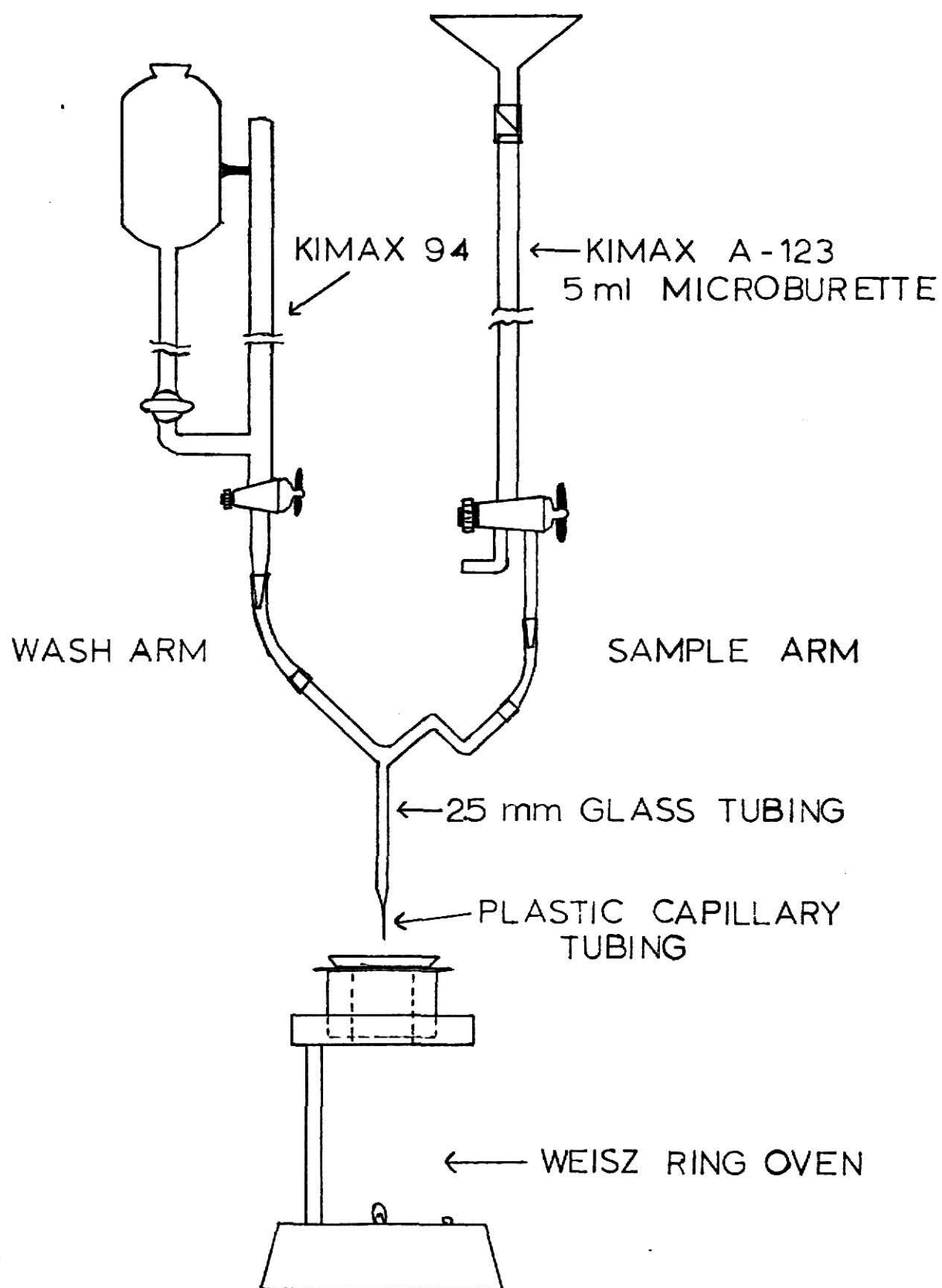


Figure 2 Sample and Wash Water Delivery System

Y-tubes caused a complete displacement of the wash water by the more dense KMnO_4 solution. The use of small diameter glass tubing and the proper bending of the sample arm of the Y-tube eliminated the seepage problem.

Using the initial procedure, the apparatus was set up to drop both sample and wash solutions on the spot of black acid. After testing several metal cations, it was determined that there was no appreciable advantage to the attempt to concentrate the water-soluble compounds in the ring by using wash water. The relatively high dilution of the test solutions resulted in adequate concentration in the rings. Also, without the addition of wash water, a concentration gradient was set up. The highest concentration of water-soluble compounds was in the ring formed. The concentration of material deposited decreased gradually from just inside the ring to the spot of black acid. This gradient was helpful when observing the results with highly colored metal solutions, such as $\text{Co}(\text{NO}_3)_2$, $\text{Cu}(\text{NO}_3)_2$, and $\text{Fe}(\text{NO}_3)_3$.

The testing procedure is outlined below.

- 1) The sample arm of the apparatus was rinsed with several portions of metal ion solution, then filled with the same metal ion solution. The flow rate was set to be one drop per 75 ± 15 sec.
- 2) The piece of filter paper was placed on the ring oven and allowed to reach the temperature of the oven.
- 3) The timer was set for 15 min if a black filter paper was being tested or 30 min if a spotted filter paper was being tested.
- 4) The timer was started as the oven was placed in position under the Y-tube.
- 5) After the appropriate elapsed time, the oven was removed from under the Y-tube; the piece of paper tested was removed,

labeled, and set aside; a new piece of filter paper was placed on the ring oven.

- 6) The timer was re-set and started as the oven was replaced under the Y-tube.
- 7) After the tests had been completed, the sample arm was drained of metal ion solution and rinsed with several portions of distilled water.
- 8) A new sample solution was selected to be tested. Steps 1-7 were carried out using the new sample.

For each metal ion solution, five timed tests were run. The initial test used a blank piece of filter paper and an exposure time of 15 min. The next three tests utilized spotted pieces of filter paper that were exposed for 30 min. The last test was identical to the first.

Results and discussion:

The results of the testing are listed in Table II. A (+) refers to a possible reaction taking place. If the ring or the area between the ring and the spot was (a) different in color from the color of the metal ion solution, if colored, (b) different from the color formed by the action of the sample acid on the black acid, or (c) different from a seemingly likely combination of (a) and (b), then it was assumed that some reaction had taken place. Table III indicates the effects of water and acids used on the black acid. If the concentration of hydrochloric acid becomes too great, a bleaching effect occurs; the black acid turns to a white substance. Investigations into the causes of such reactions and the products involved were not carried out.

Table II

Reaction of Metal Cations and
Oxohydroxybis(8-hydroxyquinolino-)vanadium(V)

Compound	Reaction	Effect
$\text{Fe}(\text{NO}_3)_3$	+	Formed a dark green product
$\text{Al}(\text{NO}_3)_3$	+	Formed a yellow green product
$\text{Ba}(\text{NO}_3)_2$	-	
$\text{Ca}(\text{NO}_3)_2$	-	
$\text{Cr}(\text{NO}_3)_2$	-	
$\text{Cu}(\text{NO}_3)_2$	-	
$\text{Ce}(\text{NO}_3)_3$	-	
CsNO_3	-	
$\text{Co}(\text{NO}_3)_2$	-	
$\text{Pb}(\text{NO}_3)_2$	-	
$\text{ZrO}(\text{NO}_3)_2$	-	
$\text{Zn}(\text{NO}_3)_2$	+	Formed a grayish-green product
$\text{UO}(\text{NO}_3)_2$	-	
$\text{Ni}(\text{NO}_3)_2$	-	
$\text{Mg}(\text{NO}_3)_2$	-	
AuCl	-	
AgNO_3	-	
$\text{Ti}(\text{SO}_4)_4$	+	Dissolved spot of black acid
TiCl_3	+	Formed an orange-brown product
		Dissolved spot of black acid
FeSO_4	-	
SnCl_4	-	

Table II (continued)

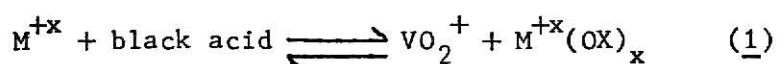
Compound	Reaction	Effect
SnCl	+	Formed a yellow product
$\text{Bi}(\text{NO}_3)_3$	+	Formed a reddish-brown product Dissolved spot of black acid
SbCl_3	+	Formed a yellow-green product Dissolved spot of black acid
AsCl_3	+	Formed a brown product
CuBr	-	
$\text{Be}(\text{NO}_3)_3$	+	Formed a grayish-green product
$\text{Sr}(\text{NO}_3)_2$	-	
$\text{Cd}(\text{NO}_3)_2$	+	Formed a yellow green product
$\text{Mn}(\text{NO}_3)_2$	+	Formed a gray product
$\text{Hg}_2(\text{NO}_3)_2$	+	Formed a rose-pink product
LiCl	-	
KNO_3	-	
NaNO_3	-	
$\text{La}(\text{NO}_3)_3$	-	
$\text{Th}(\text{NO}_3)_3$	+	Formed a yellow product
TlNO_3	-	

Table III
Effects of Acidity
on Diffusion of Color using Ring Oven

Compound	Effect
H ₂ O	Slight formation of a green ring; probably a mixture of acidified and non-acidified black acid
HCl (pH $\leq$ 0.0)	Formation of a green compound which concentrates into a brown ring
HNO ₃ (0.016 N)	Formation of a yellow compound which concentrates into a brown ring
HNO ₃ (0.08 N)	Same as above, only greater
HNO ₃ (0.16 N)	Same as above, only greater
HNO ₃ (0.40 N)	Same as above, only greater
HNO ₃ (0.80 N)	Same as above, only greater

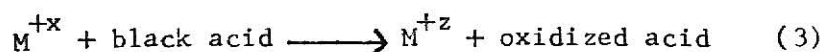
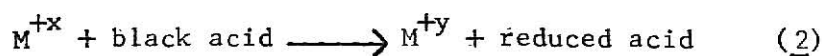
When positive color changes were obtained, one of three possible reactions could have been occurring: (a) the metal cation could have displaced the vanadium(V) and formed a new metal complex; (b) the metal cation could have been either oxidized or reduced by the black acid, yielding an oxidized or reduced metal cation and a corresponding product of the black acid; or (c) the metal cation simply could have replaced the hydrogen in the V-O-H position.

The reaction (a) would probably proceed as depicted below.



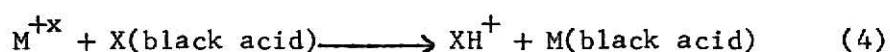
The form of the complexed vanadium(V) is VO_2^{+} . The (OX) refers to oxine, the common name of 8-hydroxyquinoline. If this reaction were taking place, it would be expected that the stability of the newly formed metal-oxine complex would be greater than that of VO_2^{+} oxinate. Irving^{23, 24} showed that the relative order of stability of oxine complexes was $Mn^{+2} \cong Mg^{+2} < Fe^{+3} < Zn^{+2} \cong Co^{+} < Ni^{+2} < VO_2^{+2} < Cu^{+2}$. An inspection of Table II shows that while Mn^{+2} , Fe^{+3} , and Zn^{+2} reacted, the remainder of the series did not. Thus, the metal complex stability was not a means of predicting which reactions, if any, would occur according to reaction (1). It should be noted that Fe(III)-oxinate complex is green in color, a color which was exhibited in the tests.¹³ The majority of the metal-oxinates are yellow; such a color was exhibited by Al^{+3} , Sn^{+2} , Sb^{+3} , Cd^{+2} , and Th^{+3} . Therefore, the possibility of these metal ions displacing vanadium(V) according to reaction (1) can be considered.

The oxidation or reduction of a metal ion probably would proceed in the following manners:



Metals such as Sn^{+2} , Sb^{+3} , and As^{+3} possess the ability to reduce, which would be necessary for equation (2) to occur. Of those metals that did react, none apparently would have the ability to engage in an oxidation of the black acid, as in equation (3). Information concerning the products obtained when the black acid is oxidized or reduced was not available, nor were any investigations of such products carried out.

The replacement of the hydrogen in the black acid may proceed according to the reaction.



Metal which reacted to produce colors that could not be attributed to the formation of metal-oxinates may react according to equation (4). The rose-pink color exhibited by Hg^{+2} and the orange-brown color exhibited by Ti^{+3} are examples of colors which could be attributed to hydrogen ion displacement.

Further investigation into the reaction mechanisms of the metal ions was not carried out. As stated previously, the purpose of this investigation was to determine if the black acid could be used to detect trace quantities of the metals tested in aqueous solutions. A study of those metals that reacted in concentrations ranging from 100 to 250 ppm showed no positive results. Hence, the study was discontinued.

CHAPTER III

THE PREPARATION AND CALIBRATION OF SOLID PHASE
ADSORBENTS FOR THE DETECTION OF ACIDIC GASES

The desire to know the concentration of pollutant gases has spurred the development of numerous methods to accomplish that task. The methods available to detect SO_2 , NO_2 , and HCl range from bench top systems to complex instrumental methods. A majority of the methods for the detection of pollutant gases are specific for one of the pollutants. Very few methods have been developed that are designed to measure the amount of all three of the pollutant gases simultaneously. In addition, very few solid phase reagents have been developed for the determination of SO_2 , NO_2 , and HCl . The use of indicator tubes for SO_2 ^{25, 26} and gels sensitive to HCl and SO_2 ²⁷ has been reported. Also, solid adsorbents have been employed to concentrate SO_2 .²⁸

The greatest amount of activity in the development of solid adsorbents is in the industrial setting. The requirements imposed in relation to maximum allowable emission of pollutant gases has spurred such development. Total adsorbents for SO_2 are receiving the greatest amount of attention. The adsorbents investigated include activated charcoal,²⁹ manganese dioxide,³⁰ limestone,³⁰ and molecular sieves.³¹ The use of such adsorbents to determine the concentration of SO_2 is limited by the ability of the adsorbents to desorb SO_2 . The adsorbents which are being developed to remove SO_2 can also be applied to the adsorption of both NO_2 and HCl .

The research described in this chapter deals with the development of a reagent which is a total adsorbent and a self indicator. The development involved a series of attempts to use the yellow sodium salt of oxohydroxybis(8-hydroxyquinolino-)vanadium(V) to detect HCl ,

NO_2 , and SO_2 . The detection of these gases is possible because they form acidic solutions when absorbed in water. If the combination of the yellow sodium salt and a small amount of water is possible in a solid form, the adsorption of an acidic gas (HCl , SO_2 , or NO_2) on that solid will cause the formation of an acid which will change the sodium salt from yellow to black.

The determination of the amount of reagent which has reacted with an acidic gas can be made in one of three ways. The reacted reagent can be placed in a solution containing I^- and IO_3^- . The acid will supply the necessary hydrogen ion to cause the formation of I_2 . The amount of I_2 formed is detected by the addition of CdI_2 -linear starch reagent. The color intensity will be directly related to the amount of reacted reagent. This determination is referred to as the I^- - IO_3^- system in the remainder of this chapter.

A second means of determining the amount of reagent reacted involves the use of 95% ethanol. As was stated in Chapter II, the black acid reacts with alcohols to form a red compound.²¹ The reacted reagent was added to a given volume of 95% ethanol and the red compound allowed to form. The intensity of the color was an indication of the amount of reagent reacted. The choice of 95% ethanol was made because 95% ethanol reacts very quickly with the black acid, and it has a sharp peak at 480 nm. This means of determination is referred to as the 95% ethanol system throughout the entire chapter.

A final means of determining the amount of reagent reacted after exposure to an acidic gas is simply to form a column of the reagent and to measure the length of reagent that has turned black.

The chapter is divided into seven sections. Each section describes a method of preparation of a solid phase adsorbent and the success or failure of that adsorbent.

A. Use of the Yellow Sodium Salt of Oxohydroxybis(8-hydroxyquinolino-)vanadium(V)

It was found that the dry yellow sodium salt did show a slight tendency to turn black when exposed to SO_2 , NO_2 , or HCl . Attempts to use the yellow sodium salt as a reagent were limited both by the amount of surface area which was available to react with acidic gases and by the amount of water which was incorporated in its crystalline structure. Even when finely powdered, the reaction which formed the black acid was limited to the surface of the material. It was due to this limited amount of reaction that the use of the yellow sodium salt alone for the detection of acidic gases was ruled out.

B. Use of a Mixture of Anhydrous MgSO_4 and the Yellow Sodium Salt of Oxohydroxybis(8-hydroxyquinolino-)vanadium(V)

A mixture of the yellow sodium salt and anhydrous MgSO_4 was made in a 1:10 ratio, respectively. It was hoped that anhydrous MgSO_4 would aid the reaction between acidic gases and the yellow sodium salt in two ways. It was believed that the mixture would cause the reactive surface area of the yellow sodium salt to increase, thereby enhancing the reaction. Anhydrous MgSO_4 , when exposed to a water vapor-containing atmosphere, forms $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ by adsorption of water. This adsorption of water would facilitate the adsorption of an acidic gas, the formation of the corresponding acid, and finally the reaction of this newly formed acid with the yellow sodium salt.

The mixture of yellow sodium salt and MgSO_4 failed to react as expected. There was little or no increase in the reactivity of the yellow sodium salt, and even when placed in a water saturated atmosphere, the anhydrous MgSO_4 failed to form the heptahydrate.

An attempt was also made to recrystallize a mixture of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and the yellow sodium salt from a slurry. $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ was added to 50 ml of deionized water until a slurry was formed. To this slurry approximately 0.1 g of the yellow sodium salt was added. After mixing thoroughly, the slurry was placed in a vacuum oven at room temperature and dried. A similar sample was dried by merely exposing it to air. The formation of a solid mixture by this method would incorporate the desired waters of hydration.

A qualitative test of the reactivity of the mixture when exposed to SO_2 was made while the mixture was drying and also when it had dried. It was found that the slurry reacted quite readily with SO_2 , forming a black mass. As the mixture dried, the reactivity decreased. The dried mixture was approximately 10% as reactive as the slurry. This was only a slight improvement over the dry mixing previously described. Because of the poor results obtained, further investigations of the $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ - yellow sodium salt mixture were not conducted.

C. Absorption of the Yellow Sodium Salt of Oxohydroxybis(8-hydroxy-quinolino-)vanadium(V) in Strong Base Resin

Four strong base resins were selected for the experimentation.

The resins selected were:

- (1) Dowex 1-X8, 20-50 mesh, Chloride form
- (2) Rexyn 201, 16-50 mesh, Chloride-Sulfate form

(3) Doulite ES-109, (DS-6490K), Chloride form

(4) Dowex 21K, (08127-A1), 20-50 mesh, Chloride form

All resins were strong base quaternary ammonium type resins.

A solution of yellow sodium salt was prepared by the addition of 0.5 g of yellow sodium salt to 150 ml of deionized water. To each 150 ml solution, 10 ml of resin was added. After exposure to the solution of yellow sodium salt for 30 min, the solution was decanted and the resin was washed with deionized water. The wet resin was placed in a vacuum oven and dried at room temperature. Attempts to dry the resin in an oven at 110°C caused the conversion of the absorbed yellow sodium salt to the black acid. Also, it was necessary to pretreat resins (3) and (4) with NH_4OH to prevent the formation of the black acid upon initial exposure of the resin to the yellow sodium salt solution.

Samples of the resins were exposed to 100% SO_2 . The response pattern to SO_2 exhibited by the damp versus dry MgSO_4 - yellow sodium salt was observed in testing the resins that had absorbed the yellow sodium salt. Damp or slightly wet resins reacted very sharply to SO_2 , while dry resins reacted slowly and only to a slight extent. A comparison of the resins revealed that resins (3) and (4) were far superior to resins (1) and (2) in regard to response to SO_2 . Therefore, all further work that was done employed resins (3) and (4).

More water had to be incorporated in the strong base resins if they were to serve as acceptable supports. Since the incorporation of ethylene glycol into the resin bead would cause a greater amount of water to be retained by the resin bead, an ethylene glycol-water mixture (2:1) was used to dissolve the yellow sodium salt. A resin

that had been treated with the ethylene glycol-water mixture retained a greater degree of reactivity when exposed to 100% SO_2 . Whereas previously the dry resin was about 5% as reactive as the damp resin, the resin prepared retained about 25% of the reactivity of the damp resin.

Studies of the ability of loaded resins to absorb SO_2 in the 50 ppm range were conducted. The gas dilution apparatus described in the Appendix was used to produce the concentration necessary for the set of experiments. Visual observation indicated that there was no apparent darkening of the resins when exposed to 50 ppm SO_2 . The time of exposure was 30 min and the air flow rate was 1 l/min. In this 30 min test, the resins were exposed to a total volume of 1.5 ml of 100% SO_2 . The exposed resin was placed in 20 ml of deionized water; 5 ml of 0.5 M KI and 5 ml of 0.5 M KIO_3 were added. The addition of two drops of Cd-linear starch reagent indicated that no I_2 had been formed: therefore, the loaded resin had no absorbed SO_2 as had been expected.

Further examination yielded two interesting results. Resin which had been loaded using a water mixture and then exposed to 100% SO_2 caused a greater formation of I_2 from the acid-induced reaction of I^- and IO_3^- than did the resin which had been loaded using an ethylene glycol-water mixture. Also, both methods of loading the resins resulted in a reagent that failed to react with $\text{C}_2\text{H}_5\text{OH}$, after the reagent had been exposed to 100% SO_2 .

The limiting factor in the use of strong base resins as supports for the yellow sodium salt was the apparent lack of absorption of SO_2 when exposed to an air stream containing 50 ppm SO_2 . The failure of proper response may have been caused by the small ratio of surface

area of the beads to dead space between the beads. Also, the small amount of water that was absorbed was a source of limitation. An additional limiting factor was the lack of reaction of blackened resin with ethanol to form the red complex or with I^- and IO_3^- to form I_2 . For these reasons, further studies were not conducted.

D. Absorption of Yellow Sodium Salt of Oxohydroxybis(8-hydroxy-quinolino-)vanadium(V) on Weak Base Resins

The weak base resin used in the experiment was Bio-Rex 9, 20-50 mesh, Pyrdenium type, Chloride form. The loading procedure was similar to that used in the strong base resin experiment. Again it was found that it was advantageous to use an ethylene glycol mixture in the loading procedure. The reactivity of this resin to SO_2 bore similarities to previous experiments; that is, damp resin was very reactive while dry resin was much less reactive. The relative degree of reactivity was approximately the same for both the weak base resin and the strong base resins.

Loaded weak base resins that had been exposed to SO_2 reacted with 95% ethanol to give the red color; however, no reaction occurred in the I^- - IO_3^- system when similar samples of the resin were added. Also, the use of the ethylene glycol-water mixture in the loading of the resin decreased the reaction of the exposed sample of the resin with 95% ethanol. A sample that had been exposed to 50 ppm of SO_2 for 30 min in the same manner as previously described did not react with either the 95% ethanol system or the I^- - IO_3^- system.

Weak base resins were employed to determine if the idea of using a loaded resin was at fault or if the active site needed to be different from the strong base quaternary ammonia site. From evidence which

was accumulated, it was apparent that loaded resins could not be used. Therefore, other supports were examined.

E. Formation of Salts of Oxohydroxybis(8-hydroxyquinolino-)vanadium(V)

Research done on the MgSO_4 - yellow sodium salt mixture had revealed that MgSO_4 would dissolve to some extent in an aqueous solution of the yellow sodium salt. The introduction of a large amount of MgSO_4 resulted in the formation of a precipitate. The precipitate, the Mg^{+2} salt of the black acid, was formed by Mg^{+2} displacing the Na^{+2} from the yellow salt. The Mg^{+2} salt of the black acid was yellow in color and exhibited some tendency to react with SO_2 to form the black acid.

Two types of salts of the black acid were made: (a) salts of metal cations and (b) salts of complex cations. The metal salts were made using Ba, Va, Mg, Ag, Pb, and Cd. The larger cations investigated were tetraphenylarsonium ion, tetraphenylphosphonium ion, benzyltriphenylphosphonium ion, tetramethylammonium ion, and tetraethylammonium ion. The salts were prepared by dissolving 0.5 g of the yellow sodium salt in 150 ml of deionized water. Ten drops of concentrated NH_4OH were added to insure basic conditions. Approximately 0.1 g of the cation to be used was dissolved in 20 ml of deionized water. After all solids had dissolved or apparently reached equilibrium, the 20 ml of cation solution was slowly added to the 150 ml of yellow sodium salt solution. The mixture was continuously stirred with a magnetic stir bar. The solid thus formed was removed from solution via suction filtration. A medium pore glass frit funnel was used. The solid collected was washed with several portions of deionized water.

The solids were dried at room temperature in a vacuum oven and stored in glass vials.

No salts of the quaternary ammonium or phosphonium ions were collected. All of the ions formed oil-like substances when added to the solution of the yellow sodium salt. The oil-like substance settled out of the solution, and it was soluble both in acetone and in 95% ethanol.

All of the metal cations produced solid masses that were easily collected. A qualitative evaluation of the solubility of the metal salts revealed the following relative solubilities, Mg being the most soluble:



The relative solubilities exhibited in aqueous solutions also were exhibited in solutions of acetone and in solutions of 95% ethanol.

The dried metal salts were finely powdered and exposed to SO_2 . In all cases, the yellow salts turned dark green when exposed to SO_2 . The reaction was confined to a thin layer on the surface of the metal salts. Continued exposure to SO_2 produced no reaction of the metal salt below this thin surface layer.

Additional limitations regarding the use of the metal salts were encountered. After ten days, the metal salts had decomposed and were completely unreactive to 100% SO_2 . Storage of the metal salts in brown glass vials and in drawers failed to prevent decomposition. Investigations into the decomposition products were not attempted. Also, metal salts that had been exposed to SO_2 failed to react with the I^- - IO_3^- system. A cloudy solution was formed. Similar problems were encountered when using the 95% ethanol system.

The investigation of metal salts of the black acid was conducted to determine if such salts would form porous solids and would incorporate a greater amount of water than was incorporated in the yellow sodium salt. Both the failure of the metal salts to conform to these expectations and the problems previously indicated led to the abandonment of further research of this method.

F. Formation of Yellow Sodium Salt of Oxohydroxybis(8-hydroxyquinolino-) vanadium(V) on Anionotropic Alumina

Experimental:

The reagents used for the formation of the yellow sodium salt on anionotropic alumina were reagent grade. The same reagents were used in the preparation of the yellow sodium salt as had been indicated previously. Two types of anionotropic alumina were employed:

- (1) Aluminum Oxide; Woelm Acid; (anionotropic)
- (2) Alumina, Activated; Alcoa, Type F-1; 60-80 mesh; AX612-3

A majority of the research used the Woelm alumina.

The formation of the yellow sodium salt on anionotropic alumina was carried out in the following manner.

- 1) A 1.0 M solution of NaVO_3 was prepared by dissolving 30.48 g of NaVO_3 in 250 ml of deionized water.
- 2) Ten g of alumina were placed in a beaker and washed several times with deionized water.
- 3) To the beaker containing the wet alumina, 100 ml of the 1.0 M NaVO_3 solution was added. When the VO_3^- was adsorbed on the alumina, the alumina became light yellow in color. The mixture was stirred for 30 min. During the stirring

period, the stirring was momentarily stopped and a small portion of the solution was placed in a test tube. A small amount of 8-hydroxyquinoline was added to the test tube and the color was noted. If a yellow solution was formed, it implied that excess VO_3^- was present. If no color resulted from this addition, 20 ml of the 1.0 M NaVO_3 solution was added to the beaker containing the alumina to ensure that an excess of VO_3^- was available to be adsorbed by the alumina.

- 4) If an excess of NaVO_3 was present after 30 min of stirring, the alumina was allowed to settle and the solution was decanted. The alumina was washed several times with deionized water and was placed in an oven to dry at 110°C .
- 5) The dried alumina was allowed to cool to room temperature and steps 3 and 4 were carried out again.
- 6) After the twice-treated alumina had cooled, 100 ml of CHCl_3 was added to the beaker. 8-Hydroxyquinoline slowly was added to the beaker while the mixture was stirred with a magnetic stir bar. Since it was desirable to have an excess amount of 8-hydroxyquinoline available, the CHCl_3 solution was checked for an excess after an apparently sufficient quantity of 8-hydroxyquinoline had been added. To test the solution, a small portion of the solution was added to alumina, which had been treated with NaVO_3 . Formation of a yellow color indicated that the desired excess was present.
- 7) After 20 min of stirring, the alumina was allowed to settle in the beaker, and the CHCl_3 was decanted. Fresh portions of CHCl_3 were used to wash the alumina. The wet alumina then was placed in a vacuum oven and dried at room temperature.

- 8) The dry alumina was placed in a glass container and stored until use. This loaded alumina was a deep yellow and is further referred to as Reagent A.

Variations of the amount of NaVO_3 used, the stirring time, the amount of 8-hydroxyquinoline added, etc., were studied before the above procedure was established. Optimum results were obtained using the above method of preparation.

The apparatus used to conduct quantitative evaluation of Reagent A is diagrammed in the Appendix. The apparatus was adapted for use in the evaluation of solid reagents by the construction of a sample holder shown in Figure 3. (The sample holder was constructed by Mr. Mitsugi Ohno.) For later evaluation, the apparatus was modified again as shown in Figure 4. The second modification allowed the use of 1 mm glass tubes.

The gases used in the evaluations were SO_2 and NO_2 . The initial set of tests involved the use of 0.55% SO_2 - and 0.58% SO_2 -by-volume Lif-O-Gen Chemispheres. Later tests of the reagent used a gas permeation tube as a source of SO_2 . This permeation tube was a Sulfur Dioxide Permeation Tube #11-5, National Bureau of Standards. The NO_2 had two sources: a 0.55% NO_2 -by-volume Lif-O-Gen Chemisphere and a lecture cylinder of 100% NO_2 (Air Products). The permeation rates for the SO_2 permeation tube are listed in Table IV.

The evaluation procedure differed slightly according to which gas was used, which source of gas was used, which sample holder was used, and which treatment the reagent received after it had been exposed to the acidic gas. The general procedure was established as follows:

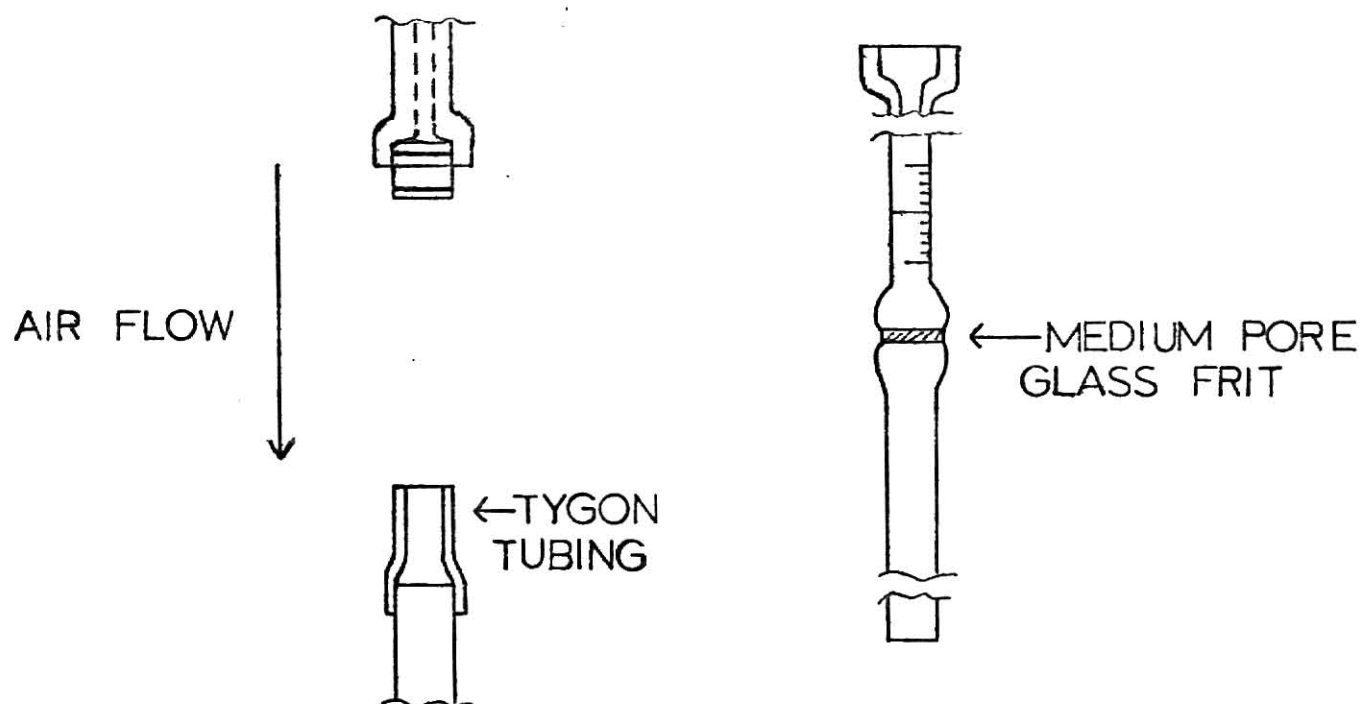


Figure 3 Sample Holder Constructed for Use With Solid Reagent

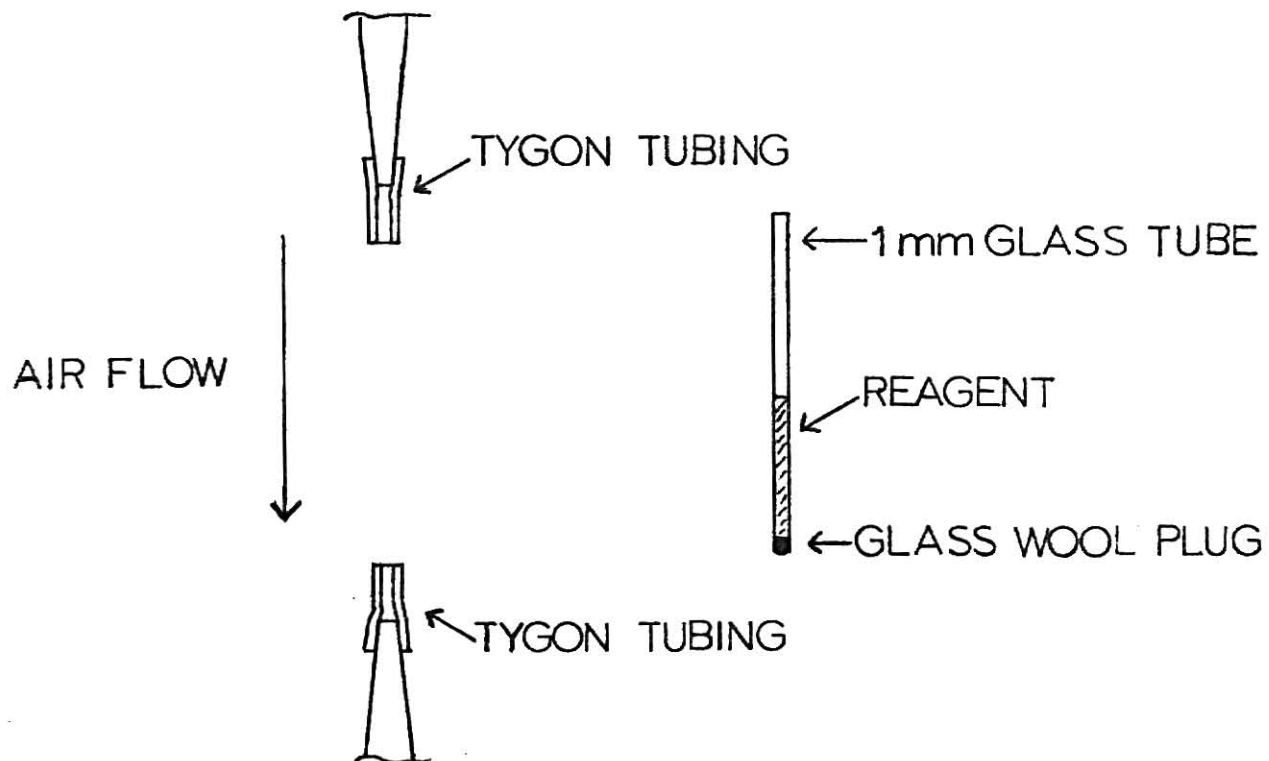


Figure 4 Modification Using 1 mm Glass Tubing

Table IV

Certified Permeation Rates for Tube No. 11-5

Temperature, ° C	Permeation Rate, SO ₂ , μg/min
20.00	1.745
21.00	1.885
22.00	2.036
23.00	2.300
24.00	2.376
25.00	2.567
26.00	2.773
27.00	2.996
28.00	3.237
29.00	3.496
30.00	3.777

The permeation rate is represented by the equation

$$\text{Log } R = M(273.15 + T) - B$$

where $M = .033537$, $B = 9.58870$, $T = \text{Temperature in } ^\circ \text{C}$

- 1) The syringe was filled with the proper gas at the desired concentration.
- 2) The proper amount of Reagent A was placed in the sample holder. The sample holder was then fitted into the gas dilution system.
- 3) The flow rate was adjusted to the desired level and the syringe drive was started.
- 4) After a pre-determined amount of time, the sample holder was removed from the gas dilution system and the syringe drive was stopped.
- 5) When using the sample holder shown in Figure 3, Reagent A was poured from it and the exposed reagent was treated with a 95% ethanol solution. If the 1.0 mm glass tubing was used as a sample holder, the length of darkening in the column of Reagent A was measured with a callipers.

The exposed Reagent A that was to be treated with 95% ethanol was poured from the sample holder into a 50 ml erlenmeyer flask. Ten ml of 95% ethanol was pipetted into the flask and the flask was placed in a shaker (Warner-Chilcott Laboratories). After shaking the mixture for 30 min, the alumina was allowed to settle and the solution was decanted into a test tube. The residual solids in this solution were removed by centrifugation. The clear supernatant was poured into a 1 cm glass cell, and the absorbance of the solution was measured at 480 nm in a Coleman 124 spectrophotometer.

Results and discussion:

In preliminary analysis, the blackened reagent formed by exposure of Reagent A to SO_2 was not able to catalyze the formation of I_2 in

the I^- - IO_3^- system. The failure of the blackened Reagent A to give the desired results stems from the fact that the black acid which was formed is insoluble in water and is a weak acid. Also, the addition of the CdI_2 -linear starch reagent to a beaker containing the exposed Reagent A in the I^- - IO_3^- solution caused a precipitate to form. The precipitate was probably the insoluble Cd salt of the black acid. For the above reasons, no extensive work using the I^- - IO_3^- system was done.

Further evaluations employed 95% ethanol to determine the amount of Reagent A which had reacted when exposed to SO_2 . Table V lists the results which were obtained when Reagent A reacted under the following conditions:

Total Flow Rate	1000 ml/min
Gas Flow Rate	0.97 ml/min
Gas Source	0.58% SO_2
Time of Exposure	20 min

Table V

Absorbance Measurements of 95% Ethanol Solution
Reacted with Reagent A Following Exposure of Reagent A to SO_2

Run #	Absorbance	Date Run
Blank	0.37	7/31/73
1	0.52	7/31/73
2	0.62	7/31/73
3	0.59	7/31/73
4	0.59	7/31/73
Blank	0.18	8/1/73
1	0.37	8/1/73
2	0.37	8/1/73

The sample results that are listed in Table V are typical of those obtained. During any one day of testing, it was possible to obtain a series of consistent results. However, it was impossible to obtain the same results using the same conditions one day later. As Reagent A aged, the difference between an exposed sample and a blank sample would decline as would the absolute value of absorbance measured. No difference could be detected between the absorbance of a blank sample and an exposed sample after Reagent A had aged for one week.

Visual comparison indicated that the amount of Reagent A that was darkened remained approximately constant, although the response to 95% ethanol was decreasing. An attempt was made to compare the amounts of blackened Reagent A by using a 1 mm glass tubing. Table VI contains the results of those measurements. The experimental conditions are listed below.

Total Flow Rate	75 ml/min
Gas Flow Rate	2.4 μ g/min (0.94 μ l/min)
Gas Source	SO ₂ Permeation Tube
Time of Exposure	30 min
Temperature	24.0 $\pm$ 0.5° C

A comparison of results in Table V and Table VI indicated that the instability that was evident in Table V was due to the use of 95% ethanol in determining the amount of reacted Reagent A. Reagent A itself is stable and could be useful as a self-indicating adsorbent for acidic gases. No plausible explanation was made in regard to the failure of 95% ethanol to determine consistently the amount of reacted Reagent A.

Table VI

Length of Darkened Column of Reagent A After Exposure to SO_2

Run #	D in mm	Date
1	10.0	9/10/73
2	10.0	9/10/73
3	10.4	9/12/73
4	10.5	9/12/73
5	10.2	9/14/73
6	10.4	9/14/73
7	10.5	9/16/73
8	10.5	9/16/73
9	10.0	9/23/73
10	9.7	9/23/73
11	10.5	9/30/73
12	10.3	9/30/73
13	10.0	10/10/73
14	10.1	10/10/73

Mean D = 10.2 mm; s = $\pm$ 0.3 mm

Studies relating to the stability of Reagent A revealed that this reagent is light sensitive. Exposure to laboratory lighting caused a color change from yellow to reddish-brown. The reddish-brown reagent showed less tendency to react with SO_2 . No investigation of the products formed by the light-induced reaction were performed.

The ability of Reagent A to detect acidic gases results from the ability of the reagent to overcome the problems associated with surface area and with adsorbed water. The formation on alumina of a thin, mono- or multi-layer coating of the yellow sodium salt

removed the problems associated with the crystalline structure of the yellow sodium salt. In addition to increasing the amount of yellow sodium salt available to react with acidic gases, alumina adsorbs water quite readily. The adsorption of water on the surface of the alumina created the necessary conditions for the acidic gases to be adsorbed on the surface of Reagent A. The adsorbed acidic gas reacted with the adsorbed water to form either a hydrated acid, as in the case of HCl, or the acid, as in the case of NO_2 and SO_2 . The water-acidic gas product then was able to react with the yellow sodium salt to form the black acid. Table V presents evidence that Reagent A. functions in this manner.

Extensive investigations into the quantitative ability of Reagent A were not made. A more useful reagent, which is described in the next section, had been prepared and extensive investigation of that reagent were made.

G. Formation of Yellow Sodium Salt of Oxohydroxybis(8-hydroxy-quinolino-)vanadium(V) on Silica Gel

Experimental:

The reagents used for the formation of the yellow sodium salt on silica gel were reagent grade. The chemicals which were used to prepare the yellow sodium salt also were used in the preparation of this salt on silica gel (Reagent B). Silica Gel S-157, 28-200 mesh, Grade 12, (Fisher Scientific Co.), was employed. This gel was powdered in a mortar and pestle. A small amount of force was applied to prevent complete powdering of the silica gel. The ground silica gel was placed in a stack of standard sieves: 60 mesh, 150 mesh, and

200 mesh (U.S. Standard Sieve, Cual Mfg, Co.). Silica gel having a mesh size of 150-200 mesh was used.

The formation of the yellow sodium salt on silica gel was carried out in the following manner:

- 1) Ten g of silica gel (150-200 mesh) were washed with several portions of deionized water. To the damp silica gel, 150 ml of 2.0 N NaOH was added. After mixing the silica gel mixture with a magnetic stir bar for 30 min, the NaOH solution was decanted and the silica gel was washed several times with deionized water.
- 2) To the washed silica gel, 100 ml of a saturated NaVO_3 solution was added. After 30 min of stirring with a magnetic stir bar, the excess solution was decanted and the wet silica gel was placed in an oven and dried at 100°C .
- 3) The dried silica gel was allowed to cool before adding 100 ml of CHCl_3 . While stirring with a magnetic stir bar, 8-hydroxyquinoline was slowly added. To insure an excess of 8-hydroxyquinoline, a small portion of the solution was removed and tested with a small sample of anionotropic alumina that had been treated with NaVO_3 .
- 4) After the mixture had stirred for 30 min, the CHCl_3 was decanted, and the loaded silica gel (Reagent B) was washed several times with fresh CHCl_3 . After drying at room temperature in a drying oven, the reagent was placed in a glass vial and stored in a laboratory bench drawer.

Although other variations were attempted before the above preparation was developed, this preparation afforded optimum results. The reasons for using a saturated NaVO_3 solution and not washing the support after step 2 was to compensate for the fact that silica gel is a cationotropic support. If the silica gel had been washed, a large portion of the NaVO_3 would have been removed. The resulting reagent would have had a very small amount of the yellow sodium salt adsorbed on the surface of the support.

The apparatus described in the previous section was used also in the evaluation of Reagent B. This apparatus was modified as depicted in Figure 4. Hamilton gas-tight syringes (1.0 ml, 10.0 ml, and 20.0 ml) were employed.

The gases used in the evaluation of Reagent B were HCl , NO_2 , and SO_2 . The sources of SO_2 and NO_2 are described in the previous section, whereas the source of HCl was a lecture cylinder (Air Products).

The evaluation procedure was similar to that described in the previous section. To obtain the desired concentration of HCl and NO_2 , a gas-tight syringe was filled with a sample of the pure gas. This gas was injected into the 20 ml Hamilton syringe on the gas dilution apparatus. After much practice, uniform injections could be made, resulting in a uniform concentration of NO_2 or HCl in the 20 ml Hamilton syringe. The most frequent ratios of pure gas to laboratory air were 2:18, 4:16, 4:15, and 8:12. The use of these concentrations facilitated syringe flow rates that prevented problems with diffusion effects.

Results:

Confirmation of the total adsorbent nature of Reagent B is indicated in Table VII. The total flow rate was 75 ml/min.

Table VII

Comparison of Concentration of Acidic Gases Using Reagent B

Gas	Concentration in ppm	Exposure Time in min	D in mm
NO ₂	65	30	5.8
NO ₂	130	15	6.0
HCl	26	30	4.0
HCl	52	15	3.9

Calibration curves were made using Reagent B for detection of HCl, NO₂, and SO₂. A minimum of four determinations were made at each of the microgram levels indicated. A callipers was used to measure the length of darkening in the 1 mm glass sample holder. The accuracy of the measurement was to the nearest 0.1 mm. Standard deviation was calculated according to the equation

$$s = \sqrt{\frac{(D_i - \bar{D})^2}{N - 1}}$$

where s is the standard deviation, D_i is the length of a particular determination, $\bar{D}$ is the average length, and N is the number of D_i . The results are given in Table VIII and Figure 5.

Table VIII

Reaction Distance and Standard Deviation
for Calibration Curves for Reagent B

Gas	μ l of gas	μ g of gas ^a	D in mm ^c
HCl	19.4	28.2	$1.7 \pm .2$
HCl	38.8	56.3	$3.0 \pm .4$

Table VIII (continued)

Gas	μl of gas	μg of gas ^a	D in mm ^c
HCl	58.2	84.5	$3.9 \pm .4$
HCl	77.6	112.6	$4.7 \pm .3$
HCl	97.0	140.8	$5.5 \pm .4$
HCl	116.4	169.0	$6.1 \pm .4$
HCl	155.2	225.2	$7.7 \pm .2$
HCl	174.6	253.5	$8.4 \pm .3$
HCl	236.8	338.0	$10.5 \pm .2$
Gas	μl of gas	μg of gas ^a	D in mm ^d
NO ₂	48.5	88.8	$2.0 \pm .2$
NO ₂	97.0	177.6	$3.8 \pm .4$
NO ₂	145.5	266.4	$5.6 \pm .2$
NO ₂	194.0	355.2	$7.0 \pm .4$
NO ₂	242.5	444.0	$8.7 \pm .2$
NO ₂	291.0	532.8	$10.0 \pm .2$
Gas	μl of gas	μg of gas ^b	D in mm ^e
SO ₂	4.34	11.88	$2.0 \pm .1$
SO ₂	8.68	23.76	$4.0 \pm .3$
SO ₂	13.68	35.64	$6.0 \pm .2$
SO ₂	17.36	47.52	$7.7 \pm .4$
SO ₂	21.70	59.40	$9.0 \pm .3$
SO ₂	26.04	71.28	$10.0 \pm .2$
SO ₂	39.06	106.92	$14.0 \pm .4$
SO ₂	52.08	142.56	$17.0 \pm .2$

- a) μg of gas were calculated from μl using $PV = nRT$
- b) μg of gas were calculated by using Table IV
- c) $s = \pm 0.1 \text{ mm}$ is equivalent to $\pm 2.6 \mu\text{g}$ or $1.8 \mu\text{l}$
- d) $s = \pm 0.1 \text{ mm}$ is equivalent to $\pm 5.0 \mu\text{g}$ or $2.6 \mu\text{l}$
- e) $s = \pm 0.1 \text{ mm}$ is equivalent to $\pm 0.6 \mu\text{g}$ or $0.24 \mu\text{l}$

Discussion:

Qualitative evaluation of Reagent A and Reagent B led to the use of Reagent B. Besides being less sensitive to heat and light, Reagent B responded to acidic gases with a more definite color change, facilitating a more accurate determination of reaction distance. A comparison of Tables VI and VIII indicates that the reagents give nearly the same response to equal amounts of SO_2 ($10.2 \pm .3 \text{ mm}$ of Reagent A vs $10.0 \pm .2 \text{ mm}$ of Reagent B).

Table VII illustrates the total adsorbent nature of Reagent B. The sequence of reactions relating to the adsorption of an acidic gas on Reagent A, discussed in the previous section, also applies within limits to Reagent B. If the concentration of NO_2 or HCl is greater than needed to react with the yellow sodium salt. In the case of HCl , a bleaching effect takes place. If the reagent is subsequently placed in a stream of air free from HCl or NO_2 , a slow diffusion process takes place. Again in the case of HCl , the bleached reagent slowly darkens until black. For this reason, the data for the calibration curves is based upon Reagent B being exposed to a constant concentration of an acidic gas for a variable amount of time.

As explained in the preparation of Reagent B, the silica gel ranged in size from 150-200 mesh. The mesh size affects both the surface area of the reagent and the total flow rate of air through a

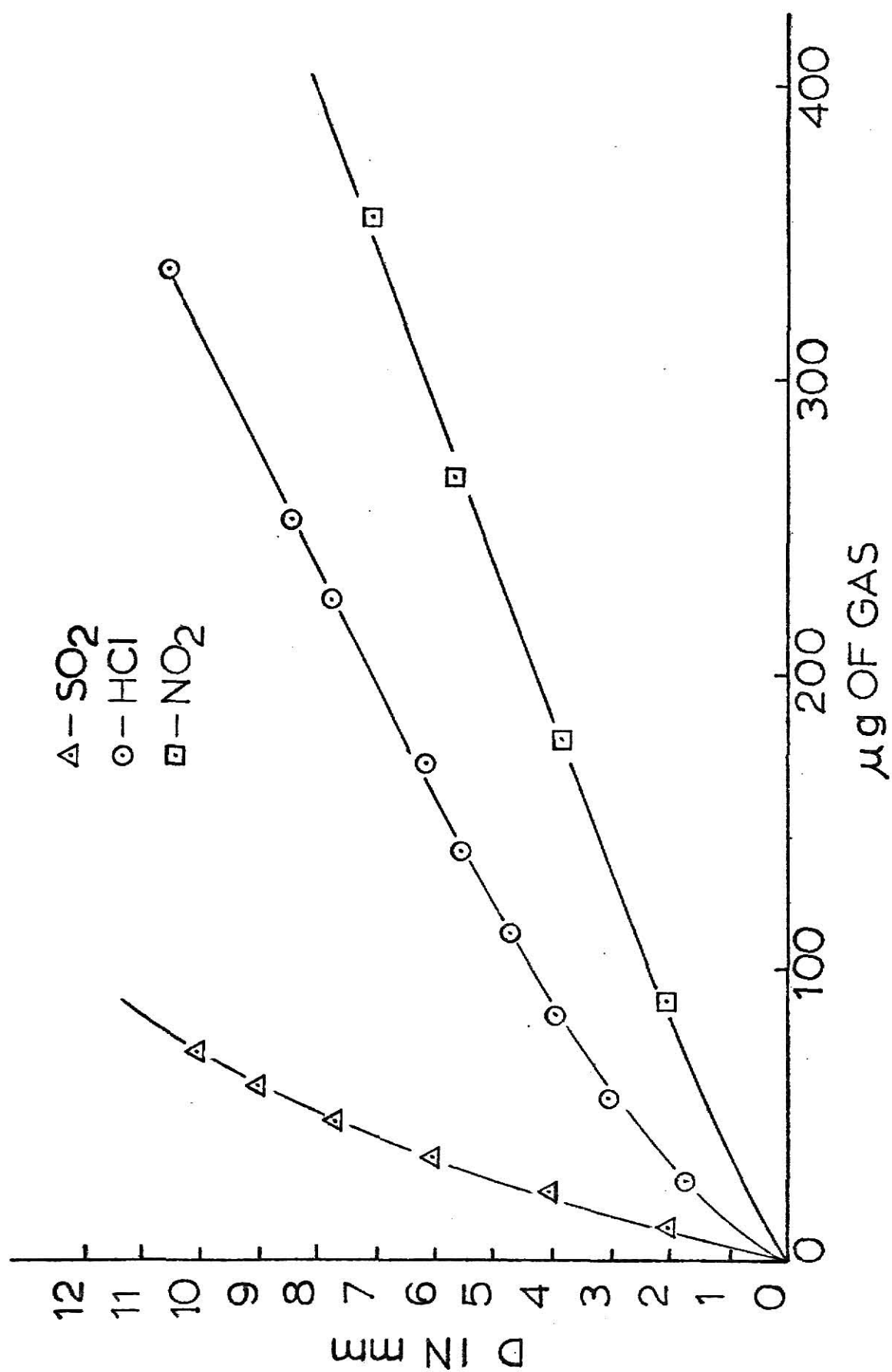


Figure 5 Calibration Curves for Reagent B

15 mm by 1 mm column of the reagent. If a smaller mesh size had been employed, the maximum flow rate through the 1 mm column would have been less than 40 ml/min. The 150-200 mesh silica gel gave the best results.

The calibration curves indicate a slightly nonlinear response of Reagent B to acidic gases. The nonlinearity of the response can in part be explained in terms of the reaction sequence described in the previous section. The adsorption of the acidic gas molecules on the surface is the initial step of the sequence. The other two steps of the sequence involve the combination of the adsorbed gas with the water adsorbed on the surface, followed by the reaction of this combination product with the yellow sodium salt, resulting in the formation of the black acid. After the yellow sodium salt of a particular area of the surface has completely reacted, it may adsorb gas molecules from the passing air. The adsorbed gas molecules do not undergo any reactions, but are adsorbed and desorbed setting up an equilibrium between the air stream and the surface of the support. The support surface available for this type of equilibrium increases as the length of the darkened column increases. An additional factor that may explain the nonlinearity is the bleaching effect, which was described previously. If the concentration of strong acids, such as HCl and HNO_3 , becomes too large, the nitrogen on the 8-hydroxyquinoline may become protonated. The protonation causes the coordination of the nitrogen with the vanadium to uncouple. This uncoupling destroys the resonance in the system, and the color changes from black to white. The bleaching process is an equilibrium reaction which will occur only with strong acids. Both of the above mentioned equilibria may cause the slight nonlinearity evident in Figure 5. The significance

of the nonlinearity is minimal provided it is considered in determining the concentrations of acidic gases.

The comparison of calibration curves in Figure 5 shows that the amounts of different acidic gases required to cause a given length of reaction vary to a substantial extent. Part of this variation can be explained in terms of the strength of the acid formed when the acidic gas is adsorbed on the surface of the support. When a strong acid is formed, it will readily react with the yellow sodium salt. The formation of the black acid effectively stops the reverse reaction and desorption from taking place. A weak acid, on the other hand, will have less tendency to react with the yellow sodium salt and will be more susceptible to the reverse reaction and desorption. Based upon this reasoning, the amount of acidic gas needed to darken a given length of column should be greater for HCl and NO₂ than for SO₂. It is assumed that H₂SO₃ is formed when SO₂ is adsorbed. To form H₂SO₄, SO₂ would have to be oxidized to form SO₃. The possibility of vanadium(V) oxidizing SO₂ does exist; however, because of the complexed nature of the vanadium(V), it is expected that such a reaction is not likely to occur. H₂SO₃ is a weak acid, pK₁ = 1.81 and pK₂ = 6.91, in relation to HCl and HNO₃.

As can be concluded from the above statements, an amount of SO₂ darkened a larger volume of the reagent than did the same amount of NO₂ or HCl. Although SO₂ darkened a larger volume, NO₂ and HCl produced a blacker reagent upon exposure. If the quantities of intensity of darkening and of length of darkening could be included in a single measurement, the acidic gases would have produced nearly the same results.

The difference in the amount of HCl versus the amount of NO_2 required to darken a given length of a column of Reagent B, as shown in Figure 5, cannot be predicted on the basis of acid strength. HCl and HNO_3 are approximately equal in acid strength; thus, for a given length of reaction, the same amount of both HCl and NO_2 should be required. The only explanation of the unexpected behavior of NO_2 versus HCl is based upon the purity of the NO_2 used. When exposed to visible light, NO_2 both dimerizes to form N_2O_4 and decomposes to form NO and O. Although this may explain part of the discrepancy, it is not believed to be the entire cause of the differences observed. No other plausible causes are advanced and no investigations into the purity of the NO_2 were made.

Qualitative studies of possible interfering gases were made. Reagent B did not react when exposed to 100% H_2S , 100% CO_2 , and 100% CO. In an additional study, black Reagent B did not respond to NH_3 vapor. However, it cannot be assumed that Reagent B would respond to a mixture of SO_2 and NH_3 as it responded to SO_2 . No extensive studies were done in the area of interferences.

In summary, a new solid phase, total adsorbent, self-indicator for acidic gases has been prepared. The adsorbent shows an excellent response to SO_2 , NO_2 , and HCl. Reagent B may have a possible practical application in situations requiring both an indication of the amount of acidic gases present and a means of removing them.

CHAPTER IV

EXTENSIONS AND CONTINUATIONS

Calibration studies of Reagent A need to be done. A qualitative study indicated that Reagent A responded in a consistent and quantitative manner to SO_2 . Further studies need to be done using HCl , NO_2 , and acetic acid. Along with such studies, more information is needed on the effects of possible interferences such as NH_3 . Also, the ability of Reagent A to adsorb acidic gases, as affected by temperature, humidity, and gas flow rate needs to be examined.

Similar studies need to be conducted with Reagent B. Studies of the capacity of the reagent need to be done. The results of such a study would shed light on the practical use of Reagent B as a total adsorbent. Attempts to incorporate an oxidizing agent in Reagent B were unsuccessful; however, further studies into such possibilities are needed to determine if an oxidizing agent which is milder than persulfate can be incorporated.

The possible usefulness of an inexpensive reagent such as Reagent A and/or Reagent B should cause continued experimentation. The commercial development of such reagents is a possibility which should be explored.

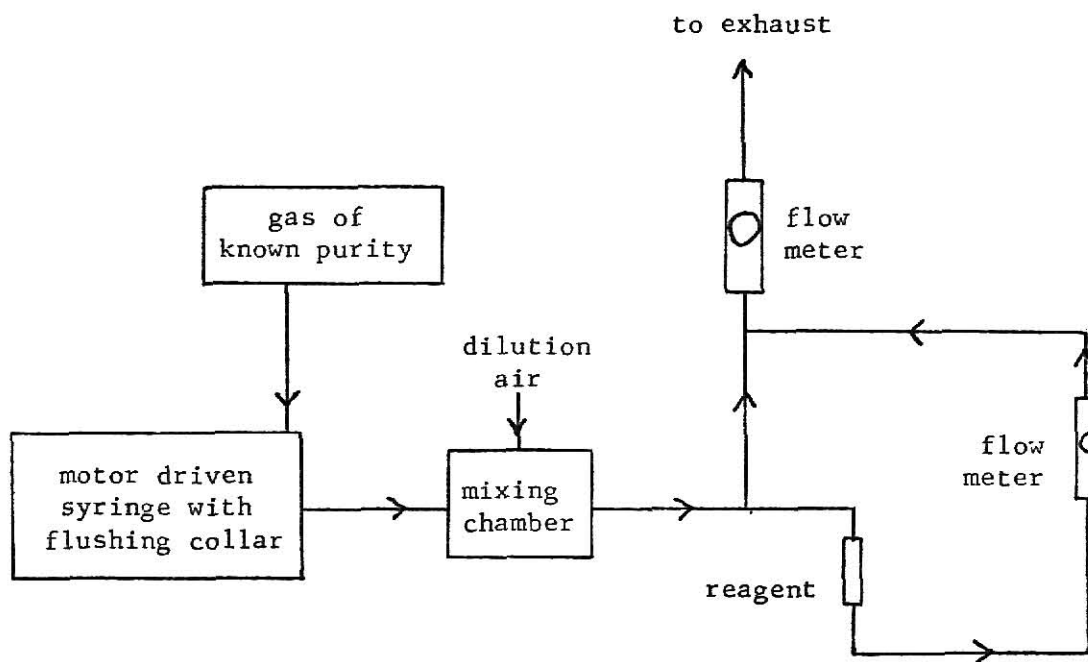
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APPENDIX

A schematic diagram of the gas dilution apparatus is shown below. The motor driven syringe was capable of delivering: 19.4, 9.7, 3.88, 1.94, 0.388, 0.194, 0.097, 0.0388, 0.0194, 0.0097, or 0.00388 ml per min. Total flow could be controlled between 250 ml per min and 12,000 ml per min. Flow through the reagent could be controlled between 20 ml per min and 800 ml per min. The system was entirely glass, except for valves, which were either glass or teflon.



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VITA

David A. Heying was born on Nov. 10, 1948, in St. Cloud, Minn. He lived on a small farm near the rural community of Richmond, Minn., until he graduated from Albany High School in 1966. He was the fifth child born to Ambrose and Leona Heying. He continued his education at St. John's University, Collegeville, Minn., starting in Sept. of 1966. St. John's University awarded him a B. S. in chemistry in May of 1970. In Sept. of 1970 he began his studies as a full time graduate student in chemistry at Kansas State University. He married Jean M. Silvers on Aug. 12, 1972.

STUDIES OF SOME LEAD AND VANADIUM COMPOUNDS
FOR USE AS ANALYTICAL REAGENTS

by

DAVID A. HEYING

B. S., St. John's University, 1970

AN ABSTRACT OF A MASTER'S THESIS

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Studies were conducted to determine the feasibility of using lead paraperiodate as an oxidizing agent for the determination of Mn^{+2} in aqueous solutions. The studies were based upon the use of periodate oxidation of Mn^{+2} to MnO_4^- as a standard method. The reasons for using $\text{Pb}_3(\text{IO}_5)_2$ included the insolubility of $\text{Pb}_3(\text{IO}_5)_2$ and the possible formation of $\text{Pb}_3(\text{IO}_5)_2$ on supports. The results of the study indicated that $\text{Pb}_3(\text{IO}_5)_2$ did not form on supports as desired. In addition, the formation of MnO_2 and a detection limit of 3 ppm Mn^{+2} , led to the abandonment of further research in this area.

A second set of investigations dealt with the possible reaction of oxohydroxybis(8-hydroxyquinolino-)vanadium(V), referred to as the black acid, with metal ions in aqueous solution. A method of detecting possible reactions included the construction of an apparatus to deliver a sample solution at an uniform rate to a spot of the black acid on a piece of filter paper. The apparatus was used in conjunction with a Weisz Ring Oven. From the colors of the reaction products obtained, several reaction schemes were discussed. The reaction schemes included the displacement of VO_2^+ from the black acid by a metal cation, an oxidation or reduction reaction between the black acid and a metal cation, and the formation of a metal salt of the black acid by displacement of the acidic hydrogen. Tests of those metals reacting revealed that no appreciable reaction occurred in solution of metal ion concentration of less than 150 ppm.

A third series of investigations involved attempts to form an adsorbent to detect acidic gases. Seven different adsorbents were prepared using the yellow sodium salt of the black acid. The conversion of the yellow sodium salt to the black acid was used to detect acidic gases. The adsorption of the acidic gas on the

adsorbent results in the formation of an acid which converts the salt from yellow to black. Of those adsorbents prepared, only two responded in a quantitative manner. The two adsorbents, Reagent A and Reagent B, were prepared by forming the yellow sodium salt on anionotropic alumina and silica gel, respectively. Calibration curves for Reagent B were developed using HCl, NO₂, and SO₂. Reagent B was found to respond in an approximately linear fashion to increases in the quantity of an acidic gas. Strength of the acid formed by the adsorption of the acidic gas on Reagent B accounts for the differences exhibited in the calibration curves using HCl, NO₂, and SO₂.