Determination of Complexed and Ionic Metal in Aqueous Solution. Determination of Stability Constants at Low Concentrations and Kinetic Studies of Complex Formation Using Accelerated Electrodeposition

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DETERMINATION OF COMPLEXED AND IONIC METAL IN AQUEOUS

SOLUTION.   DETERMINATION OF STABILITY CONSTANTS AT LOW

CONCENTRATIONS AND KINETIC STUDIES OF COMPLEX FORMATION

USING ACCELERATED ELECTRODEPOSITION.

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INTRODUCTION

Metal speciation has become one of the most important areas

of concern for today's analysts. Metal complexes can be more

readily assimilated by living systems than inorganic forms of

the same metals. Conventional atomic absorption spectroscopy

is the most widely used technique for the determination of

trace metals. By using atomic absorption spectroscopy in

conjunction with accelerated electroplating it is possible to

distinguish between ionic metal and organically bound or

complexed metals in solution.

Using the stripping electrode described in the preceeding

article (1), it was discovered that complexed metal was not

removed from water but traveled through the electrode without

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depositing. This observation led to the development of a new
method of analysis of aqueous samples for inorganic and organic
or complexed metal determinations.

The method proposed here involves the passage of the test
solution through the stripping electrode and the analysis of the
test solution before and after passage through the electrode in
order to obtain total metal present in solution and total
complexed metal species in solution. The capabilities of the
accelerated electrode system to distinguish between ionic and
complexed metals can be applied to the determination of stability
constants of metal complexes at very low concentrations to
observe exchange reactions between different metals competing for
the same ligand, to observe the molecular ratio of total concentration
versus concentration of complexed metal and to study the rate of
formation of some complexes such as EDTA chelates.

The increasing importance of complexing agents in chemistry
has created a demand for reliable values of equilibrium constants.
The stability constants of many enzymes involving metal centers
are also of significance. Because of the low concentrations of
these species in biological systems, very sensitive techniques
are needed for their determinations.

The determination of stability constants is no trivial matter.
The mathematical and graphical methods which are often employed
utilize concepts and parameters unfamiliar to analytical chemists
(2). Not only the determination of stability constants is

difficult but also the data obtained depend upon the experimental
conditions (3).

Stability constants are of great importance because they
enable the analyst to determine the concentration of the different
species in solution and may allow the prediction of conditions
required for maximum formation of a given complex. The chemist
and biochemist both are very interested in the concentrations of
species present in solution in order to predict optical and kinetic
properties as well as partition equilibria, biochemical behavior,
and free energy change of a reaction (2,4,5).

The introduction of chelons such as EDTA has virtually
revolutionized the analytical approach to metal ion chelation.
EDTA titrations are currently used for the determination of more
than 50 elements and many books have been published dealing with
EDTA complexes (6,7).

Chelating agents form acid, basic and binuclear complexes in
addition to normal chelates. Ringbom (1) stated that for an
aqueous system where M is the metal ion and L is the ligand, the
following species are possible: ML, MHL, MH_2L, $M(OH)L$, $M(OH)_2L$,
M_2L, M_2HL, M_2H_2L, $M_2(OH)L$, $M_2(OH)_2L$, ML_2, MHL_2, MH_2L_2, $M(OH)L_2$,
$M(OH)_2L_2$. Usually it is not as important to know exactly the
true concentration of every species present in solution as
it is to know the degree of completeness of the main reaction.
Ringbom (8) introduced the term "conditional constant" in order

to stress the fact that this 'constant' is not a constant but depends on experimental conditions.

The thermodynamic stability constant for a normal mononuclear complex is defined as follows:

In the reaction $M^{2+} + Y^{4-} \rightleftharpoons [MY^{2-}]$
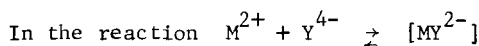
$$K_{MY} = \frac{[MY]}{[M][Y]}$$

The charges are omitted for simplicity. K_{MY} is the stability constant. [MY] is the actual concentration of the complex of interest. [M] and [Y] are the concentrations of the metal and ligand present in solution. No attention is paid to side reactions in this elementary approach.

At different pH different forms of the ligand and of the complex may be present, e.g., H_2MY, MY^{2-}, HMY^-, etc. Literature values do not always take into account that the ligand may react with other species in solution and therefore, is not readily available for complex formation with the species of interest. The protonated complexes have different stability constants and could account for errors in stability constant determinations of the normal complex, i.e., MY^{2-} (9).

Ringbom's "conditional constant" $K'_{M'Y'}$ is defined by the following expression:

$$K'_{M'Y'} = \frac{[MY]}{[M'][Y']}$$

where $[M']$ denotes the concentration of free ion M^{2+} as well as the concentration in solution of the metal that has not reacted with EDTA but that may be involved in side reactions. $[Y']$ denotes the concentration of all forms of EDTA that are not coordinated to the metal of interest.

Schwarzenbach (7) introduced the α coefficients which are measures of the extent of side reactions:

$$\alpha_M = \frac{[M']}{[M]} \, , \qquad \alpha_Y = \frac{[Y']}{[Y]} \, , \qquad \alpha_{MY} = \frac{[(MY)']}{[MY]}$$

α_M gives the ratio of total metal in solution not involved with EDTA to the amount of free ions available for EDTA complex formation. α_Y is the ratio of all forms of EDTA to the actual free Y^{4-} in solution. This expression is extremely dependent on pH:

$$\alpha_Y = \frac{[Y']}{[Y^{4-}]} = \frac{[Y^{4-}] + [HY^{3-}] + [H_2Y^{2-}] + [H_3Y^-] + [H_4Y]}{[Y^{4-}]}$$

$\alpha_{(MY)}'$ denotes the ratio of the sum of $[MY]$ and the concentrations of the acid or basic (1:1) complexes to the $[MY]$ formed. Those terms are pH dependent. Thus, the conditional constant and its relationship to the stability constant are given by the following expression:

$$K'_{M'Y'} = \frac{[MY]}{[M'][Y']} \qquad \text{and} \qquad K_{MY} = K'_{M'Y'} \frac{\alpha_M \alpha_Y}{\alpha_{ML}}$$

$$(1,7)$$

This conditional constant give the relationship between quantities of interest to the analyst such as the concentration of product formed [MY], the total concentration of uncomplexed metal [M'] and the total concentration of uncomplexed reagent [Y']. This conditional constant is the one of importance for analytical and biochemical studies.

Because of protonation and complexing side reactions that interfere with the formation of the complex of interest, the conditional formation constants are usually smaller than the literature values.

Table I shows the effect of pH on α_Y for EDTA (10).

TABLE I

Logarithmic values of $\alpha_{Y(H)}$

pH	EDTA	Used Constants:
0	21.4	Log K_1 10.34
1	17.4	Log K_2 6.24
2	13.7	Log K_3 2.75
3	10.8	Log K_4 2.07
4	8.6	
5	6.6	Where
6	4.8	$K_1 = \dfrac{[H_3Y^-][H^+]}{[H_4Y]}$
7	3.4	
8	2.3	
9	1.4	etc.
10	0.5	
11	0.1	
12	–	

The various competitive equilibria in solution were summarized
by Reilley and others (9) as follows:

$$M \quad + \quad Y \quad \rightarrow \quad MY$$

+	+	+	+		H$^+$
xOH$^-$	yZ	nH$^+$	N	MLY	HMY$^-$
↓	↓	↓	↓	M(OH)Y	
M(OH)$_x$	MZy	H$_n$Y	NY		
(Hydrolysis effect)	(Complex effect)	(pH effect)	(competing metals in solution effect)		

(with L, OH$^-$ branches from MY)
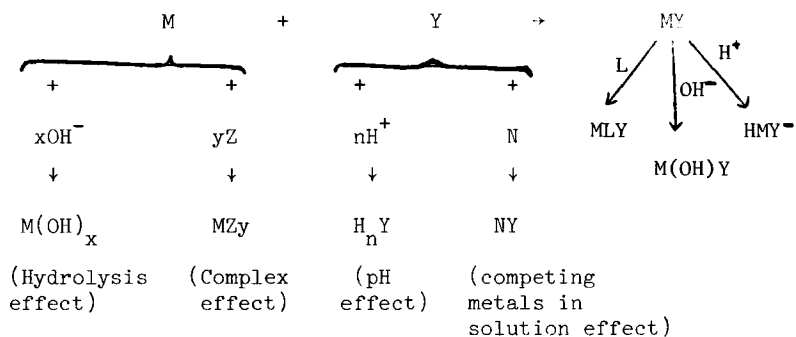
It can be deduced that for complete conversion of the
conditional constant to the stability constant assessment of all
side reactions is needed, as well as a constant ionic medium. It
is not always possible to produce a solution where all of the
metal ions are in the aquo ion form and all of the EDTA is as Y^{4-},
therefore, the values of some conditional constants never approach
the value of the stability constants even after all obvious
corrections have been applied.

Beck (5) and Rossotti et al. (4) have stated that the
reliability of a stability constant depends on the adequacy of
the experimental method, the exactness of the experimental work,
the consideration of all relevant equilibria, the calculation
method and the reliability of the auxillary data used.

The experimental methods for the determination of stability
constants usually involve the measurement of a solution property

that changes due to complex formation. Most of the constants determined in recent decades were determined by means of pH measurements and pM measurements (1). The latter measurements are usually restricted to limited concentration ranges and within a certain pH range. A comprehensive list of methods that have been used for the determination of stability constants was compiled by Beck (5). None of these methods have been used for the determination of stability constants at concentrations lower than 10^{-5} $\underline{M}$.

The method proposed here introduces the use of atomic absorption spectroscopy for the determination of conditional stability constants of metal complexes. The superior sensitivity of AA methods allows the determination of stability constants of complexes at physiological levels.

Many enzymes have metal centers and are essentially metal complexes. These biologically important reactions usually take place at very low concentrations and information regarding the rate of formation of these complexes is not available.

Exchange reactions are also of extreme importance since many toxic effects of metals are thought to be due to the replacement of essential metals on enzymes by the toxic species.

The method described is employed in the determination of conditional stability constants of some EDTA complexes at different concentrations, in the study of the rate of formation of the Pb-EDTA complex at different concentrations, and in the study of the exchange of Cd for Fe for the Cd-EDTA complex.

EXPERIMENTAL

A. Equipment: The equipment used in this work is the same as that previously described (1).

B. Chemicals:

1000 ppm stock solution of Cd (as $CdCl_2$)

1000 ppm stock solution of Cd (as $CdSO_4$)

1000 ppm stock solution of Pb (as $Pb(NO_3)_2$)

1000 ppm stock solution of Zn (as $ZnSO_4$)

$8.90 \times 10^{-3} \underline{M}$ Na_2 EDTA solution (equimolar with 1000 ppm Cd)

$4.83 \times 10^{-3} \underline{M}$ Na_2 EDTA solution (equimolar with 1000 ppm Pb)

$1.53 \times 10^{-2} \underline{M}$ Na_2 EDTA solution (equimolar with 1000 ppm Zn)

$8.90 \times 10^{-4} \underline{M}$ Fe solution (as $FeSO_4$) (equimolar to 100 ppm Cd solution)

Distilled deionized water; Bromocresol green solution (0.004%) pH range 4.0 to 5.4

HNO_3; H_3PO_4; KOH; pH_4 buffer; pH_{10} buffer

C. Experimental Procedures:

1. Determination of Conditional Stability Constants of Cd and Zn EDTA Complexes at Different Concentrations: Cd-EDTA complex was studied at two concentration levels. A solution containing $4.448 \times 10^{-5} \underline{M}$ Cd (5 ppm) and $4.448 \times 10^{-5} \underline{M}$ EDTA was prepared and run through the stripping electrode system at a voltage of -0.8v. The total Cd concentration was determined by AA at 3261 $\overset{o}{A}$. The solution as it emerged from the electrode was also analyzed to determine the total complexed Cd. The electrode

effluent was collected using an Eppendorf pippette from the drop
formed at the bottom of the electrode before the drop fell into
the collecting resevoir. This procedure avoided contamination
problems from the container. Each solution was analyzed at least
five times and as many as twenty times for statistical purposes.

The Cd-EDTA complex was also studied at the 15 ppb level
using the 2288 Å line. The solutions were prepared by mixing
$1.334 \times 10^{-7} \underline{M}$ Cd with an equimolar EDTA solution.

The pH of these solutions was difficult to measure due to
the low ionic strength of these unbuffered solutions. A combina-
tion of colorimetry and potentiometry was used in order to determine
the pH of these solutions.

A series of distilled deionized water samples were prepared
with the pH adjusted between 3.0 to 6.0 with dilute KOH and H_3PO_4
using the pH meter. To these solutions, bromocresol green indicator
solution was added. These solutions were then placed in test tubes
with screw tops. The pH of the test solution was measured by
adding bromocresol green indicator and comparing the color to the
color of the solutions of known pH. This is only an approximate
method but was probably more accurate than using a pH meter alone
which was not reliable when used with very dilute solutions.

The solutions at the $10^{-7} \underline{M}$ concentration were heated at about
92°C to complete the reaction.

Zn-EDTA complex was studied by preparing a $1.53 \times 10^{-3} \underline{M}$ Zn
solution (100 ppm) with an equimolar concentration of EDTA. The

zinc was determined by atomic absorption using the weak resonance line at 3076 Å.

All solutions were allowed to sit for at least 1 hour prior to analysis.

2. Rate of Formation of Pb-EDTA Complex with Respect to Time for Different Concentrations and with Respect to Different Mole Ratios: A series of solutions of Pb with EDTA at different mole ratios were prepared and ran through the electrode system at -0.8v. The mixtures were analyzed half an hour and one day, respectively, after the solutions were prepared. The Pb concentration was about 0.2 ppm.

In order to investigate the effect of concentration on the speed of reaction, two solutions were analyzed (both equimolar in Pb and EDTA) one containing 0.5 ppm Pb and the other 0.25 ppm Pb. The solutions were analyzed until complete complex formation was evident.

3. Study of an Exchange Reaction of Fe^{3+} with the Cd:EDTA Complex: To a two day old solution containing $1.334 \times 10^{-7} \underline{M}$ Cd and $1.334 \times 10^{-7} \underline{M}$ EDTA, an equimolar amount of Fe^{3+} was added. The amount of complexed Cd was monitored in order to study the rate of replacement of complexed Cd by Fe.

RESULTS AND DISCUSSION

A. Determination of Conditional Stability Constants of Cd and Zn-EDTA Complexes at Different Concentrations: The Cd-EDTA complex was studied at the ppm level and at the ppb level using two

resonance absorption lines for Cd at 3261 Å and 2288 Å
respectively.

The solution containing 5 ppm Cd ($4.45 \times 10^{-5}\underline{M}$ Cd) and an
equimolar amount of EDTA was prepared and the rate of formation
of the complex was followed by analyzing the solution by AA
before and after passing through the electrode system. Figure 1
shows the results obtained. After one hour only about 42% of
the Cd was complexed and the solution was at pH 3.3. Five hours
later, about 74% of the Cd was complexed and the pH had dropped
to 3.1. After 24 hours, the percent Cd complexed was about 75% and
the pH was still about 3.1. At a 5 ppm Cd concentration, and pH
3.1 and taking only pH effects into account, theoretically 84.5%
Cd should be complexed in order to obtain log K=16.5, the
reported literature value for the normal Cd-EDTA complex (7).
It was suspected that at this concentration level, the rate of
complex formation may be slow and heating the solution should
speed up the reaction.

As shown in Figure 1, after the solution was heated at about
92°C for 17 hours in an oven, about 83% of the Cd was found to
have complexed with EDTA giving a log K=16.1 when pH correction
was taken into account (log α_Y = 5.8).

Using AA, Cd can be determined at the ppb level. When
solutions of Cd and EDTA were prepared at the 15 ppb level ($1.334 \times 10^{-7}\underline{M}$), the pH was difficult to measure but was estimated to
be between 4.6 and 4.7. At pH 4.6, for 15 ppb Cd and log K 16.5
(assuming no side reactions other than those due to pH effects)
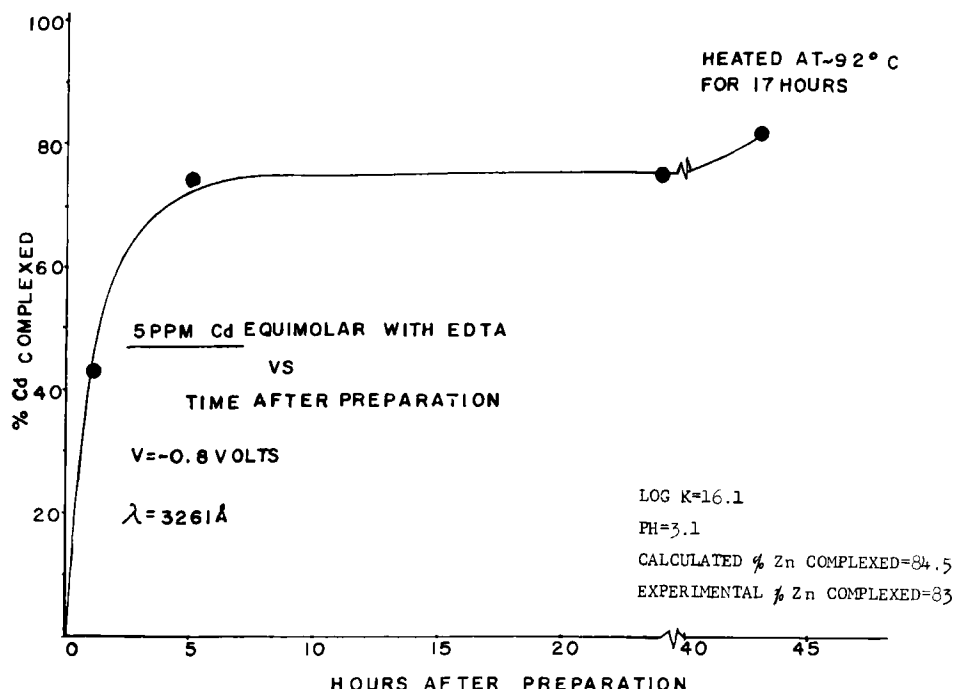
FIGURE 1:   DETERMINATION OF THE CONDITIONAL STABILITY CONSTANT AND RATE OF FORMATION
            OF Cd-EDTA COMPLEX AT THE PPM LEVEL.

82% of the Cd should be complexed. However, everytime that a

solution in the range 5 to 15 ppb were prepared with equimolar

quantities of Cd and EDTA, the complexation was always found to

be only 35 to 45% complete.   Figure 2 shows a typical analysis of these

solutions using the stripping electrode - AA method described here.

The complex formation at these levels seems to be kinetically

inhibited.   There may also be other ions present in solution

competing with Cd for the available EDTA or that at the pH of the

solutions, some of the protonated Cd:EDTA complexes were present.

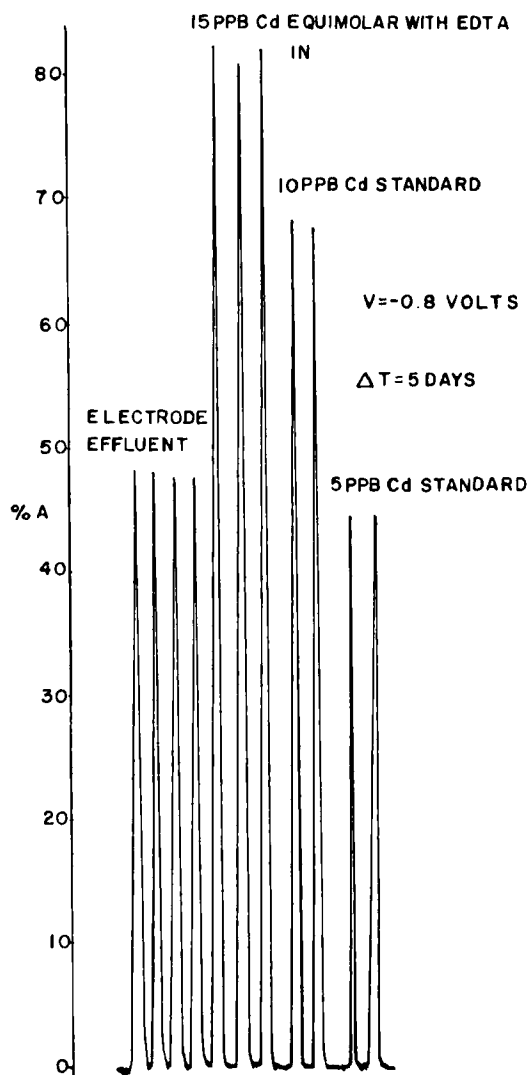The reasons for the low complexation obtained could be one or

FIGURE 2: ANALYSIS OF A SOLUTION CONTAINING 1.33×10^{-7}
$\underline{M}$ Cd and 1.33×10^{-7} EDTA.

more of the above mentioned factors on a combination of some or
all of them.

Since it was necessary to heat solutions containing 5 ppm
to complete complexation, the more dilute solution of 15 ppb would
probably need prolonged heating to complete equilibrium.

Heating the solutions favors the entropy term of the
expression relating log K with ΔG. With heating, the collision
rate among species in solution increases and so does the
probability for the reaction to take place. Figure 3 shows the
results obtained when solutions containing equimolar mixtures
of Cd and EDTA were heated at 92°C for several hours in a
polyethylene container. As heating time was increased, the pH
decreased indicating increasing complexation. This was
expected since the solutions were not buffered. As pH decreased,
the amount of complex that could be theoretically formed also
decreased because of fewer available Y^{4-} ions. This is indicated
by the asterics in Figure 3 which represent the calculated
theoretical % Cd that should be complexed at the particular pH
for a 15 ppb total Cd concentration if only hydrogen effects were
considered.

Because heating increased the amount of complex formed, it
can be stated that at the ppb level the Cd-EDTA complex formation
was kinetically inhibited. Further studies with solutions by
these concentrations for periods of up to 3 months indicated no
change in a complexation of about 35 to 45% Cd indicating an
equilibrium. When these solutions were heated, the percent Cd
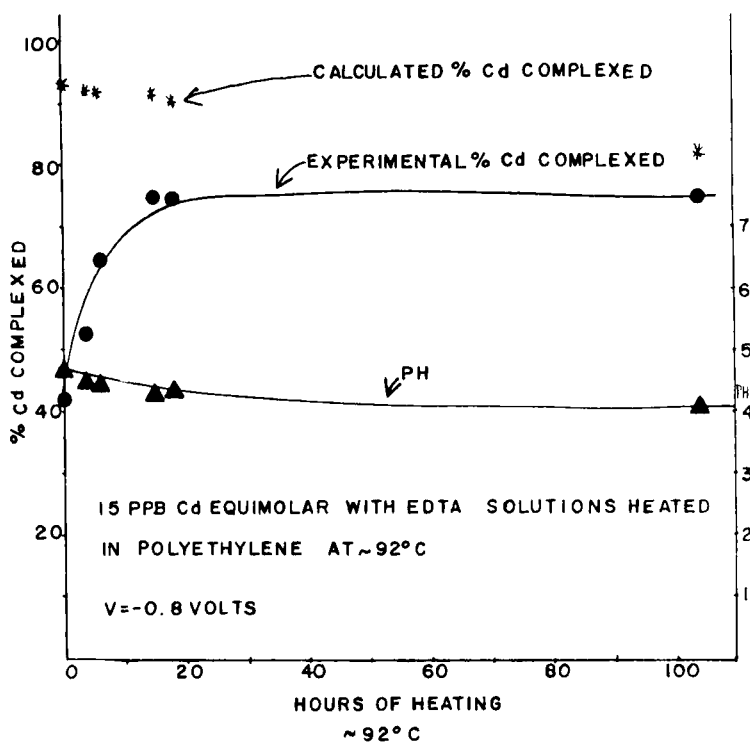
FIGURE 3:   EFFECT OF HEATING ON THE FORMATION OF THE Cd-EDTA COMPLEX
            AT PPB LEVEL.   THE CONDITIONAL STABILITY CONSTANT
            (PH CORRECTED ONLY) WAS FOUND TO BE 16.3.

complexed increased up to a maximum of 75% at a pH of 4.1 giving

log K 16.3 when pH corrected.

The discrepancy between the experimentally obtained values

and the literature value of 16.5 (8) for the Cd:EDTA complex could

be due to several factors: The ionic strength of the solutions

was far from 0.1 which is the ionic strength most often used to

report stability constant values.   Errors in pH measurements of

these very dilute solutions could account for the lower values

obtained. There could be other cations present in solution that
could compete with Cd for the available EDTA. These cations could
be present in distilled deionized water, in the container walls
or as impurities in the reagents used. There could also be
different forms of the metal-EDTA complex such as MHY^- and MH_2Y
(2,5,8) which have different stability constants.

Studies of the Zn-EDTA Complex

The Zn:EDTA complex was studied at 100 ppm level (1.53 x
$10^{-3}\underline{M}$) and it was found to form readily at this concentration.
The solution was passed through the electrode system at a voltage
of -1.6 volts (slightly above twice the E° for Zn^{2+}) and analyzed
before and after by AA using the 3076 Å absorption line which
allowed determination of Zn at this high concentration level.
Figure 4 shows the results obtained. It was found that about 92%
of the Zn was complexed under the experimental conditions. The
log K was found to be 16.3 after correcting for EDTA dissociation
at pH 2.7. The value was fairly close to the literature value of
16.5 (7). A theoretical percent of 93 was predicted by the
literature value of log K. This was well within the experimental
errors of the method.

These studies indicate that as the concentration of the
species to be complexed decreases, so does the reaction probability.
Stability constants do not predict kinetic behavior. This is well
documented. For example, Cu is 20,000 times more effective than
Ni in replacing each other in EDTA complexes even though their
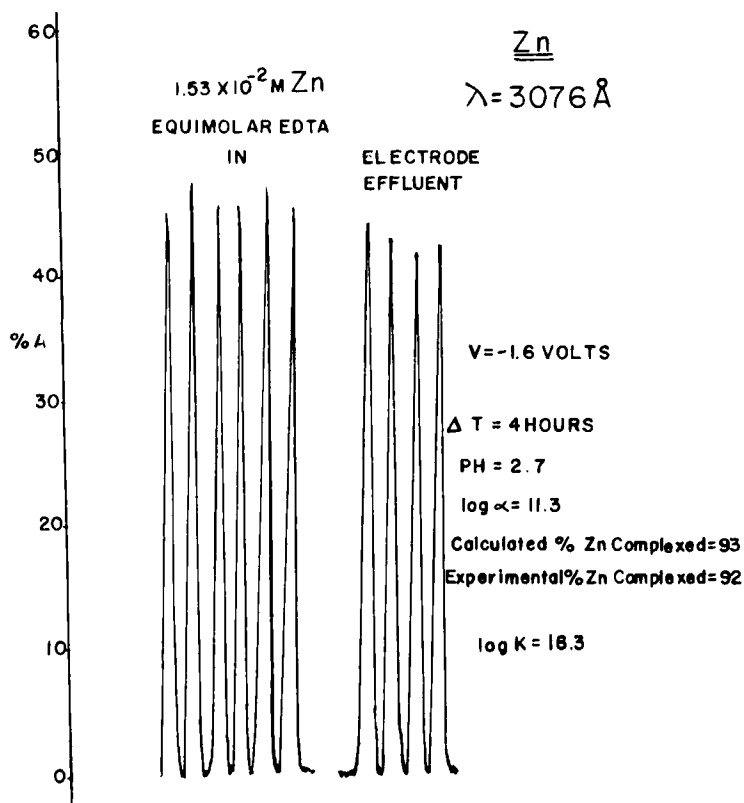
FIGURE 4:   DETERMINATION OF ZINC CONCENTRATION AND CALCULATION OF
            THE CONDITIONAL STABILITY CONSTANT OF THE Zn-EDTA
            COMPLEX AT THE PPM LEVEL.

stability constants are nearly identical, i.e. 18.8 and 18.6

respectively (11).

     Other factors that may account for the low complex formation

observed at low concentrations may be that some complexes

dissociate upon dilution (12) and to crystal field theory

considerations (12).

B.   Rate of Formation of Pb-EDTA Complex with Respect to Time for

Different Concentrations and with Respect to Different Mole Ratios:

To illustrate the capabilities of the electrode system in the

study of the rate of formation of metal complexes the Pb:EDTA

system was studied.   Figure 5 shows the results obtained after

half an hour for solutions of Pb and EDTA of different mole

ratios of EDTA at the 0.2 ppm Pb level.   The solutions were
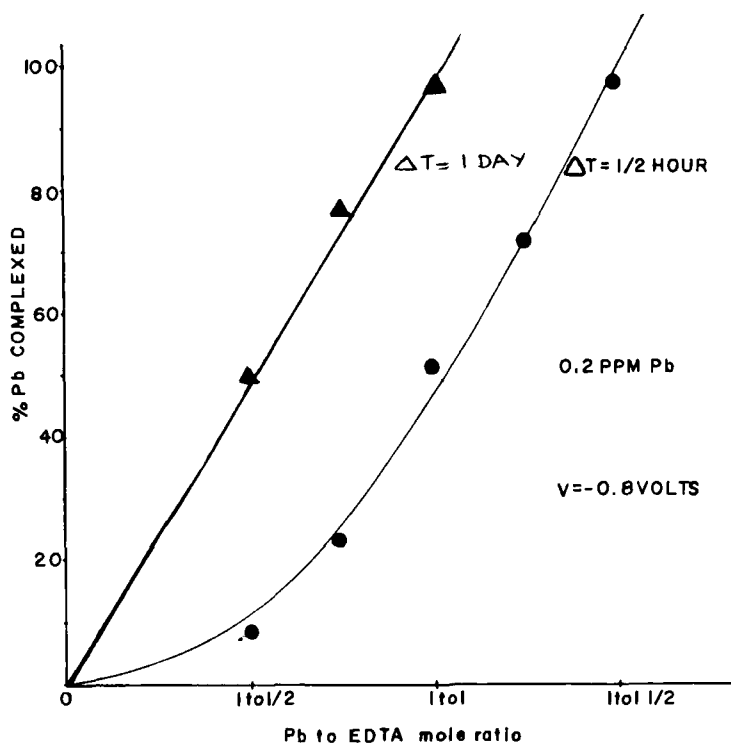
FIGURE 5:   FORMATION OF Pb-EDTA (IN SOLUTIONS OF DIFFERENT MOLE
            RATIOS) AFTER 30 MINUTES AND AFTER 1 DAY FROM THE
            TIME OF PREPARATION.

tested again later and were found to have gone to completion. The theoretical stability constant for the Pb:EDTA complex is 18.0 (8). This would give a near 100% completion for this reaction at pH 4.5.

Figure 6 shows a plot of the percent Pb complexed with respect to time for two equimolar Pb:EDTA solutions. One of the solutions was twice as concentrated as the other. The more concentrated solutions proceeded faster toward completion.
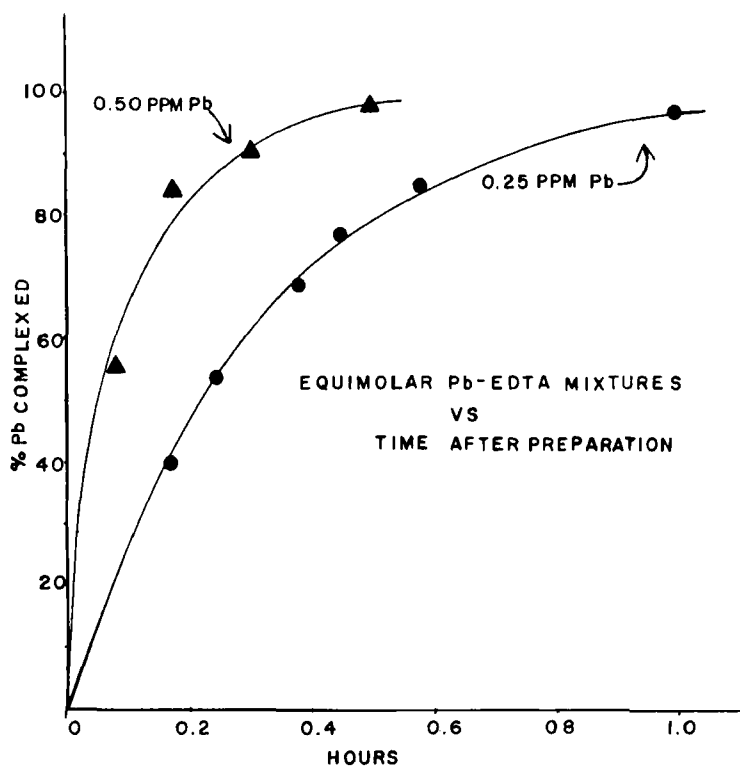

FIGURE 6:   RATE OF FORMATION OF THE Pb-EDTA COMPLEX WITH RESPECT
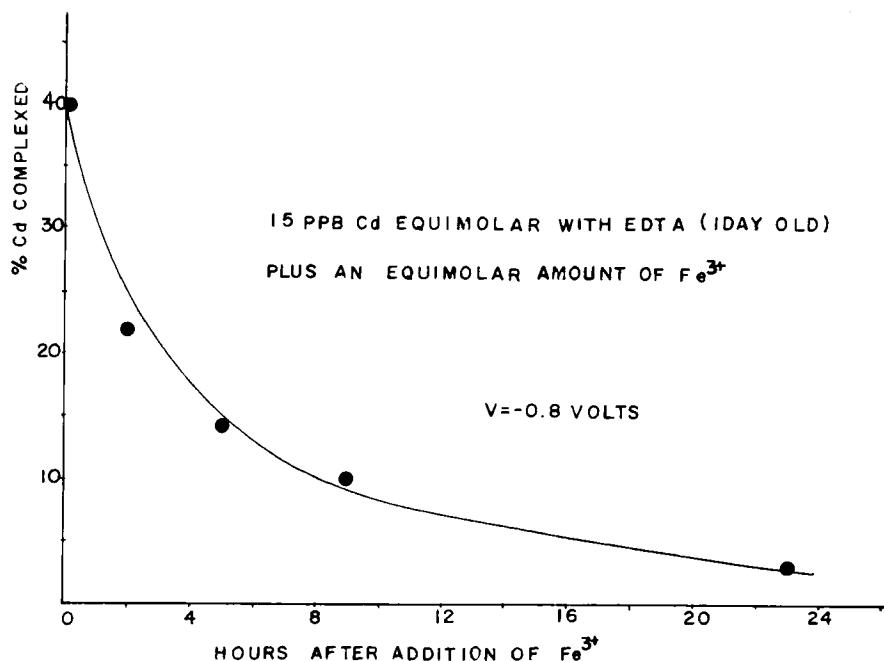   TO TIME IN SOLUTIONS OF DIFFERENT CONCENTRATIONS.

FIGURE 7: REPLACEMENT OF Cd^{2+} BY Fe^{3+} IN THE Cd-EDTA COMPLEX BY EQUIMOLAR CONCENTRATION OF Fe AT THE PPB LEVEL.

This study again shows that as the concentration is increased, the reaction rate also increases. The electrode system can best be used to follow slow reaction rates.

C. <u>Study of an Exchange Reaction of Fe^{3+} with the Cd:EDTA Complex</u>: Exchange studies are of extreme importance for the prediction of the toxic effects of many metals. It has been suspected that the principal toxic effect of Cd in humans is due to the replacement of Zn by Cd in the many enzymes that contain Zn in the body.

The method described here can also be used for the study of exchange reactions as illustrated in Figure 7. A solution containing

15 ppb Cd $(1.33 \times 10^{-7}\underline{M})$ and an equimolar amount of EDTA is only about 40% complexed after 2 days. At this point Fe^{3+} $(1.33 \times 10^{-7}\underline{M})$ was added and the amount of complexed Cd was monitored with respect to time by analyzing total Cd and then complexed Cd by means of passing the solution through the stripping electrode system. Even though 60% of the EDTA was not complexed with Cd, Fe^{3+} is able to take that and also to displace Cd from its EDTA complex. After 23 hours only about 3% of the Cd remained complexed. A nearly complete replacement of Cd by Fe had taken place.

CONCLUSIONS

The accelerated "stripping" electrode system in conjunction with atomic absorption spectroscopy has been demonstrated to be successful in the determination of complexed and inorganic heavy metal concentrations in liquid samples at very low concentrations. These complexation reactions seem to be somewhat inhibited at low concentrations which raise the question of how accurate it is to determine these constants at higher concentrations and then to extrapolate to low concentrations as it is the case for most bio-logical experimental determinations of enzyme formation. It is also of great importance to know how much of a particular complex is present in a given system to assess accurately toxic effects.

This method can be used as an efficient method to distinguish between ionic and complexed metals, to determine conditional stability constants of many heavy metals complexes, to perform kinetic studies involving reaction rate determinations of complex

or organometallic reactions that take longer than about 10 minutes and to study exchange reactions.

A practical advantage is the fact that an electrode lasts a long time. All of these studies were done with only three electrodes and all of them are still usable. If contamination occurs, reversing the voltage while running water overnight through the electrodes usually achieves cleaning of the system.

Some of the disadvantages of the method include the fact that only heavy metals can be analyzed this way, only liquid samples can be be studied and there could be interference due to anions that may solubilize the plated metals.

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