

ADSORPTION OF COPPER ON QUARTZ

BY

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ABSTRACT

The amount of copper that is adsorbed on the surface of quartz from aqueous solutions of varying copper concentration and varying pH has been investigated. The copper was determined by chemical means using dithizone. It was found that in solutions with the concentrations of copper and the pH's found in nature, the amount of adsorption varies from  $1.7 \times 10^{-12}$  to  $5.6 \times 10^{-12}$  moles of copper per square centimeter of quartz.

*Handwritten: Dept. of Geol. & Geophys. 15, 1955*

Thesis Supervisor: Herbert E. Hawkes

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TABLE OF CONTENTS		<u>Page</u>
ABSTRACT .....		2
LIST OF TABLES .....		4
LIST OF FIGURES .....		5
ACKNOWLEDGMENTS .....		6
PART 1		
I.	INTRODUCTION .....	7
	1. General Statement .....	7
	2. Water .....	8
	3. Adsorption .....	8
	4. Weathering .....	13
	5. Discussion of Copper in Solution .....	14
II.	OUTLINE OF EXPERIMENTAL METHOD .....	18
III.	EXPERIMENTAL RESULTS .....	20
	1. Chemical Results .....	20
	2. Spectrographic Results .....	26
IV.	SOURCES OF ERROR .....	27
V.	DISCUSSION OF RESULTS .....	31
VI.	CONCLUSIONS .....	35
VII.	SUGGESTIONS FOR FUTURE RESEARCH .....	36
VIII.	BIBLIOGRAPHY .....	38
PART 2	DETAILED PROCEDURE .....	41
PART 3	A METHOD FOR THE DETERMINATION OF THE HEAVY METAL CONTENT OF WATER .....	60
I.	INTRODUCTION .....	60
II.	PROCEDURE .....	61
III.	DISCUSSION OF RESULTS .....	62
BIOGRAPHICAL SKETCH .....		63

## LIST OF TABLES

TABLE		PAGE
1.	The pH of Natural Media and its Relation to the Precipitation of Hydroxides .....	17
2.	Experimental Determinations of Copper Adsorbed on Quartz .....	21
3.	Comparison of Chemical and Spectrographic Results...	26
4.	Effect of Concentration of Electrolyte on Double ... Layer Thickness .....	28

## LIST OF FIGURES

FIGURE	PAGE
1. A Model of Adsorption .....	11
2. Solubility Boundaries for Heavy Metal Hydroxides.....	16
3. Amount of Copper Adsorbed on Quartz expressed in Micrograms of Copper per Gram of Quartz.....	22
4. Amount of Copper Adsorbed on Quartz expressed in Moles per Square Centimeter of Quartz Surface.....	23
5. Photomicrograph of Quartz Particles.....	25
6. Solubility of Silica versus pH.....	30
7. Quartz Structure.....	30
8. Adsorption of Several Cations on Quartz at pH = 6 .....	34
9. Water Demineralizer and Cenco-Meinzer Seive Shaker.....	42
10. Beckman Model N pH Meter.....	42
11. Ro-tap used in Sizing the Quartz Particles.....	46
12. Weighing Bottles Nested with Outer One used as a Dessicator .....	46
13. Increase in Weight of Cooling 20 mm Weighing Bottle.....	49
14. Oxidation Rate of Dithizone in Various Solvents.....	52
15. Transmittancies of Dithizone and Cupric Keto Dithizonate ..	52
16. Photometer Calibration of 0.001% Dithizone in Toluene versus Copper.....	53
17. Adapted Centrifuge Tubes.....	55
18. Ground Glass Stoppered Pyrex Test Tubes.....	55
19. Conversion Chart.....	59

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PART 1

## I. INTRODUCTION

## 1. General Statement

The object of the investigation is to determine the amount of copper that is adsorbed on a unit area of quartz from aqueous solutions of varying copper concentration and varying pH. These measurements and a consideration of the solubility field of copper ions were undertaken as a means of investigating the complex subject of the weathering of mineral deposits and the subsequent history of the released components.

In the Department of Metallurgy at M.I.T. similar studies have been carried out on the adsorption of sodium on quartz (Bell, 1953; Laxen, 1951) and on the adsorption of barium on quartz (Chang, 1951). In those studies radioactive tracers were used as a means of measuring adsorbed material. Chemical methods for determination of very small quantities of heavy metals exist (Sandell, 1950). Because of the familiarity of the writer with chemical rather than radioactive tracer techniques, the possibility of using a chemical technique was investigated. It was found in preliminary work that the very small amounts of adsorbed copper could be measured chemically. As a result, work was begun to develop the technique so it would give readings precise enough to investigate small variations of adsorbed copper.

Briefly, the thesis describes the study of the amounts of copper adsorbed on quartz utilizing a chemical technique for measuring the copper.

The experimental procedures and techniques are described in detail in part 2. Part 3 is a description of a method for

determining very small amounts of heavy metals in water.

## 2. Water

Adsorption in the experiments and in nature takes place in water. The pertinent properties of water have been summarized in Mason (1952). As a solvent, water is unequalled and the key to its properties is the structure of the water molecule. The hydrogens are deeply embedded in the oxygen atom with the bond angle of the lines joining the hydrogen nuclei to the oxygen nucleus being  $105^\circ$ . This results in an uneven distribution of charge and, as a result, the water molecule is a dipole. The mutual attraction of the dipoles makes the cohesive forces between the water molecules much higher than for normal liquids. This causes water to have a high dielectric constant, e.g. 78.4 compared with 2.2 for carbontetrachloride. This is responsible for the activity of water as a solvent for ionic compounds because the force of attraction between ions varies inversely as the dielectric constant of the medium and the solution of ionic compounds is essentially a dispersion of the ions by the molecules of the solvent.

The radius of hydrated ions is 5 to 6 Å (Eigen and Wicke, 1954). The unit is made up of the ion plus usually two hydration shells. Under some circumstances one or both shells may be removed. These shells are impenetrable for ions of like sign but can intermesh to some extent when the ions are of opposite sign because of the reverse orientation of the oriented water molecules.

## 3. Adsorption

Adsorption is the concentration of a substance at an interface



between two phases. There are two main types of adsorption. Physical adsorption is the physical concentration of a substance at an interface. The concentrating substance is known as an adsorbent. Chemical adsorption, or chemisorption, is the concentration of a substance at an interface by reaction of the concentrated substance with the adsorbent. In the case of a solid in contact with a solution, physical adsorption on the solid is an enrichment, near the solid, of the substance in solution relative to its concentration in the bulk of the liquid (Glasstone, 1946). Negative adsorption is an impoverishment of a solute near the solid-liquid interface.

It has been found that an empirical relationship of the form

$$a = kc^n$$

is adequate for adsorption from solution over a considerable range of concentration (Freundlich, 1930) where

$a$  is the amount of solute adsorbed by a unit mass of adsorbent

$c$  is the concentration of solution

$k$  and  $n$  are constants for the given adsorbent and solute.

$n$  is greater than 1.

It is apparent from the form of the isotherm that the amount of adsorption decreases less rapidly than the concentration of the solution.

According to the ideas of Stern (1924), physical adsorption requires a triple rather than a double layer model of adsorption (fig 1) (Fuerstenau, 1955). Quartz, the mineral being investigated in this thesis, has a negative potential and is used as an example

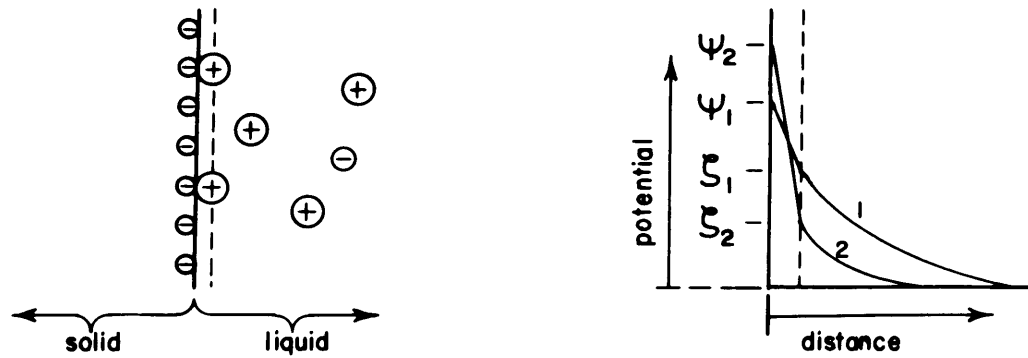
in the diagram. The outer layer of the solid is made up of ions which are not completely neutralized by other components of the solid and which are the potential-determining ions. In the case of quartz in contact with an aqueous solution, the potential-determining ions are oxygen. Because the ions are of one sign, ions of the opposite sign are attracted to the solid from the bulk of the solution. These "counter ions" are held near the interface and their concentration grades off into the solution. An equilibrium is set up between the attracting forces of the potential-determining layer and the forces of dispersion originating from thermal agitation in the liquid.

Beside the solid surface one thickness of counter ions (not necessarily a complete monolayer) is held firmly; beyond this extends a gradually more rarified diffuse layer. The force attracting the diffuse layer to the surface has been named the zeta potential. The zeta potential may be measured experimentally and is found to be of the order of 0.1 volts. Measurement is made of the potential generated by forcing a stream of liquid of known pH and salt concentration past a substance with a non conducting surface, e.g., quartz. The diffuse layer is sheared and moved and an electric potential arises which sets up a conduction current through the liquid in a direction opposite to the convection current. For quartz the zeta potential is zero at a pH of 3.72 when the salt concentration is low.

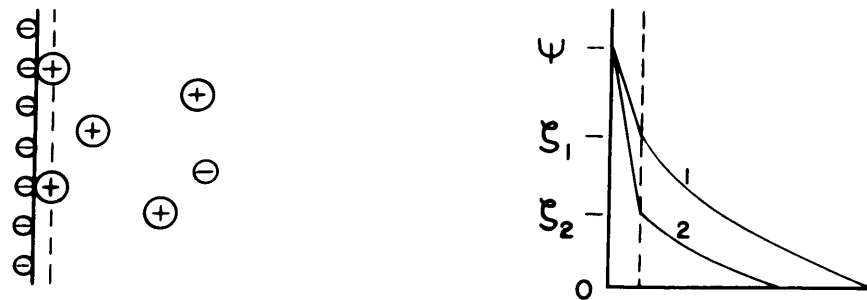
This model of adsorption departs slightly from previous models. It is illustrated in figure 1. In the boundary of the solid is a tightly bound layer of ions, the potential-determining ions.

# FIGURE I- A MODEL OF ADSORPTION

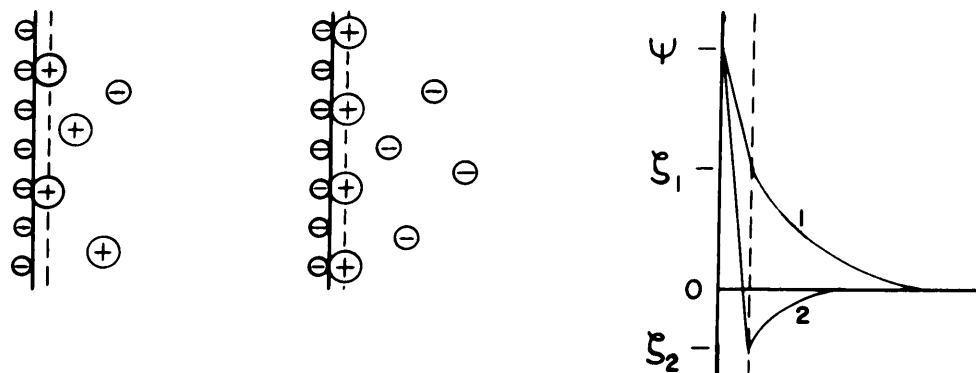
## A- Role of Potential-Determining Ions



## B- Role of Non-Surface-Active Counter Ions



## C- Role of Surface-Active Counter Ions



Note: Line 1 portrays low concentrations, Line 2 much higher concentrations  
 $\Psi$  = the potential of the surface of the solid  
 $\zeta$  = the zeta potential

For quartz in contact with aqueous solution, these are considered to be oxygen; from the point of view of the liquid, the potential-determining ions are hydrogen and hydroxyl. When the pH is varied, the total charge on the quartz surface, the thickness of the adsorbed layer, and the zeta potential all vary (fig 1-A).

The adsorbed ions in solution, the counter ions, may have no effect on the surface charge but can still affect the thickness of the adsorbed layer. If this is the case, they are ions of a non-surface-active indifferent electrolyte (fig 1-B). Because their concentration affects the thickness of the adsorbed layer, they affect the potential holding the diffuse layer to the surface. Systems containing constant amounts of potential-determining ions and varying amounts of non-surface-active indifferent ions illustrate this. The term "indifferent" indicates that the ion in question is not potential determining.

Surface-active indifferent electrolytes do not affect the potential of the solid surface but are bound closely to the surface and if the solution is sufficiently concentrated may actually reverse the sign of the zeta potential (fig 1-C). If the sign is reversed, as in the example illustrated, anions rather than cations would make up the diffuse layer and, in effect, distinct triple layer adsorption would be realized.

In summary, for quartz the hydrogen and hydroxyl ions are the potential-determining ions in solution. Monovalent non-surface-active ions, such as sodium and chlorine ions, which do not react with the solid phase, do not affect the potential of the surface but affect the zeta potential if they vary in concentration. Ions

of higher valence, such as barium, affect the zeta potential to the extent of reversing its sign but they are not nearly as potential-determining as hydrogen and hydroxyl ions.

#### 4. Weathering

When a sulfide mineral deposit is subjected to the agencies of weathering, the metals are released forming ionic solutions. The rate and completeness of the removal of the heavy metals is dependent on the mineral assemblage and on the environment in which oxidation takes place. The soluble components of the weathered mineral deposit are transported in the surface and underground drainage. Those parts of the mantle through which the underground water flows and over which the surface drainage flows retain, at least temporarily, some of the migrating metals.

Soil and stream sediments are made up of particles of the resistates, clays, organic material, and numerous partly altered fragments of rocks and minerals. These various particles retain a portion of the heavy metals by adsorption when the heavy metals are available in water in contact with the particles. The extent of retention varies enormously depending on the size and kind of adsorbing particle, the pH of the water, and other materials in solution. A given mass of organic material or clay adsorbs much more metal than the same mass of very fine quartz sand.

When water or soil contains a more than normal amount of heavy metal as a result of the weathering of a metalliferous deposit, the area of concentration is termed a "geochemical anomaly." In recent years water, stream sediments, and soils have been sampled to find geochemical anomalies and to trace

them to the mineral deposits from which they originated (Hawkes, 1955). The heavy metals copper, zinc, lead, and nickel are most commonly sought after by this method.

Because in any given anomaly various types of soil are present and because the extent of retention of heavy metals depends on the size and kind of particle, it is desirable to know the relative retention power of the soil components in order to understand the significance of variations of metal in samples of different soil type. It should be possible to decide if the collection and analysis of any given soil type is of use in tracing a geochemical anomaly.

Using geochemical techniques, it is impossible to predict the size and tenor of the mineral deposit undergoing weathering. However, a more complete knowledge of the nature of geochemical anomalies should facilitate recognizing them and tracing them to their sources. Consequently, it is especially desirable that adsorption experiments should include determinations which cover the entire range of pH and metal concentrations found in nature.

##### 5. Discussion of Copper in Solution

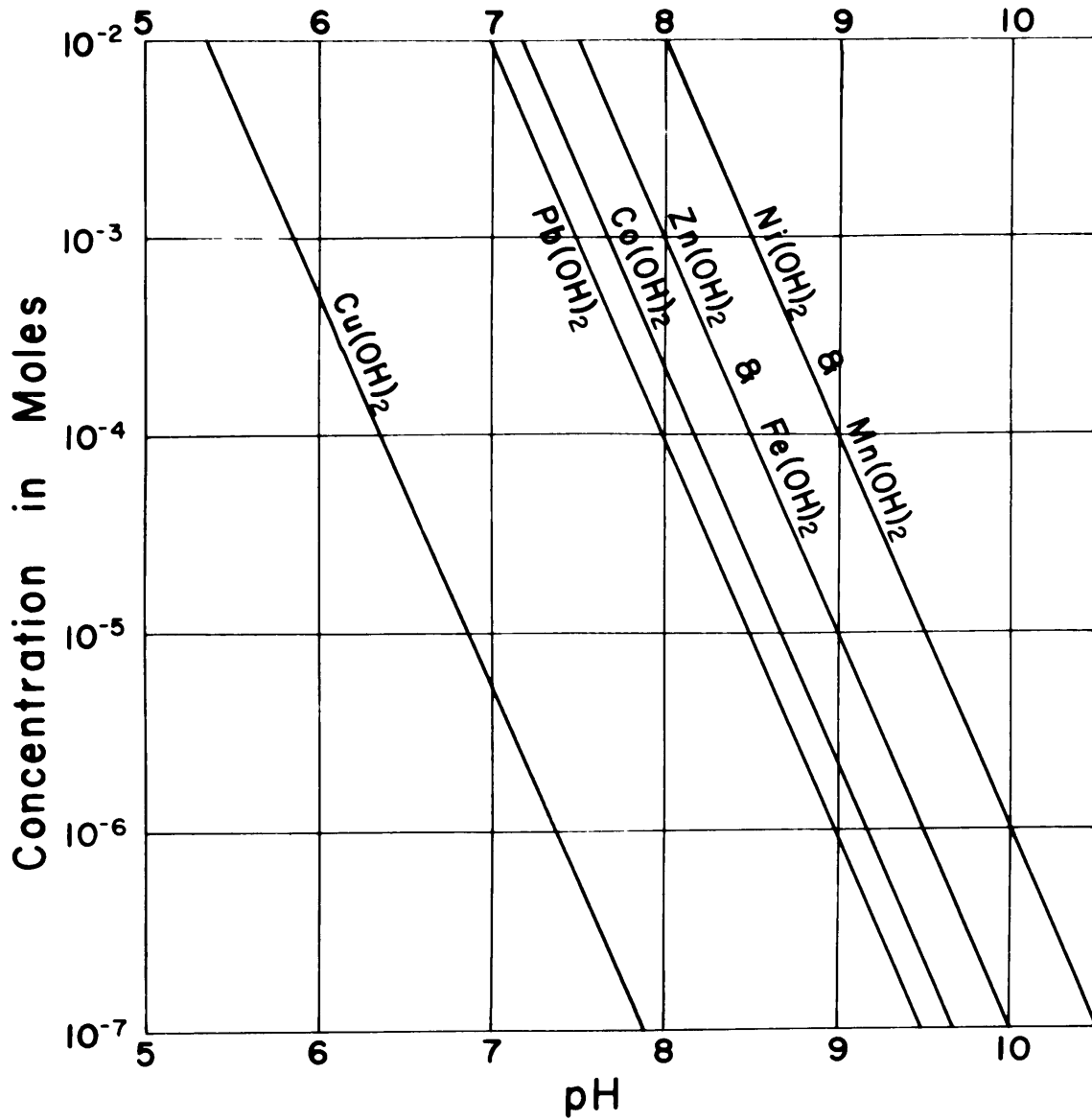
The concentration of copper in ionic solution in most stream waters is limited by the amount of copper available for solution rather than by its insolubility (fig 2). Exceptions are those streams of high pH which flow from limestone areas. Not all the copper in the streams is carried as ionic copper; some is adsorbed on suspended organic and inorganic material. There is however, no reason to think that there is any limit to the load that the stream may carry other than the supply. This is even more the

case for the other heavy metals (fig 2).

Upon reaching the ocean, however, different conditions prevail. These are shown in table 1 which is by Mason (1952, p. 140). It will be noticed that the sea is slightly alkaline, whereas most terrestrial waters are somewhat on the acid side of neutrality. The pH of many terrestrial waters is controlled by the buffer system  $\text{CaCO}_3 - \text{CO}_2 - \text{H}_2\text{O}$ ; a saturated solution of  $\text{CO}_2$  has a pH of 5, and one of  $\text{Ca}(\text{HCO}_3)_2$  a pH of 6.4.

Riley (1939, p.53) in a study of Connecticut lakes found a variation of copper content from 0.005 to 0.6 ppm. He found that the content varied greatly with the season. The greatest amount was present in the autumn and least in late winter and spring. Riley (1937-8) also investigated the copper content of water near the mouth of the Mississippi. Here he found the normal variation of dissolved copper to be 0.001 to 0.015 ppm with the highest values in water of low salinity and the lowest in sea water approaching normal salinity.

Wattenberg (1943, p. 87) has stated that the copper content of sea water is 0.0002 to 0.001 ppm in contrast to the earlier generally accepted content of 0.001 to 0.01 ppm.



$K_{SP}$ :	$\text{Cu(OH)}_2 = 6.0 \times 10^{-20}$	$\text{Mn(OH)}_2 = 1.0 \times 10^{-14}$
	$\text{Pb(OH)}_2 = 1.0 \times 10^{-16}$	$\text{Fe(OH)}_2 = 1.0 \times 10^{-15}$
	$\text{Zn(OH)}_2 = 1.0 \times 10^{-15}$	$\text{Co(OH)}_2 = 2.0 \times 10^{-16}$
	$\text{Ni(OH)}_2 = 1.0 \times 10^{-14}$	

FIGURE 2 - SOLUBILITY BOUNDARIES FOR  
HEAVY METAL HYDROXIDES



TABLE 1

The pH of Natural Media and its Relation to the Precipitation of  
the Hydroxides

pH	Precipitation of Hydroxides	Natural Media	pH
11			11
.	Magnesium		
10		Alkali Soils	10
9			9
	Bivalent Manganese	Sea Water	
8			8
7	Bivalent Iron	River Water	7
6	Zinc, Copper	Rain Water	6
5	Aluminum		5
4		Peat Water	4
3		Mine Waters	3
	Trivalent Iron		
2			2
		Acid Thermal Springs	
1			1

## II. OUTLINE OF THE EXPERIMENTAL METHOD

Samples of quartz particles with a surface area of 900 square centimeters per gram were agitated in water of varying copper concentration and pH. After agitation, the pH of the solution was measured and the liquid was decanted. The moist quartz was transferred from the shaking bottles to gooch crucibles with glass frits. The crucibles were placed in centrifuge tubes and centrifuged to reduce the water content of the samples without evaporating the water. The samples were transferred to tared weighing bottles and weighed. The weighing bottles were heated to 120°C to evaporate the remaining water and then weighed again. From these weights the amount of water was found and thus the amount of copper deposited on the quartz by the evaporation of water. This would be the total amount of copper on the quartz if there were no adsorption.

The quartz was transferred to ground glass stoppered test tubes to which sodium citrate dissolved in water and dithizone dissolved in toluene were added. The tubes were shaken. The citrate released the copper from the quartz and the dithizone reacted with the copper causing a color change in the organic (toluene) phase. This color change may be measured quantitatively with a colorimeter. The colorimeter reading was compared with a previously prepared standard curve to obtain the amount of copper that was on each quartz sample. From this experimentally determined amount of copper on the quartz samples was subtracted the amount of copper precipitated on the quartz by evaporation of the water not removed by centrifuging. The difference was the

amount of copper adsorbed by the quartz sample. The total amount of copper adsorbed by each quartz sample was divided by the weight of the sample to obtain the amount of adsorption of copper per gram of quartz. The amounts may then be calculated to moles of copper adsorbed per square centimeter of quartz or any other convenient units.

An independent check of the order of magnitude of the copper on the quartz was made using the optical spectrograph (Benson, 1955).

## III. EXPERIMENTAL RESULTS

## 1. Chemical Results

The experimental determinations are tabulated in table 2. Figures 3 and 4 show the amount of adsorption of copper on one gram of quartz particles with a surface area of 900 square centimeters per gram. The ordinate shows the concentration of copper in the solutions and the abscissa shows the final pH of the experimental solutions. The copper concentration is plotted on log scale because of the extreme variation of concentrations used. In figure 3 adsorption is plotted as micrograms of copper per gram of quartz and in figure 4 as moles of copper per square centimeter of quartz surface.

The area investigated is limited on the right by a line representing the solubility boundary of copper in water. The solubility product of  $\text{Cu}(\text{OH})_2$  is  $6 \times 10^{-20}$  (Pauling, 1953, p.468). The left boundary of the investigated area is the isoelectric line for quartz in aqueous solution. To the left of the isoelectric line the surface charge on the quartz is positive and anions rather than cations are attracted to the surface. At copper concentrations greater than five parts per million (ppm) the isoelectric line departs from the pH of 3.7. It may be seen in figure 3 that the deviation takes place where the concentration of the copper ion approaches that of the hydrogen ion. The upper concentration boundary of the area is 100 ppm copper. This is much higher than copper anomalies found in nature and about 20,000 times normal background in natural stream waters. The lower limit of investigation is 0.1 ppm. This concentration is between 10 and 20 times normal background found in nature.

TABLE 2

## Experimental Determinations of Copper Adsorbed on Quartz

	Copper Conc in ppm	Copper Conc in moles	Initial pH	Final pH	Adsorption in Micrograms of Cu per gm of Quartz	Adsorption in Moles of Cu per cm <sup>2</sup> of Quartz Surface (x10 <sup>-12</sup> )
1	10	1.57x10 <sup>-4</sup>	3.80	3.80	-.01	-0.18
2	10	1.57x10 <sup>-4</sup>	4.50	4.40	.17	2.9
3	10	1.57x10 <sup>-4</sup>	6.08	5.79	.32	5.5
4	1	1.57x10 <sup>-5</sup>	3.98	3.92	.04	0.67
5	1	1.57x10 <sup>-5</sup>	4.95	4.92	.18	3.1
6	1	1.57x10 <sup>-5</sup>	6.07	5.82	.26	4.5
7	10	1.57x10 <sup>-4</sup>	5.38	5.29	.24	4.2
8	50	7.85x10 <sup>-4</sup>	5.32	5.30	.52	9.1
9	100	1.57x10 <sup>-3</sup>	5.37	5.24	.59	10.3
10	100	1.57x10 <sup>-3</sup>	4.55	4.50	.03	0.50
11	100	1.57x10 <sup>-3</sup>	5.66	5.61	.96	16.7
12	100	1.57x10 <sup>-3</sup>	3.98	3.90	-.31	- 5.4
13	100	1.57x10 <sup>-3</sup>	4.94	4.86	.36	6.3
14	50	7.85x10 <sup>-4</sup>	5.85	5.70	.65	11.3
15	0	0	5.69	5.43	0.00	0.0
16	0.1	1.57x10 <sup>-6</sup>	5.50	5.38	0.08	1.4

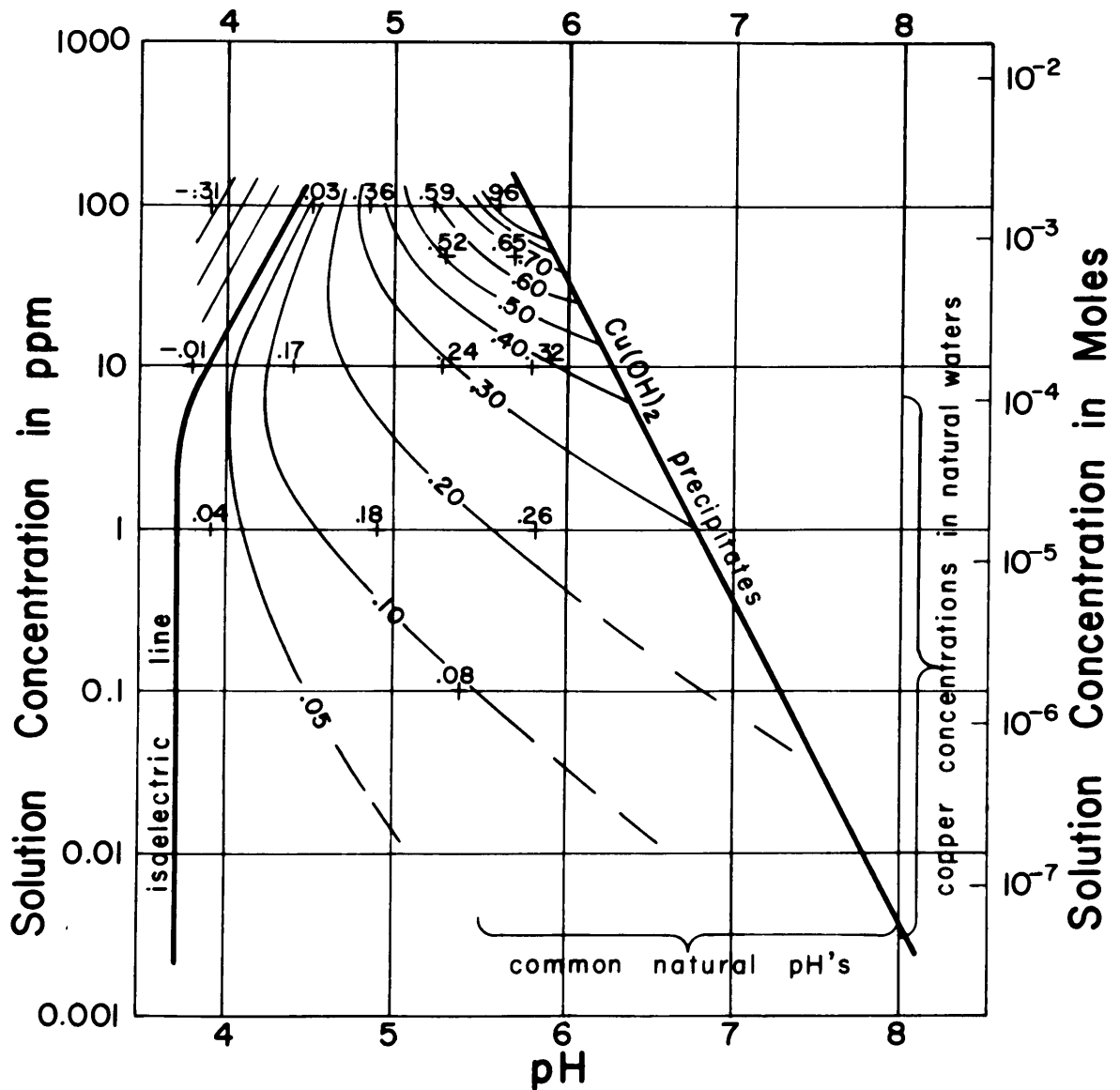


FIGURE 3

AMOUNT OF COPPER ADSORBED ON QUARTZ  
 expressed in  
 Micrograms of Copper per Gram of Quartz

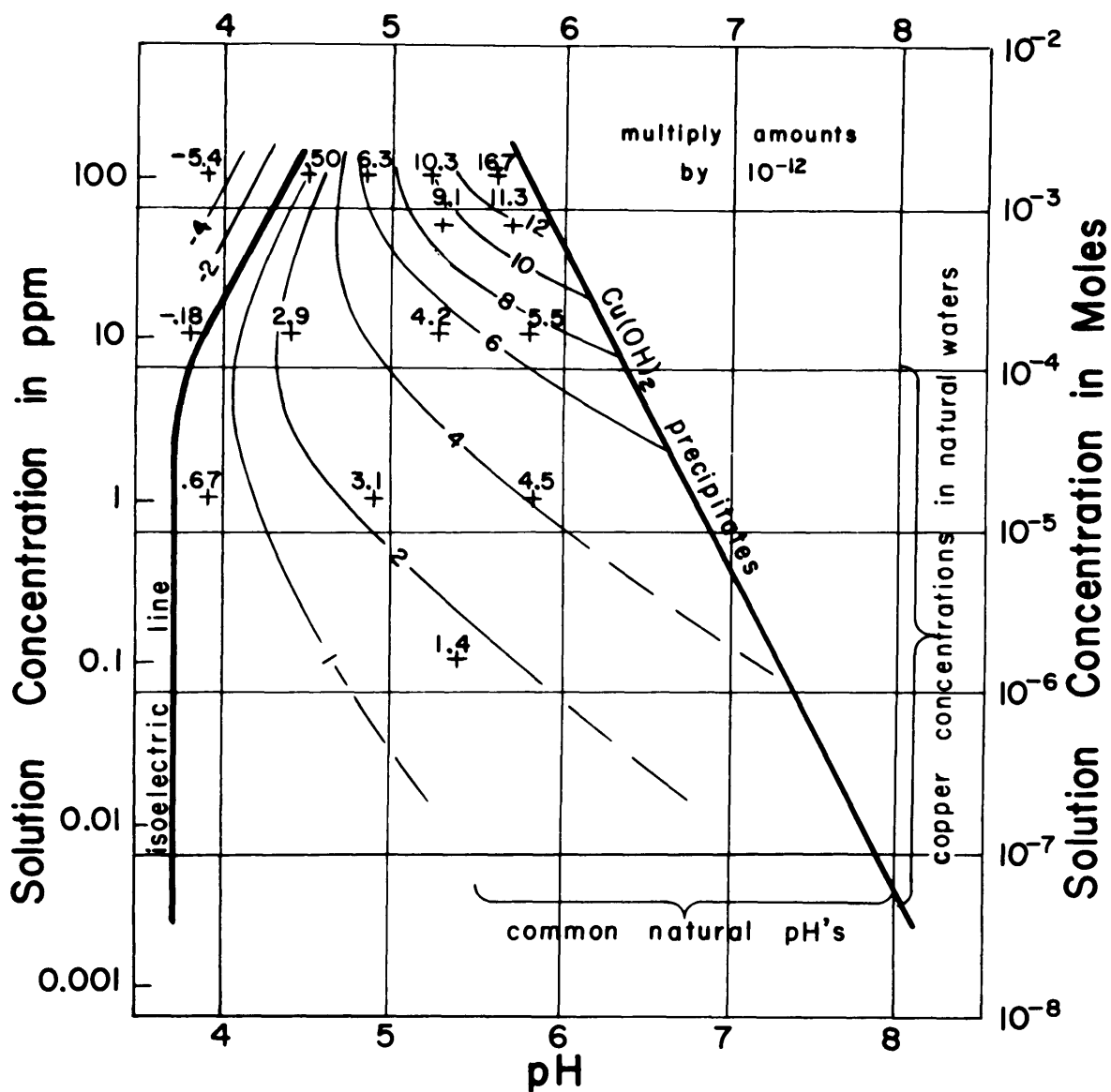


FIGURE 4

AMOUNT OF COPPER ADSORBED ON QUARTZ  
expressed in  
Moles per Square Centimeter of Quartz Surface

At the appropriate concentration and pH coordinates the measured amounts of adsorbed copper are plotted. Each of these values is the average of four determinations. The contoured values show an increasing amount of adsorption with increasing copper concentration of the solution and with increasing pH. The amount of copper adsorbed from solutions of concentration and pH which might be encountered in nature varies from 0.1 to 0.3 microgram per gram of quartz of this particle size. This is equivalent to  $1.7 \times 10^{-12}$  to  $5.6 \times 10^{-12}$  moles of copper per square centimeter of quartz.

Assuming a hydrated radius of  $5 \text{ \AA}$  and therefore a parking area of  $100 \text{ \AA}^2$ , the surface is respectively 10% and 1% covered when 1.0 microgram and 0.1 microgram of copper is adsorbed per gram of quartz.

The average grain has about 10 exterior corners, 300 microns of edges, and 8000 square microns of facial area. It is very irregular in outline (fig. 5). Assuming a hydrated radius of  $5 \text{ \AA}$  this would give positions for 10 ions on the corners,  $6 \times 10^5$  ions on the edges, and  $3 \times 10^{10}$  ions on the faces per gram for quartz grains of this size.

It was found that the average amount of water remaining after centrifuging was 4%. If the area of the quartz was 900 square centimeters per gram, the average thickness of the water was  $4.4 \times 10^{-5}$  cm or  $4400 \text{ \AA}$ .



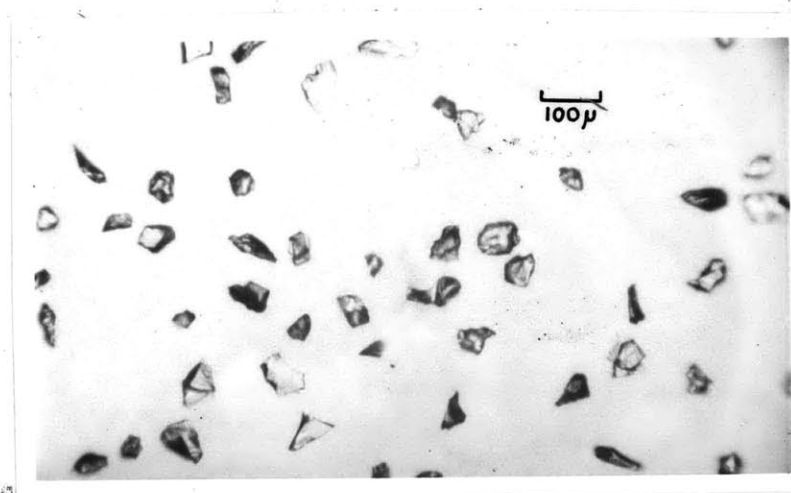


Figure 5 - Photomicrograph of Quartz Particles

## 2. Spectrographic Results

Benson (1955) used the optical spectrograph to analyse quartz specimens which had been exposed to copper solutions. The results are shown in table 3.

Table 3  
Comparison of Chemical and Spectrographic Results

Sample	Concentration of Solution	pH of Solution	Micrograms of Copper Adsorbed per Gram Quartz	
			Benson	Richardson
1	100	4.66	0.06	0.15
2	0.1	6.15	0.20	0.16

Each of Benson's results are averages of four determinations. The readings under Richardson are taken from figure 3. Sample 1 was exposed to copper solutions under conditions where citrate soluble copper was very low, where the precipitated copper was accurately known, and where there was possibly some tightly bonded copper which was not citrate soluble. Benson's results show that there was little or none of the last. Sample 2 was exposed to copper solutions under conditions where the amount of precipitated copper was very low (0.004 ppm). The object of this sample was to confirm the order of magnitude of the experimentally determined values of adsorbed copper in figure 3.

## IV. SOURCES OF ERROR

- (1) A very small quantity of water may have been evaporated during the transfer of the quartz samples before and after centrifuging. The amount of copper precipitated by such evaporation is assumed to be negligible.
- (2) Very small errors might be introduced by the surfaces of the tared weighing bottles not being identical. The maximum weighing error here was about 0.0005 gram which is negligible.
- (3) It is difficult to weigh out 0.01 gram of dithizone and to transfer it quantitatively to a graduated cylinder. This resulted in the dithizone solutions varying slightly in concentration but blanks spiked with known amounts of copper were used to standardize the dithizone solutions when they were being used to determine copper on quartz.
- (4) It was found that one sample in six or eight gave an anomalous answer. By being very careful of contamination it was possible to reduce the number of spoiled runs but they could not be completely eliminated. Perhaps soot containing heavy metals settled into the occasional sample. These erratic errors necessitated quadruplicate runs.
- (5) Very small amounts of contaminants were in the water used in the experiments. Six litres were boiled to dryness and a residue of 1-2 milligrams remained.
- (6) It is possible that centrifuging might disturb the adsorbed layers to the extent of making the determinations unreliable. When the centrifuge was spun at 2400 rpm, the sample was subjected to 805 gravities. This may have caused differential movement of the copper with respect to the water. Actually,

probably all the water that was removed was gone by the time the centrifuge got up to speed so there was no migrating water available in which the copper could move differentially.

Some indication that migration of copper ions relative to water has not taken place is afforded by the statement that solid particles can be subjected to mechanical forces and to gravity and thus give rise to electrokinetic phenomena while hydrated ions can not (Weyl, in Gomer and Smith, 1953).

In addition to disturbances from equilibrium caused by copper ions migrating relative to water ions, there might be disturbances caused by the removal of most of the water. Bull (1943, p. 182) gives the thickness of the electrical double layer in the presence of electrolytes. His values are listed in table 4. Copper sulfate solution is di-divalent.

Table 4

Effect of Concentration of  
Electrolyte on Double Layer  
Thickness

Concentration moles per litre	Thickness of Double Layer in Angstroms		
	Uni-univalent	Uni-divalent	Di-divalent
$10^{-7}$	10,000	5600	4800
$10^{-6}$	3200	1800	1530
$10^{-5}$	1000	560	480
$10^{-4}$	320	180	153
$10^{-3}$	100	56	48
$10^{-2}$	32	18	15

For dilute solutions the thickness of the double layer is of the same order of magnitude as the thickness of water remaining on the quartz after centrifuging.

(7) Solubility of  $\text{SiO}_2$  might cause readings that are too high.

It was noticed that during almost every run the pH decreased a small amount (table 2). It may be seen in figure 6 that the solubility of silica decreases with decreasing pH.

During a run there could initially be a period of dissolving of quartz to reach equilibrium with the initial pH then, as the pH decreased, a precipitation of colloidal  $\text{SiO}_2$  and adsorption of copper on it.

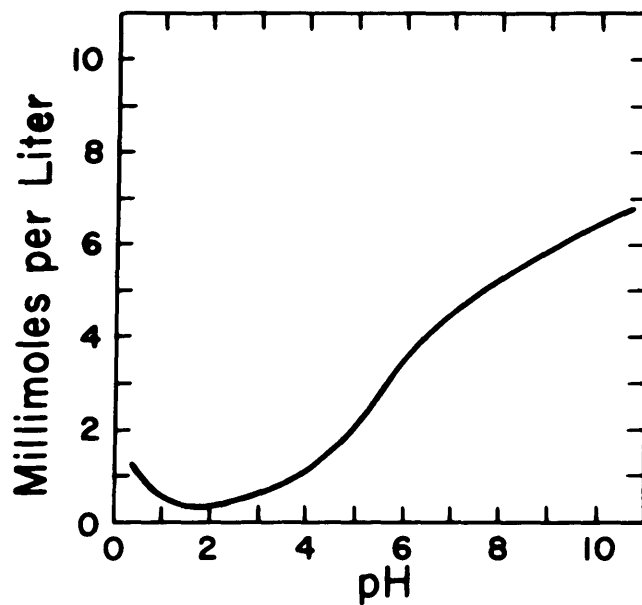


FIGURE 6 - SOLUBILITY OF SILICA VERSUS pH

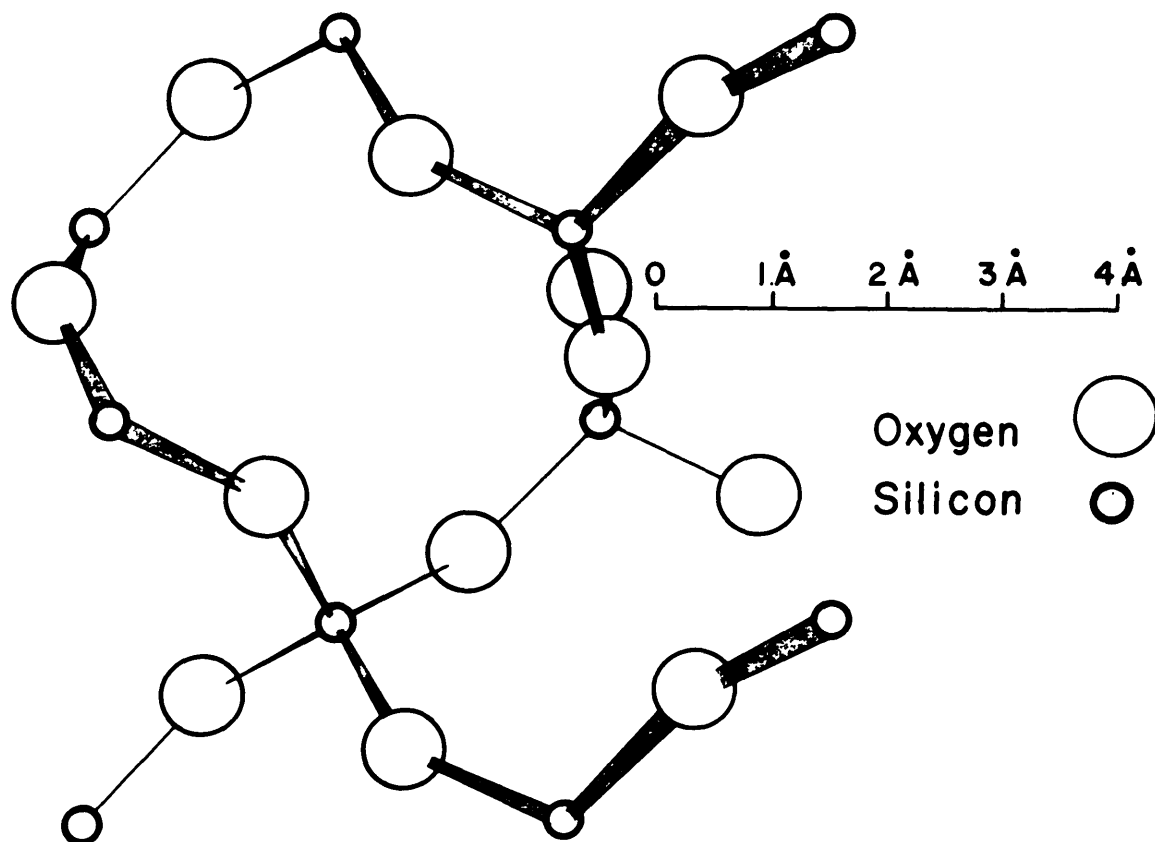


FIGURE 7 - QUARTZ STRUCTURE

## V. DISCUSSION OF RESULTS

Because of the limited solubility of copper hydroxide, the field of the adsorption of copper on quartz was restricted to a low pH range. This was a disadvantage from the point of view of making the measurements because the amount of adsorption is much less where the pH is low. However, there was an advantage because more attention had to be paid to a smaller area in which the amounts of adsorption compared to the concentration of solution departed from the usual exponential relationship. The main cause of the deviation from the normal increase is the changing of the pH of no copper adsorption from 3.72 at low copper concentrations to 4.4 at a concentration of 100 ppm (see fig. 3). This results, at a pH of 4.6, with there being as much adsorption at 1 ppm as at 100 ppm. It is difficult to explain the change of pH of zero adsorption and the rather high negative adsorption to the left of the isoelectric line.

There are two possible explanations. If copper is considered a surface-active-indifferent electrolyte (see definition in introduction) high concentrations of copper might lead to less total copper adsorbed. With low concentrations, the zeta potential would be negative and there would be copper ions in both the first layer of the liquid and the diffuse layer. If copper is present in such amount that the zeta potential becomes positive, it is assumed in the model of adsorption that there is a relatively large amount of copper in the first layer of the liquid and that the diffuse layer is made up predominantly of anions.

The reason that the ions are attracted to the quartz is the presence of a charged surface on the quartz. The charged surface is supposed to originate when the quartz is crushed and to be caused by the presence of silicon ions at the surface (figure 7). It has been postulated that rearrangement of many ionic layers takes place upon production of new faces in order to mask the silicon ions with oxygen ions (Wehl, in Gomer and Smith, 1953). If this is the case, there is still some charge remaining after rearrangement and the remaining charge is neutralized by the presence of ions near the solid surface but in the adjacent solution. Perhaps ions in the liquid which can array themselves very near the interface are more effective neutralizers than those ions further away in the diffuse layer. In other words, one ion close to the surface can exert the same neutralizing power as several ions at a distance from the surface. In this manner, at high concentrations of copper solutions and at low pH's there could actually be less copper near the surface than if there were no adsorption at all.

Another possible explanation of the change in the position of the pH of no adsorption is a change in the form of copper in solutions of differing concentration. An investigation of the different states of hydrolysis of copper in nitrate solution has indicated that the relative amounts of the different forms varies with concentration (Pederson, 1943, p. 23). It was concluded that, besides  $\text{Cu}^{2+}$ , there existed in solution  $\text{CuOH}^+$ ,  $\text{Cu}_2\text{OH}^{3+}$ , and  $\text{Cu}_2\text{O}^+$ . It was found that the concentrations of the three hydrolysed ions were of the same order of magnitude when the concentration was



0.1 to 0.01 molar. In more concentrated solutions, the ion  $\text{Cu}_2\text{OH}^{3+}$  gains more and more predominance while the ion  $\text{Cu}_2\text{O}^{2+}$  and, more especially, the ion  $\text{CuOH}^+$  gradually disappear. In solutions more dilute than 0.01 molar, the form  $\text{Cu}_2\text{OH}^{3+}$  gradually disappears. At sufficiently high dilutions only the ion  $\text{CuOH}^+$  remains of the three ions resulting from hydrolysis.

Qualitatively, it can be assumed that a similar hydrolysis of copper takes place in the sulfate solutions which were used in the experiments. A solution of copper in the presence of sulfate ions is probably even more complicated than a nitrate solution because of the power of sulfate ions to form complexes with cupric ions.

Considering the two ions  $\text{Cu}_2\text{OH}^{3+}$  and  $\text{CuOH}^+$  it will be noticed that the copper to ionic charge ratios are 2:3 and 1:1 respectively. The ion which is more abundant at high concentrations has less copper for a given amount of charge. Figure 3 shows that the adsorption at high concentrations does not increase as quickly as would be expected.

The adsorption of several cations on quartz has been investigated by several workers (Chang, 1951; DeBruyn, 1952; Laxen, 1951; Mao, 1955). The results of the above investigations have been plotted in figure 8 to compare the results with the amounts of copper obtained in this investigation. No attempt is made here to explain the different amounts of metals adsorbed on quartz but attention is drawn to the wide difference of the amounts of copper found in the work by Mao and in this thesis. This latter subject is discussed in the section on future work.

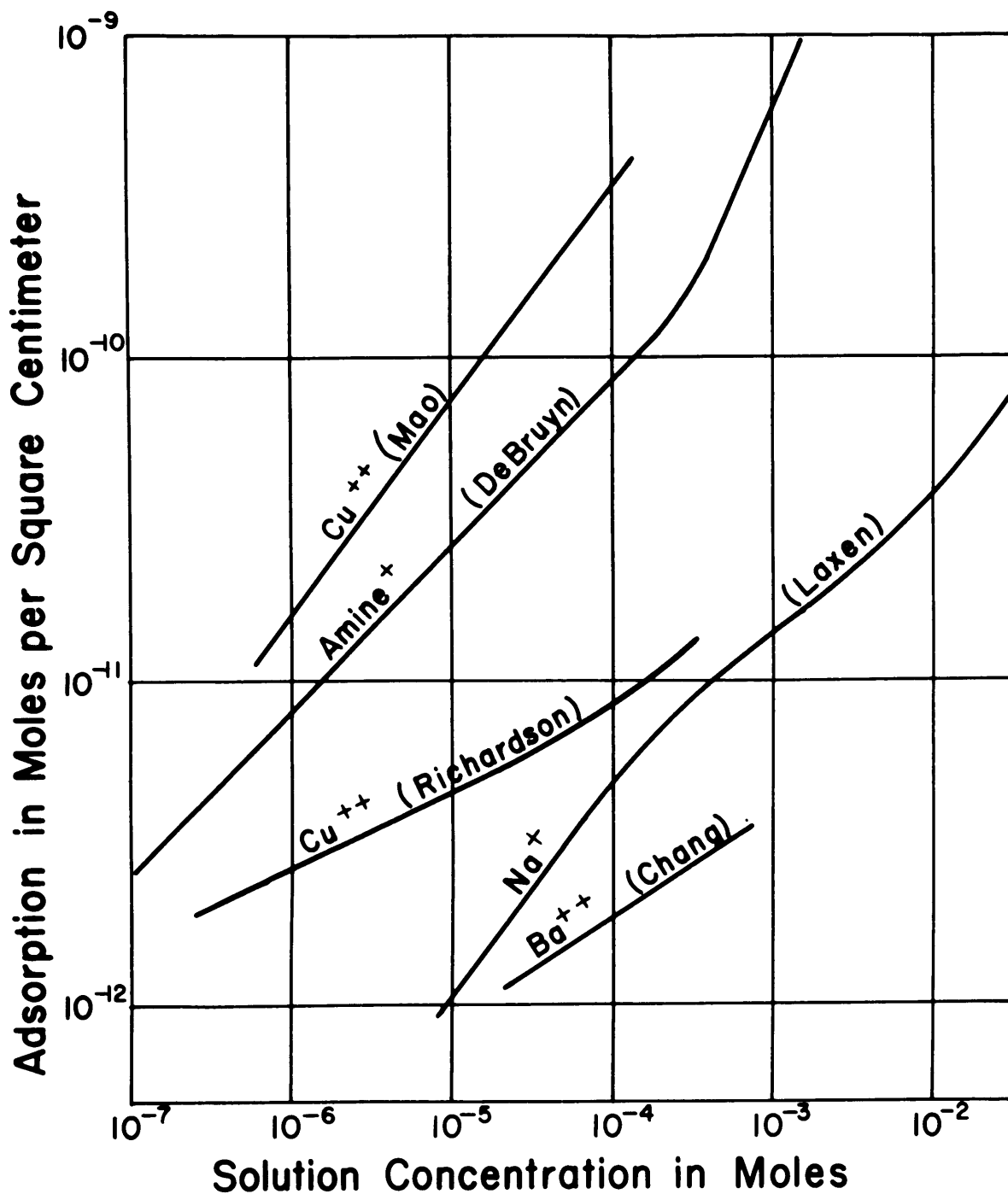


FIGURE 8

ADSORPTION OF SEVERAL CATIONS ON QUARTZ  
AT pH = 6

## VI. CONCLUSIONS

The amount of copper adsorbed on quartz is measurable but very small. The amount of adsorption increases roughly as the square root of the increase of concentration. For solutions of constant pH and varying concentration, this relationship is modified by the presence and shape of the isoelectric line. The field where copper can exist in ionic solution is very limited in solutions of high pH because of the very low solubility of  $\text{Cu}(\text{OH})_2$ .

As a result of the formation of  $\text{Cu}(\text{OH})_2$  at high pH's, very little copper is carried in true solution in streams with a pH above 7. Of course, copper can be transported as  $\text{Cu}(\text{OH})_2$  in suspension or on suspended particles. From a consideration of the solubilities of the other heavy metals (fig.2) it appears that they can be transported at normal stream pH's in ionic solution.

In a stream containing 0.01 ppm copper and with a pH of 6, quartz particles 41 microns in size adsorb only 0.1 microgram of copper per gram of quartz. In the usual geochemical prospecting field test using a 0.1 gram sample, this concentration of copper would be undetectable.

## VII. SUGGESTIONS FOR FUTURE RESEARCH

The investigation started in this thesis could be extended to quantitative measurements of other simple phenomena which are combined in the weathering, transportation, and deposition of the components of mineral deposits.

Specifically, this would include an investigation of adsorption of copper and other heavy metals on quartz, clay, and organic material. Complex systems containing more than one adsorbent or more than one type of cation would approach more closely the systems found in nature. It would be a distinct improvement to use natural waters or artificial mixtures containing the salt content of natural waters.

Further work on details of the experimental technique would also lead to valuable results. Two aspects of the technique are especially interesting. One is the use of the centrifuge. There can be little doubt that the application of 800 gravities and the removal of most of the water disturbs the environment set up in the water when the quartz samples and copper solutions are shaken together. This could be checked by very slow centrifuging of the samples exposed to copper solutions in the low concentration range where a several fold increase of the usual water content after centrifuging would not cause very much copper to be precipitated during the subsequent heating.

The methods of analysing for copper on the quartz need further investigation. Mao (1955) used the radioactive tracer technique and obtained, at a pH of 6, several times the amount of adsorption the writer obtained (figure 8). Benson (1955) used the optical spectrograph to determine the copper content of eight quartz

samples. His results were similar to those of the writer but the different results obtained by Mao have not been explained. It seems that a single person must use all three modes of analysis in order that all the sample preparation and techniques be identical. Only in this manner can the various techniques be evaluated for their use in the determination of micro amounts of heavy metals.

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PART 2

## DETAILED PROCEDURE

In this section, the procedure is described in detail so that the work of this thesis could be duplicated and related research could be undertaken without a long initial period of becoming familiar with the techniques. Both preparation of reagents and analytical techniques are included.

## I. REAGENTS AND MATERIALS

## 1. Demineralized Water

Demineralized water is used in large quantity in the experiments and for washing equipment. It is prepared by passing distilled water through a Barnstead Bantam Demineralizer, model BD1 (fig 9). The demineralizing column consists of cation and anion exchange resins. The output water passes through an ohmmeter where the resistance of the water is measured and a scale of NaCl equivalent content is given. The water used in the experiments had a resistance of 900,000 ohms which indicates a NaCl equivalent content of 0.2 ppm.

The salt content of output water from new demineralizing cartridges is much higher than 0.2 ppm. The cartridge used to prepare water for the experiments was conditioned by pouring large quantities of hot distilled water through it.

The demineralized water was tested for copper content with a method which has a detection limit of 0.002 ppm copper. The copper was undetectable. The water has a pH of 5.4. No attempt was made to exclude atmospheric CO<sub>2</sub> because the experiments were intended to investigate the adsorption of copper on quartz

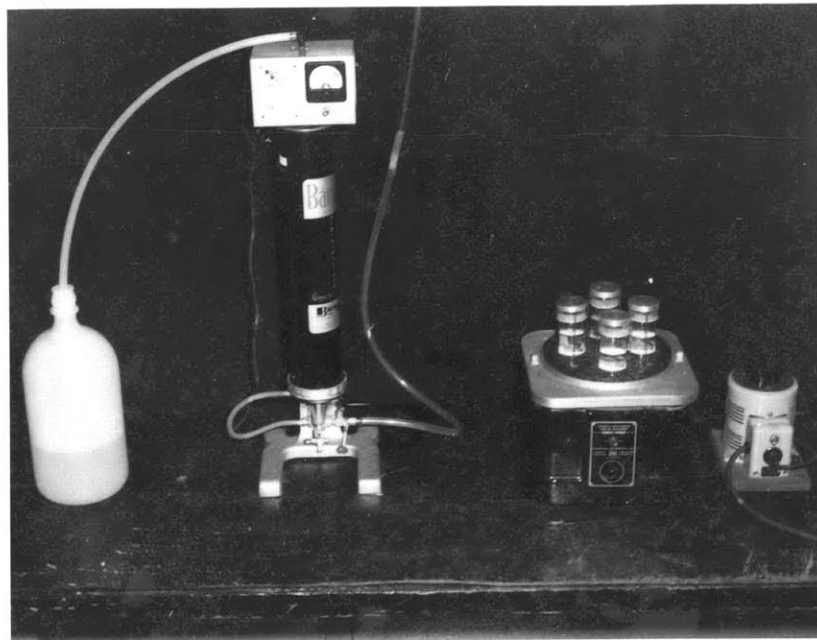


Figure 9 - Water Demineralizer  
and Cenco Meinzer Seive Shaker

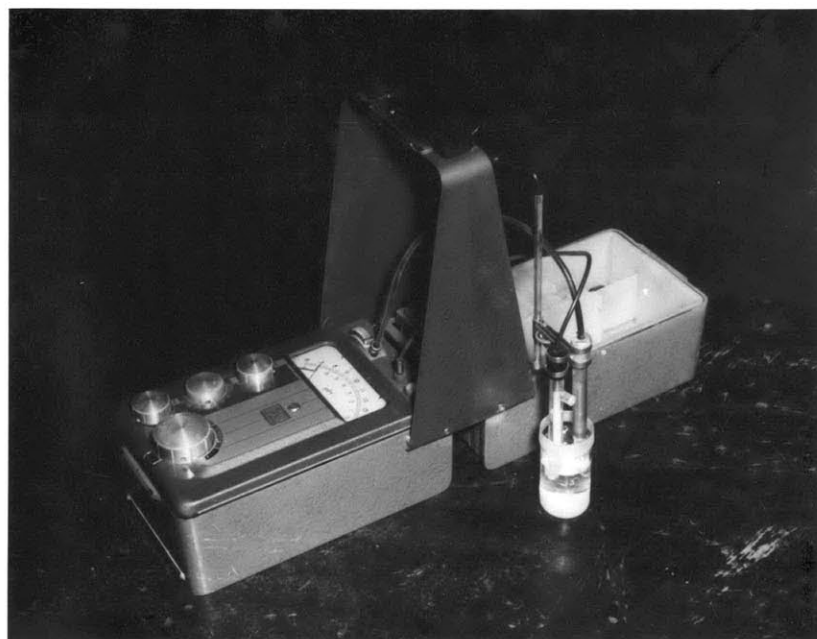


Figure 10 - Beckman Model N pH Meter

under simple but not too unnatural conditions.

The water was stored in one gallon, capped, polyethylene bottles.

## 2. Copper Standard

Two litres of 0.1 mole (6357 ppm) copper standard were made by dissolving 49.839 grams of crystalline hydrated copper sulfate ( $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ ) in demineralized water (final pH=4.35). The  $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$  was tested for water content by weighing a specimen, heating until the blue salt changed to white, anhydrous  $\text{CuSO}_4$ , and then re-weighing. The proportion of  $\text{H}_2\text{O}$  to  $\text{CuSO}_4$  was found to be 5.005 to 1. The strength of the standard solution was checked by electrolytically depositing copper from solution on platinum electrodes with an electrolysing apparatus in the analytical chemistry laboratory. The measured amount of copper in the electrolysed sample was 0.205% lower than the calculated amount of copper present.

## 3. Copper Solutions for the Adsorption Experiments

Copper solutions for the adsorption experiments were prepared by pipetting standard copper solution into a polyethylene beaker and making the volume up to 200 ml. If the standard copper solution had to be diluted more than 50 times to make a desired strength of working solution, the dilution was done in two stages.

The pH of the solution was adjusted using  $\text{H}_2\text{SO}_4$  or  $\text{Na}(\text{OH})$ . The pH was measured with a Beckman model N pH meter (fig. 10). Readings could be taken to 0.02 of a pH unit. When the solution had had its pH adjusted it was divided into four 50 ml portions in order to do each run in quadruplicate.

#### 4. Sulfuric Acid and Sodium Hydroxide

Sulfuric acid was prepared by bubbling vapour from a pyrex still containing 6 N  $\text{H}_2\text{SO}_4$  through demineralized water.

Sodium hydroxide solution was prepared by dissolving analytical grade sodium hydroxide pellets in demineralized water. The pellets contained 30 ppm heavy metals but the amounts of sodium hydroxide solution required to adjust the pH of the working solutions of copper were so small that contamination from this source was negligible.

These reagents were not standardized but were used in small increments until desired pH's were obtained.

#### 5. Preparation of Sodium Citrate Solution

The sodium citrate solution is the Solution "A" very commonly used in geochemical prospecting (Bloom, 1953). Solution "A" is made by combining 200 grams of sodium citrate and 16 grams of hydroxylamine hydrochloride in a 4 litre separatory funnel and adding 1500 ml of water. The funnel is shaken until the salts dissolve and then sodium hydroxide pellets are added until the pH is 8.5. The volume is made up to 2 litres.

The solution contains rather large amounts of heavy metals which were introduced by the reagents. To remove the metals, the solution is extracted with successive 20 ml portions of 0.01% dithizone in carbontetrachloride until a bluish green dithizone color is obtained in the organic phase after the separatory funnel is shaken vigorously. The aqueous phase is now metal-free but is saturated with dithizone. The solution is extracted with successive portions of chloroform in which dithizone is much more soluble

than in water at a pH of 8.5. When the chloroform layer remains almost colorless after the separatory funnel is shaken, the dithizone has been removed from the aqueous phase and the Solution "A" is ready for use.

#### 6. Preparation of Quartz

Several kilograms of unsorted, finely ground, vein quartz was obtained from the Department of Metallurgy at M.I.T. This was deslimed to about 5 microns (.005 mm) and wet screened to -200 + 400 mesh. This fraction was dry screened on a ro-tap (fig. 11) and 500 grams of -325 + 400 mesh was retained.

The quartz was transferred to an 8 inch evaporating dish and was cleaned by boiling in twelve changes of 6N hydrochloric acid. The quartz was washed with demineralized water until the discarded wash water had a pH of 5.5. Sodium hydroxide was added to make the pH basic and the quartz was washed with demineralized water until the pH was 7.0. The moist quartz was dried in an oven at a temperature of 90°C and stored in a capped polyethylene bottle.

The cleaned quartz was tested with dithizone and contained about .05 micrograms of available copper per gram. This copper was introduced to the quartz by the wash water. The surface area of the quartz was found to be 900 cm<sup>2</sup> per gram using a krypton adsorption apparatus in the comminution research laboratory of the Metallurgy Department.

Using a method describing the area of screened fractions of quartz, the area was also calculated (Gaudin and Hukki, 1946, p.67). The average diameter of the quartz grains in the sample is 41  $\mu$  .



Figure 11 - Ro-tap Used in Sizing the Quartz Particles



Figure 12 - Weighing Bottles Nested with Outer One Used  
as a Dessicator

It was found in the study of quartz areas that a grain of crushed vein quartz with an average size of 41 has 1.80 times the area of a sphere of this diameter. The calculation is as follows:

$$\begin{aligned} \text{volume of sphere} &= \frac{4}{3} \pi r^3 = \frac{4}{3} (3.14) (20.5)^3 (10^{-4})^3 \\ &= 3.62 \times 10^{-8} \text{ cm}^3 \end{aligned}$$

$$\text{volume of 1 gram of quartz} = \frac{1}{2.65} \text{ cm}^3$$

$$\begin{aligned} \therefore \text{number of spheres} &= \frac{1}{2.65} \left( \frac{1}{3.62} \right) 10^8 \\ &= 1.04 \times 10^7 \end{aligned}$$

$$\text{Area per sphere} = 4 \pi r^2 = 4(3.14) (20.5)^2 (10^{-4})^2 = 5.27 \times 10^{-5}$$

$$\text{Area per gram} = 1.04 (10^7) 5.27 (10^{-5}) = 548 \text{ cm}^2/\text{gram spheres}$$

$$\text{Surface Factor} = 1.80$$

$$\therefore \text{area per gram quartz} = 1.80 (548) = 985 \text{ cm}^2/\text{gm}$$

In all calculations the experimentally determined area of 900 square centimeters of surface area per gram of quartz will be used.

#### 7. Use of Tared Weights

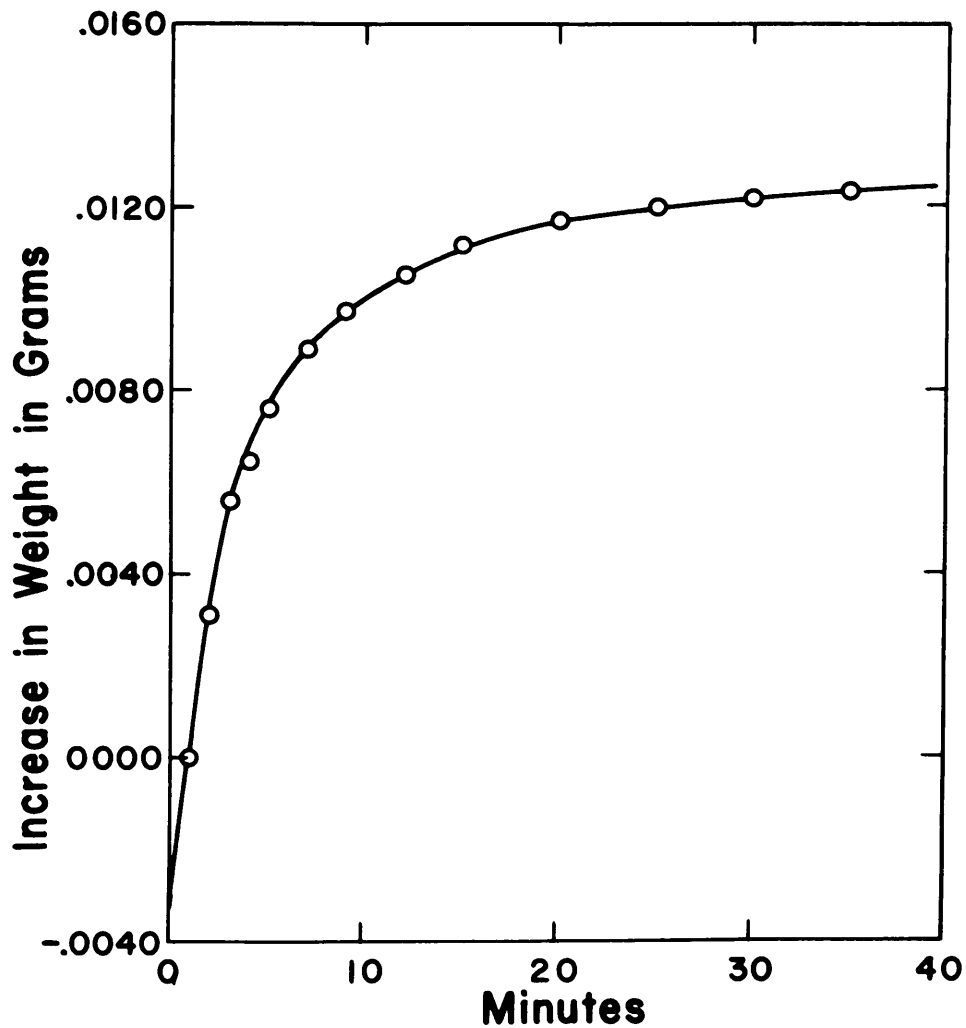
All weighings were done in tared weighing bottles. Each weighing bottle which was used to hold samples had a similar but slightly lighter weighing bottle which was submitted to identical cleaning and heating processes and which was placed on the right hand or weight pan of the balance whenever the weighing bottle containing a sample was weighed. Thus the samples could be

weighed immediately after heating with no danger of errors introduced by the condensation of water vapour on the cooling weighing bottles. In fact, however, the weighing bottles were cooled in a dessicator so they could be weighed cold because the balance could not weigh hot objects sufficiently accurately.

A plot was made of the weight of a weighing bottle versus time after removal from the furnace (fig 13). The curve was extrapolated to time zero to obtain the total weight change upon cooling. The weight gain was 0.0155 gram for a 25 mm weighing bottle. This weight gain was checked by using a larger 40 x 80 mm weighing bottle as a dessicator (fig. 12). The 25 mm weighing bottle and the dessicator were air cooled and then weighed separately. The weighing bottle was heated, quickly put into the cool dessicator, and the nested bottles were weighed immediately. The weight difference between the 25 mm weighing bottle when it was weighed cool and when it was weighed hot was 0.0164 grams. This checks closely with the previously obtained weight of water using the cooling curve.

Some of the solutions used in the experiments contained 100 ppm copper. If the error in weighing caused by cooling bottles is not avoided, errors in copper determination arise which are the same order of magnitude as the experimentally determined amounts of copper adsorbing on quartz. For example, if the weighing error is 0.005 grams, the amount of copper in this weight of 100 ppm copper solution is 0.5 microgram, a very important amount.

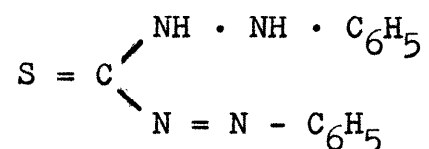




**FIGURE 13**  
**INCREASE IN WEIGHT**  
**OF**  
**COOLING 20 mm WEIGHING BOTTLE**

## 8. Use of Dithizone to Analyze Copper

The amount of copper adsorbed on the quartz samples was determined using the organic compound dithizone (diphenylthiocarbazon) which has the following formula:



Dithizone is soluble in many organic solvents. It is also soluble in water above a pH of 8 but only to a slight extent at lower pH's. Dithizone forms compounds called dithizonates with the heavy metals. In the case of copper, two dithizonates are formed depending on the amount of copper present relative to dithizone. If there is only one copper ion present for each dithizone molecule, a red keto dithizonate is formed. If there is more than enough copper to go around once, a yellowish brown enol dithizonate begins to form. In this thesis the red keto dithizonate was used to measure the amounts of copper present.

The rate of formation of dithizonates is much faster when a reaction takes place at high pH's than when it takes place at low pH's. The rate also depends on the organic solvent used. The dithizone may be dissolved in numerous organic solvents such as xylene, toluene, acetone, carbontetrachloride, and tetrachlorethylene. In these experiments it was desired to use one that would be insoluble in water and lighter than water. Xylene and toluene fulfill these requirements. Xylene is not too desirable a solvent for dithizone because the dithizone quickly oxidizes. Dithizone dissolved in toluene does not oxidize nearly

as quickly (fig 14). The writer tested the stability of copper dithizonate in xylene and toluene and found it much more stable in toluene. It was decided to use toluene as the organic solvent.

Early in the experimentation an attempt was made to use the excellent colorimetric end point obtainable in dithizone reactions with heavy metals. A solution of dithizone is green and a solution of copper dithizonate is strawberry pink. When not all the dithizone present reacts with heavy metal, a "mixed color" results. With less and less heavy metal present, a sequence of colors is produced. The sequence is pink, purplish-pink, bluish purple, blue, bluish green, and green. The blue color is very characteristic and may be used as a colorimetric end point. It was found that one ml of 0.002% dithizone neutralized about one microgram of copper. It was also found, however, that this end point could not be found precisely enough to give the degree of precision necessary to determine the amount of copper adsorbed on the quartz because of the extremely small amounts adsorbed.

The necessary accuracy was obtained using a colorimeter. A Bausch and Lomb monochromatic colorimeter was used with a 505 m $\mu$  (green) filter. At this wavelength the keto copper dithizonate has low transmittancy and dithizone has high transmittancy. The figure given shows transmittancies for dithizone in carbon-tetrachloride. Toluene solutions have very similar transmittancies. (fig 15). The colorimeter was calibrated by shaking various amounts of copper in 7 ml of Solution "A" with 5.5 grams of quartz and 10 ml of 0.001%, weight to volume, dithizone dissolved in toluene (fig 16).

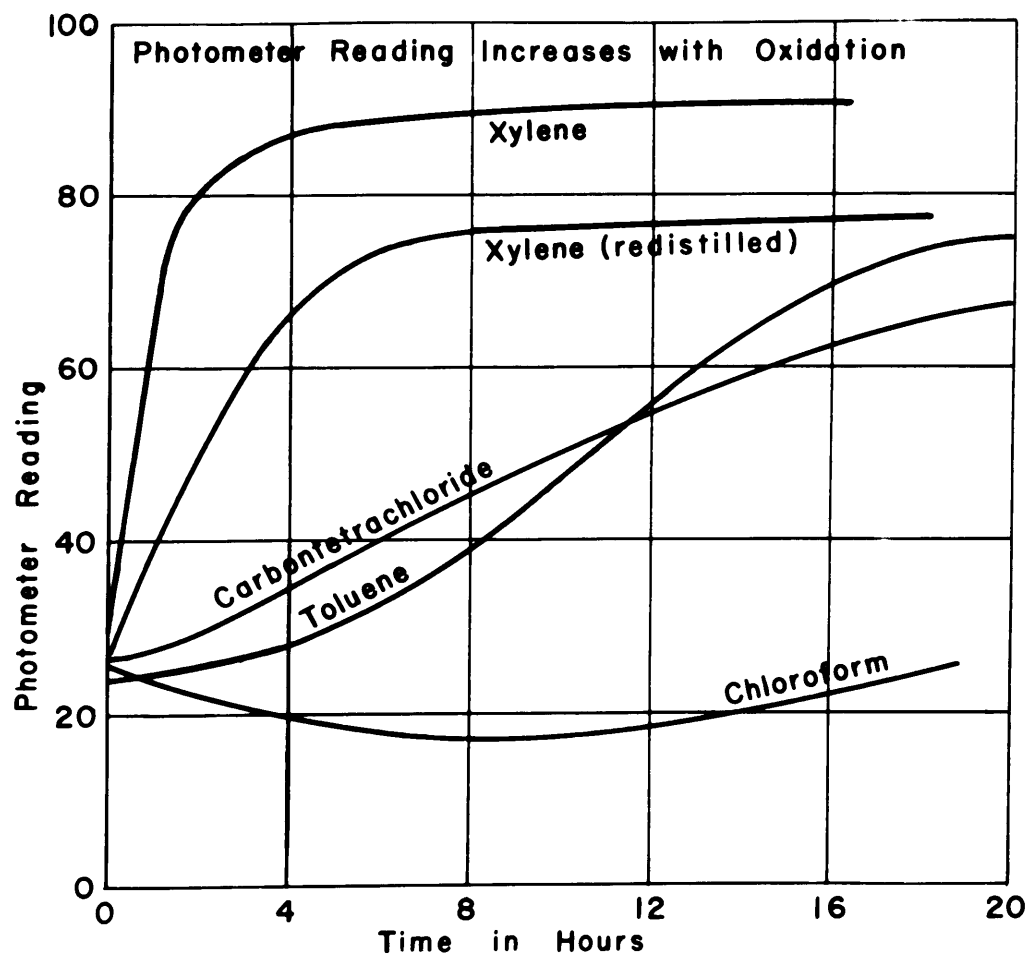


FIGURE 14- OXIDATION RATE OF DITHIZONE IN VARIOUS SOLVENTS

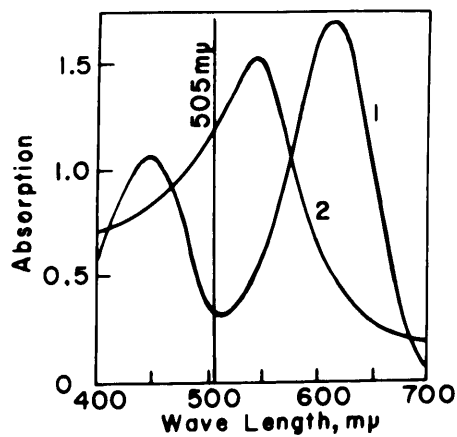


FIGURE 15- TRANSMITTANCIES OF DITHIZONE<sup>1</sup> AND CUPRIC KETO DITHIZONATE<sup>2</sup>

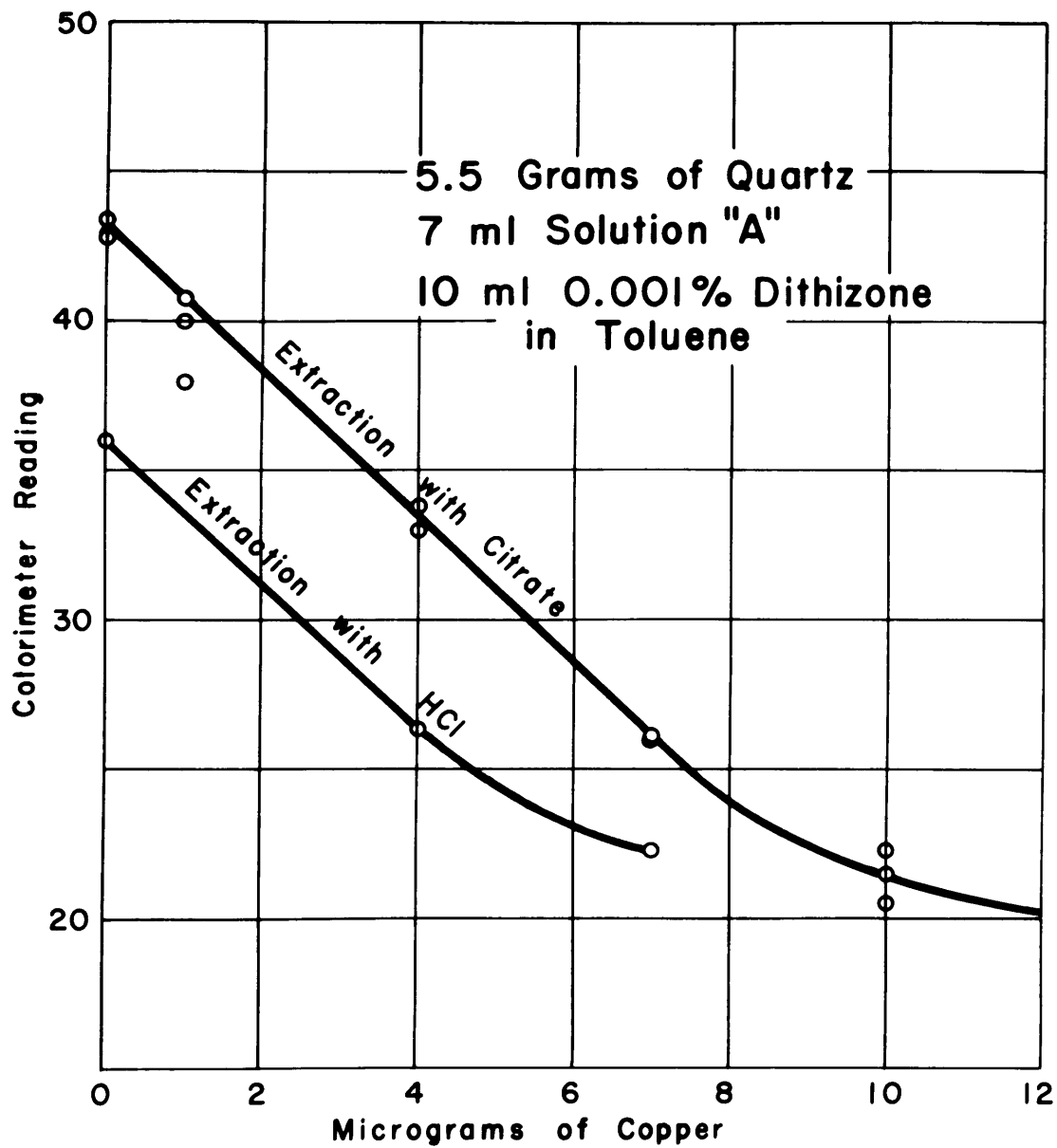


FIGURE 16  
PHOTOMETER CALIBRATION

## II. EXPERIMENTAL PROCEDURE

### 1. Adsorption of Copper on Quartz

Fifty ml portions of solutions of known copper content were poured in each of four 40 x 80 mm weighing bottles with outside caps. To these bottles were added quartz samples varying from one to five grams in weight depending on the strength of the copper solution. For runs with 100 ppm copper, quartz samples of one gram were used because with larger samples too large an amount of copper for convenient analysis was precipitated on the quartz when it was dried later in the procedure.

The bottles were placed on an adapted Cenco-Meinzer Seive Shaker (fig 9) and were agitated 30 minutes. At the end of this time the pH of the solution was measured, the copper solution decanted and discarded, and the four moist quartz samples quickly transferred to four 15 mm gooch crucibles with medium porosity fritted discs. The transfer was made using a glass spatula and was done as quickly as possible to avoid evaporation of water. The gooch crucibles were placed in adapted centrifuge tubes (fig. 17) and covered immediately.

The centrifuge tubes were spun at 2500 rpm for ~~five~~ minutes in an International Centrifuge, model SB-1. The fast speed and short period of spinning were desirable in order to reduce the water content as much as possible before the machine heated too much. It was found that the water content of the quartz sample was reduced to between 4 and 4 1/2 %.

The samples were removed from the centrifuge and quickly transferred to tared weighing bottles. The samples were weighed

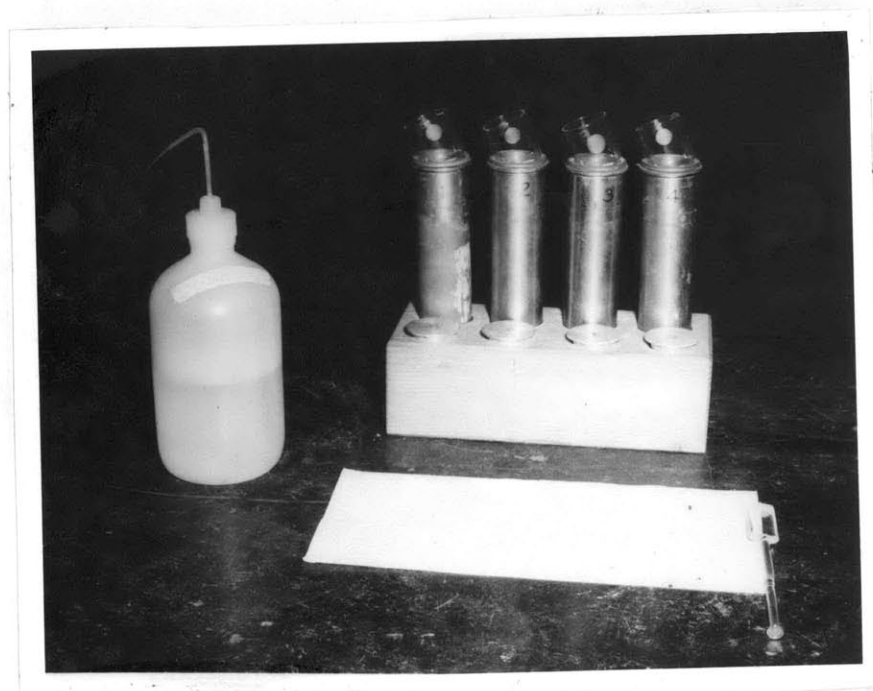


Figure 17 - Adapted Centrifuge Tubes, Gooch Crucibles, and Aluminum Caps



Figure 18 - Ground Glass Stoppered Pyrex Test Tubes

to the nearest 0.1 milligram, heated to 125°C for one hour in a Cenco, de Khotinsky constant temperature furnace. The weighing bottles were cooled in a dessicator and then weighed. The difference in weight before and after heating gave the amount of water that was evaporated during heating.

## 2. Removal of Copper from Quartz

The copper was de-adsorbed from the quartz with a solution of sodium citrate. There was some concern whether the extraction was complete using this extractant but because the copper was loosely attached to the quartz and because the extraction was carried on concurrently with the determination of the amount of copper the extraction was complete. This was confirmed by using an acid extraction on three samples which were identical with three samples from which the copper had been extracted with a citrate solution. The amount of copper obtained from each was similar within experimental limits (fig. 16). The difference in height of the two curves is probably the result of some copper or other heavy metal being introduced by the hydrochloric acid used in the acid extraction or by different amounts of reaction of dithizone with copper because of the different treatment of the quartz. The essential feature is that the slopes of the two curves are identical.

## 3. Analysis of Copper

The weighed, dried quartz samples were transferred to calibrated, ground glass stoppered, pyrex test tubes (fig 18) and 5 ml of citrate solution added. The quartz was allowed to stand until it was wetted and then 10 ml of 0.001% dithizone in toluene was added. The test tube was shaken five minutes,



allowed to stand two minutes to let the organic phase separate from the aqueous phase, transferred to a photometer tube, allowed to stand one minute, and then the tube was read in the photometer. The tube was allowed to stand in the photometer two minutes and read again. The definite time sequence is necessary because copper dithizonates do not form instantaneously. In addition, the dithizone apparently oxidizes to some extent so the time until the colorimeter reading is taken is important because the oxidation product has a different transmittancy than the keto copper dithizonate.

From the photometer readings the approximate amount of copper present was read from the copper versus photometer reading graph (fig. 16) and blank quartz samples of the same weight as the quartz sample being analysed were spiked with this amount of copper. The blanks were analysed as described above. Through the copper versus photometer reading point on figure 16 was drawn a line parallel to the calibration curve. From this line was read the amounts of copper present in the unknowns.

When the analytical procedure was completed, the amount of copper adsorbed on the quartz was calculated by subtracting the weight of copper contained in the evaporated water from the total amount of copper on the quartz sample and then dividing by the weight of the quartz sample to find the amount of copper adsorbed per gram of quartz. Figure 19 is a graph to convert micrograms of copper per gram of quartz to moles of copper per square centimeter of quartz surface.

On the following page is a facsimile data and calculation sheet.

April 2, 1955

Initial Solution of 50 ppm Cu at pH = 5.86

	Final pH	Spike blanks with 7 $\gamma$	
		immed	after 2 min
1	5.66		
2	5.72	5	26.7      27.2
3	5.72	6	<u>26.6</u> 27.1
4	<u>5.72</u>		26.65
average = 5.705			

Sample	1	2	3	4
Tare + Qtz + Water	2.9779	2.8091	2.6742	2.9078
Tare + Qtz	2.8695	2.7034	2.5707	2.7952
Tare weight	.3566	.2214	.1803	.1384
Wt quartz	2.5129	2.4820	2.3904	2.6568
Wt water	.1084	.1057	.1035	.1126
Photometer Reading (immed)	26.0	26.8	27.4	26.0
after 2 minutes	26.0	27.0	27.6	26.6
Total Copper on Qtz ( $\gamma$ )	7.25	6.82	6.70	7.25
Copper in evap water	<u>5.42</u>	<u>5.28</u>	<u>5.18</u>	<u>5.63</u>
Cu adsorbed/sample	1.83	1.54	1.52	1.62
Cu " /gram of qtz	.730	.621	.636	.610

average = .730

.621

.636

.610

4)2.597

.649 = .65 micrograms Cu/gm qtz

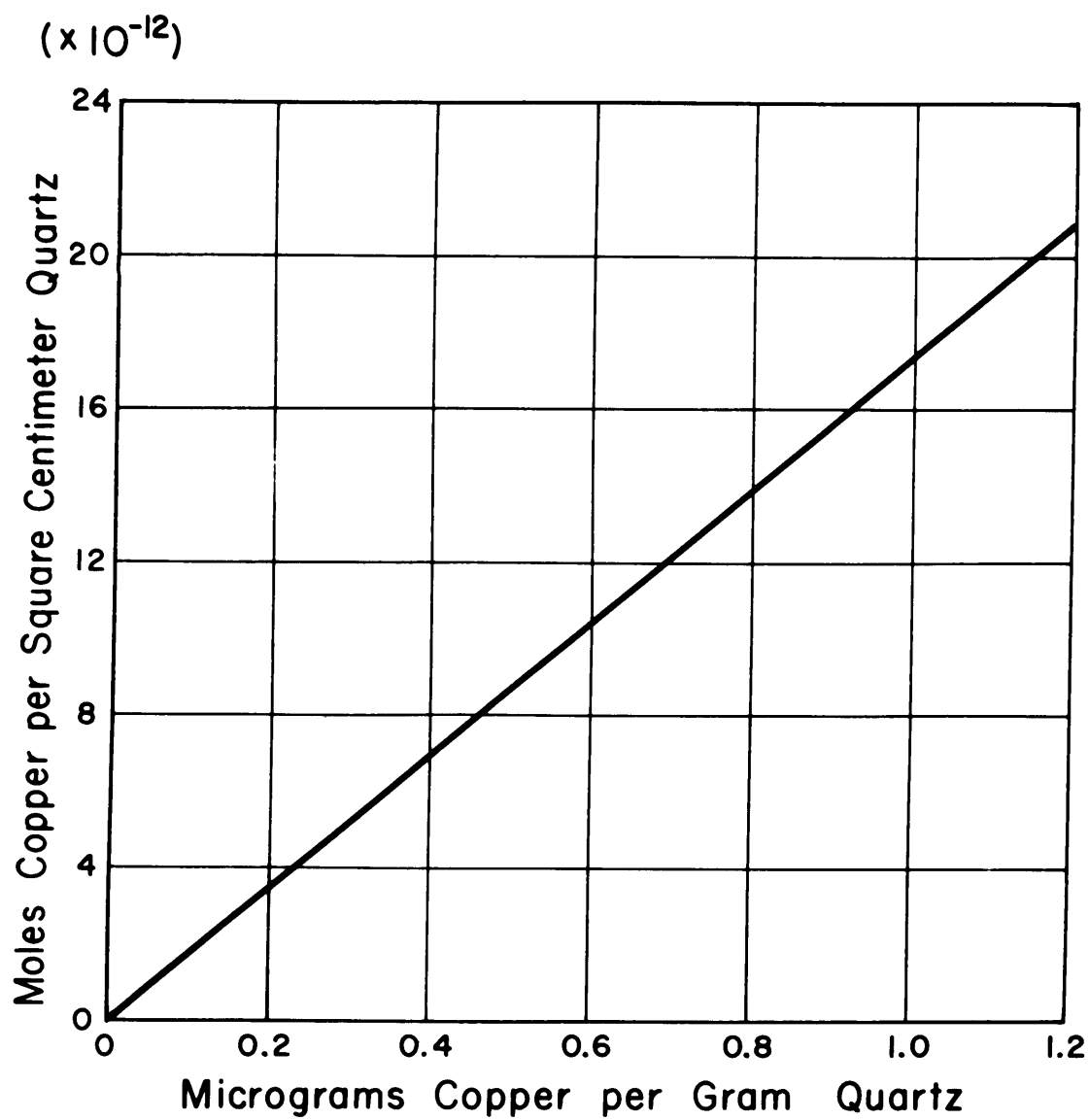


FIGURE 19

## CONVERSION CHART

PART 3

## A METHOD FOR THE DETERMINATION OF THE HEAVY METAL CONTENT OF WATER

## I. INTRODUCTION

There were two reasons for developing a water testing kit of very low detection limit. One was to permit accurate measurement of heavy metals in water in experiments designed to determine the amounts of metals adsorbed on mineral particles. The other was to develop a method with a sensitivity sufficient to measure the background heavy metal content of natural fresh water.

A method described by Warren and Delavault (1953) was used as a starting point. This method of determining the heavy metal content of water was used by the writer for field work in the summer of 1953. The method was valuable but the smallest positive reading obtainable was above background; as it later turned out, about three times background. As a result, a great majority of brooks gave "negative" readings and small anomalies could not be detected.

The McPhar Geophysics Company developed a water testing method rather similar to the one developed in the M.I.T. geochemistry laboratory (Wark, 1955, p. 111). The McPhar method and the presently described method as well as the Warren method and one by Riddell have been compared in a project carried out in the geochemical laboratory (Benson and Stewart, 1955). The presently described method compares favourably with the others.

## II. PROCEDURE

To a pyrex, ground glass stoppered, one litre erlenmeyer flask add 500 ml of streamwater. Add 5 ml citrate solution (Solution "A") and 3 ml of 0.002% (weight to volume) dithizone in carbontetrachloride ( $\text{CCl}_4$ ). Shake the flask for one minute and then allow the organic phase to settle. The bubble of  $\text{CCl}_4$  is almost always light pink. Add 3 ml of dithizone solution and shake 30 seconds. After the second 3 ml increment of dithizone solution, the color of the organic phase is almost always light purple or blue-grey. If the organic bubble is still pink continue adding increments of dithizone solution and shaking until the blue end point is reached. The total number of ml of dithizone necessary to reach the blue end point is recorded. This number is a measure of the heavy metal content of the stream.

If after the first three increments of dithizone solution the bubble of  $\text{CCl}_4$  remains bright red, discard the 500 ml water sample and take a 100 ml sample. Treat this exactly as in the above procedure for a 500 ml sample and multiply the answer by 5. The conversion is not strictly quantitative but is sufficiently accurate for a field procedure.

Although the usual shaking time used in water tests is 30 seconds, an initial shaking time of one minute is used in this procedure because copper dithizonate forms slowly and small copper anomalies could be missed with a shorter shaking time.

## III. DISCUSSION OF RESULTS

A method capable of measuring down to 0.002 ppm copper in water has been developed. The precision is low. Readings can not be made closer than about 20%. This is entirely insufficient to measure the change in metal content of a copper solution after quartz has been agitated in the copper solution and some of the copper has been withdrawn from the solution by adsorption on the quartz. The percentage of copper withdrawn from the water during the adsorption experiments varied from 0 to 10% with the change during most of the runs less than 1%. It is possible that with the use of measuring equipment such as a spectrophotometer the precision could be sufficiently increased to make the procedure of value in adsorption experiments.

The writer used this method for detecting heavy metals in natural stream water during the summer of 1954. Readings were recorded as the number of ml of 0.002% dithizone in  $\text{CCl}_4$  required to react with the heavy metals present in 500 ml of brook water. The background amount of heavy metals in ~~streams~~ in the Stirling area of Nova Scotia reacted with 6-8 ml of dithizone solution. It is important to have an expanded scale of readings, for example twice background content would be about 12 on this scale, because some anomalies at relatively great distances from their sources are not very much higher than background and can be detected only if a large spread is used. For example, one anomalous stream was observed to enter a small river. The amounts of dithizone solution necessary to react with the metal in the river above and below the tributary were 8 and 11 ml. respectively. The anomaly in the river would have been undetectable with a less sensitive method.

## BIOGRAPHICAL SKETCH

The author was born in Vancouver, Canada, on September 30, 1926. He was married to Erlyne Kirkpatrick on June 28, 1951. They have one son, Christopher, born February 1, 1955.

The author attended public and high schools in Vancouver and entered the University of British Columbia in September, 1944. He graduated with the degree of Bachelor of Applied Science in Geological Engineering in May, 1949 and received the degree of Master of Applied Science at the same university in October, 1950. He then worked two years as a geologist and entered the Massachusetts Institute of Technology in September, 1952.

The writer's professional experience has consisted of nine summers of field work with Granby Consolidated Mining and Smelting Company, the British Columbia Department of Mines, Consolidated Mining and Smelting Company, and Mindamar Metals Corporation and a period of one and one-half years at the Sullivan Mine of Consolidated Mining and Smelting Company. While at Massachusetts Institute of Technology the writer has assisted in courses in mineralogy, general geology, engineering geology, and geochemical prospecting.

The writer received the William S. Knudsen Fellowship for the year 1954-55.