THE RELATIVE STABILITIES OF METAL - ORGANIC
COMPLEXES IN RECENT LAKE SEDIMENT

Thesis for the Degree of M. S.
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THESIS

THE RELATIVE STABILITIES OF METAL-ORGANIC COMPLEXES
IN RECENT LAKE SEDIMENT

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A THESIS

Submitted to
Michigan State University

in partial fulfillment of the requirements
for the degree of

MASTER OF SCIENCE

Department of Geology

ABSTRACT

THE RELATIVE STABILITIES OF METAL-ORGANIC COMPLEXES
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A series of potentiometric titrations was carried out to examine the effects of metal interaction with organic-rich sediment from Lake Lansing, Michigan. The objective was to determine the relative affinities of several metals for organic-rich sediment with respcct to complexing and displacement.

A constant amount of well-stirred sediment to which 50 ml of distilled water has been added was used for each titration. Known amounts of several environmentally-important, complex-forming metals were added, and a titration curve was determined for each using 0.1N KOH as titrant. The metals used were: Cr^{+3}, Fe^{+2}, Fe^{+3}, Co^{+2}, Ni^{+2}, Cu^{+2}, Zn^{+2}, Cd^{+2}, Hg^{+2}, Pb^{+2}. Relative stabilities for each complex were computed using the method of differential precipitation.

ACKNOWLEDGEMENTS

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CHAPTER 1

Introduction

What is the "fate" of metals disposed of into lakes? In these
days of profound environmental concern, the answer to this question
is of major importance. Do metals disposed into lakes remain in
solution on the overlying water or are they taken up by the organic
sediment to form complexes? If the latter is the case, what can we
say about the relative stabilities of these metal complexes? These are
the two prime questions which this experiment attempts to answer.

Radiotracers are a method that can be used in determining the
competition of metals in sediment. However, there are a number of
problems involved in using this method. This method requires a labo-
ratory that is well-equipped in nuclear material. Thus extra precau-
tion have to be taken in handling the radioactive material.

By contrast, the potentiometric method, used in this study, offers
a safer, less complex and equally reliable technique for measuring
the competition of metals in any natural environment. However, the
radiotracer method could be useful in providing supplementary infor-
mation on the competition kinetics of metals in natural environments.

For this study, a series of potentiometric titrations were carried
out using sediment from Lake Lansing. Metal ions were introduced
into the sediment before titration with 0.1N KOH. The aim was to deter-
mine whether or not chelation occurs between these metals and the
sediment. The relative stability of each metal complex was also
determined.

According to Martell and Calvin(1952), the pH of a solution is directly affected by chelate formation since all chelating agents are also acids (or bases), and formation of the chelate is accompanied by the displacement of a proton from the acid, or by a decrease in the concentration of the base. The potentiometric method is a good technique for detecting chelate formation.

Hoffman(1969) points out the importance of dissolved organic complexes in natural aqueous environments. In many such environment, especially in sediment pore waters, organic complexes probably act as the controlling factor for solution or precipitation of minerals. Organic complexes cause cation activities to behave as complicated functions of Eh, pH, and the total amount of dissolved organic matter. Presence of these complexing agents can cause the dissolution of minerals whose cation concentrations is at a level of saturation.

A knowledge of the relative order of stability of metal complexes is useful to the understanding of ore formation. Helgeson(1964) has shown that the deposition of sulphides in ore proportions is a function of changes in the stabilities and degrees of formation of complexes in solution. Such deposition may be localized over a short depth range by dilution with cool ground water, or by its mixing with other hydrothermal solutions of different composition.

Complexes of the non-ore-forming metals may be responsible for sulphide deposition or hydrothermal leaching through their changing degrees of formation in response to varying geothermal and compositional environments. Whether or not a metal ore would be deposited depends on the stability of the metal complex (ore-forming metals

are generally transported in the form of metal complexes), and on the type of chelating agent.

Helgeson(1964) computed the order of stability for chloride complexes of the ore-forming metals at 25 degrees centigrade as:

$$Cu^{++} \angle Zn^{++} \angle Pb^{++} \angle Ag^{++} \angle Hg^{++} .$$
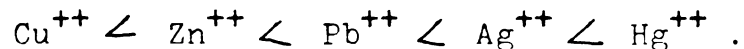
This proved to be the reverse of what was observed for the metal complexes of the organic sediments in this study.

SAMPLE COLLECTION

Sediment sample was collected from the deepest part of Lake Lansing. This was done with a bottom dredge lowered from a small boat. The dredge was hand-lowered with a rope and tripped with a messenger. The contents of the dredge were placed in a plastic collection bag which was then sealed and taken to the laboratory. About 250 ml of this sediment was put in a one-litre glass beaker. Distilled water was added up to $1/4$ inch from the top of the beaker and covered with an airtight cover. This beaker was kept in a water-bath at a temperature of $20^{\circ}C$ for a week.

EXPERIMENTAL TECHNIQUE

A small vial of about 7.5cc in volume was used to measure the amount of sediment used for each potentiometric titration. Samples were taken from the 1-litre beaker of sediment. The sediment in the beaker was stirred for about ten minutes, until a uniform mixture was obtained. Several small vials were filled with the sediment and sealed.

For each titration, the contents of one vial was emptied into a 100 ml beaker and 50cc of distilled water was added. This was again stirred thoroughly and then allowed to settle. 0.1N KOH was prepared and used for the titrations. A 5ml burette was used.

<u>Procedure:</u> An Orion Research pH meter with Beckman electrodes was used. The meter was standardized with a buffer solution of pH 10.

The first titration of the sediment was done in the absence of metal cation. Each titration was carried out by adding a few drops of the titrant, at a time, stirring the sample, giving it time to settle, and recording the changes in pH (see Appendix).

Subsequent titrations were carried out by adding 5,000mg of different metal solution to each sample before titrating.

Standard stock solution of the following metals were used:

$$Cu^{++}, Zn^{++}, Cr^{+++}, Co^{++}, Ni^{++}, Pb^{++}, Hg^{++}, Cd^{++},$$

$$Fe^{++}, Fe^{+++}, \text{ and } Mn^{++}.$$

The titration curves for each metal are presented shortly.

A sediment sample from the small vial was dried at $105^{\circ}C$ and weighed:

```
Weight of sediment = 0.4519gm
Volume of water added to sediment
   before each titration = 50ml
```

$$\text{Density of sediment} = \frac{0.4519}{50} = 0.009gm/cc$$

$$\text{Density of sediment at each titration} = 0.009gm/cc.$$

CHAPTER 3

THEORY OF POTENTIOMETRIC TITRATIONS

Potentiometric titrations are concerned with the reactions of
ions. Electrolytes may be classified as strong or weak. By the
theory of Arrhenius, strong electrolytes in solution are in the
main dissociated into ions and the **degree of dissociation** decreases
with increasing concentration of the electrolyte.

Consider a 0.1Molar solution of a strong electrolyte BA. We have:

$$[B^+] = [A^-] = 0.1 = 10^{-1}$$

where,

$[B^+]$ is concentration of cation

and,

$[A^-]$ represents concentration of anion

Following in the tradition of Sorensen, we can express the ion
concentration as the ion exponent, PI, which is the negative loga-
rithm of the ionic concentration. Thus:

$$PI = -\log[I] = \frac{1}{\log[I]}$$

During a titration, the ion concentration changes over a considerable
range and in a pattern elaborated upon by Kolthoff and Furman(1926)
(Chapter 1).

The Equivalence Potential: The potential of a metal electrode is
a linear function of the metallic ion exponent in the solution.
Therefore the change in potential during a titration is an indication
of the change of the metallic-ion exponent.

At the theoretical end-point of a titration, there is, as a rule, a sudden change of the ion exponent which is indicated by a corresponding jump of the **potential** at the electrode. Thus the electrode can be considered a specific indicator for the corresponding metallic-ions in the solution; consequently, it is called an **indicator electrode**

Titration Curves and Detection of Equivalence Point: The change of the pH of the solution and the variation in the potential of the electrode during titration, can be represented by a plot of pH versus volume of **titrant** added. This then will be a <u>titration curve</u>. The titration curves obtained under different conditions are shown in Figures 1-6. The maximum change in potential occurs at the equivalence point, or, if the titration curve is not symmetrical. at both sides of the point, very close to the equivalence point. This means that the equivalence point is located at the point where:

$$\frac{\Delta pH}{\Delta V}$$ reaches a maximum, or its 2nd derivative

$$\frac{d^2 \Delta pH}{d \Delta V^2} = 0 \ .$$

Close to the equivalence point, we add the reagent drop by drop and note the readings when the potential remains constant with additional drops.

CHELATE FORMATION

The main purpose of the experiments was to find out whether or not complex or chelate formation takes place when metals are presented into organic-rich sediment. The pH of a solution is directly affected by chelate formation since all chelating agents are also acids (or bases) and formation of the chelate is accompanied by the

displacement of a proton from the chelate. The H^+ liberated can be
titrated with NaoH or KoH.

pH Effect: According to Martell(1952), all metal chelates may be
considered as formed by the displacement of one or more usually weak
acidic protons of the chelating agent by a metal ion. Thus the addi-
tion of glycine to a solution of cupric salt causes a drop in the pH
due to the equilibrum:

$$Cu^{+2} + 2H_3\overset{+}{N}CH_2COO^- \rightleftharpoons \begin{matrix} CO \text{---} O \diagdown & \diagup NH_2 \text{---} CH_2 \\ | & Cu & | \\ CH_2 \text{---} NH_2 \diagup & \diagdown O \text{---} CO \end{matrix} + 2H^+$$
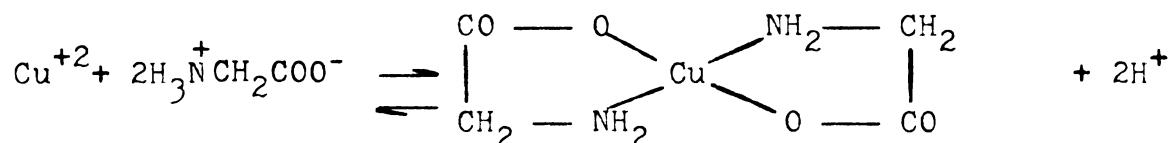
The reaction may also be considered as the combination of the metal
ion with the anion of the chelating agent, accompanied by a shift in
the ionization equilibrum of the amino acid:

$$Cu^{+2} + H_2NCH_2COO^- \rightleftharpoons \begin{matrix} CO \text{---} O \diagdown & \diagup NH_2 \text{---} CH_2 \\ | & Cu & | \\ CH_2 \text{---} NH_2 \diagup & \diagdown O \text{---} CO \end{matrix}$$
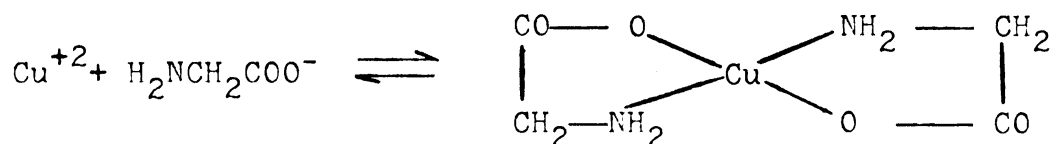
The result is the same in both cases.

Although it is difficult to fully and accurately define the orga-
nic species in sediments, we can safely assume that the complexing
agents include humic acids, amino acids or folic acids. In that case,
the reaction would be as explained above. In a qualitative sense
therefore, we can conclude that chelate formation of metal ions with
amino acids and with the acid form of other chelating agents results
in pH drop(Martell,1952). The greater the tendency for metals to
combine with a given chelating agent, the greater the pH drop.
In this experiment, the addition of metal ions to the sediment resul-
ted in an appreciable drop in pH for some metals (fig.3) and a rise
in pH for some others (figs 2, 5).

TITRATION OF SEDIMENT
in absence of metal ion

Fig. 1

pH

vol. of 0.1N KOH (mls.)
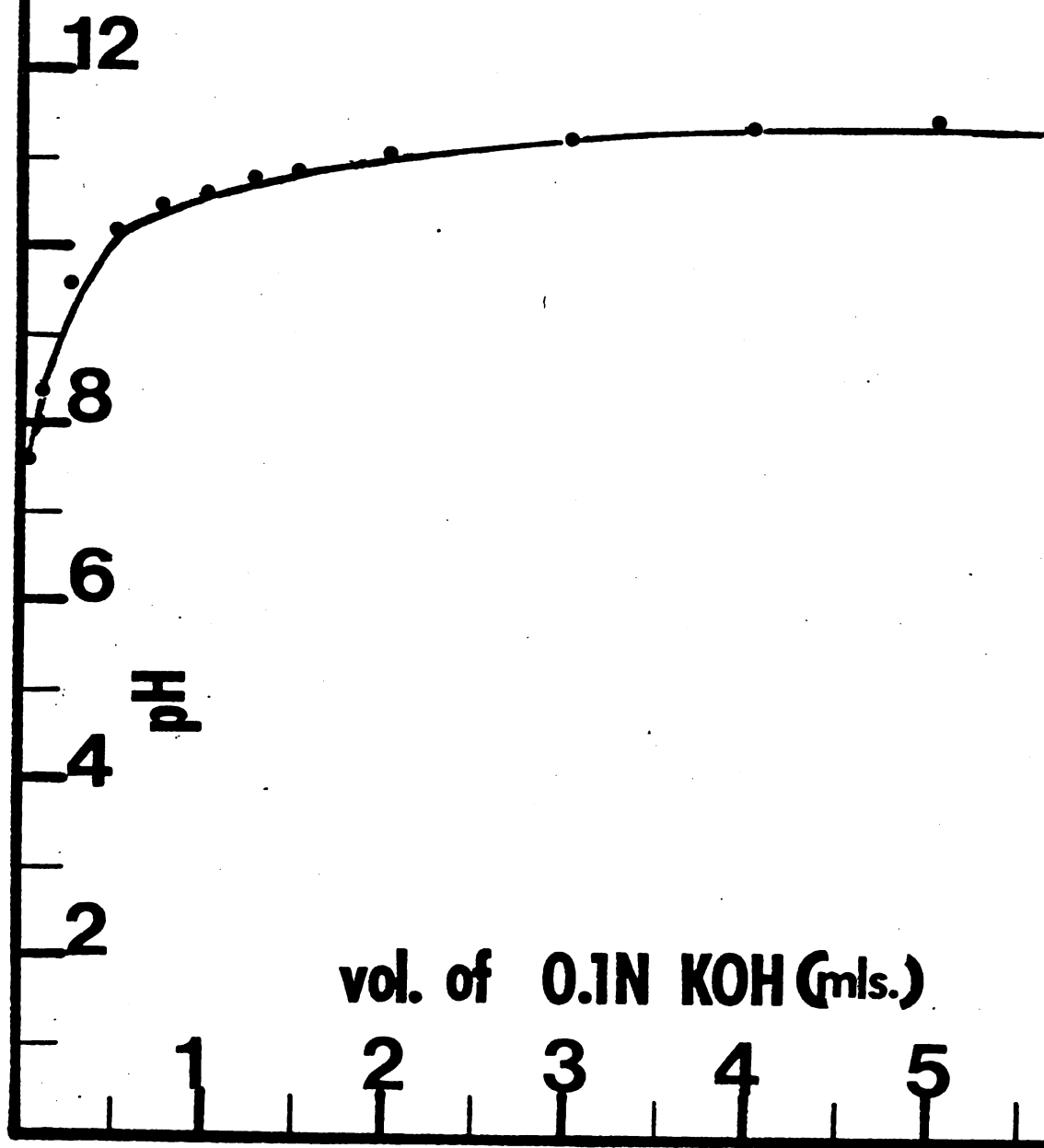
Fig.2

TITRATION OF SEDIMENT
in presence of 5000 µg of
metal ion
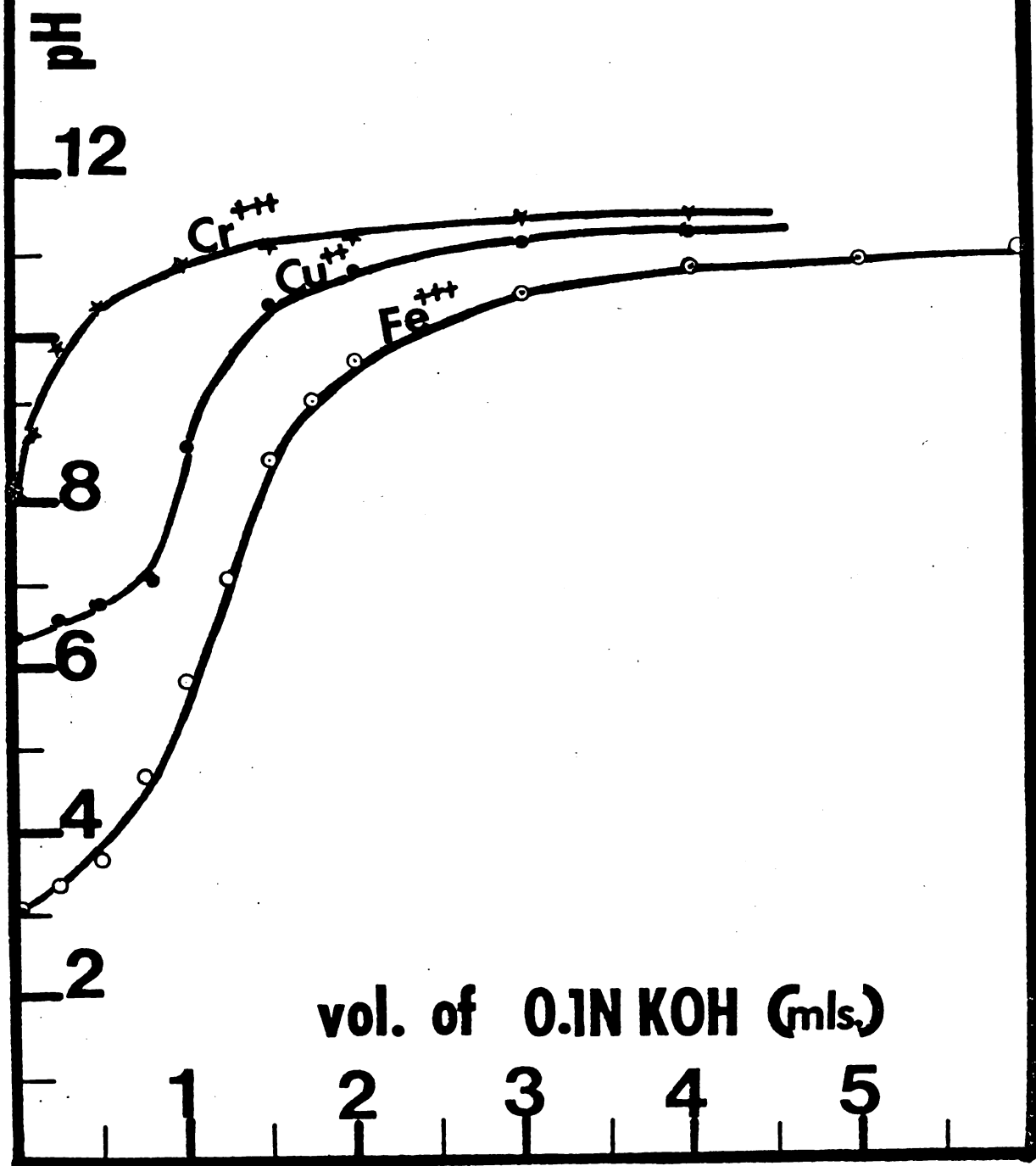
Fig.3

TITRATION OF SEDIMENT in presence of 5000μg of metal Cation
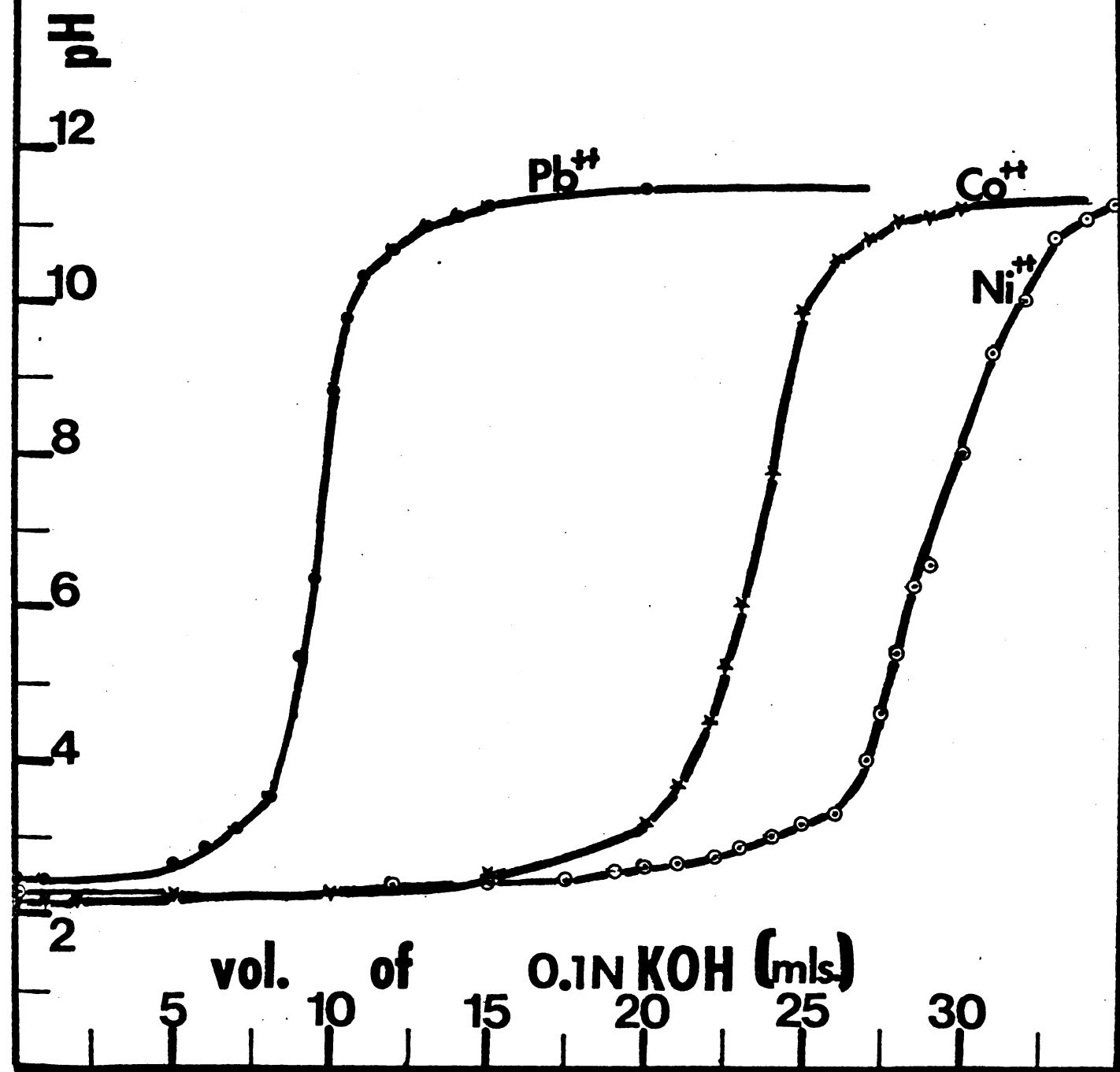
TITRATION OF SEDIMENT in presence of 5000 μg of metal Cation. Fig. 4

Fig. 5

TITRATION OF SEDIMENT in presence of 5000 μg of metal Cation

pH vs. vol. of 0.1N KOH (mls)

Curves: Mn⁺⁺, Zn⁺⁺, Ca⁺⁺
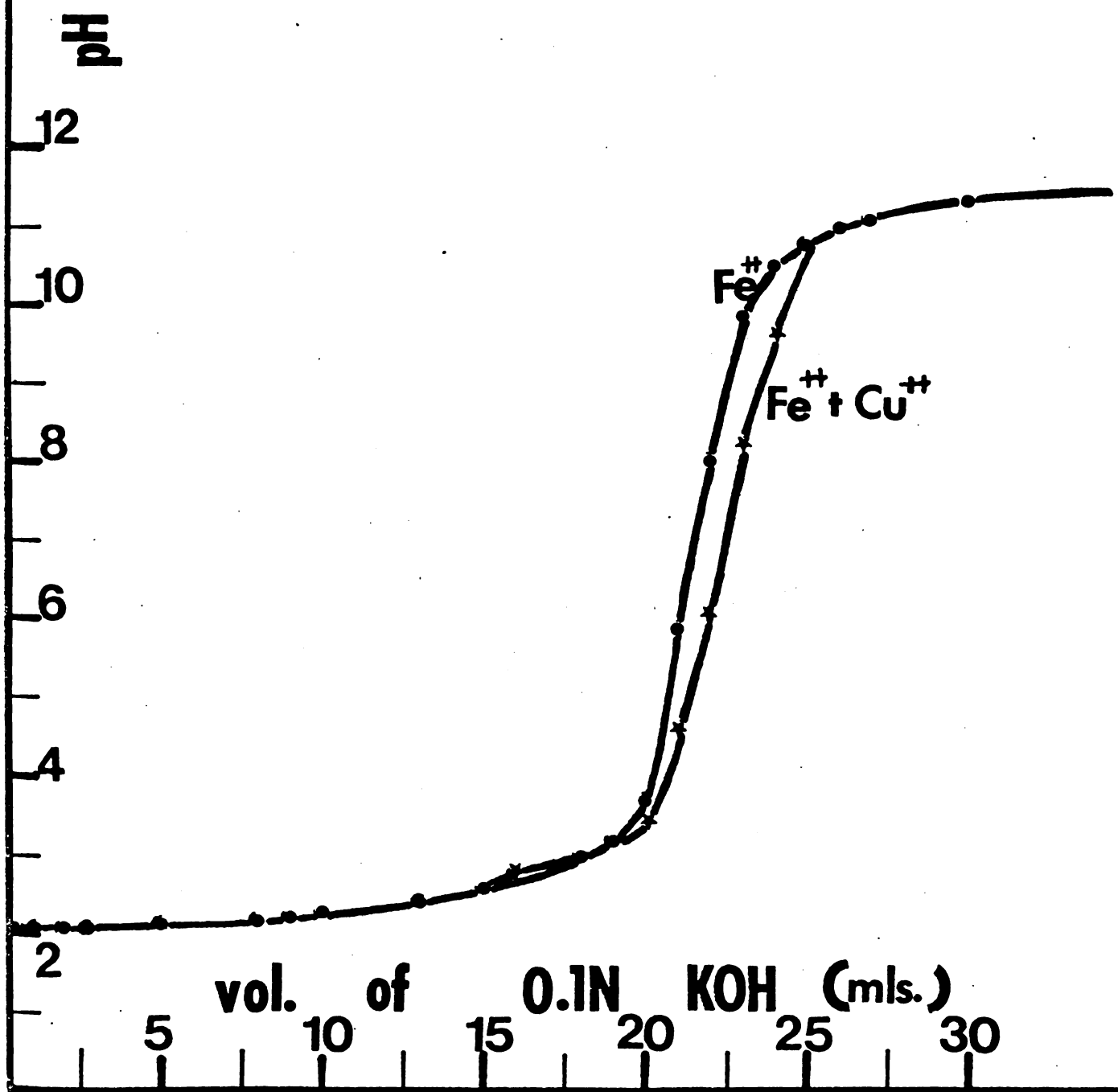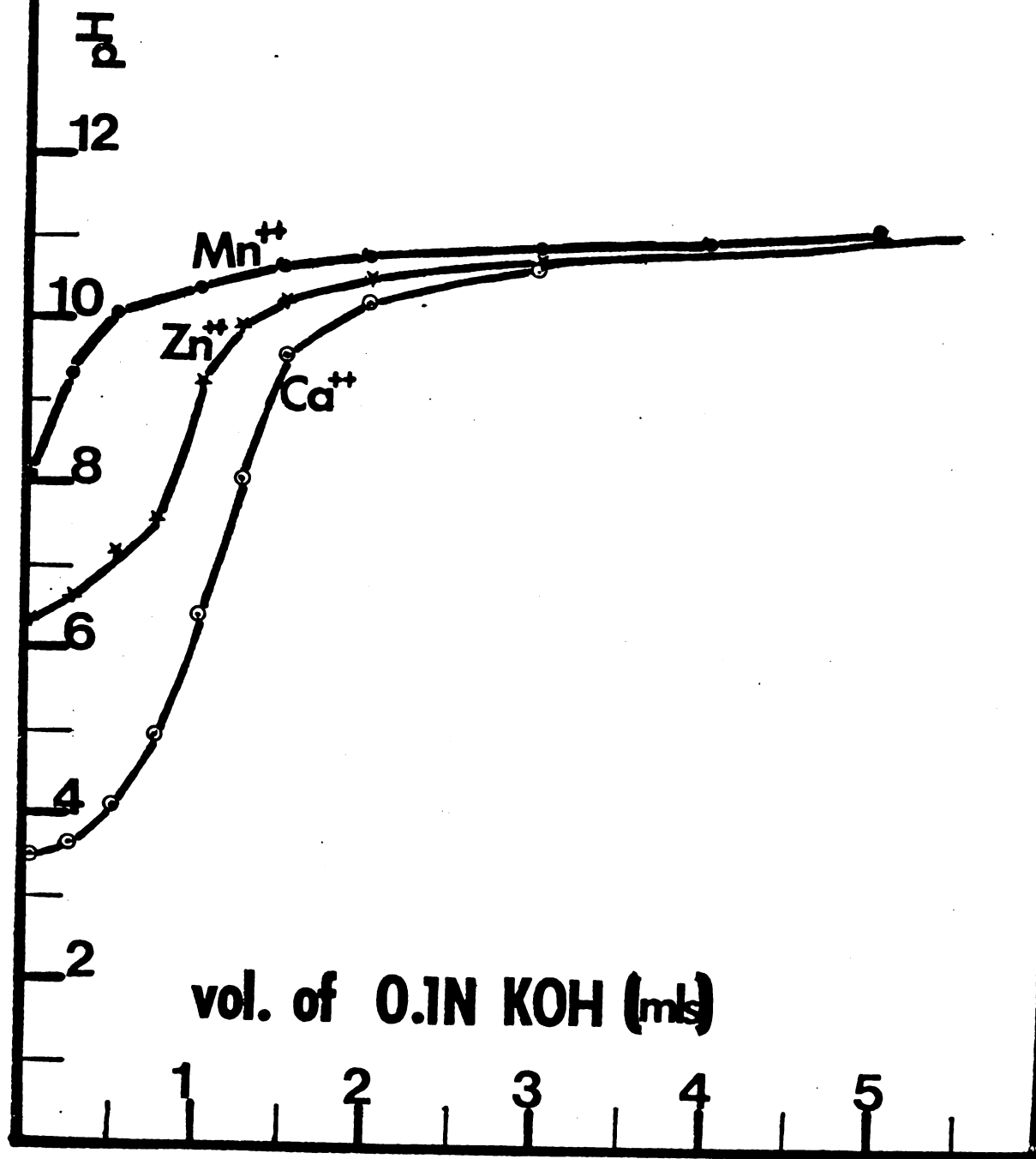
Fig.6

TITRATION OF SEDIMENT
in presence of 5000 µg
of metal Cation
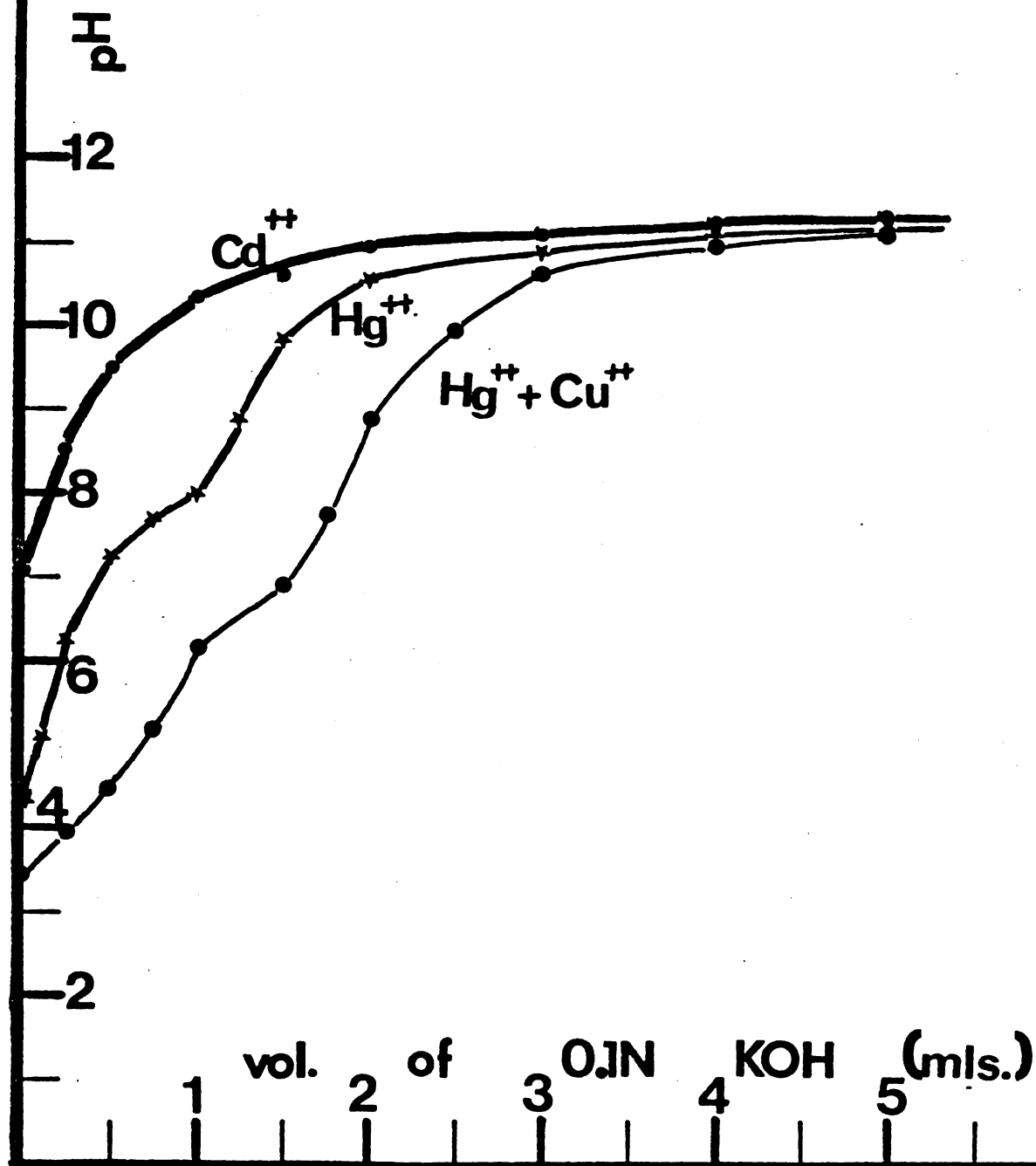
Fig. 7

TITRATION OF SEDIMENT: PRECIPITATION

Turbid
Overlying
water

Sediment

Clear
overlying water

Colored
metal ppt
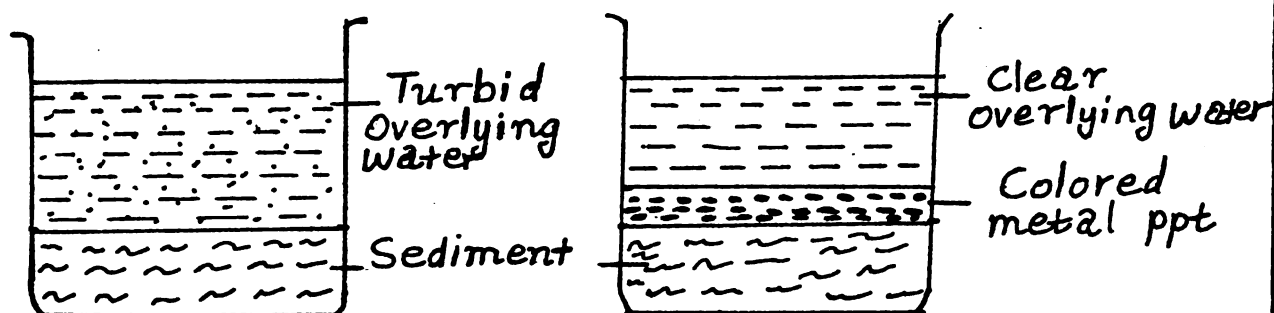
Before Titration.

After Titration.

CHAPTER 4

RESULTS AND DISCUSSION

TABLE 1

Changes in pH and Equivalence Points

(pH of pure sediment = 7.55)

Metal	pH change on adding metal to sediment	pH at equivalence point(precipitation begins)	Comment
Divalent-transition			
Mn^{++}	8.05 *	9.30	
Fe^{++}	2.05	5.85	$Fe(OH)_2$ ppt
Co^{++}	2.15	5.20	pink ppt
Ni^{++}	2.25	5.40	blue ppt
Cu^{++}	6.35	8.65	blue $Cu(OH)_2$ ppt
Zn^{++}	6.35	7.55	$Zn(OH)_2$ ppt
Trivalent-transition			
Cr^{+++}	8.05*	8.80	yellow ppt
Fe^{+++}	3.05	5.80	brownish ppt of $Fe(OH_3)$
Other divalent			
Pb^{++}	2.45	5.35	
Cd^{++}	7.05	9.45	
Hg^{++}	4.30	5.05	first inflection point
Ca^{++}	3.50	6.40	

* No **complexing** occurred with these metals

Explanation of what happened during the titrations:

Formation of chelate is accompanied by a drop in pH, due to the liberation of H^+ ions. For example:

$$M^{+2} + Ke \longrightarrow MKe + 2H^+$$
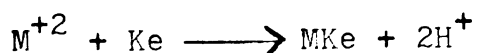
When the hydrogen ions are titrated with a base (e.g. KOH), the H^+ liberated is neutralized by the OH^- from the base to form water. Therefore, when all the H^+ are neutralized, that is at the equivalence point, the metals come out of the sediment to form hydroxides such as in:

$Cu(OH)_2$ ———— which gives blue ppt.
Co^{++} ———— pink ppt
Ni^{++} ———— light blue ppt
Fe^{++} ———— yellowish brown ppt
Fe^{+++} ———— brownish ppt

For those metals which do not form insoluble hydroxides there was no precipitate; the metal merely remained in solution (Fig.7).

The equivalence point was extrapolated from the titration curve and also from the maximum $\frac{\Delta pH}{\Delta V}$ which is the increase in potential with each addition of 0.1N KOH.

Mn^{++} and Cr^{+++} were not taken up by the sediment since there is no drop in pH below the pH of the pure sediment(see Table 1 & Figs 2,5)

Fe^{++}, Co^{++}, Ni^{++}, Pb^{++} show the greatest drops in pH. This means that these metals have the greatest tendency to be taken up by the sediment. Fe^{+++}, Hg^{++}, and Ca^{++} also show a considerable drop in pH when they were added to the sediment, also implying a readiness to be taken up. Cu^{++}, Zn^{++}, and Cd^{++} show the least drop in pH but unlike Mn^{++} and Cr^{+++}, they did form complexes with the sediment(.Table 1 and Figs 1-6).

In Fig.6, the titration curve of Hg^{++} shows two inflection points. Martell and Calvin(1952) provide an explanation for this(pg 44). The first inflexion point represents the completion of the normal chelation of the metal:

$$M^{+2} + HN^+ \begin{cases} CH_2COO^- \\ CH_2COO^- \\ CH_2COO^- \end{cases} \rightleftharpoons \left[\text{(structure)} \right]^{-1} + $$
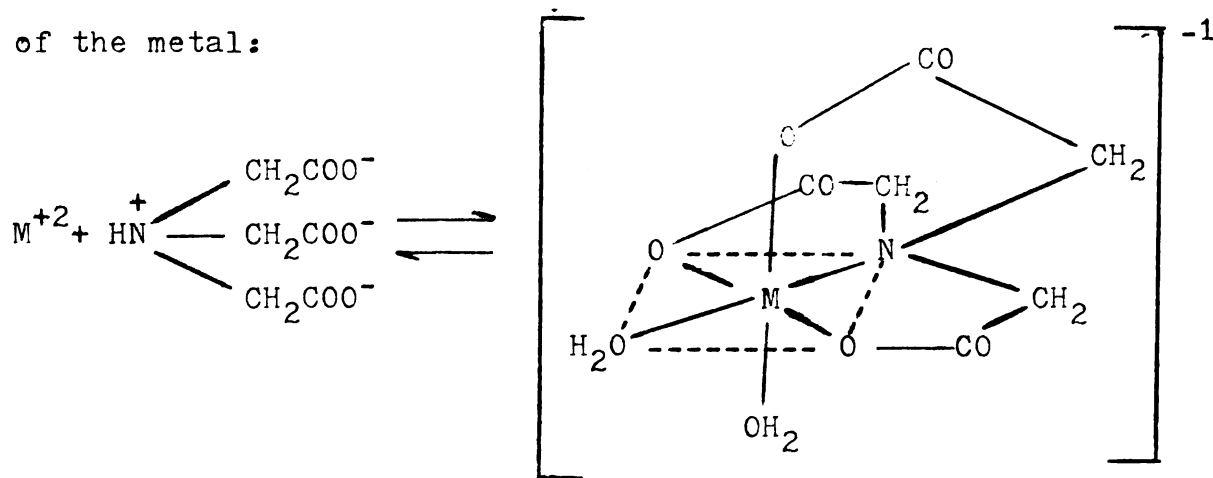
The second inflexion point indicates another reaction with base. This could be due to interaction with excess chelating agent to form a higher chelate:

$$\text{(structure)} + HN^+ \begin{cases} CH_2COO^- \\ CH_2COO^- \\ CH_2COO^- \end{cases} \rightleftharpoons$$

$$\left[\text{(structure)} \right]^{-4} + H^+$$
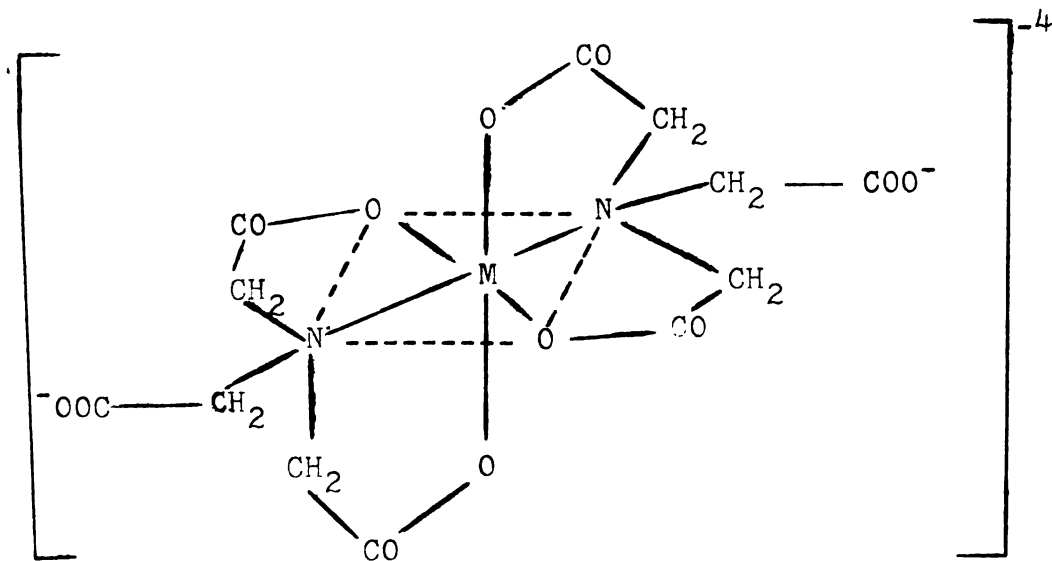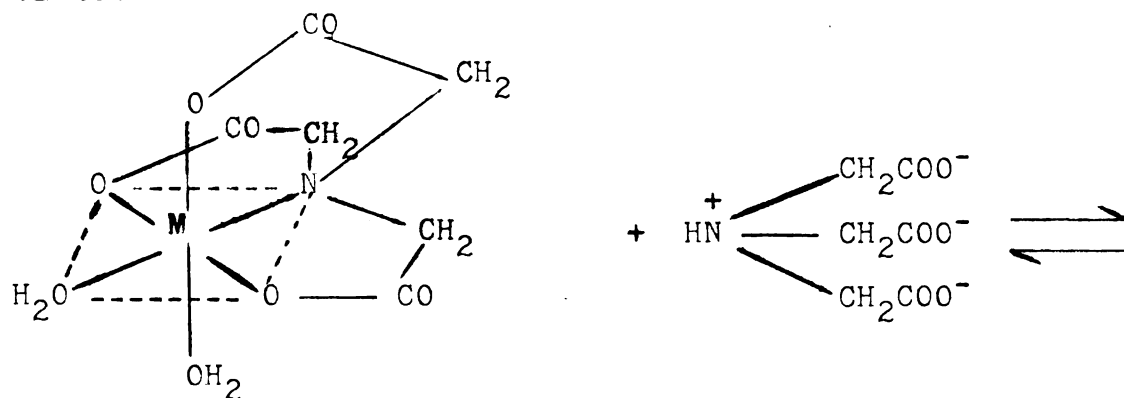
Schwarzenbach(1948), found that this behavior is characteristic of the divalent positive ions of Ca,Co,Cu,Fe,Mg,Mn,Ni,Hg,Pb and Zn as well.

Relative Stability of the Metal Complexes: Mellor and Maley(1947) have determined that the stability of complexes of bivalent metal ions follow the order:

$$Pd > Cu > Ni > Pb > Co > Zn > Cd > Fe > Mn > Mg ,$$
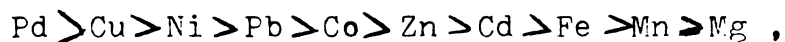
irrespective of the nature of the ligands involved. The stability also seemed to decrease with increasing basicity of the metal.

Irving and Williams(1948), also corroborated the findings of Mellor and Maley(1947) on the successive stability constants of the divalent ions of the first transition series. This is generally:

$$Cr > Mn < Fe < Co < Ni < Cu < Zn.$$
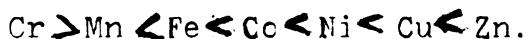
This trend results from differences in ligand field stabilization energies between the aquated and complexed ions. In this series, the ionic radius decreases and the ionization potential increases up to Cu.

Irving and Williams, and their contemporaries concluded that the stability of metal complexes was dependent on the nature of the metal ion involved. However, recent work with various chelating agents indicate that the nature of the chelating agent and its pH also affect stability. Most prominent of these are the works on humic acids by Adhikari and Hazra(1970), Ovcharenko and Gordienko(1969) and Courpron(1967), all of which show how the nature of the chelating agent affects the stability of metal complexes.

The nature of the organic fraction of sediment is very complex and we assume, for the sake of simplicity, that humic acid, the organic matter found in soil, is contained in the organic fraction of our sediment. Humic acid is capable of complexing metals and the stability of

such complexes are generally very high.

In Adhikari and Hazra(1970), humic acid extracted from Chinsura subsoil was fractionated by solvent extraction. Stability constant values calculated on the basis of average molecular weight of humic acid, 670, followed the following order at pH 4; $Cu^{++} > Co^{++} > Zn^{++} > Ni^{++}$ which did not conform to the Irving-Williams series for stability constants of metals with ligands. This **difference** is probably due to the fact that humic acid is heterogenous in nature and has a complicated structure. Because of this, no exact mechanism of reaction between metal and humic acid could be ascertained.

In my study, titration of humic acid was carried out but no inflection points, from which the equivalent weight of humic acid could be calculated, were obtained. As Breger(1963) pointed out, the titration curve resembles the adsorption isotherms of colloidal substances. Later experiments however proved that this was true chelation rather than adsorption. Also in my study, titration of humic acid in the presence of 5,000mg each of Cu^{++}, Co^{++}, Zn^{++}, Hg^{++} and Cd^{++} showed the trend of stability similar to the findings of Adhikari and Hadzra(1970): $Cu^{++} > Co^{++} > Zn^{++}$. In addition, the metals were not precipitated during titration, indicating the formation of a soluble metal organic complex.

Ovcharenko and Gordienko(1969) also observed that the stability of the humic acid metal ion complexes deduced from the potentiometric curves for the titration (with 0.01N NaoH) of the acids in the presence of varied concentrations of metal salts was in the following order: $Fe^{++} > Cu^{++} > Co^{++} > Mn^{++}$. This too did not agree with the Irving-Williams series.

TABLE 2

Relative Stability Of Metal Complexes
Of Lake Lansing Sediment

Metal	pH at equivalence point	Order of stability
Hg^{++}	5.05	1.00
Co^{++}	5.20	1.03
Pb^{++}	5.35	1.06
Ni^{++}	5.40	1.09
Fe^{++}	5.85	1.16
Ca^{++}	6.40	1.27
Zn^{++}	7.55	1.50
Cu^{++}	8.65	1.71

Computation of Relative Stability: Relative order of stability of
the metals which formed complexes with the organic sediment (divalent
metals only) was calculated as follows: Hg^{++} has the least pH at the
equaivalence point; therefore using the pH of Hg^{++} at equivalence
point as a standard, we can divide the pH of the other metals at the
equivalence point by the pH of Hg^{++} at equivalence point, to give
the relative order of stability of these other metals. Hence the order
of stability of Co^{++} is 5.20/5.05 = 1.03.

Relative stability deduced from pH at equivalence point in this
manner shows the following order for the metals compared:

$Cu^{++} > Zn^{++} > Ca^{++} > Fe^{++} > Ni^{++} > Pb^{++} > Co^{++} > Hg^{++}$. This does not con-
form with the Irving-Williams series in which Fe^{++} is the least stable.

Although calculation of the actual stability constants of the metals
using the Bjerrum method for example would be valuable,we cannot do this
in this case because the molecular weights of the complexing agents in
our sediment are not known. Hence the resort to relative stabilities
which are also useful.

TABLE 3

Summary Of Relative Stabilities Of Humic Acid
Fractions In Four Studies

	Order Of Stability	Average molecular wt. of humic acid
Adhikari & Hazra(1970) Adhikari & Hazra(1970)	$Cu^{++} > Co^{++} > Zn^{++} > Ni^{++}$ (2.494 2.453 2.126 1.385)	670
Gordienko & Ovcharenko (1969)	$Fe^{++} > Cu^{++} > Zn^{++} > Mn^{++}$	-
Courpron (1967)	$Cu^{++} > Zn^{++}$	-
Present study	$Cu^{++} > Co^{++} > Zn$	-

Displacement of One Metal By Another

5000mg of Fe^{++} plus 5000mg of Cu^{++} were added to the sediment
before titration. pH drop was 2.05. During titration with 0.1N KOH,
Fe^{++} was precipitated at pH 6.05. Similarly, when Cu^{++} and Hg^{++} were
added, the pH dropped to 3.45.

Explanation

The metal that forms the most stable species complexed first, but
Fe^{++} and Hg^{++} have a greater tendency to form chelates with the sedi-
ment; hence the considerable drop in pH. On titration, Fe^{++} and Hg^{++}
were precipitated showing that Fe^{++} and Hg^{++} have been displaced from
the sediment into the overlying water.

Summary and Conclusion

The results of this study show that Fe^{++}, Co^{++}, Ni^{++}, and Pb^{++} have the greatest tendency to form complexes with the organic sediment used. The relative stabilities are of the order:

$$Cu^{++} > Zn^{++} > Ca^{++} > Fe^{++} > Ni^{++} > Pb^{++} > Co^{++} > Hg^{++} ; \; Cd^{++} > Hg^{++} ; \; Fe^{+++} > Fe^{++}$$
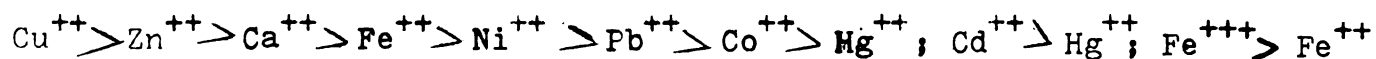
In defining relative stabilities, the important factor is the pH at equivalence point. We assume that all the metal complexes, in the same environment, are initially at the same pH level. Thus as pH increases, the metals are differentially pushed out of the metal complexes are either precipitated as insoluble hydroxide or remain in solution.

The experimental procedures used in this study could be used in defining the profile of a lake; specifically to find out the capacity for metals of a Lake sediment. It is thus applicable to environmental pollution studies, and in explaining some aspects of ore formation, and why one metal is not found in association with another.

APPENDIX A

Test For Reproduceability Of The Method Used

The pure sediment was titrated with O.1N KOH, three times. The 95% confidence level for each of the points is repoted below:[*]

TABLE A

Confidence Level Of Titration Points

| Vol.of 0.1N KOH added | pH Readings | | | $\sum R$ | Confidence Level | |
	1st Titration	2nd Titration	3rd Titration		$\bar{X}$	$A(\sum R)$
0.00	6.85	6.85	6.95	0.10	6.883	± 0.1301
0.10	8.35	8.35	8.35	0.00	8.350	± 0.0000
0.25	9.65	9.75	9.65	0.10	9.683	± 0.1301
0.50	10.15	10.15	10.15	0.00	10.150	± 0.0000
0.75	10.35	10.30	10.45	0.15	10.367	± 0.1952
1.00	10.60	10.45	10.55	0.15	10.533	± 0.1952
1.25	10.75	10.55	10.75	0.20	10.683	± 0.2602
1.50	10.85	10.80	10.85	0.05	10.833	± 0.0651
2.00	11.00	10.95	11.00	0.05	10.983	± 0.0651
3.00	11.20	11.15	11.20	0.05	11.183	± 0.0651
4.00	11.30	11.30	11.30	0.00	11.300	± 0.0000
5.00	11.40	11.40	11.45	0.05	11.417	± 0.0651

[*] The formula used for calculating the 95% confidence level (three observations per point) was:

$$CL = \bar{X} \pm A(\sum R)$$

where $\bar{X}$ is the mean of the three observations,

A is the confidence interval constant for three observa-tions per point, and,

$\sum R$ represents the range of the observations per point.

A.   Titrations Of Sediment Sample (From 1st Collection)
      With 0.1N KOH.

1. **In The Absence Of Metal Ions.**   2. **In the presence of metal cations.**

Vol.of 0.1N KOH added (in mls)	pH Readings
0.0	7.55
0.1	8.35
0.25	9.55
0.50	10.15
0.75	10.45
1.00	10.60
1.25	10.75
1.50	10.85
2.00	11.05
3.00	11.20
4.00	11.35
5.00	11.45

2nd titration

Vol.	pH
0.0	7.60
0.1	8.45
0.25	9.75
0.50	10.15
0.75	10.45
1.00	10.60
1.25	10.75
1.50	10.85
2.00	11.00
3.00	11.20
4.00	11.35
5.00	11.45

3rd titration

Vol.	pH
0.0	7.55
0.1	8.30
0.25	9.80
0.50	10.20
1.00	10.65
1.50	10.85
2.00	11.05
3.00	11.25
4.00	11.35
5.00	11.45

Vol.of 0.1N KOH added (in mls)	pH Readings

With 5000μg of Cu^{++}

Vol.	pH
0.0	6.35
0.25	6.55
0.50	6.75
0.75	7.00
1.00	8.65
1.50	10.35
2.00	10.75
3.00	11.15
4.00	11.25

With 5000μg Cr^{+++}

Vol.	pH
0.0	8.05
0.1	8.80
0.25	9.85
0.50	10.35
1.00	10.85
1.50	11.05
2.00	11.15
3.00	11.40
4.00	11.40

With 5000μg Cu^{++} and 5000μg of Cr^{+++}

Vol.	pH
0.0	6.55
0.25	6.90
0.50	7.40
1.00	10.05
1.50	10.85
2.00	10.90
3.00	11.25
4.00	11.35

Vol.of 0.1N KOH added (in mls)	pH Readings	Vol.of 0.1N KOH added (in mls)	pH Readings
With 5000 μg Mn^{++}		21.00	3.65
		22.00	4.50
0.0	8.05	22.50	5.20
0.25	9.30	23.00	6.00
0.50	10.05	24.00	7.75
1.00	10.35	25.00	9.85
1.50	10.65	26.00	10.50
2.00	10.75	27.00	10.75
3.00	10.90	28.00	11.00
4.00	10.95	29.00	11.05
5.00	11.15	30.00	11.15
With 5000 μg Ni^{++}		**With 5000 μg Pb^{++}**	
0.0	2.25	0.0	2.45
0.25	2.25	0.25	2.45
0.50	2.25	1.00	2.45
5.00	2.25	5.00	2.65
10.00	2.25	6.00	2.85
12.00	2.35	7.00	3.10
13.00	2.35	8.00	3.50
15.00	2.40	9.00	5.35
17.50	2.45	9.50	6.35
19.00	2.55	10.00	8.80
20.00	2.60	10.50	9.75
21.00	2.65	11.00	10.25
22.00	2.75	12.00	10.65
23.00	2.85	13.00	10.95
24.00	3.00	14.00	11.05
25.00	3.15	15.00	11.20
26.00	3.30	20.00	11.45
27.00	4.00	**With 5000 μg of Fe^{+++}**	
27.50	4.60		
28.00	5.40	0.0	3.05
28.50	6.25	0.25	3.35
29.00	6.55	0.50	3.65
30.00	8.00	0.75	4.65
31.00	9.30	1.00	5.80
32.00	10.00	1.25	7.05
33.00	10.80	1.50	8.50
34.00	11.05	1.75	9.20
35.00	11.25	2.00	9.65
With 5000 μg Co^{++}		3.00	10.50
		4.00	10.80
0.0	2.15	5.00	10.90
0.25	2.15	6.00	11.05
0.50	2.15		
1.00	2.15		
2.00	2.15		
5.00	2.25		
10.00	2.25		
15.00	2.50		
20.00	3.15		

Vol.of 0.1NKOH added (in mls)	pH Readings	Vol.of 0.1NKOH added (in mls)	pH Readings
With 5000 μg Fe^{++}		With 5000 μg Ca^{++}	
0.0	2.05	0.0	3.50
0.25	2.05	0.25	3.65
0.50	2.05	0.50	4.10
1.00	2.05	0.75	4.95
2.00	2.05	1.00	6.40
3.00	2.05	1.25	8.05
5.00	2.10	1.50	9.55
8.00	2.15	2.00	10.20
9.00	2.20	3.00	10.75
10.00	2.25	4.00	11.05
13.00	2.40	5.00	11.20
15.00	2.55	With 5000 μg of Cd^{++}	
18.00	2.95	0.0	7.05
19.00	3.15	0.25	8.50
20.00	3.65	0.50	9.45
21.00	5.85	1.00	10.30
22.00	7.95	1.50	10.55
23.00	9.80	2.00	10.90
24.00	10.45	3.00	11.05
25.00	10.70	4.00	11.20
26.00	10.90	5.00	11.25
27.00	11.00	With 5000 μg Hg^{++}	
30.00	11.25	0.0	4.30
With 5000 μg Zn^{++}		0.1	5.05
0.0	6.35	0.25	6.20
0.25	6.65	0.50	7.20
0.50	7.15	0.75	7.65
0.75	7.55	1.00	7.95
1.00	9.20	1.25	8.85
1.25	9.90	1.50	9.80
1.50	10.20	2.00	10.50
2.00	10.50	3.00	10.85
3.00	10.85	4.00	11.05
5.00	11.15	5.00	11.15
With 5000 μg Fe^{++} and 5000 μg Cu^{++}		With 5000 μg Hg^{++} and 5000 μg Cu^{++}	
0.0	2.10	0.0	3.45
5.00	2.15	0.25	3.95
10.00	2.25	0.50	4.45
15.00	2.60	0.75	5.20
16.00	2.75	1.00	6.15
18.00	2.95	1.50	6.85
19.00	3.10	1.75	7.70
20.00	3.40	2.00	8.85
21.00	4.60	3.00	10.60
22.00	6.05	4.00	10.90
23.00	8.20	5.00	11.05
24.00	10.65		
25.00	10.70		
30.00	11.20		

B. Titration Of Sediment, 2nd Collection.
   (for testing reproduceability of method)

Vol. of 0.1N KOH added (in mls)	pH Readings

In The Absence of Metal Ions

0.0	6.85
0.10	8.35
0.25	9.75
0.50	10.15
0.75	10.30
1.00	10.45
1.25	10.55
1.50	10.80
2.00	10.95
3.00	11.15
4.00	11.30
5.00	11.40

2nd titration

0.0	6.85
0.10	8.35
0.25	9.65
0.50	10.15
0.75	10.35
1.00	10.60
1.25	10.75
1.50	10.85
2.00	11.00
3.00	11.20
4.00	11.30
5.00	11.40

3rd titration

0.0	6.95
0.10	8.35
0.25	9.65
0.50	10.15
0.75	10.45
1.00	10.55
1.25	10.75
1.50	10.85
2.00	11.00
3.00	11.20
4.00	11.30
5.00	11.45

C. Titration Of Humic Acid. (10gm Humic acid in 1000mls H_2O; 50mls aliquot used for each titration)

Titration In Absence Of Metal Ions.

Vol.of 0.1N KOH added (in mls)	pH Readings		Vol.of 0.1N KOH added (in mls)	pH Readings
0.0	3.65		8.00	8.25
0.10	3.75		9.00	8.65
0.25	3.85		10.00	9.45
0.50	4.00		11.00	10.00
0.75	4.15		12.00	10.45
1.00	4.25		13.00	10.95
1.25	4.45		14.00	11.05
1.50	4.75		15.00	11.25
1.75	4.90			
2.00	5.05			
2.25	5.15		With 5000μg Co^{++}	
2.50	5.35		0.0	2.35
3.00	5.75		0.50	2.35
3.50	5.90		2.00	2.35
4.00	6.25		5.00	2.35
4.50	6.55		7.00	2.40
5.00	6.70	starts dissol-	10.00	2.45
5.50	6.90	ving.pH reading	13.00	2.55
6.00	7.05	unsteady.Takes	15.00	2.65
6.50	7.15	up to 5 mins. to	17.50	2.65
7.00	7.25	get constant	20.00	2.85
8.00	7.75	reading.	22.50	3.05
8.50	7.95		25.00	3.45
10.00	8.75		27.00	4.15 — disso-
15.00	11.25		28.00	4.75 lution
			29.00	5.35 starts

With 5000μg Cu^{++}

Vol.of 0.1N KOH added (in mls)	pH Readings		Vol.of 0.1N KOH added (in mls)	pH Readings
0.0	3.45		30.00	5.95
0.1	3.45		31.00	6.55
0.25	3.50		32.00	7.45
0.50	3.55		33.00	8.45
1.00	3.75			
1.25	3.85		34.00	9.10
1.50	4.05		35.00	9.40
2.00	4.25		37.00	10.50
2.50	5.25		40.00	11.25
2.75	5.45			
3.00	5.75			
3.25	6.05			
3.50	6.15			
3.75	6.25			
4.00	6.55			
4.50	6.85			
5.00	6.85			
5.50	7.25	dissolution		
6.00	7.90	starts		
6.50	7.70			
7.00	7.85			

Titration with 5000mg Zn^{++}

Vol.of 0.1NKOH added (in mls)	pH Readings	
0.0	3.55	
0.25	3.55	
0.50	3.65	
1.00	3.75	
2.00	4.35	
3.00	4.95	
3.50	5.35	
4.00	5.65	
4.50	5.95	
5.00	6.20	
5.50	6.50	
6.00	6.75	
7.00	7.45	solution
8.00	7.80	starts
9.00	8.65	
10.00	9.00	
11.00	9.15	
14.00	10.50	
15.00	10.65	
20.00	11.35	

With 5000mg of Cd^{++}

Vol.of 0.1NKOH added (in mls)	pH Readings	
0.0	3.50	
0.50	3.65	
1.00	3.85	
2.00	4.45	
3.00	5.25	
4.00	5.95	
5.00	6.70	solution
6.00	7.85	starts to
7.00	8.45	form
8.00	9.45	
9.00	9.75	
10.00	10.45	
15.00	11.35	

With 5000µg Hg^{++}

Vol.of 0.1NKOH added (in mls)	pH Readings	
0.0	3.35	
0.50	3.35	
1.00	3.45	
2.00	3.85	
3.00	4.45	
4.00	5.15	
5.00	5.65	
6.00	6.15	
7.00	6.85	
8.00	7.05	solution
9.00	7.65	starts
10.00	8.05	
11.00	8.45	
12.00	9.05	
14.00	9.95	
15.00	10.25	
18.00	11.00	
20.00	11.15	

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