An investigation of the effects of acid solutions of vanadium in column chromatography
by Theodore Van Vorous

A THESIS Submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree
of Master of Science in Chemistry
Montana State University
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Abstract:
During an investigation of the possibility of using column chromatographic methods for the analysis of. Vanadium minerals it was found that the concentration of acid in the test solution determined to a great extent the distance Vanadium will migrate in certain absorbents. The purpose of this thesis is to show the effect of this phenomenon with various absorbents, solvents, and concentrations of acid.

Since the analysis of Vanadium minerals necessarily involves to a great extent the Geochemistry of that element, a brief outline of the Geochemistry of Vanadium has also been included in the introduction.

AN INVESTIGATION OF THE EFFECTS OF ACID SOLUTIONS
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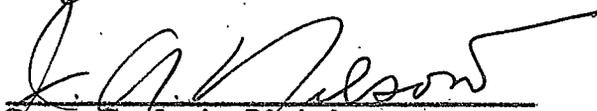
for the degree of

Master of Science in Chemistry

at

Montana State College

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August, 1954

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ABSTRACT

During an investigation of the possibility of using column chromatographic methods for the analysis of Vanadium minerals it was found that the concentration of acid in the test solution determined to a great extent the distance Vanadium will migrate in certain absorbents. The purpose of this thesis is to show the effect of this phenomenon with various absorbents, solvents, and concentrations of acid.

Since the analysis of Vanadium minerals necessarily involves to a great extent the Geochemistry of that element, a brief outline of the Geochemistry of Vanadium has also been included in the introduction.

II. INTRODUCTION

Since this study is not only concerned with the effect of acid concentration on the migration of vanadium, but is also somewhat a study of the separation of vanadium from other ions, it is important to know what ions occur with vanadium. For that reason, a brief summary of the geochemical character-istics of vanadium is included in this introduction.

Part A: Geochemistry of Vanadium

The wide distribution of vanadium throughout the earth's crust has been clearly established, not only in ores and coals but in clays, limestones, sandstones and igneous rocks. Vana-dium occurs in appreciable amounts in the more basic igneous and metamorphic rocks, up to .08% or more of vanadium trioxide, but seems to be absent or nearly so from the highly siliceous rocks. Some of the igneous and metamorphic rocks can carry up to .13% of vanadium trioxide in ferric aluminous silicates, especially in a biotite separated from a pyroxene gneiss. In general, the search for vanadium should be limited to rocks containing less than 60% silica.

In the upper lithosphere vanadium is oxyphile, a behavior dictated by the fact that it has three stable oxidation states, i.e., tri-, quadri-, quinquivalent vanadium. Because of its position in the periodic table, vanadium resembles phosphorous and titanium in its manner of occurrence but differs from them in several respects. It does not occur in the early pentlandite

assemblages or the late magmatic sulfides. On the other hand, vanadium does become enriched in titaniferous iron ores due to the replacement of titanium. It also concentrates in basic rocks, but has no connection with the phosphorous content in that respect.

In igneous rocks vanadium usually does not form independent minerals, but instead is concealed in the structure of other minerals. An exception is Ardennite, a complex manganese-aluminum-arsenic-vanadium silicate in which the vanadium occurs as VO_4.

Because of the similar ionic radii of vanadium in its three oxidation states and ferric iron, aluminum and quadrivalent titanium, vanadium has a great many replacement possibilities. Quinquivalent vanadium also easily replaces phosphorous in Apatite.

Feldspars are nearly devoid of vanadium, but the pyroxenes, amphibole, and the micas are normally carriers of vanadium. In this respect one mica, roscoelite, can be considered to be a vanadium mineral because much of the aluminum in its structure has been replaced by vanadium.

Vanadium minerals of secondary origin are more common because they become more highly concentrated. Because of the higher redox potentials they occur as vanadates. The minerals might be considered to be mineralogical curiosities because the conditions that form them are seldom met. The vanadium in these

minerals normally comes from enriched ground waters and thermal waters. The chief metals found with these vanadates are calcium, manganese, (ferric) iron, uranium, lead, copper, zinc and bismuth. They may form simple vanadates such as pucherite (bismuth vanadate) and steigerite (aluminum vanadate) or complex vanadates such as descloizite (a lead-copper-zinc vanadate) and carnotite (potassium uranyl vanadate).

Vanadium is found in the biosphere in a number of plants and small sea animals as well as in crude oil. In Persian crude oil, vanadium can occur as high as 2.82%. In any event, it constitutes a poison for cracking catylists.

In the Geochemical cycle of vanadium several important things are to be noted. Solution and migration takes place at relatively high redox potentials and in the quinqui-valent state it has a tendency to form anion complexes. When vanadium is mobilized it moves with the ground water until heavy metals such as copper, zinc, or lead are met and then vanadates will form. This is especially true in the presence of dolomitic and calcitic limestones which give the water and appropriate pH for precipitation. Vanadium will also precipitate in the presence of sulfide ion, a condition often met in crude oil.

When a study was made of the effects of organic material on the concentration of vanadium in clays and shales it was shown that as the organic material percentage went up so did the vanadium percentage. This is true in general for all

sedimentary material containing organic material.

These generalities I have mentioned are the more important characteristics of the Geochemistry of vanadium. They should serve at least as a partial guide to understanding the mode of occurrence of vanadium.

Part B: Considerations of the Thesis

Up to the present time no publications have been mentioned in Chemical Abstracts concerning the effect of acid concentration on the migration of vanadium ions in column chromatography. In addition, very few references were found concerning the use of column chromatography for the separation and determination of vanadium. Of the references available, the most comprehensive was written by T. Ashizawa (B-11). This study covered various solvents, absorbents, and color developing agents that were tried in order to develop inorganic analysis methods for water samples, minerals, and various rocks found in Japan.

Since there was a general lack of information concerning appropriate solvents, absorbents and color developing agents for inorganic column chromatography, a brief study had to be made of these subjects as they apply to vanadium analysis. After usable combinations of the above-named factors were found, experimentation could proceed. During this experimentation, it was observed that in a hydrated calcium silicate (Silene E.F.) absorbent as well as in other similar absorbents there was a

definite tendency for the migration distance of vanadium to be affected by the acid concentration of the test solution. A series of tests was set up to further investigate this fact. Columns were set up in which several possible factors such as vanadium, acid, and other ion concentrations were varied, one at a time. The effect of varying these factors is the basis for this Thesis.

III. APPARATUS

A. Apparatus Setup for Vacuum System

The original equipment used by the author is illustrated in Figure 1. It consisted of a column made of various diameters of soft glass tubing pulled out at the bottom to constrict it and enlarged at the top to allow easy application of test solutions. The diameter of glass tubing was varied in size from 6mm to 1cm (O.D.) to find a suitable size to use. The bottom of the tube was packed with a small wad of glass wool to prevent the absorbent from being pulled out by the vacuum. This column was placed in a cork of suitable size to fit a 500ml suction flask of the conventional type, and connected to a water suction pump. A test tube of suitable length was placed below the tip of the column inside the flask to collect the solvent coming through the column.

It was found that this type of setup had the disadvantage of packing the absorbent too tightly and also drying out at the bottom.

B. Original Setup for Gravity Feed System

To overcome the disadvantages of the suction system, a gravity fed column was tried. The apparatus consisted of a separatory funnel suspended about four feet above the column and connected to it with rubber tubing. The columns were made of 8mm (O.D.) glass tubing about 30cm long, and pulled out at the bottom. The columns were filled with the absorbent in the

form of a slurry to about one half of their length, and the solution to be tested was applied at the top. The columns were then connected to the rubber tubing and a pinch clamp opened to allow the solvent to flow.

Although this system worked well, it had the disadvantage of allowing only one sample to be run at a time unless a number of such setups were used.

C. Apparatus Setup for a Multiple Column System

The multiple column setup (Fig. 3) was essentially the same as the original gravity system except that calcium chloride drying tubes were used in place of a separatory tube. The multi-outlet tube was made in such a way that a source of air or nitrogen pressure could be applied, thus obtaining gravity and gas pressure at the same time on the columns. It was found later that the system flowed sufficiently fast with no gas pressure applied, so this part of the apparatus was removed.

This system allowed twelve columns to be run at once with two six multi-outlet tubes. This greatly increased the speed of the method and also its versatility. It too had a bad point in that the rubber tubing was attacked by the solvents being used. This was remedied by using glass tubing with surgical rubber joints as shown in Fig. 4.

Simple Suction Feed System

- -Soft Glass Column
(1cm I.D.) 25cm long

- -Solvent

- -Test Solution

- -Absorbent

- -One Hole Rubber Cork

- -Glass Wool
Collection Test Tube
- - - - - - - - - - - - - - To a Water Suction Pump

- -Vacuum Flask
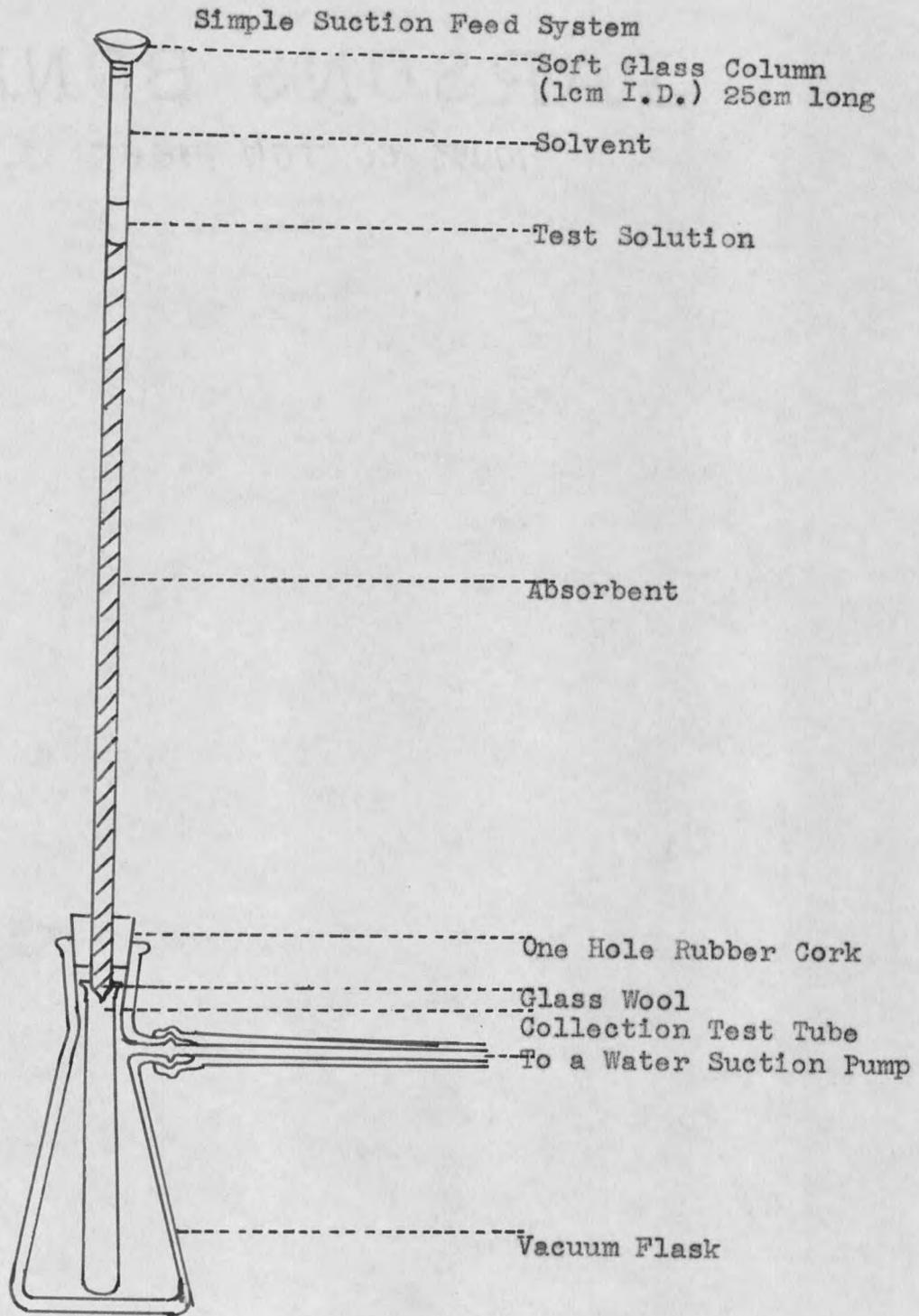
Figure 1

Simple Gravity Feed System

------------------------- Separatory Funnel

------------------------- Solvent

------------------------- Rubber Tubing

------------------------- Test Solution

------------------------- Absorbent

------------------------- 8mm Soft Glass
Column

------------------------- Glass Wool

------------------------- Collection Beaker

Figure 2

Multiple Column Gravity Feed System

----Multiple Outlet Tube

----Rubber Tubing

----Calcium Chloride Drying Tube

----Solvent

4'

----Tube Clamp

----8 mm (O.D.) Column

----Test Solution

----Column Stand

----Absorbent

----Glass Wool

----Collection Test Tube
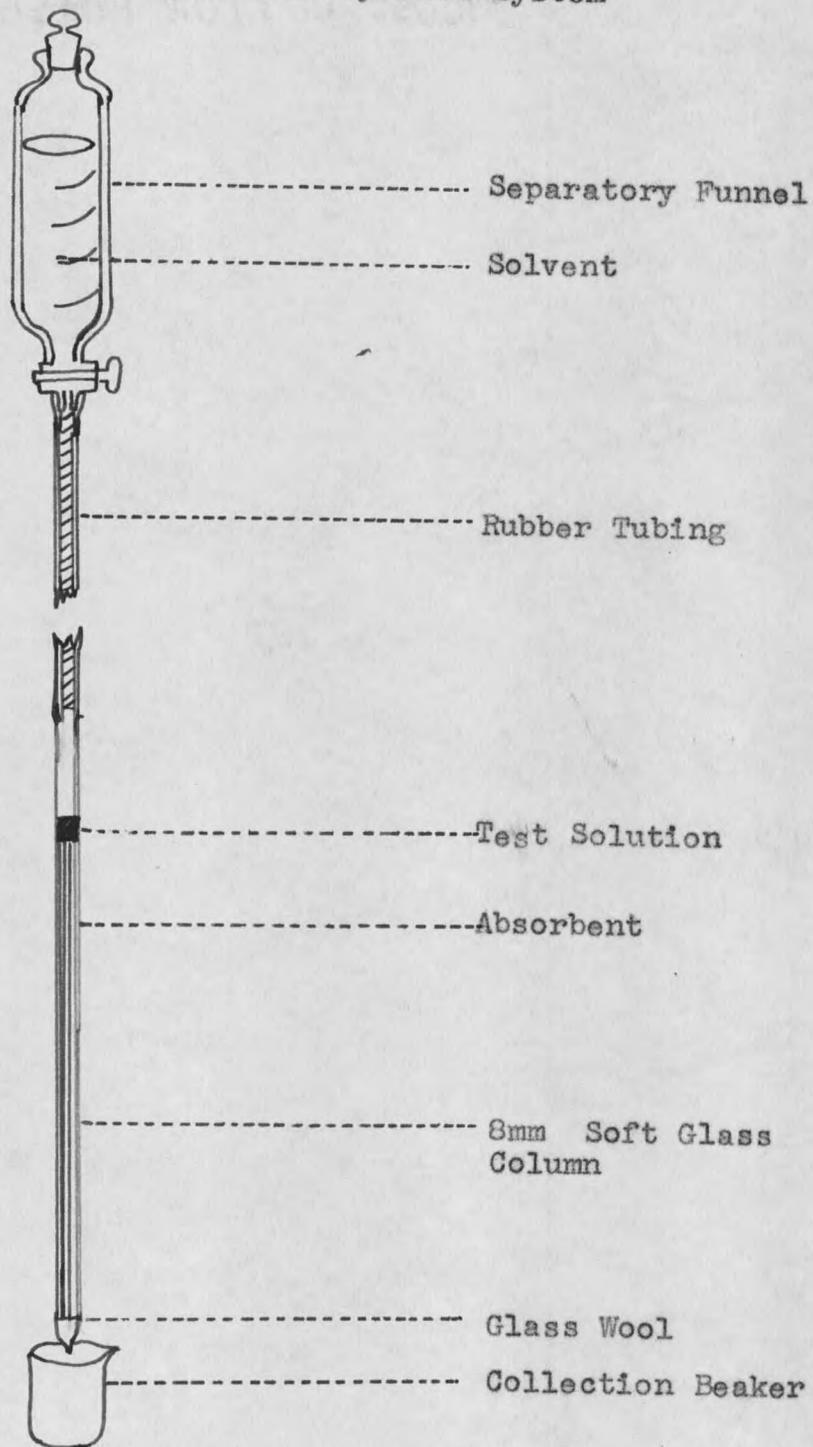
Figure 3

Modified Column Assembly

- - - - - - - - - - - - - - - - - Rubber Tubing

- - - - - - - - - - - - - - - - - Glass Tubing
- - - - - - - - - - - - - - - - - One Hole Rubber Cork

- - - - - - - - - - - - - - - - - Calcium Chloride
                                  Drying Tube

- - - - - - - - - - - - - - - - - Gum Rubber Tubing

- - - - - - - - - - - - - - - - - 8 mm Glass Tubing

- - - - - - - - - - - - - - - - - Gum Rubber Tubing
- - - - - - - - - - - - - - - - - Clamp

- - - - - - - - - - - - - - - - - 8 mm (O.D.) Glass
                                  Tubing

- - - - - - - - - - - - - - - - - Glass Wool
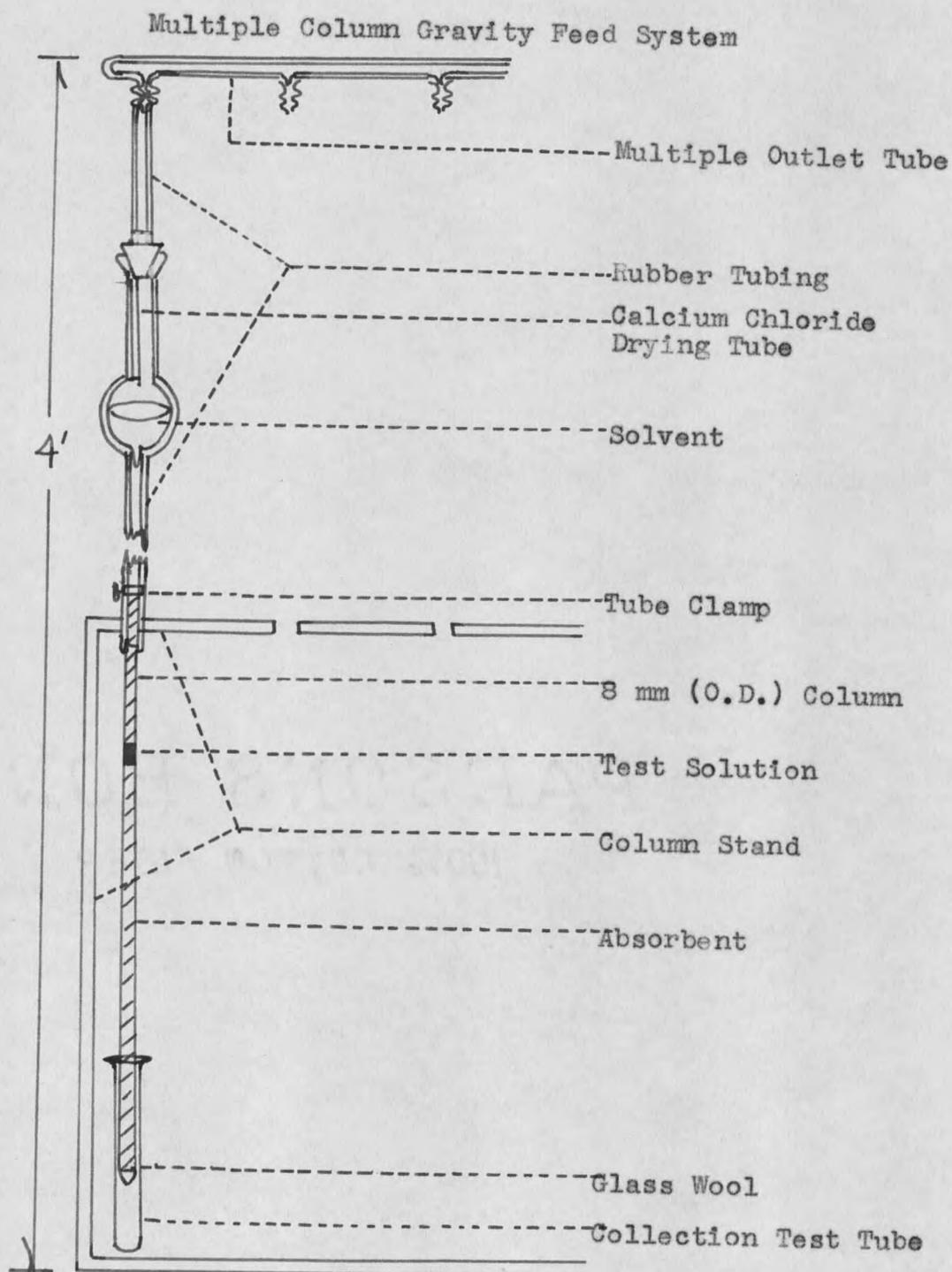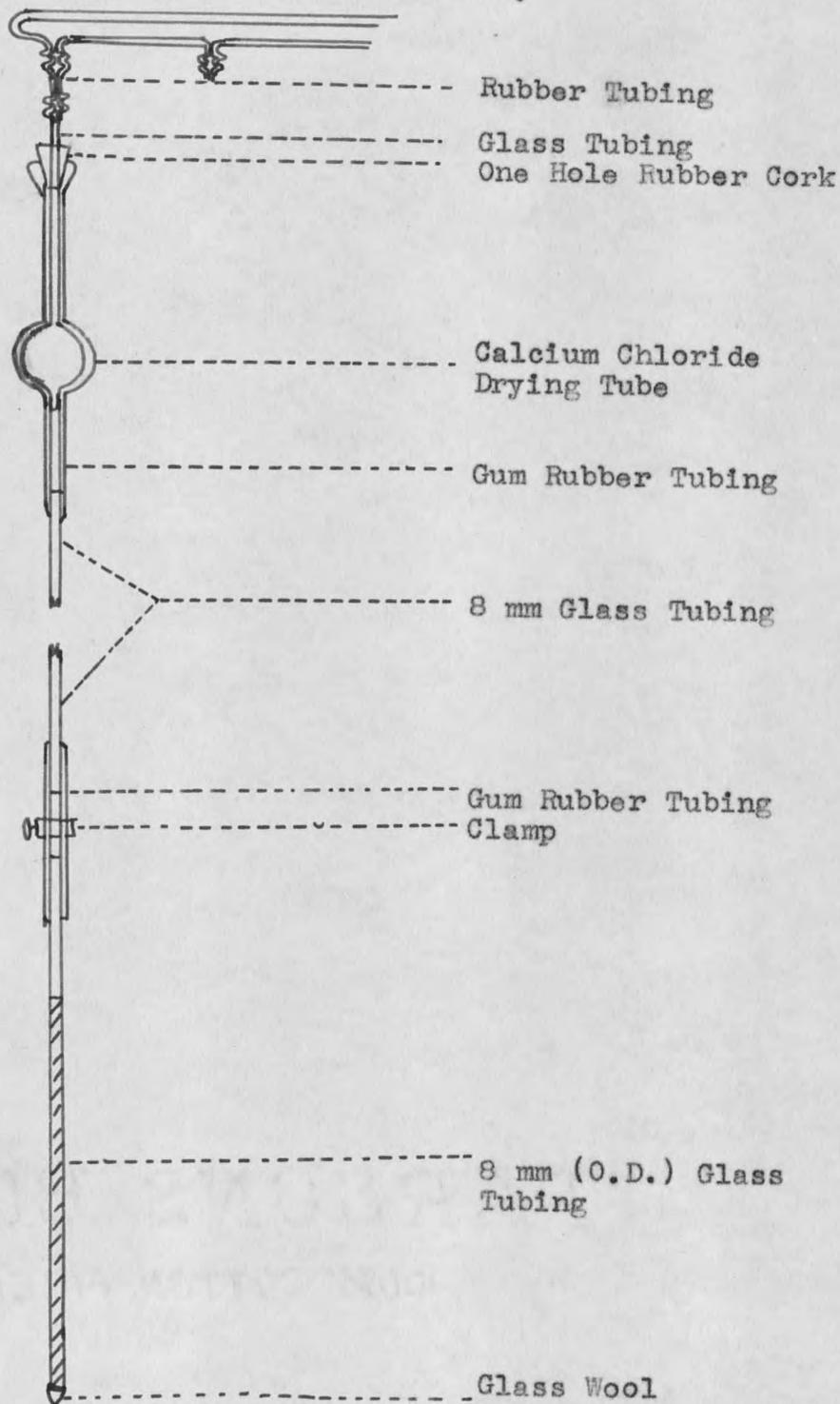
Figure 4

IV.   EXPERIMENTAL PROCEDURES

The following conditions and procedures were followed for all of the experimentation except where deviations are specifically noted. These conditions are not listed in any particular order.

1.   Except in the early experimentation, the absorbent being used was washed and then poured into the columns as a thick slurry. This was done with a partial vacuum applied to the bottom of the column to insure an even flow and no bubble formation.

2.   The absorbents used were as follows:

   a.   Aluminum Oxide--Baker Reagent Grade (ignited) thru #100 mesh.

   b.   Hydrated Calcium Silicate (Silene E.F.)--Columbia Southern Corp.--thru #100 mesh.

   c.   Tricalcium Phosphate--Malinkrodt Reagent Grade-- ground to pass #100 mesh.

   d.   Bone Ash--unknown analysis for impurities-- unknown producer.

   e.   Diatomaceous Earth--Tech. Grade

   f.   Fullers Earth--

   g.   Magnesium Carbonate--Baker C.P.

   h.   Calcium Carbonate--Baker C.P.

3.   The eluting solvents used were as follows:

   a.   Methyl Alcohol - Water (1:1)

b. Ethyl Alcohol - Water (1:1)

c. n-Propyl Alcohol - Water (1:1)

d. iso-Propyl - Alcohol (1:1)

e. n-Butyl Alcohol - Water (1:1)

f. Carbon Tetrachloride

g. Ethyl Acetate

h. Benzene

i. n-Butyl Alcohol - 1N Hydrochloric Acid (1:1)

j. n-Butyl Alcohol - 1N Nitric Acid - Oxine (1%)

4. The color developing agents used were as follows:

a. Hydrogen Sulfide passed through the column

b. 8-Hydroxyquinoline at the correct pH

c. Ammonium Polysulfide

d. Ultra-violet light (uranium)

e. Sodium Thiocyanate .1N soln.

f. Ammonium Hydroxide 2N

g. Phosphotungstic Acid

5. The solutions containing Vanadium were made up from the following reagents:

a. Sodium ortho-vanadate--

b. Sodium meta-vanadate--

c. Ammonium meta-vanadate--

d. Vanadium Trioxide

6. Since the absorbents containing carbonates and active forms of silica evolved gas in acidic solutions, the solutions