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DETECTION OF DECONTAMINATION SOLUTION CHELATING AGENTS USING ION SELECTIVE COATED-WIRE ELECTRODES

by

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APPROVAL BY THESIS DIRECTOR

This thesis has been approved on the date shown below:

4/30/92

Dr. Morton E. Wacks
Professor of Nuclear Engineering

Date

To my parents with love and deep gratitude

To CaraLyn and Jarod for the light you brought into my life

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I would like to give recognition to some of the many people who have helped me reach this point.

I would like to give a heartfelt thanks to my Dad and Mom for their lifelong support of my desires and goals.

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ABSTRACT

It is the purpose of this thesis to explore the feasibility of using coated-wire electrodes to measure chelating agent concentration. Chelating agents are often found in radioactive decontamination solutions because they aid in the removal of radionuclides from contaminated surfaces by increasing their solubility. However, this characteristic will also enhance the mobility of the radionuclide and thus its transport out of a waste disposal site.

Coated-wire ion selective electrodes, based on a polyvinylchloride membrane using dioctylphthalate as a plasticizer and dinonylnaphthalene-sulfonic acid as a counterion, were constructed for five commonly utilized chelating agents (ethylenediaminetetracetic acid (EDTA), nitrilotriacetic acid (NTA), citric acid, oxalic acid and tartaric acid).

The EDTA and NTA electrodes' calibration characteristics exhibited acceptable behavior in pure standard solutions. From data obtained while using the EDTA and NTA electrodes in a cement environment, further research needs to be done in the area of ion interference.

CHAPTER 1
INTRODUCTION

It is the purpose of this thesis to explore the use of coated-wire electrodes as a simple method of measuring chelating agent concentration. Coated-wire electrodes have not been tested with the chelating agents used in this feasibility study. The coated-wire electrode works using the same principle as a pH electrode. The concentration of chelating agent ions can be associated with a voltage developed in the electrode circuit. If this relationship is linear in nature, then the concentration of an unknown sample can be determined quickly. The reason for investigating the feasibility of the chelating agent/electrode combination is to find a nondestructive method of determining chelating agent concentration in various environments typical of that found in ground water infiltration of waste repositories. The chelating agents studied were the following: ethylenediaminetetracetic acid (EDTA); nitrilotriacetic acid (NTA); citric acid (CA); oxalic acid (OA); and tartaric acid (TA).

1.1 Background

The technology used in the decontamination of surfaces contaminated with radionuclides has become increasingly important in the nuclear power industry, as well as medicine and other industries utilizing radioactive materials. This trend will continue as worker and public safety regulations tighten, and as the older nuclear power plants are shutdown and decommissioned. The reuse of contaminated materials also provides a large source of this contaminated waste material. Radioactive decontamination is defined as the removal of unwanted radionuclides from surfaces.[1] The need for decontamination can result from an accidental spill or the normal operating activities at a nuclear facility. Many radioactive contaminants are not readily removed with mere soap and water; therefore, specialized methods and agents have been developed. While many "off-the-shelf" cleaning methods commonly used in other industries may remove 99% of the contaminants, it is necessary to increase the efficiency of removal by a factor of 10, 100 or even more to reduce the residual radioactive levels to those specified as acceptable in the regulations. In addition to this concern, the methods and agents used in the decontamination process must not create other problems such as corrosion induced by chemical reaction with the material being decontaminated.[14]

Many methods and cleaning agents have been developed by the nuclear industry since its inception. Primarily, the decontaminates used have been solutions of acids and bases. More recently, chelating agents, a special kind of metal complexants, have been used in tandem with these methods to increase the efficiency of radionuclide removal The chelating agents are added to the cleaning solution because of their chemical ability to increase the solubility of normally insoluble metal ions such as cobalt. This then increases the ions removal rate from the contaminated surface. However, this very desirable decontamination characteristic is also very undesirable from the standpoint of disposing of the now radionuclide contaminated cleaning solution. Because water is the primary method of radionuclide transport out of a radioactive disposal site, any agent in the waste form that increases the ability of the water to transport the radionuclide is very undesirable (see Fig. 1). Thus it is important to know the concentration of any chelating agents in the waste prior to final disposal. This information, along with chelating agent solubility products and equilibrium constants, can be used to help determine the probability of the radionuclides migrating beyond the boundaries of the disposal site.

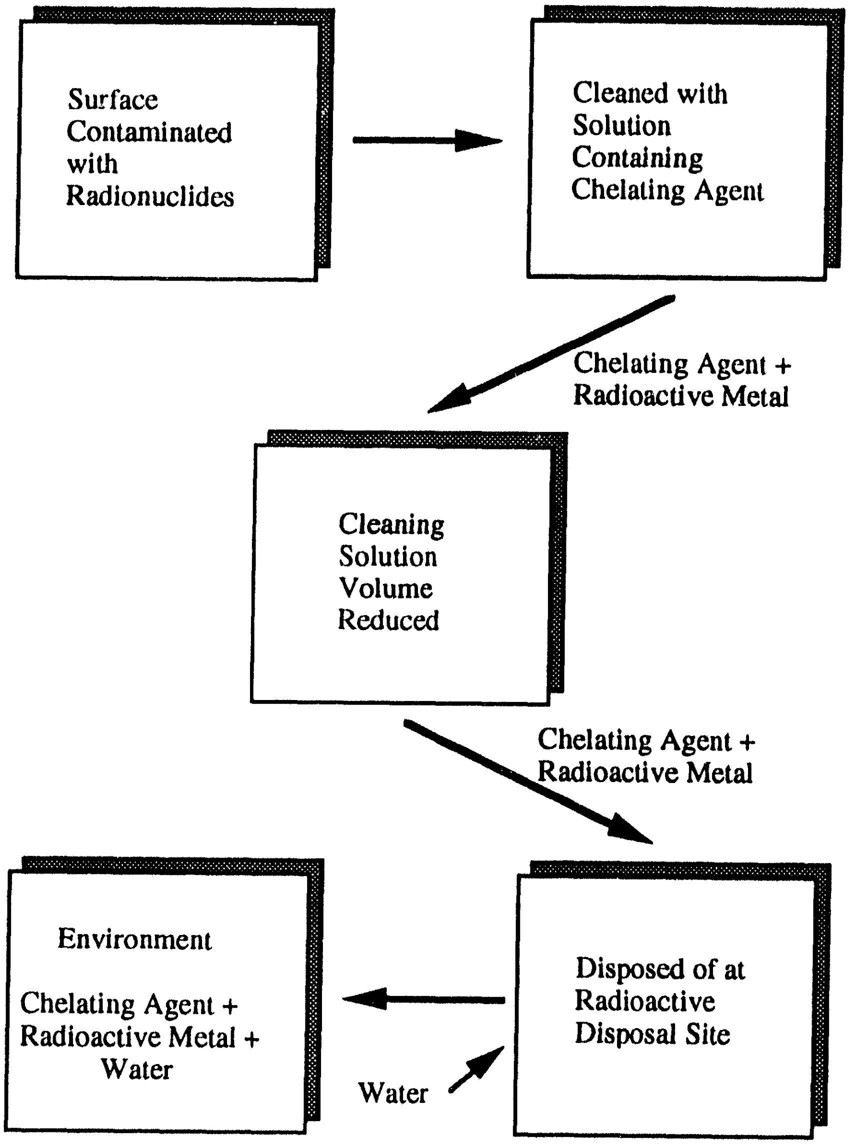


Figure 1. Pathway of Chelating Agent/Radionuclide.

1.2 Coated-Wire Electrodes

Conventional electrodes are relatively simple, but they are too expensive to be practically used as disposable devices and are not very adaptable to miniaturization. A type of ion-selective electrodes called coated-wire electrodes offers both of these desirable qualities. Coated-wire electrodes are simply copper wires with a selective membrane applied directly to the outer wire surface (see Fig. 2). At the membrane interface, an electrical potential is established due to the solubility difference between the ion in the aqueous phase and the same ion bound in the membrane. A rapid ion-exchange process takes place between the free ions of interest in the aqueous phase and the ions bound to organic site groups in the membrane.[11]

The selectivity of the electrode depends primarily on the selectivity of this ion-exchange process. That is, the bound ions should form a more stable complex with the same ion in the aqueous phase than with any other.[5] No ion-selective electrode responds exclusively to the ion which it is designed to measure, although it is often more responsive to this primary ion than to others. If an interfering ion is present at a concentration which is large with respect to the primary ion, the electrode response will have contributions from both the primary and interfering ions. It has been shown that electrodes for species which are more soluble in the membrane (more lipophilic) show greater selectivity.[11] In order to

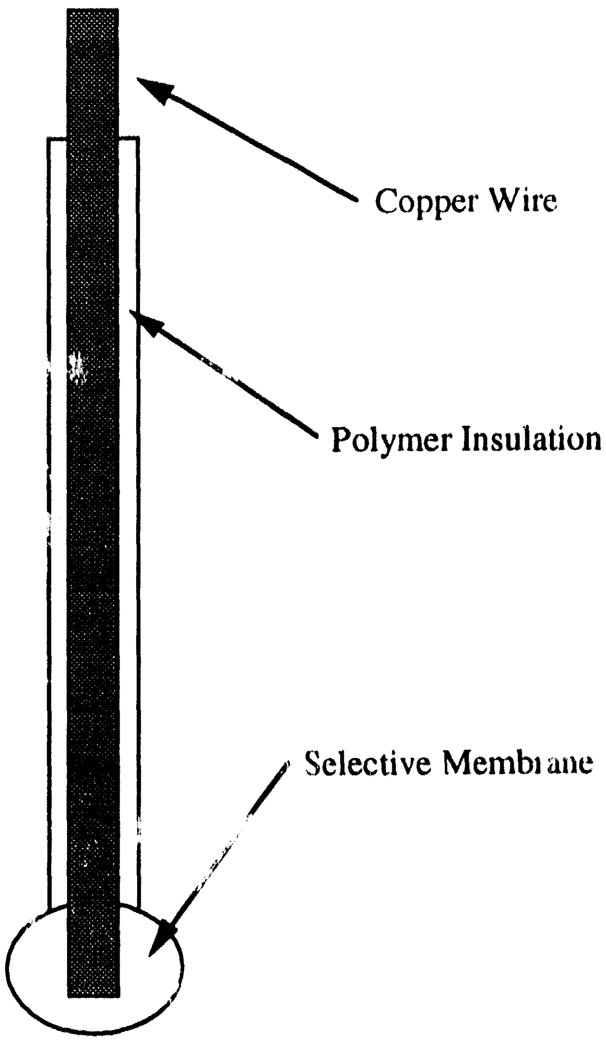


Figure 2. Basic Design of Coated-wire Electrode.

increase the solubility of the ion of interest in the membrane, a carrier or counterion is normally incorporated in the polymer. In such systems, ions which form lipophilic pairs can be detected. A plasticizer is also generally incorporated in the polymer to increase the ion pair mobility.[11]

The plasticizer also tends to reduce the diffusion potential across the membrane. This extends the life of the electrode by reducing the rate that the ion of interest and carrier ion diffuse into solution. While they are both hydrophobic, they do show a finite solubility in water, and the leaching of these species from the membrane will limit the lifetime of the electrode. Therefore, the electrodes with the more lipophilic ions and carriers should be operative longer.

When the membrane is made, the ion of interest and the carrier or counterion are usually added to the selective membrane in stoichiometric quantities. A charge separation is established as the ion of interest, being less lipophilic that the other species of the pair, partitions into the aqueous phase resulting in a charge separation. The detection limits of these electrodes are limited by the solubility of the ions in the aqueous phase, so electrodes constructed for a more lipophilic species should have a lower detection limit.[7]

Much research has been done to increase coated-wire electrode detection limits and extend their lifetimes. To this end, several carrier or counterions have been employed with various success. One of these counterions, dinonylnaphthalenesulfonic acid (DNNS) has been found to be very selective toward lipophilic organic ions.[11]

When a coated-wire electrode, together with an appropriate reference electrode, is placed in a solution containing the ion of interest, a potential is established. In order to obtain a meaningful analytical result, this potential must be converted into a concentration or activity value. Ion-selective electrodes sense the

activities of ions in solutions; if the environments of the ions is known and well defined, the activities may be related to the concentrations of the ions. The activity *[a]* of volatile constituents in a liquid mixture is defined as the partial pressure of the solute divided by the vapor pressure of the pure solvent or

$$a = \frac{p}{p^{o}} \qquad [2\text{-}1]$$

In dilute solutions, the vapor pressure of a solvent can be approximated by Raoult's Law,

$$p_1 = x_1 p_1^{o} \qquad [2\text{-}2]$$

and the vapor pressure of the solute by Henry's Law,

$$p_2 = k_m m \qquad [2\text{-}3]$$

The activity, a_x, of an ion X in solution is related to its concentration, m_x, expressed as a molality (moles of X per kilogram of solvent), by the equation

$$a_x = \gamma_x m_x \qquad [2\text{-}4]$$

where γ_x is the activity coefficient, a measure of the extent of the deviation from ideality.[4] For pure solutions of X of low concentration, the activity coefficient is close to unity and differences between activity and concentration can be ignored.[11]

The simplest calibration method is to generate a curve by measuring the potential resulting from a series of standard solutions of known concentrations of the chelating agent of interest. In this, as in all calibration methods, it is important to allow adequate time for the electrical potential to become stable in standard or sample solutions. All electrode determinations are concerned with electromotive force differences and concentration differences and can therefore be described ideally using the Nernst equation

$$E = E^{o} + \frac{RT\ (ln\ 10)}{z\ F}\ log\ a_x \qquad [2\text{-}5]$$

where E is the measured potential in mV, E^{o} is the measured potential in mV under standard conditions, R is the gas constant (8.3143 J mol^{-1} K^{-1}), T is the temperature in degrees Kelvin, z is the charge on the primary ion, F is the

Faraday constant (96,487 C mol^{-1}), a_x is the activity of the primary ion.[2] The slope of the potential versus concentration or activity is then

$$Slope = \frac{R\,T\ (ln\ 10)}{z\,F} \qquad [2\text{-}6]$$

Once the slope of the curve (assuming a linear relationship) and the intercept are determined during the calibration process, the concentration of an unknown sample may be determined simply by measuring its potential difference and finding the corresponding concentration on the curve.

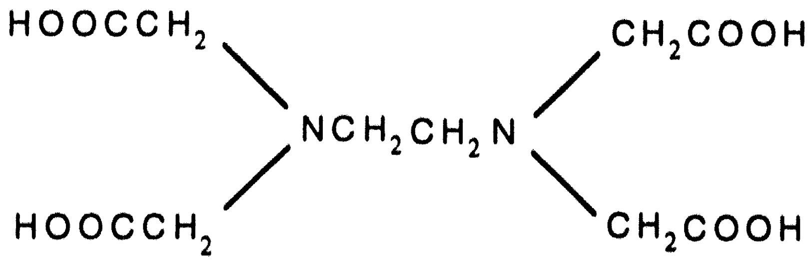
Interfering ions may be a source of nonlinearity in cases where the concentration of the interfering ion is low and the selectivity of the electrode against that interference is good. The only effect may be a slight departure from linearity at low solute concentration. If, however, the electrode is sensitive to the interfering ion or its concentration is high, the result may be a potential which does not vary with solute concentration, but is controlled by the interfering ion.[5]

At low concentrations, the relationship between potential and log[activity] ceases to be linear; the slope diminishes as the concentration falls further. This reduction of slope has the effect of increasing the error in the measured concentration caused by a given error in potential measurement. Slow response and reduced stability of the electrode system may become increasingly apparent at low levels, further reducing the overall precision of measurement.[7]

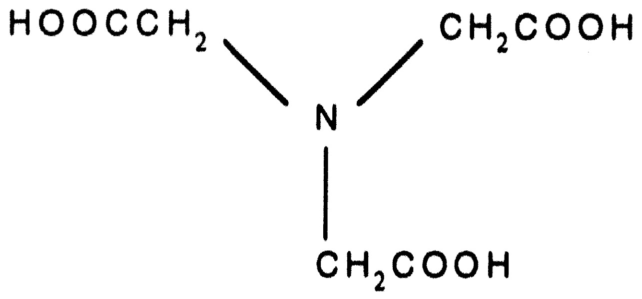
1.3 Chelating Agent Chemistry

The five chemical compounds which were studied as to their compatibility with coated-wire electrodes are the following: EDTA, NTA, citric acid, oxalic acid and tartaric acid (see Fig. 3 & 4). They all have the ability to form metal chelates. Metal chelates are defined as a special kind of metal complex. Most metal chelates consist of rather complex organic anions with two or more functional groups that are capable of sharing pairs of electrons with a centrally located metal ion. These pairs of electrons enter the vacant electron shells of the enclosed metal ion. In this way a chelate contains one or more ring structures that include the metal ion and the arms of the chelating ligand, which is either an anion or a polar molecule.[12] This process of ring formation is known as chelation. (see Fig. 5) The word chelate, which describes the ring formation, is derived from the Greek *chele*, meaning lobster claw.[8] In this respect chelates differ from complexes that have only a single bond between the metal ion and the electron donor.

A simple description of the nature of the bond between a ligand and a metal treats the ligand as an electron-pair donor and the metal as an electron pair acceptor. In other words, the metal behaves as a Lewis acid and the ligand as a Lewis base.[3] All metals form complexes, although the extent of formation and nature of these depend very largely on the electronic structure of the metal.[14]

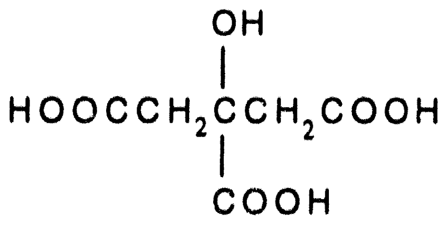


Ethylenediaminetetracetic acid (EDTA)



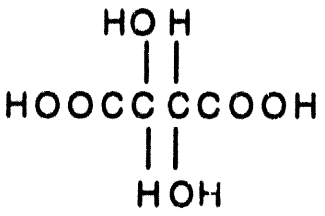
Nitrilotriacetic acid (NTA)

Figure 3. Chemical Structure of EDTA and NTA.



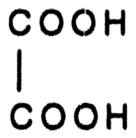
$$\mathrm{HOOCCH_2\overset{OH}{\underset{COOH}{C}}CH_2COOH}$$

Citric acid



$$\mathrm{HOOC\overset{HO}{\underset{H}{C}}\overset{H}{\underset{OH}{C}}COOH}$$

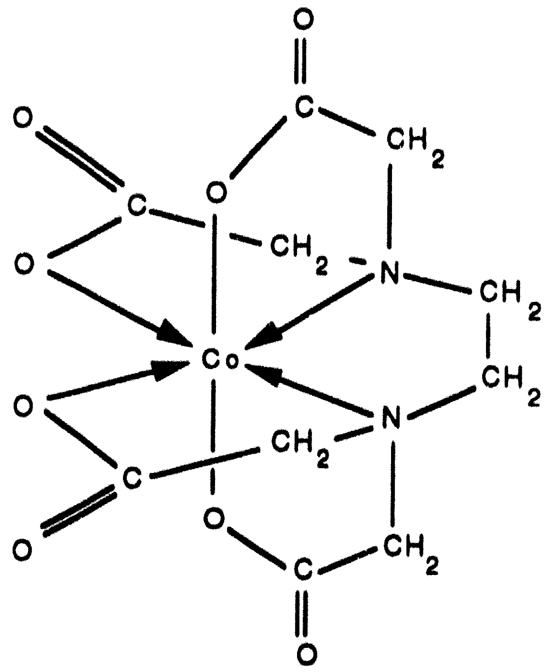
L - Tartaric acid (+)



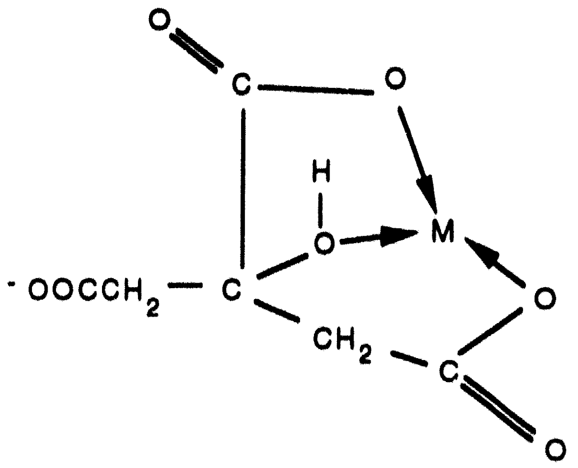
$$\begin{array}{l}\mathrm{COOH}\\ |\\ \mathrm{COOH}\end{array}$$

Oxalic acid

Figure 4. Chemical Structure of Citric Acid, Oxalic Acid and Tartaric Acid.



EDTA Chelated to Cobalt (III)



Citrate chelated to a Metal Ion

Figure 5. Examples of Metal Chelate Ring Structure.

For chelation to occur, the ligand must contain at least two donor atoms capable of bonding to the same metal atom. Elements that act as donors are the more electronegative ones on the right-hand side of the periodic table (Group V and Group VI). Another condition for chelation is that the functional groups should be so located in the ligand that the formation of a ring including the metal atom is sterically possible.[3] In this way, chelation imposes relatively little strain on the ligand molecule.

As an example of chelation, consider the chelating agent ethylenediaminetetracetic acid (EDTA), as pH increases, one or more H^+ ions dissociates from the four carboxyl groups giving a series of protonated EDTA species in solution. The higher the pH, the greater is the concentration and charge of the dissociated species. When all four H^+ ion have been removed, the free ligand, L^{4-} remains. This ligand has six pairs of electrons that can be shared with a metal ion to form a metal chelate. The EDTA ligand combines with Fe^{3+} to give $FeEDTA^-$. The centrally located Fe^{3+} is surrounded by the four carboxyls and two nitrogen donor groups.[9] Similarly EDTA combines with several different metal cations to form stable metal chelates.

CHAPTER 2

EXPERIMENTAL PROCEDURE

2.1 Electrode Construction

Table I lists the primary chemicals used in the construction of the electrodes and the suppliers from whom they were obtained. Table II lists the chemical properties of the chelating agents. After removing the outer plastic insulation, fourteen-gauge solid copper wire was straightened by applying pressure causing it to slightly elongate. The wire was then cut into ten centimeter lengths. One tip of each wire length was rounded and made smooth using 400 grit sandpaper. The sections were then cleaned with water, acetone and chloroform using an ultrasonic cleaner. The cleaning procedure was performed three times. Once clean, the wire sections were hung in a hood to dry.

Once dry, the wires were pushed through cork stoppers which had already been pre-drilled with holes whose dimensions were slightly smaller than the wire, in such a way, that the remaining rough end was approximately one centimeter above the top of the cork. Each individual wire/cork was placed in an appropriate size test tube. The first step in constructing the electrode was to coat the entire outer surface of the wire with insulation. This outer insulation was a coating of polyvinylchloride (PVC). This was prepared by dissolving an amount of PVC in tetrahydrofuran (THF) to make a 7% PVC solution by mass. The rate at which the PVC dissolved

Table I. Chemicals and Suppliers

Chemical	Suppliers
Polyvinylchloride (low molecular weight)	Aldrich
Dioctylphthalate, tech	Pfaltz & Bauer
Dinonylnaphthalenesulfonic acid 50/50 with kerosene	Pfaltz & Bauer
Dowex 20-50 Strongly Basic Anion Exchange Resin - OH	Sigma
Ethylenediaminetetracetic acid	Pfaltz & Bauer
Nitrilotriacetic acid	Pfaltz & Bauer
Citric acid	Aldrich
Oxalic acid	Aldrich
L-Tartaric acid	Aldrich

Table II. Chelating Agent Chemical Properties[13]

Chelating Agent	Molecular Weight	Melting Point °C	Density
EDTA	292		
NTA	191		
Citric acid	192	153	1.665
Oxalic acid	90	190	1.900
L-Tartaric acid	150	206	1.788

was greatly increased using a magnetic stirrer to mix the solution. The wires were then individually dipped into this solution up to within a few centimeters of the bottom of the cork. The THF was allowed to evaporate for about five minutes before the dipping procedure was repeated. The dipping procedure was repeated until the insulation was about 0.5 mm thick (approximately 25 times). Finally, the wires were allowed to dry for about 24 hours.

Once the insulation had dried, the selective membrane was applied. First, a razor blade was used to expose the bottom two millimeters of the wire (see Fig. 6). The selective membrane solution was made by dissolving 0.9 grams of dioctylphthalate (DOP), 0.1 gram of dinonylnaphthalenesulfonic acid (DNNS) and a stoichiometric amount of the chelating agent (with respect to DNNS) in 19 milliliters of THF containing 5% PVC by mass.[7] Only the stoichiometric amount of oxalic acid completely went into solution. Of the four remaining chelating agents, only a partial amount dissolved in the selective membrane solution even after vigorous attempts to dissolve the whole portion. Each had a residue on the bottom of the flask after allowing the solution to sit.

It was necessary to extract the DNNS from a 50/50 DNNS-kerosene mixture. A certain amount of DNNS solution in kerosene was diluted with an equal volume of 200 proof ethanol and then mixed with a strong anion exchange resin of the OH^- form. The amount of anion exchange resin was

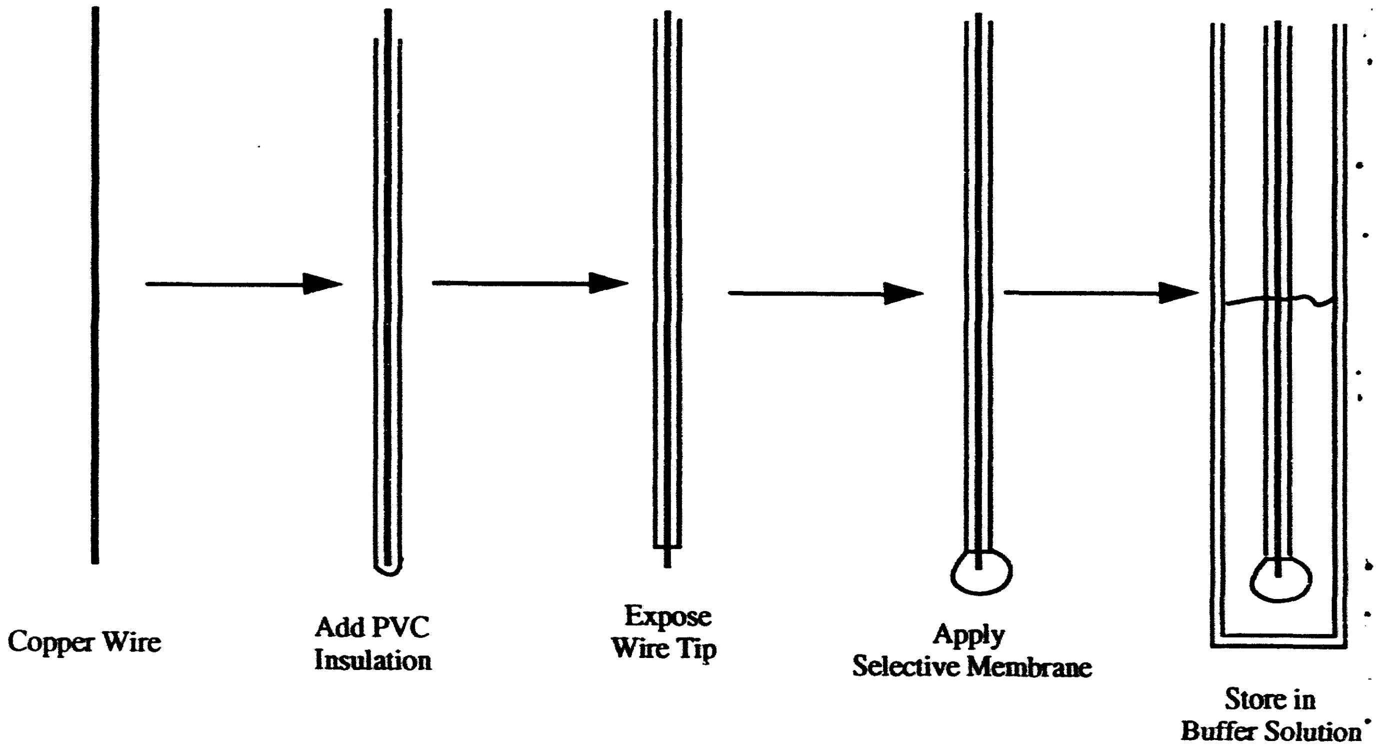


Figure 6. Process of Coated-wire Electrode Construction.

chosen to have at least ten times equivalents excess binding capability per the DNNS. After the DNNS had been adsorbed on the resin, this was washed with ethanol until a clear eluate was obtained. In this way all the neutral impurities were removed. The DNNS/resin was then eluted with a 1.0 M HCl solution in ethanol. This solution was prepared by dissolving one mole of HCl in one liter of 200 proof ethanol. The resulting eluate was evaporated to a solid brown mass at 50° C under a vacuum. The final product was repeatedly washed first with small portions of water and then small portions of ethanol, followed each time by evaporation under vacuum to remove final traces of HCl and water. The DNNS was stored under vacuum over P_2O_5.[6]

The "dip" procedure used to coat the wire lengths with insulation was then repeated using the selective membrane solution. This time only the bottom three millimeters of the wires were coated. The process was continued until the tip was coated with a bead about three millimeters in diameter. The bead was calculated to be approximately 50% PVC, 45% DOP, and 5% DNNS - chelating agent. The electrodes were then allowed to dry for 24 hours before being stored.

The electrodes were stored in a 0.1 M acetic acid buffer solution containing 10^{-4} M of the chelating agent present in the selective membrane solution. The pH of the storage solution was adjusted to 4.0 using NaOH. Each wire electrode was placed in individual test tubes containing the appropriate buffer solution.[7]

2.2 Electrode Calibration

Prior to the calibration of the wire electrodes, standard samples of the five chelating agents were made. The standards were made by first making a

0.1 M solution and diluting successive portions of that solution to make standard concentrations of 0.1, 0.05, 0.01, 0.005, 0.001, 5 x 10^{-4}, 10^{-4}, 5 x 10^{-5}, 10^{-5}, 5 x 10^{-6}, 10^{-6} M. The standard solutions were then stored in a dark cool place to prevent any decomposition.

The initial step in the calibration process was the calibration of the pH meter which was used as a voltage meter. This was done by using a standard pH electrode and standard pH buffer solutions to adjust the meter's set points according to the meter calibration instructions. The room temperature was noted and used as a part of the pH meter calibration.

Once the pH meter was calibrated, the calibration of each electrode was performed by first removing the electrode from its storage solution and washing it with distilled water. The wire electrode was then connected to the voltage input of the pH meter (see Fig 7). A silver/silver chloride (Ag/AgCl) reference electrode was connected to the reference junction of the pH meter. Both the wire electrode and the reference electrode were then placed in the most dilute standard solution of the chelating agent in question. The selective membrane was completely submerged in the test solution. The distance between the two electrodes was kept approximately the same during each subsequent standard solution calibration step. The pH meter was then turned on to the voltage setting.

The potential difference between the wire electrode and the reference electrode was given time to stabilize before the voltage reading was recorded. Once the voltage measurement stabilized for approximately one minute, the voltage was recorded and the process was repeated using the next more

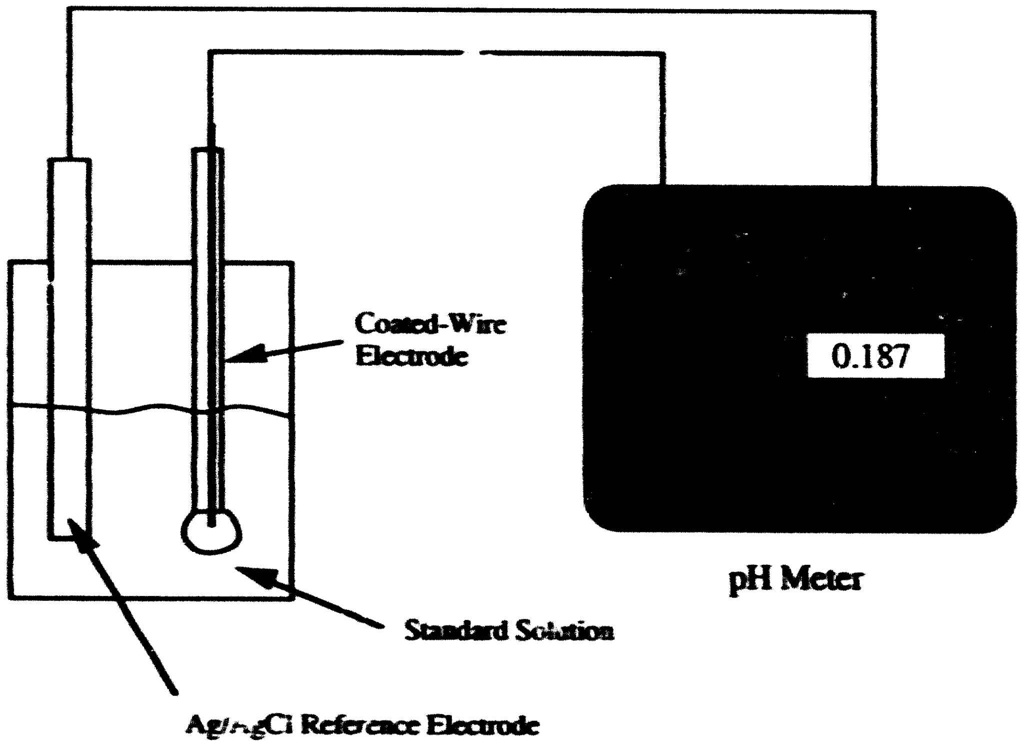


Figure [illegible]. Electrode Calibration Test Setup concentrated standard solution. Once the voltage had been recorded for the eleven standard solutions, the process was repeated for another wire electrode of the same chelating agent. More than one electrode was used to determine the similarity in slope of different electrodes of the same chelating agent. Upon completion of each electrode set, the electrodes were once again stored in their respective storage buffer solutions.

The calibration procedure was performed three times with approximately a period of 30 days between each calibration.

2.3 Electrode-Cement Test

Following the calibration of the coated-wire electrodes, the EDTA and NTA electrodes were tested with cement samples which contained a known amount of EDTA or NTA. The EDTA and NTA electrodes where chosen because of the good overall behavior they exhibited during the electrode calibration. The purpose of this test was to use the electrodes in a situation that would more closely simulate the environment found in a waste disposal site than the pure sample solutions used during the calibration portion. This test was meant to be much more qualitative than quantitative in nature. In other words, its purpose was to check the electrode reaction in a more complex environment as an indication of what direction future research might take.

The simulated waste disposal site environment consisted of cement, chelating agent and water. A large percentage of low-level radioactive waste is disposed of by mixing it with cement, commonly called grout, and placing the cement in 55 gallon steel drums. The amount of radioactivity mixed with the cement is controlled by the regulations in 10 CFR 20. If a decontamination solution containing chelating agent(s) is disposed of using cement, the cement will contain some concentration of radionuclides bound by the chelating agent(s).

The cement used was Portland cement and its composition is listed in Table III. The cement sample was prepared by adding 155 grams of cement, 70 milliliters of distilled water, 25 grams of sodium nitrate and 10 grams of the chelating agent. The resulting slurry was poured into a plastic cup and allowed to set. Once set, the plastic cup was cut away and the cement block was placed in a larger container to expose more surface area to speed drying. The cement block was allowed to dry for approximately 100 days. In addition to the cement blocks containing a chelating agents, a control sample was made using the same recipe minus any chelating agent.

For the electrode-cement test, the cement block was crushed and ten grams of the cement was finely crushed and placed in a container. 50 milliliters of distilled water was then added to the cement powder and allowed to leach. The crushing of the cement was done to reach an equilibrium concentration more quickly. Ten grams of the cement sample was calculated to contain 0.0011 moles of EDTA and 0.0023 moles of NTA. If all the chelating agent (EDTA or NTA) went into solution, the resulting solution chelating agent concentration would be 0.022 M of EDTA and 0.045 M of NTA. These concentrations were chosen so that the actual leached chelating agent concentration would fall on the linear portion of the calibration curve.

Table III. Composition of Cement Used in Waste Forms

Species	Composition (%)
SiO_2	22.63
Al_2O_3	3.84
Fe_2O_3	2.94
CaO	63.57
MgO	3.80
Na_2O	0.10
K_2O	0.58
SO_3	2.38

The electrode-cement test was performed by first calibrating the electrodes using the two point calibration described in section 3.2 of this thesis after calibrating the pH meter. The coated-wire electrode and the silver chloride reference electrode were then placed in the cement leachate of the control sample and then the cement-chelating agent sample. The first set of tests were run with the solid and leachate still together (the solids had settled). The second set of test were conducted after filtering the leachate from the solids. This was done to see if there was any response difference from condition one to condition two. As with the calibration tests, three electrodes were used for both EDTA and NTA. The three were always the same electrodes which had been used for the earlier calibration tests.

CHAPTER 3

INTERPRETATION AND RESULTS

3.1 Calibration Curve and Range

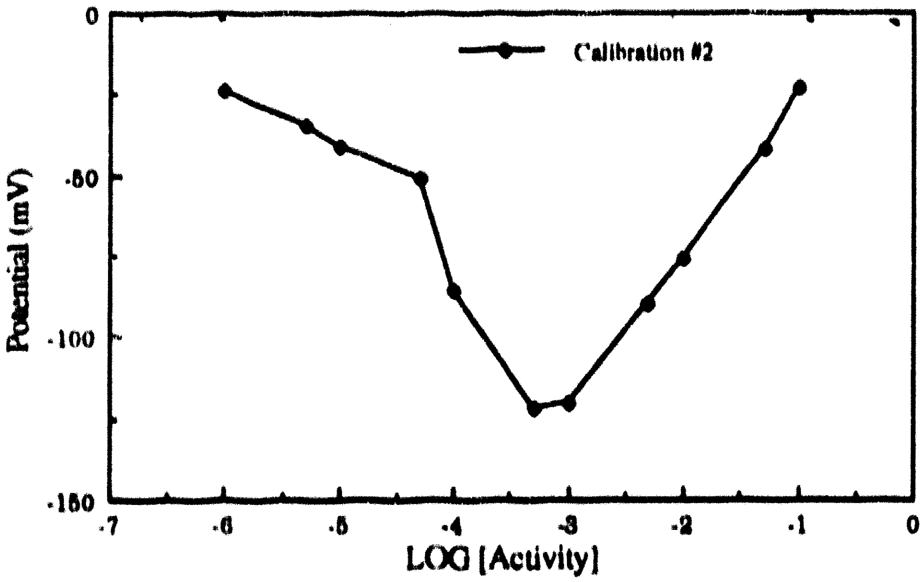
Average linear calibration characteristics: slopes, intercepts, linear limits and detection limits, determined directly from the experimental calibration curves have been listed in Table IV. These values are averages of three electrodes taken over three separate calibration experiments. The graphs of the averaged calibration curve data and the raw data from each electrode can be found in Appendix A.

A typical calibration curve of potential difference versus log[activity] consists of a linear portion that has a negative slope beginning at the higher concentrations to the lower concentrations. The linear portion of the curve will continue until other ions in solution begin to interfere with the ion of interest. At this point, the calibration curve slope will become less negative and if the interference is great enough, the slope will become positive (see Fig. 8).

The average slopes of the linear response portion of the individual chelating agent calibration curves are included in Table IV. If the slope of the electrodes were purely Nernstian in nature, their slopes should be 59.2 mV/log[a] at standard conditions.[4] As the average slopes of the electrodes show, none of the five chelating agent electrodes could be considered purely Nernstian. The slopes of the linear portions of the calibration curves were

Table IV. Calibration Curve Characteristics

Chelating Agent	Slope (mV/Log[a])	Intercept (mV)	Linear Limit (M)	Detection Limit (M)	R^2
Calibration #1					
EDTA	43.3	-66.9	10^{-3}	10^{-6}	0.997
NTA	42.5	249.9	$10^{-3.3}$	10^{-5}	0.996
Citric acid	19.7	146.7	$10^{-3.3}$	$10^{-5.3}$	0.978
Oxalic acid	27.5	268.2	$10^{-5.3}$	$10^{-5.3}$	0.987
Tartaric acid	17.0	166.6	10^{-3}	10^{-3}	0.911
Calibration #2					
EDTA	48.2	22.2	10^{-3}	10^{-6}	0.996
NTA	48.7	254.3	$10^{-3.3}$	10^{-6}	0.981
Citric acid	19.3	146.7	10^{-4}	$10^{-5.3}$	0.967
Oxalic acid	21.3	262.7	10^{-5}	$10^{-5.3}$	0.846
Tartaric acid	14.1	153.9	$10^{-3.3}$	$10^{-3.3}$	0.968
Calibration #3					
EDTA	48.2	22.2	10^{-3}	10^{-6}	0.996
NTA	42.9	250.5	$10^{-3.3}$	10^{-5}	0.986
Citric acid	22.4	159.4	$10^{-3.3}$	$10^{-5.3}$	0.957
Oxalic acid	22.5	267.7	10^{-5}	$10^{-5.3}$	0.942
Tartaric acid	19.4	194.1	10^{-3}	$10^{-3.3}$	0.823



Calibration Results of EDTA Electrodes

Figure 8. Typical Electrode Calibration Curve.

obtained using the method of least squares. The slopes of EDTA and NTA were the closest to meeting the theoretical value. Citric acid, oxalic acid and tartaric acid slopes were significantly below the theoretical value. This is not very surprising since the chelating molecules that were investigated are quite complex and are not of high ionic strength, so they would not be expected to exhibit ideal behavior.[13] The response of the electrode is also very dependent upon the interaction between the ion of interest in the aqueous phase and the counterion incorporated in the polymer. The behavior of the chelating agent/DNNS was one of the main objectives of this study. Previous work with coated-wire electrodes and organic complexes has shown that this relationship is not very well understood and the reaction of the coated-wire electrode to the organic ion of interest is difficult to predict.[11] The difference in the response of the EDTA and NTA electrodes as compared to the those of CA, OA and TA may, in part, be due to the difference in the mobility of the latter into or within the membrane, to a difference in the ion pair formation or to the inherent instability of these substances in solution which might cause interference problems even at the higher chelating agent concentrations.

An obvious difference between the two groups, EDTA, NTA and citric acid, oxalic acid, tartaric acid is the nitrogen found in the EDTA and NTA molecules. The nitrogen atoms in the molecule are like tertiary amines and will induce the tendency in the EDTA and NTA compounds to be more polar than they would otherwise be and therefore, better solubility in the selective membrane might result.[13] Thus, EDTA and NTA are probably more lipophilic than the other three chelating agents and their more Nernstian behavior would indicate this to be the case.[7] They would also have a greater tendency to be able to form ion pairs.

3.2 Electrode Response Time

The response time and characteristics of the electrodes varied depending upon the concentration of the standard solution and the chelating agent being tested. Response time is defined as the time it takes the potential difference being measured to come to equilibrium.[2] As stated previously in the section covering coated-wire electrode theory, the response time of the electrode will have a tendency to slow down as the concentration of the standard solution decreases. This tendency can be attributed to interfering ions such as H^+ present in water competing with the chelating agent ions.

This response time behavior was manifest by electrodes of each chelating agent. As the concentration of the standard sample being tested decreased, the response time increased. Since the electrodes were tested from the least concentrated standard solution (10^{-6} M) to the highest concentrated standard solution (0.1 M), the electrode response during the initial calibration took considerably longer to reach equilibrium than later in the calibration. For all the chelating agent electrodes, the point at which a transition from poor response characteristics to good response characteristics occurred approximately when the calibration curve entered the linear regime. The effect of the interfering ions became less and less significant with increasing chelating agent concentration.

EDTA exhibited the best response characteristics of all the chelating agent electrodes. Even at the lower concentrations, although the response time increased, the time to equilibrium was still acceptable. At the higher concentrations, the time to equilibrium was more dependent upon the time constant of the pH meter electronics than the EDTA electrode. This good overall behavior is clearly exhibited by the EDTA calibration curve. NTA also showed good response time behavior, similar to EDTA, but the response time associated with the lower concentrations was somewhat slower than EDTA. Both EDTA and NTA at the higher concentrations would reach an equilibrium point within one minute of the placement of the electrode in the standard solution.

Citric acid and oxalic acid exhibited response time behavior slightly less favorable than either EDTA or NTA. They both behaved similarly, taking up to five minutes to reach a potential difference equilibrium at the lower concentrations and between one and two minutes at the higher standard solution concentrations. Their calibration curves show a less favorable trend than EDTA or NTA, so their response time behavior correlates with the data. In the linear range of their calibration curves, their response times were acceptable.

Tartaric acid exhibited the worst overall response characteristics. Throughout the entire test regime the response time was considerably longer than the behavior of the other four chelating agent electrodes. At low concentrations, the response time was over five minutes and did not improve appreciably with the higher concentrations. The voltage tended to be erratic around what was determined to be the equilibrium point. This behavior also correlates with the poor calibration curve data.

With the exception of tartaric acid, the response time of the electrodes within their linear range was approximately one minute. Thus, the time to calibrate and use these electrodes is minimal and acceptable. While the linearity of the electrodes' response requires but two calibration points, any work done around the limits of the linear range will require additional calibration points. A fast response time and enables a calibration to be performed with a reasonable amount of time and effort.

Even though none of the electrodes of the chelating agents could be called truly Nernstian in nature, all but the tartaric acid electrodes produced regions where the calibration slope was linear.

The linearity of the electrodes suggests that a simple two point calibration should be sufficient to establish a relationship which provides a way of determining an unknown sample's chelating agent concentration if it falls within the linear range. Such a procedure would involve measuring the potential of two different standard solutions with concentrations in the linear range of the calibration curve. The calibration curve would then be made by drawing a line through the two points on a plot of potential versus log[activity]. The line could then be extended to the lower linear limit.

The four electrodes exhibiting a linear portion, did so at the higher concentration end of the calibration curve. While the linear region slopes of the electrodes did vary slightly from calibration to calibration, the slopes remained linear in nature and could, therefore, be used to measure EDTA, NTA, citric acid and oxalic acid concentration. None of the electrodes exhibited any decay during the time that they were tested. It has been shown in the literature that sensitivity of this type of ion-selective electrode can decay as a result of leaching of the chelating agent/DNNS.

As mentioned above, all the types of electrodes except those of tartaric acid exhibited a linear region. Of the four which did, all responded linearly at the highest concentration examined, 0.1 M. Values for the lower limit of the linear portion are in Table IV. They all averaged a linear regime of approximately three decades below the 0.1 M level.

3.3 Intercepts

The average intercepts are listed in Table IV. They were determined by extending the linear portion of the calibration curves to a value of zero for the log[activity]. Using the slopes as an indication of the intercepts, one would expect the electrodes with the largest slopes to have the largest intercepts.

The absolute intercepts in Table IV have very little significance and serve only as a means for comparing the different types of electrodes. They are however, related to the electrode's standard potential. The intercepts change from calibration to calibration which means that the electrodes need to be calibrated before each use. As mentioned before, the calibration process would only require a few minutes. Since the intercept seems to have been dependent on the number of calibrations, the change may be due to a leaching of the DOP (plasticizer), the chelating agent/DNNS complex from the membrane or to decomposition of the chelating agent. The change in concentration may also have shifted the internal reference potential at the membrane-copper wire interface.[10]

3.4 Detection Limits

The detection limits of the electrodes are also listed in Table IV. Detection limit is defined as the lowest chelating agent concentration that the electrode is able to reliably detect. This does not mean the regime on the curve that is linear, but the lowest concentration that can be merely detected to possibly verify that the chelating agent is present at some concentration. This was assumed to be the point on the graph where the curve became a straight line. EDTA electrodes responded to the lowest activity tested, 10^{-6} log[M]. Citric acid and oxalic acid both responded to $10^{-5.3}$ log[M], NTA responded to a value of 10^{-5} log[M] and tartaric acid responded to only 10^{-3} log[M].

3.5 Longevity

The electrodes used in these experiments were only three months old when the last calibration was performed and had not shown any decay or loss of function during that time. The electrodes and the standard solutions were kept in a dark, cool place to reduce or eliminate the possibility of decomposition. A harsher environment may reduce the time over which the electrodes are functional.

Theory states that the response starts to decay when the concentration of either the plasticizer or ion pair gets below some critical value.[2] Since a small amount of each substance is leached from the membrane during each calibration, it is logical that the lifetime of the electrodes depends on the number of calibrations made. The literature reports that many coated-wire electrodes have lifetimes of 25 calibrations or more and can be stored for up to 12 months before appreciable levels of electrode decay occur.[5]

3.6 Reproducibility

Standard deviations for the slopes of the three electrodes of a particular chelating agent during the same calibration were always less than 10% except one EDTA calibration which was once used with the wrong pH meter calibration. The effect of this was to change the intercept, but the slope of the linear portion remained within 10%. The standard deviation values for the intercepts were also within 10% except for the case just mentioned. The standard deviations for the slopes and intercepts between calibrations were all less than 10% for each.

Uncertainty of this magnitude should be easily tolerable in a test to determine whether or not a chelating agent is present and probably acceptable for more exact studies or quality control applications.

Since the substances in the membrane are under pressure to leach due to concentration differences present during storage, it would be advisable to use the electrodes shortly after calibration.

3.7 Drift

All the electrodes exhibited some potential drift and instability in standard solutions of low concentration. This drift was on the order of slightly more than 1 or 2 mV/min. At higher concentrations, the drift was on the order of less than 0.5 mV/min.

3.8 Electrode-Cement Test

The electrode-cement test data and results are listed in Appendix B. The two point calibration technique utilized to obtain potential versus log[activity] curves compared well with the data obtained during the calibration part of the experiment. The slopes of the curves fell between values of 40 - 50 mV/log[activity].

The selectivity of the EDTA and NTA electrodes did not appear to operate very well in the cement leachate. The potential difference measurements were consistently high for each electrode. The chelating agent concentrations determined graphically were several orders of magnitude greater than the amount of chelating agent in the cement sample. This is the type of behavior that would be expected if an ion was competing with the chelating agent and the electrode was more sensitive to the competing ion.

The control sample of cement, containing no chelating agent, consistently produced the highest reading. The filtered leachate consistently produced the lowest reading.

CHAPTER 4

CONCLUSIONS

4.1 General Conclusions

Based upon the experimental data obtained using the five chelating agent doped electrodes it can be said that coated-wire electrodes could be used to detect the presence of the chelating agents in radioactive waste solutions. Also, it was very apparent that some of the chelating agent electrodes work better than others.

The coated-wire electrodes made with EDTA performed the best of the five chelating agents investigated. The EDTA calibration curve contained a very linear portion and the overall behavior of its electrodes was very nominal. Their experimental behavior indicates that they could be used in the measurement of EDTA concentration and certainly could be used to detect EDTA. Their response time was fast and once a potential difference equilibrium was established, the voltage was very stable. This is important because characteristics such as these would allow for simple and quick two-point calibration to be performed prior to the use of the EDTA/coated-wire electrode system. EDTA is probably the most common chelating agent used in decontamination solution, so it is fortunate that it was the chelating agent which had the best overall behavior. Based upon the data, the EDTA electrode should be able to detect the presence of EDTA within the entire range that it was tested, 10^{-6} log[M] - 10^{-1} log[M].

NTA exhibited behavioral characteristics that were similar to EDTA, but not quite as well behaved. Its calibration curve linear portion was not quite as linear, but still would be considered acceptable for determining NTA concentration.

Citric acid and oxalic acid exhibited similar calibration characteristics. However, their behavior might not be such that they could be used for determining concentration. The experimental evidence indicates that citric acid and oxalic acid electrodes could be used to detect the presence of these compounds.

The tartaric acid coated-wire electrodes' behavior indicated that they would not lend themselves to being used to measure tartaric acid concentration or even detection.

This study has established that the coated-wire electrode method will work for at least four out of the five chelating agents investigated in pure solutions that do not contain any substances that might inhibit or mask their function. How the chelating agent electrodes would behave in the presence of other compounds, such as other organics found in cleaning solutions used for radioactive decontamination, is certainly a subject for further research. This behavior is known as electrode selectivity. Electrodes that are more lipophilic tend to exhibit better selective behavior. Based upon this and the experimental data for the chelating agent electrodes obtained in this study, it could be postulated that the EDTA and NTA electrodes would exhibit better selective behavior because they appeared to be more lipophilic. A substance that is more lipophilic than the chelating agent will be more successful at masking the electrode's potential dependence on the chelating agent being used.

During the time period of the experiment (three calibrations at one month intervals), the chelating agents showed no observable hysteresis. This phenomena is closely related to the rate at which the counterion diffuses out of the selective membrane; and the stability of the ion of interest, in this case the five chelating agents. The trends observed in hysteresis have been described in other studies, in which hysteresis was observed.[5]

The potential at the selective membrane-solution interface is dependent on the solubility difference between the ion of interest and its counterion. More lipophilic ions can partition into the selective membrane to a greater extent to form more ion pairs with the DNNS counterions. The potential established becomes more dependent on a particular cation as the number of ions in the membrane increases. Thus, since the more lipophilic cations partition into the selective membrane to a greater extent, more of these ions are at the membrane surface causing the potential at the membrane-solution interface to become largely dependent upon this ion. After an initial exposure to a lipophilic ion, a large number of the cations in the membrane will contain this ion. In subsequent calibrations, the interfering ion will already be present in the membrane and the response of the electrode to these interferences will become larger and larger.[7]

Also, the electrodes did not show any observable sensitivity decay. Studies of greater length would have to be performed to determine the lifetimes of the chelating agent electrodes. Lifetime is very dependent on the diffusion rate of the counterion (DNNS) out of the selective membrane and the stability of the chelating agent that was used to dope the membrane. It is logical to assume that with time both diffusion and degradation will occur, thus the electrodes will have a finite lifetime.

The results of the electrode-cement test were not very satisfactory. The coated-wire electrodes appeared to be affected by interfering ions present in the solution. In order to use these electrodes to determine the chelating concentrations in cement waste forms, additional studies would be required. If the competing ion(s) could be identified, the competing ion(s) might be removed from the leachate prior to using the electrode. A different counterion might also be investigated which might result in improved electrode selectivity. Again, it would be important to know the competing ion(s). This test has established a baseline of electrode function and is starting point for further research.

4.2 Further Studies

The results of these studies suggest a number of other projects, other than those already mentioned above, which would help in determining some of the remaining unknown characteristics of these electrodes and the conditions under which they could be used to obtain reliable data.

The concentrations of the chelating agent used to dope the selective membrane, DNNS and DOP could be varied to examine which of these chemicals has the greatest effect on electrode performance. It might be found that a certain combination would work better for electrode use under the condition which would be found at a radioactive waste disposal site.

A possible method of determining the selectivity of a particular electrode type in an environment that simulates that of a waste disposal site and the condition that would exist for radionuclide leaching to occur, would be to use a ^{14}C labeled chelating agent. In order to know if the electrode is determining the correct chelating agent concentration, the true concentration must be known. Waste form leaching studies could be performed using the labeled chelating agent and an appropriate simulated radionuclide such as ^{59}Co to determine the leach rate of the chelating agent/radionuclide. Also the equilibrium constant of the system could be obtained since the electrodes measure activity at low concentrations. If various possible environments were studied, it might be possible to determine what would be the best environment to create at a disposal site that would better keep the radionuclides within the boundaries of the site

APPENDIX [illegible]

Calibration Data

Figure A.1. Calibration Results of EDTA Electrodes.

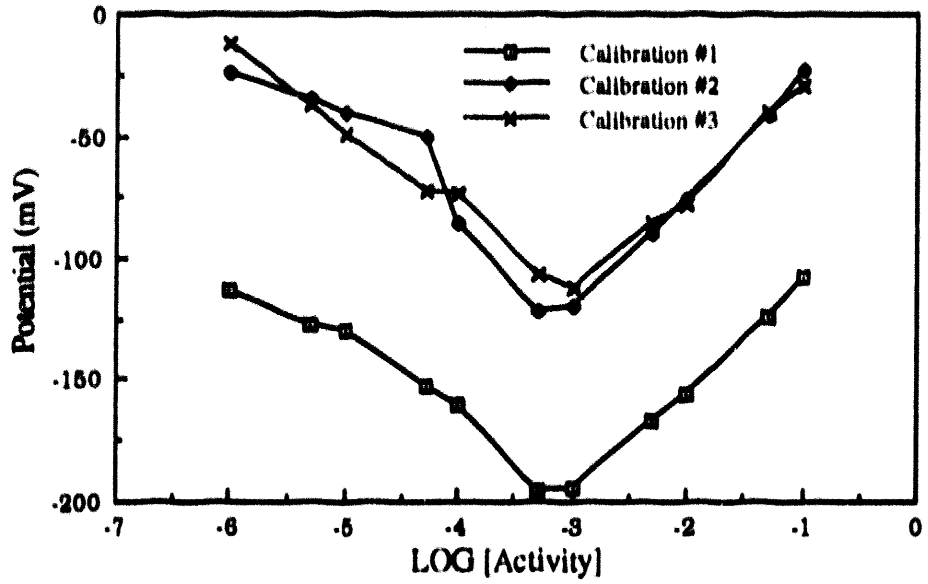


Figure A.2. Calibration #1 of EDTA Electrodes.

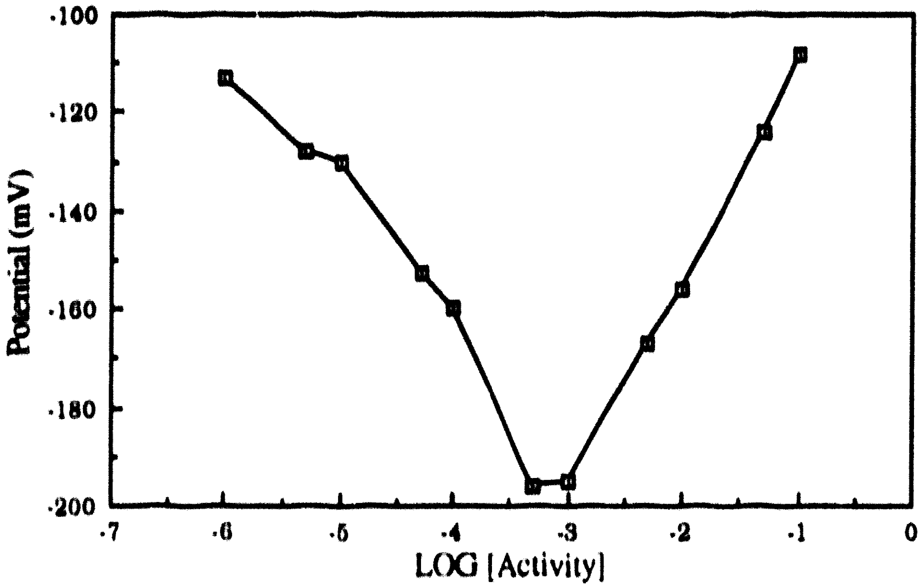


Figure A.3. Linear Portion of EDTA Calibration #1.

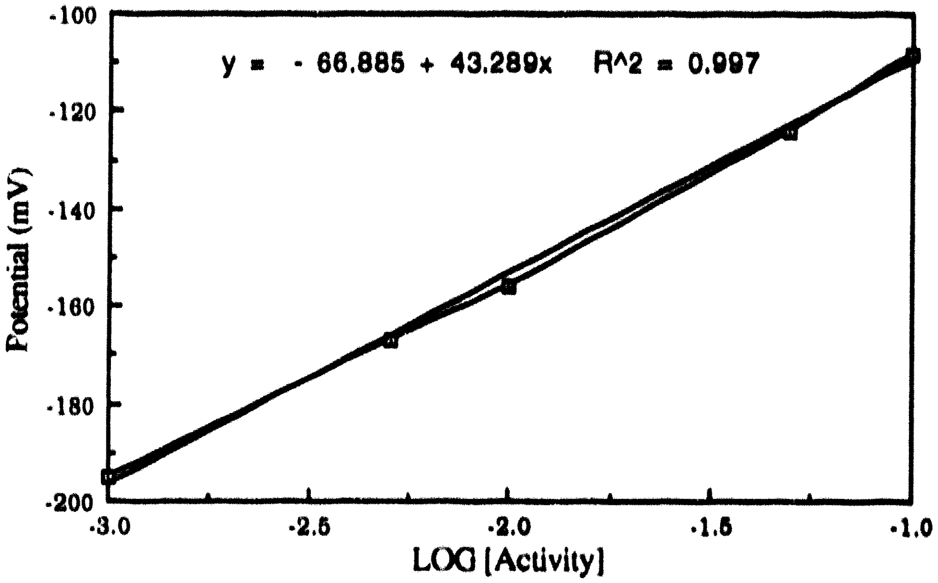


Figure A.4. Calibration #2 of EDTA Electrodes.

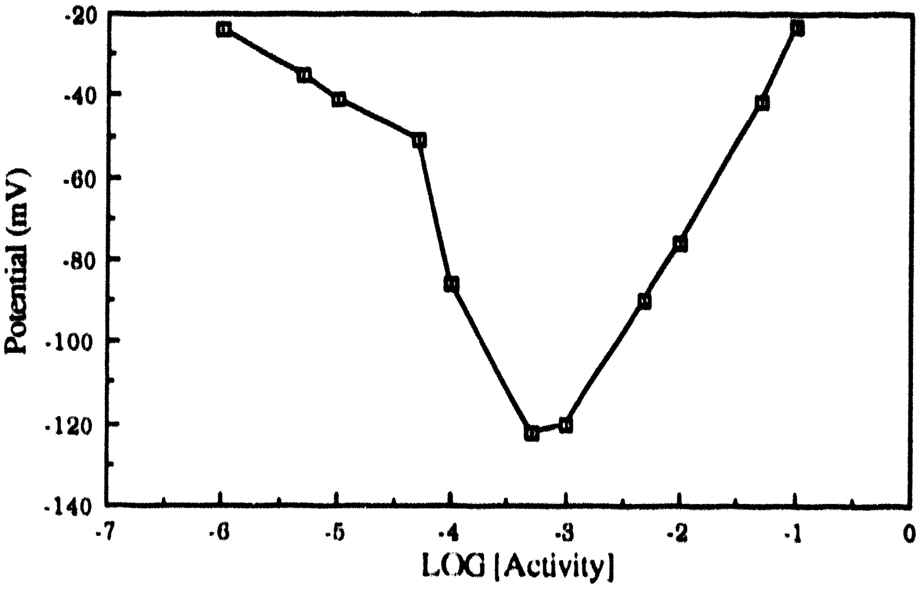


Figure A.5. Linear Portion of EDTA Calibration #2.

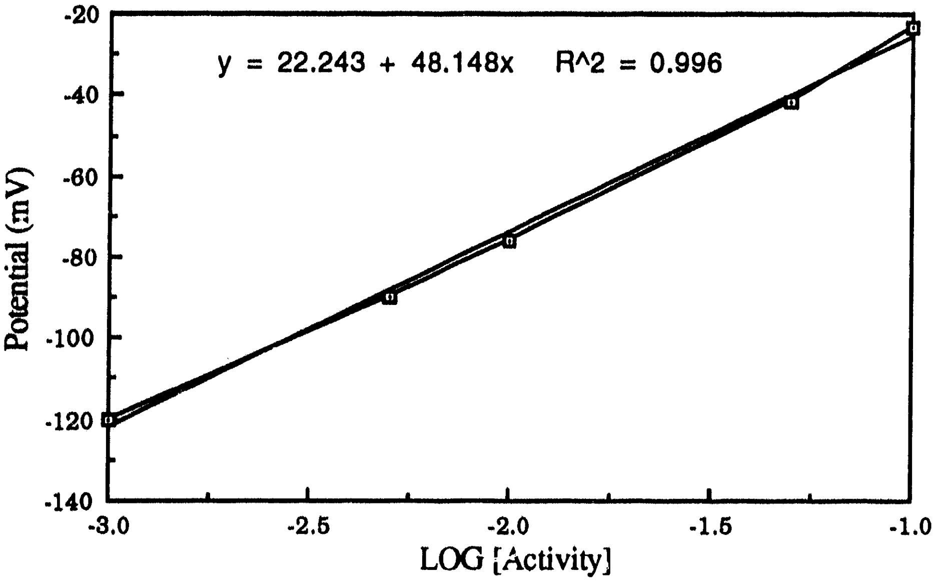


Figure A.6. Calibration #3 of EDTA Electrodes.

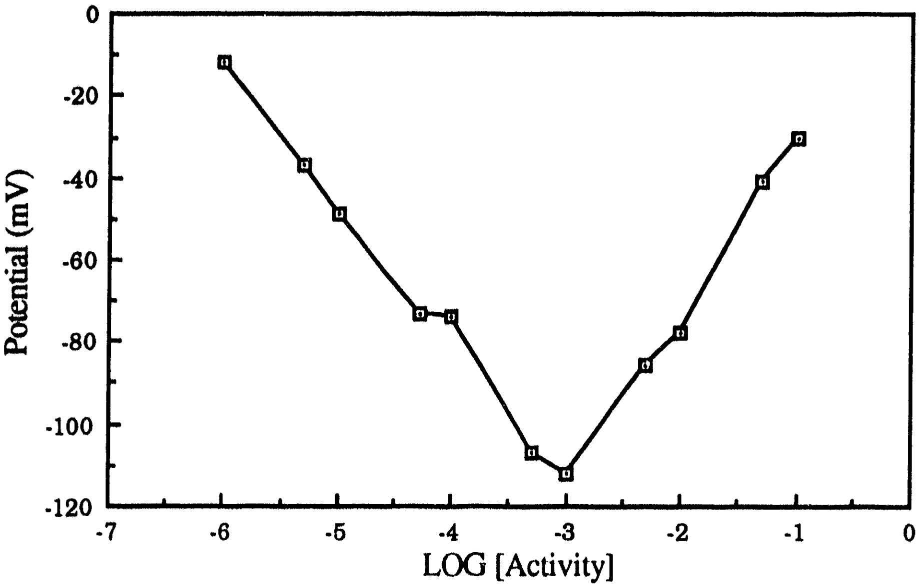


Figure A.7. Linear Portion of EDTA Calibration #3.

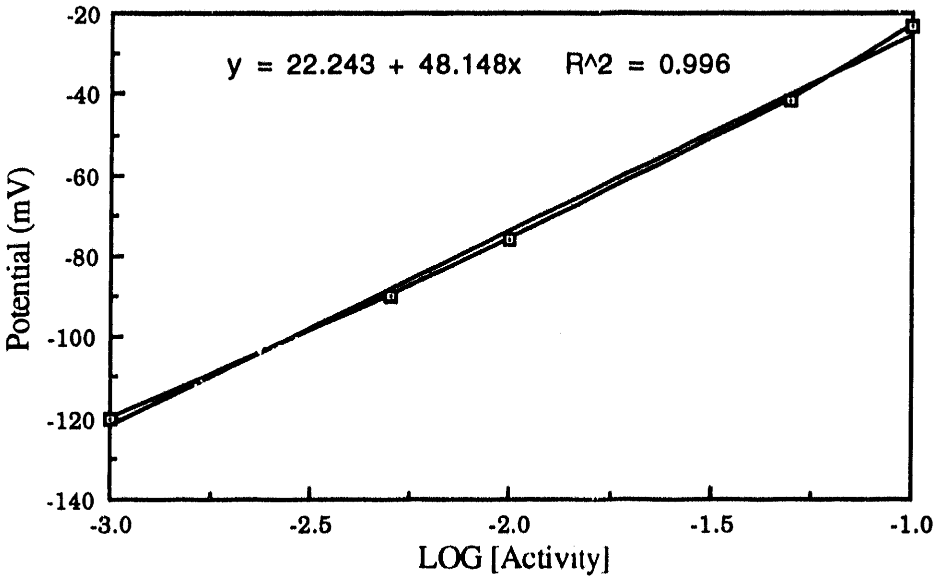


Figure A.8. Calibration Results of NTA Electrodes.

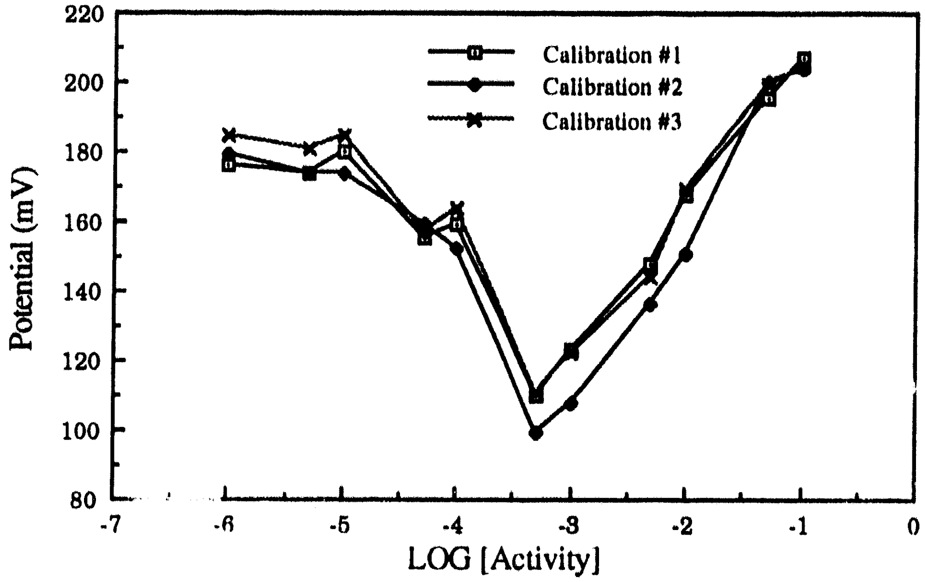


Figure A.9. Calibration #1 of NTA Electrodes.

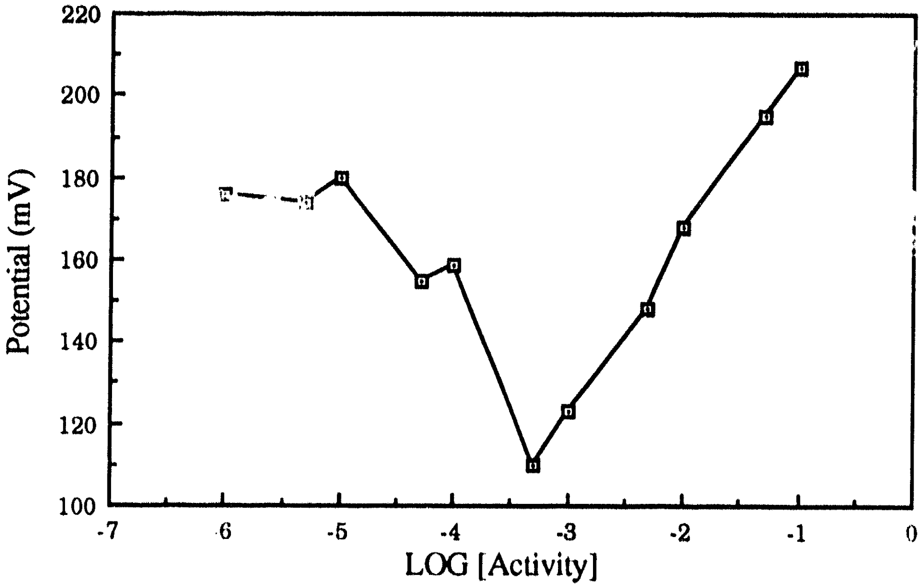


Figure A.10. Linear Portion of NTA Calibration #1.

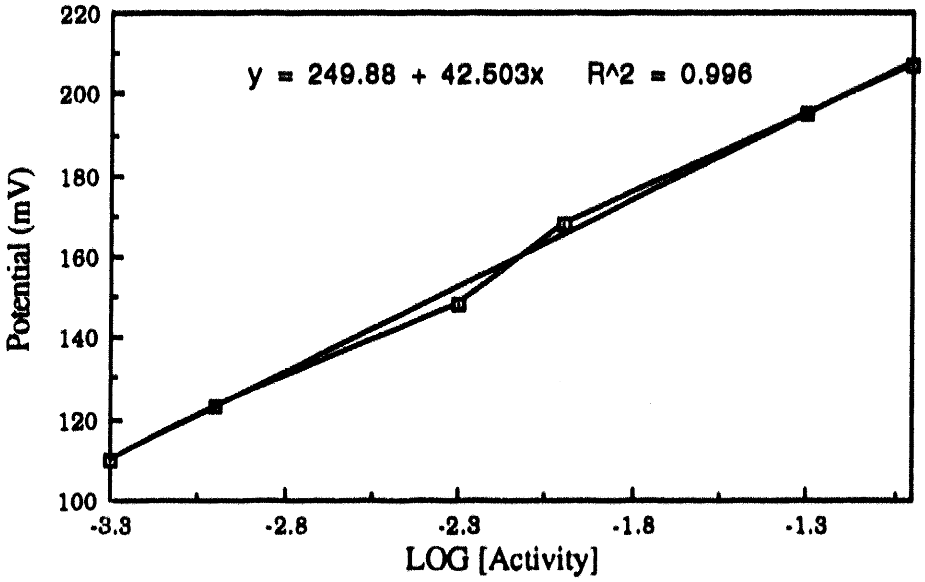


Figure A.11. Calibration #2 of NTA Electrodes.

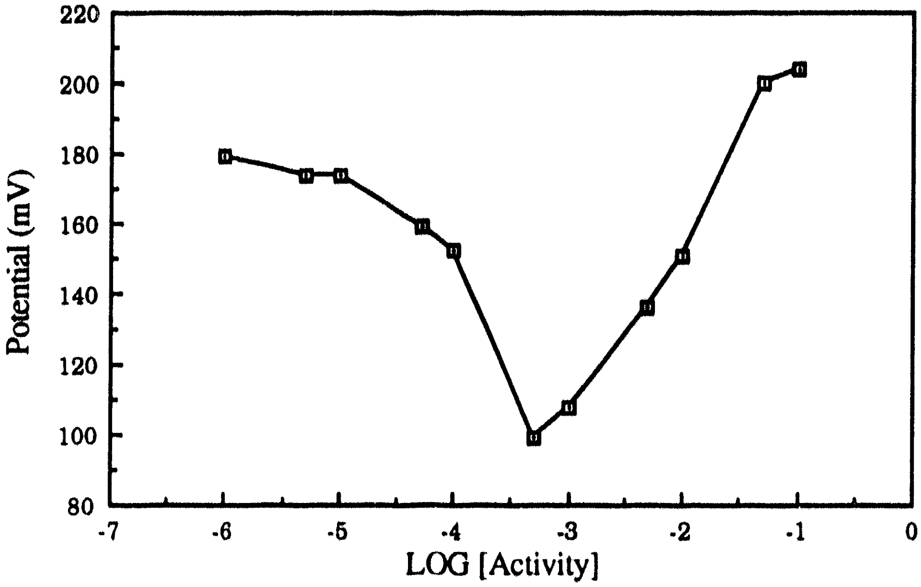


Figure A.12. Linear Portion of NTA Calibration #2.

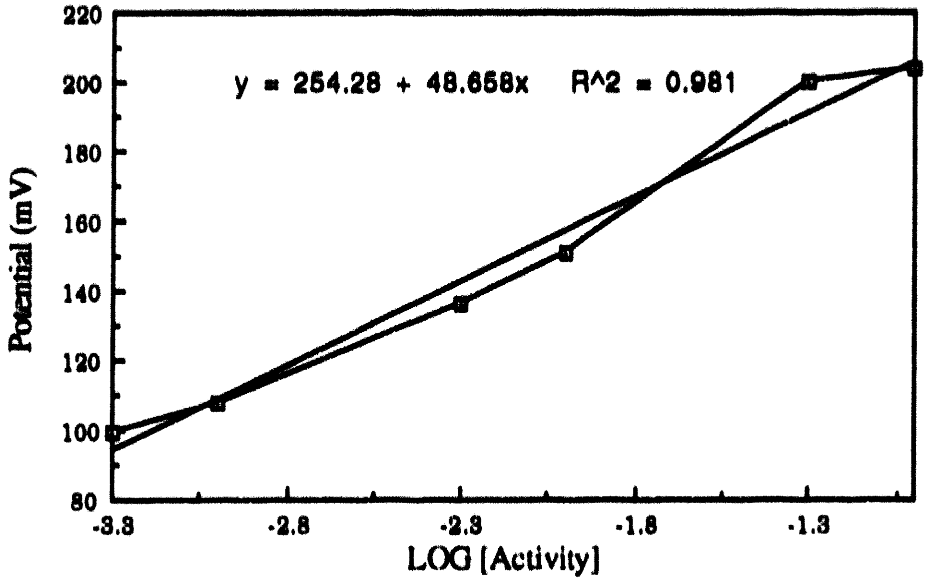


Figure A.13. Calibration #3 of NTA Electrodes.

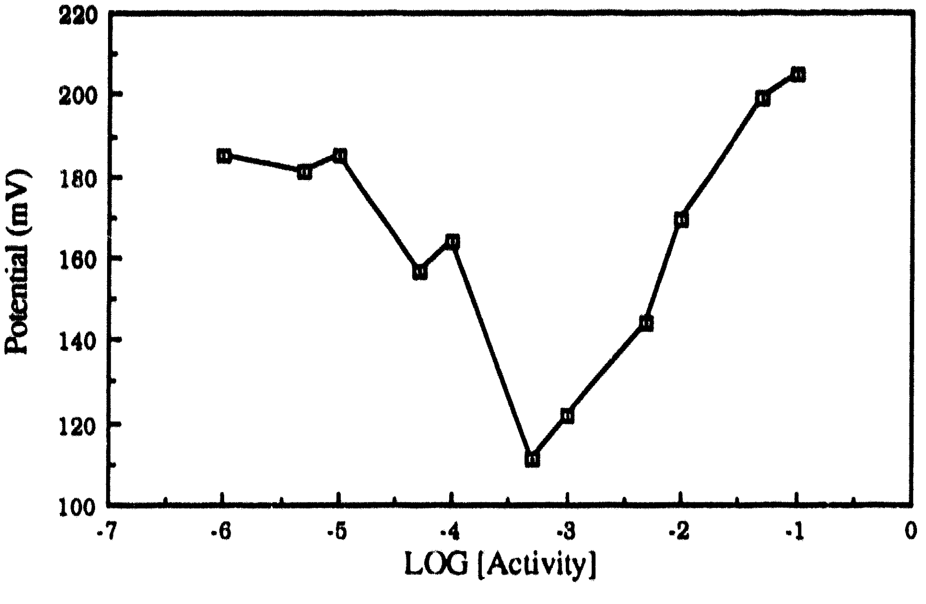


Figure A.14. Linear Portion of NTA Calibration #3.

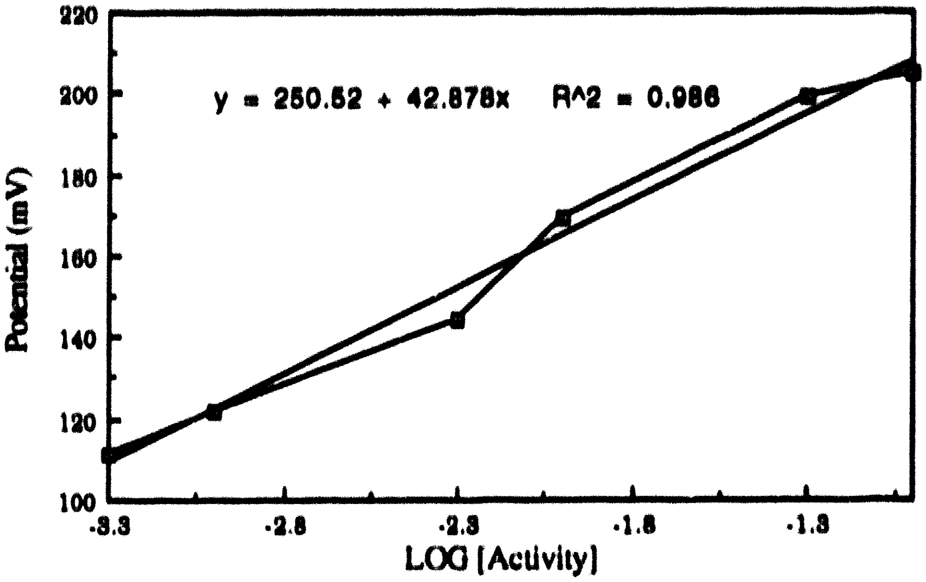


Figure A.15. Calibration Results of Citric Acid Electrodes.

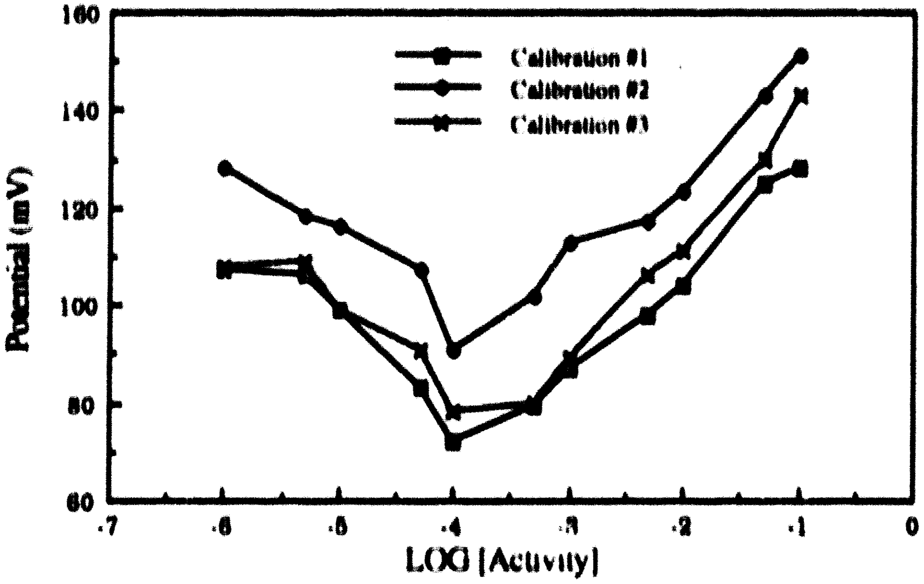


Figure A.16. Calibration #1 of Citric Acid Electrodes.

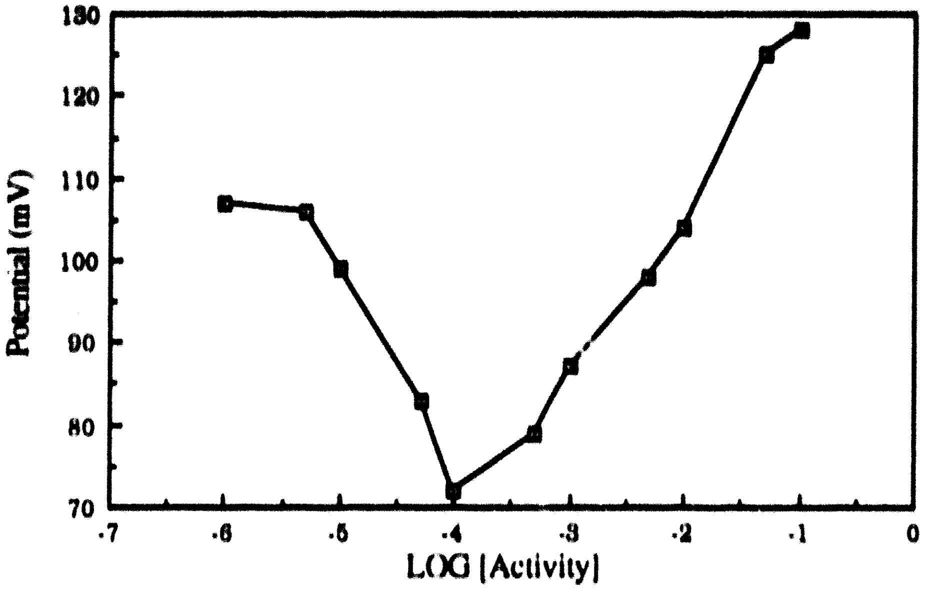


Figure A.17. Linear Portion of Citric Acid Calibration #1.

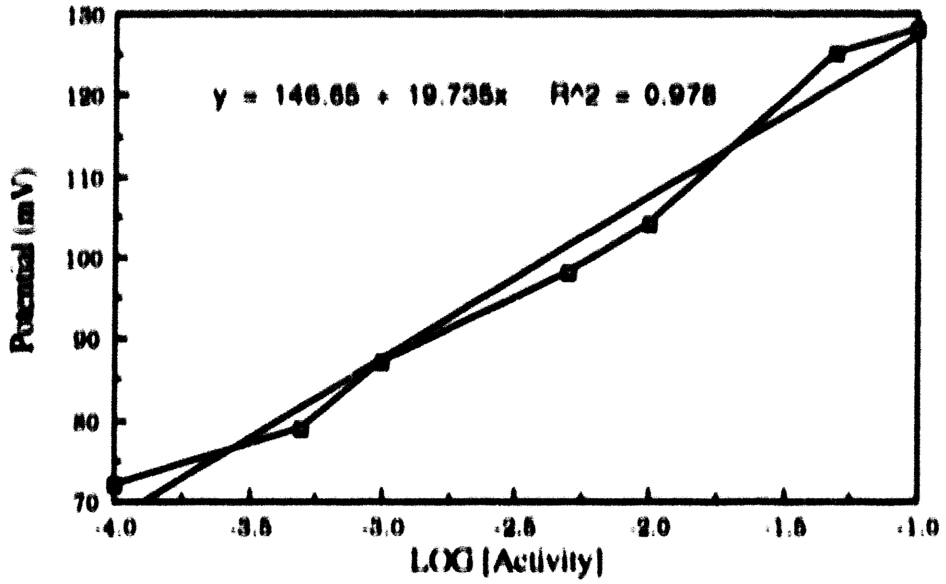


Figure A.18. Calibration #2 of Citric Acid Electrodes.

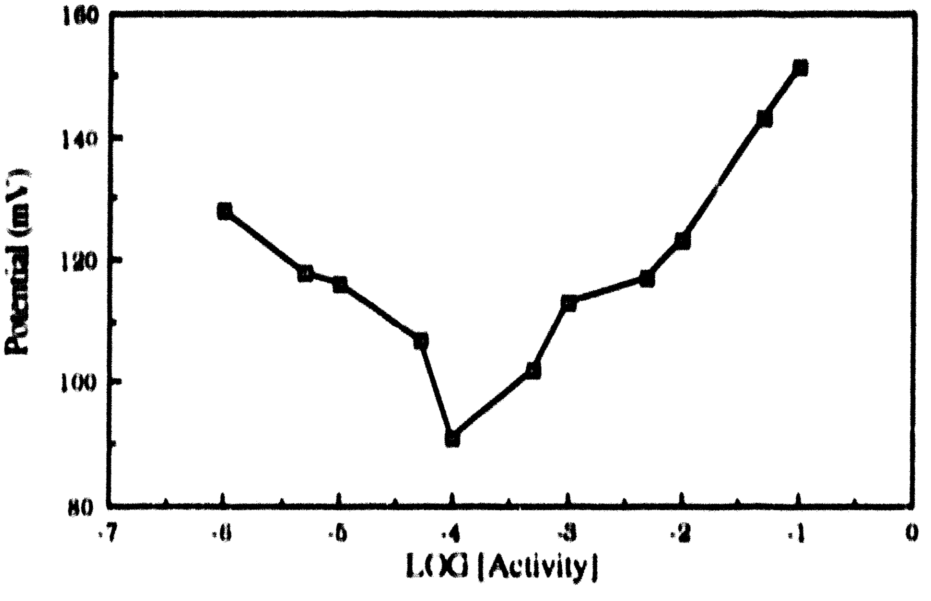


Figure A.19. Linear Portion of Citric Acid Calibration #2.

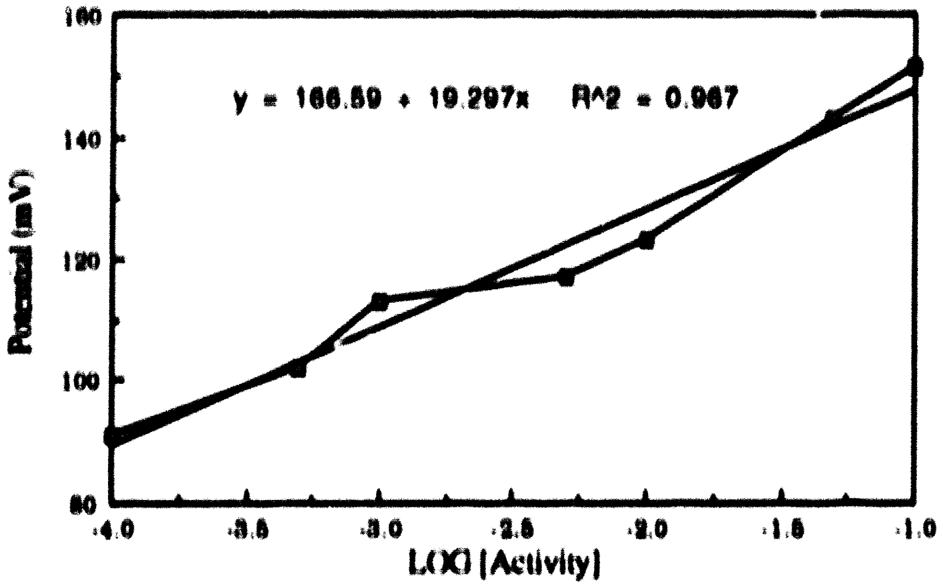


Figure A.20. Calibration #3 of Citric Acid Electrodes.

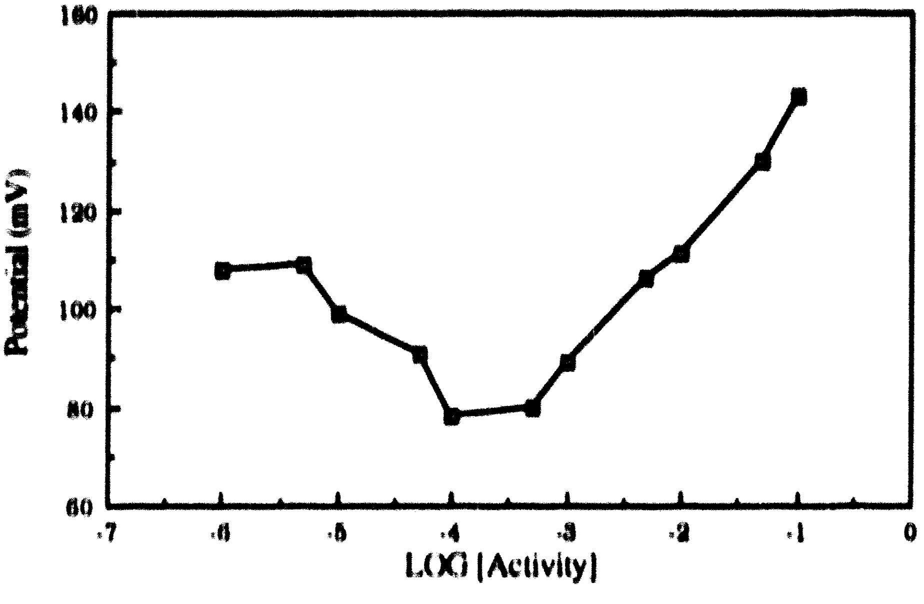


Figure A.21. Linear Portion of Citric Acid Calibration #3.

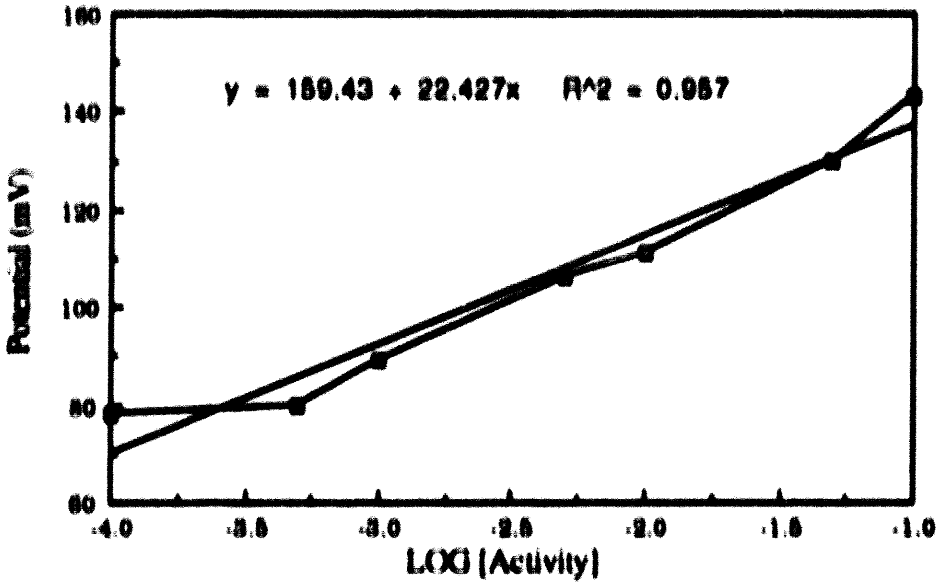


Figure A.22. Calibration Results of Oxalic Acid Electrodes.

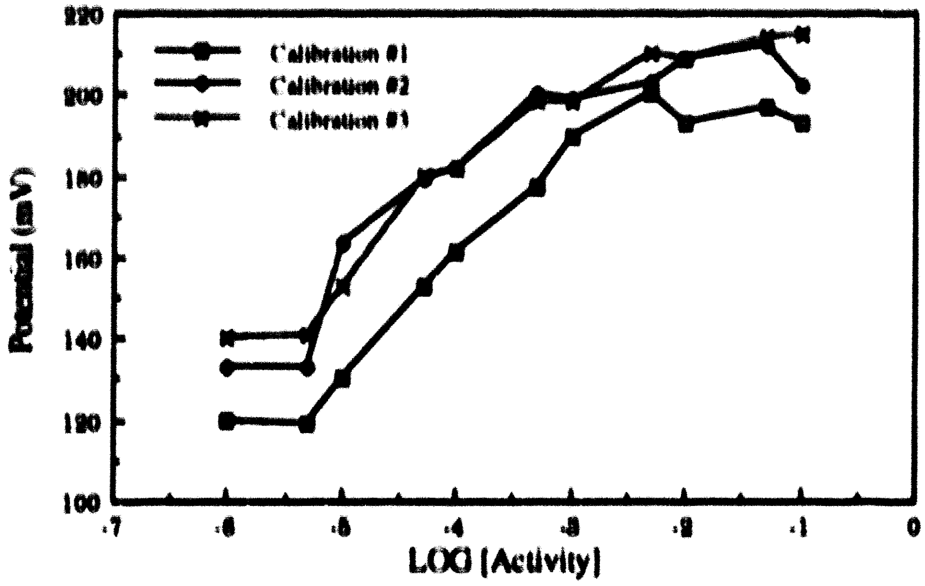


Figure A.23. Calibration #1 of Oxalic Acid Electrodes.

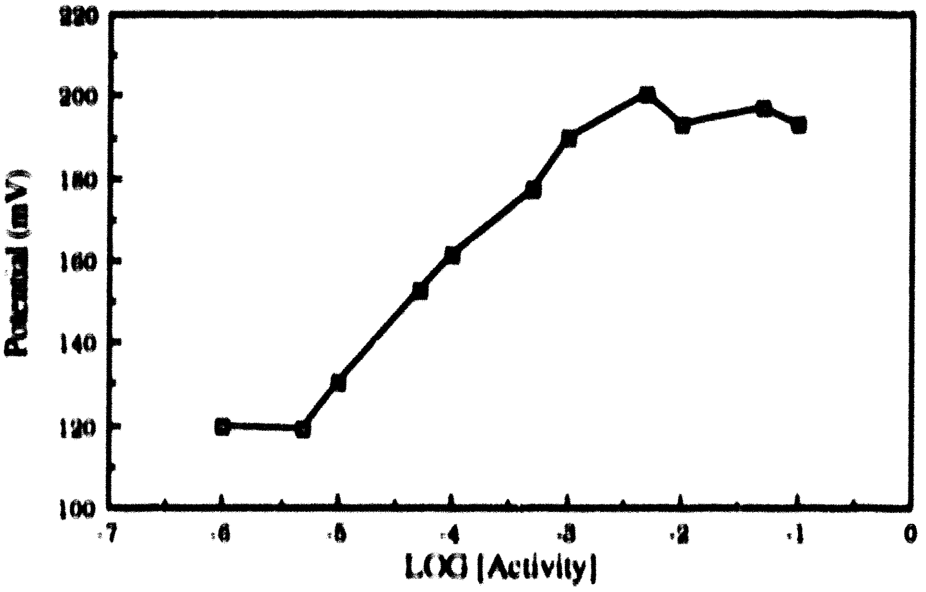


Figure A.24. Linear Portion of Oxalic Acid Calibration #1.

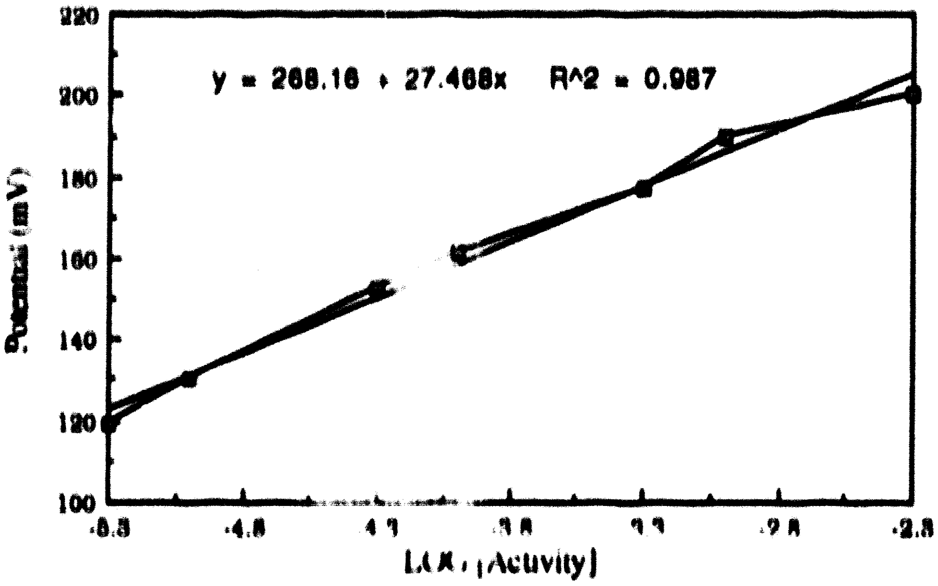


Figure A.25. Calibration #2 of Oxalic Acid Electrodes.

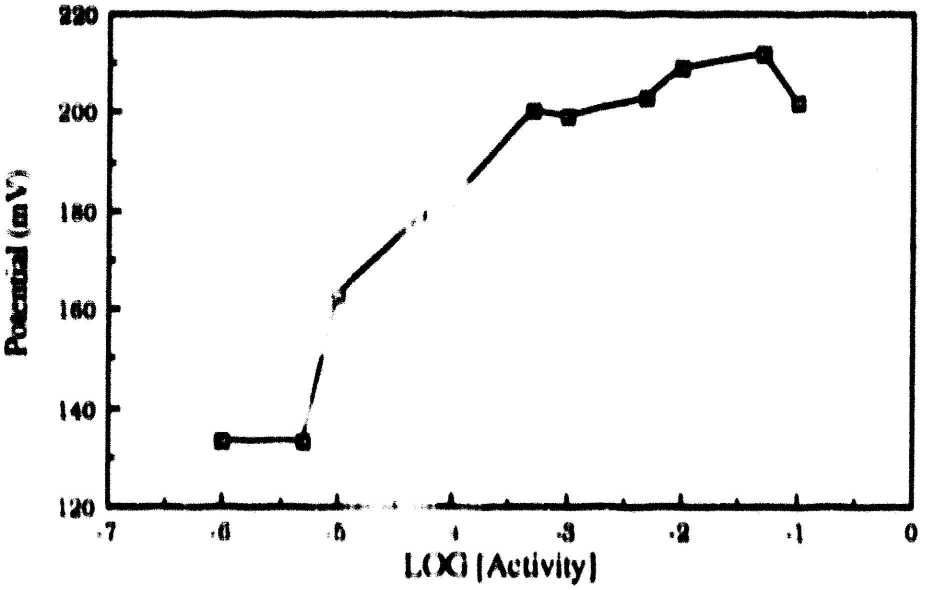


Figure A.26. Linear Portion of Oxalic Acid Calibration #2.

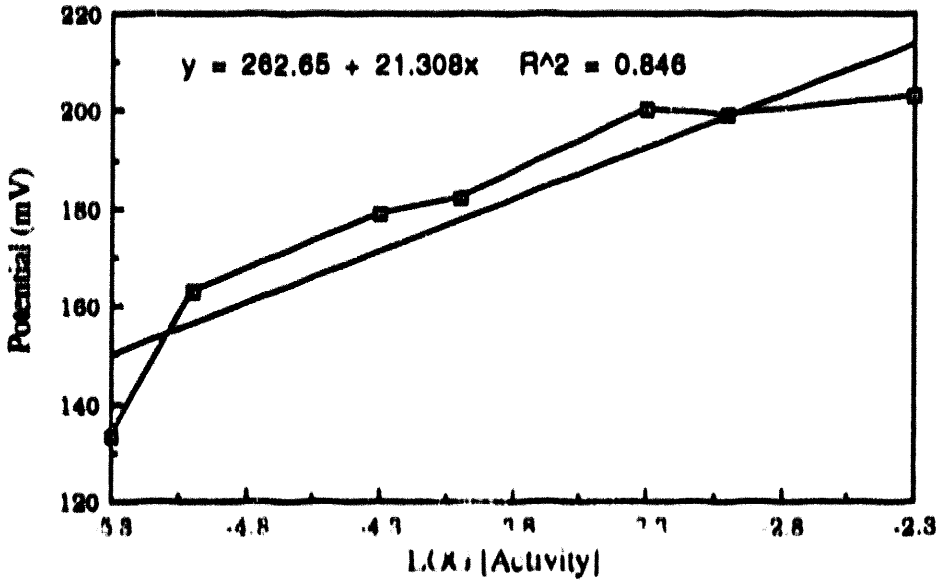


Figure A.27. Calibration #3 of Oxalic Acid Electrodes.

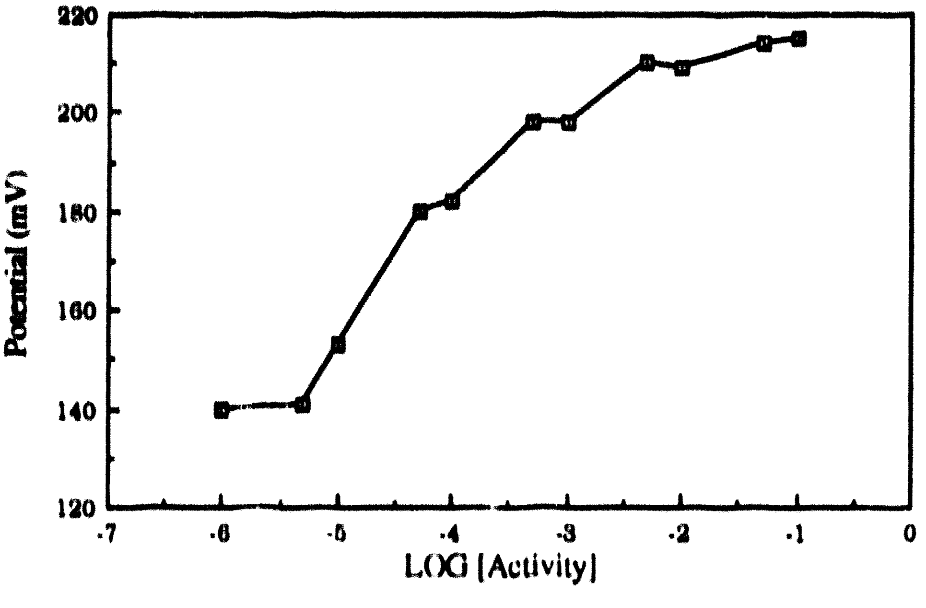


Figure A.28. Linear Portion of Oxalic Acid Calibration #3.

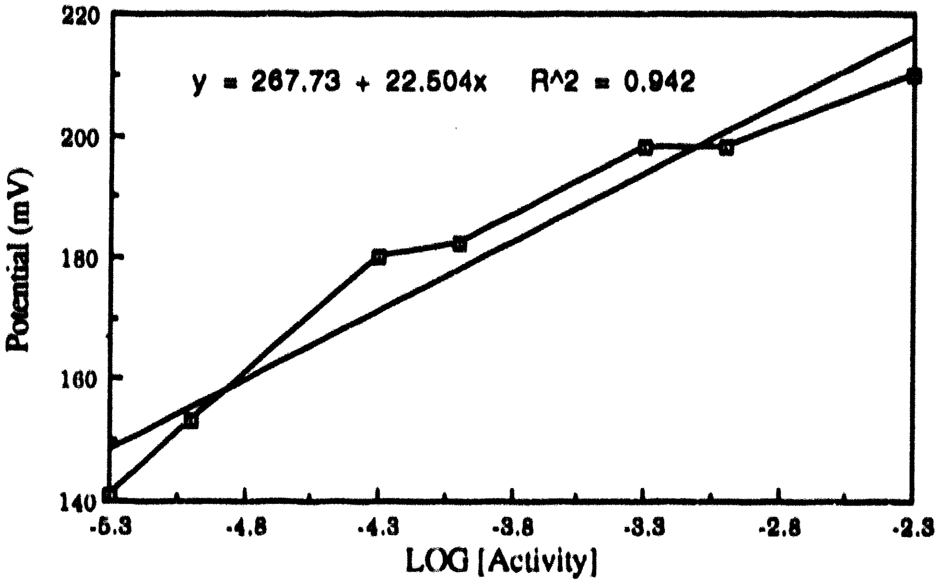


Figure A.29. Calibration Results of Tartaric Acid Electrodes.

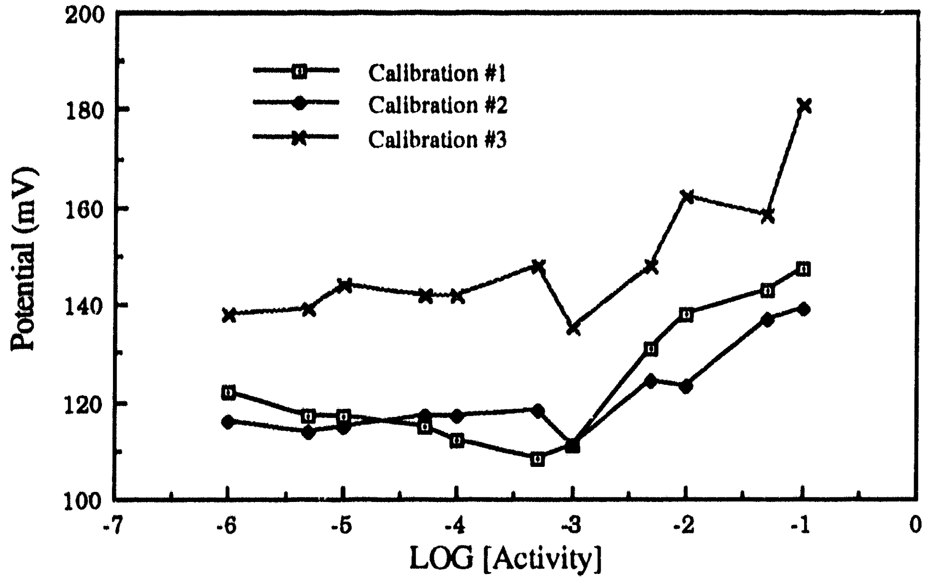


Figure A.30. Calibration #1 of Tartaric Acid Electrodes.

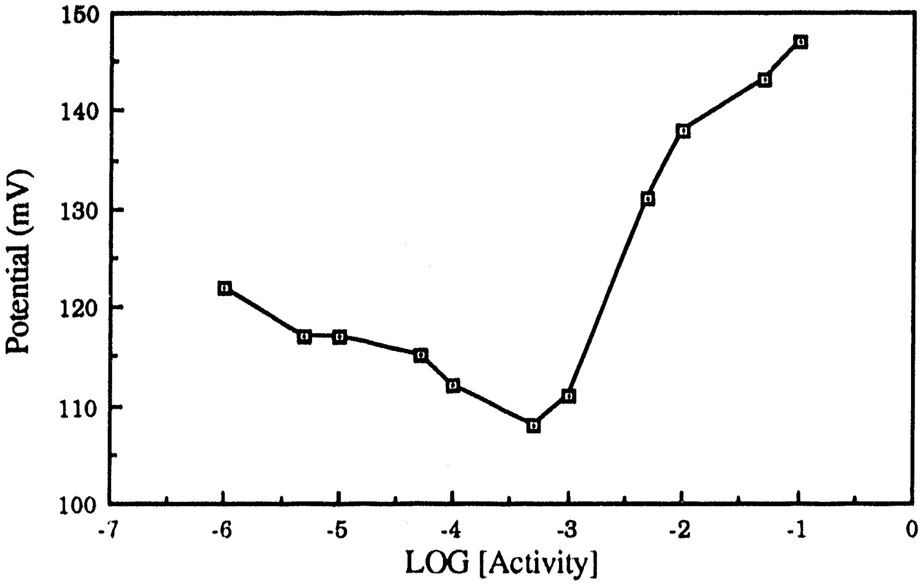


Figure A.31. Linear Portion of Tartaric Acid Calibration #1.

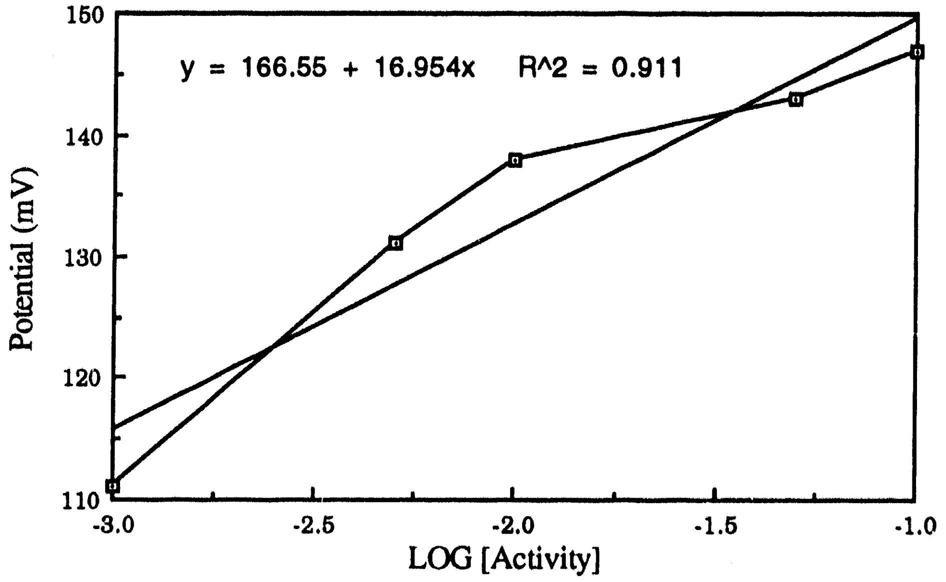


Figure A.32. Calibration #2 of Tartaric Acid Electrodes.

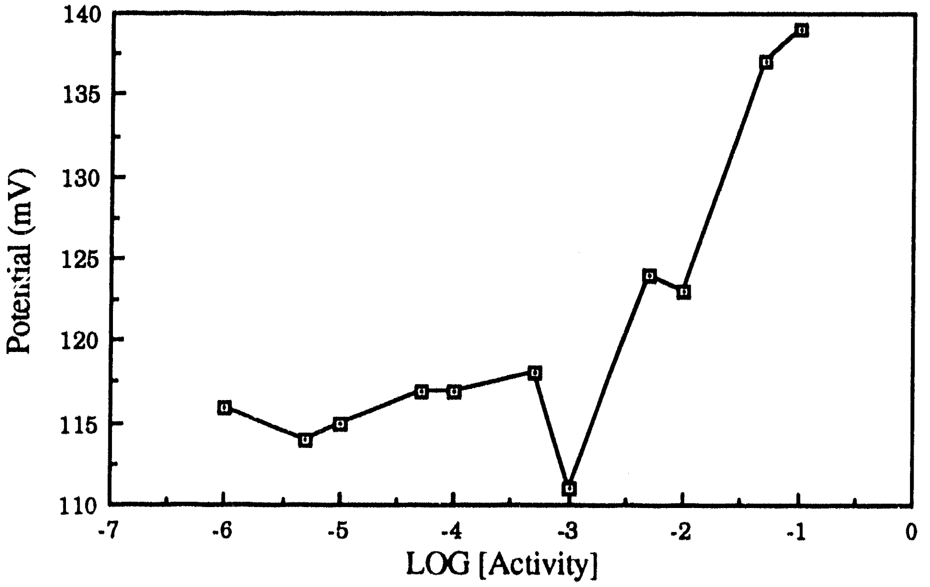


Figure A.33. Linear Portion of Tartaric Acid Calibration #2.

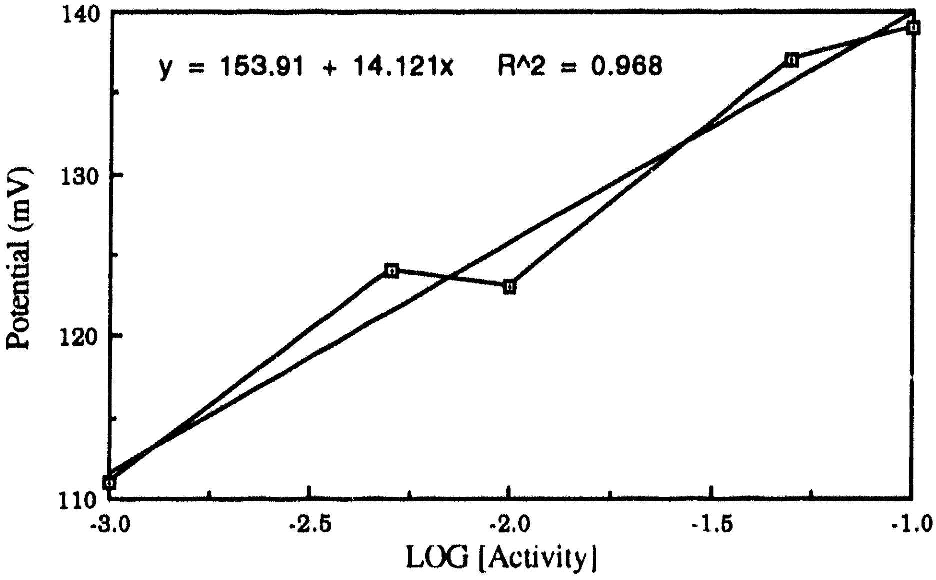


Figure A.34. Calibration #3 of Tartaric Acid Electrodes.

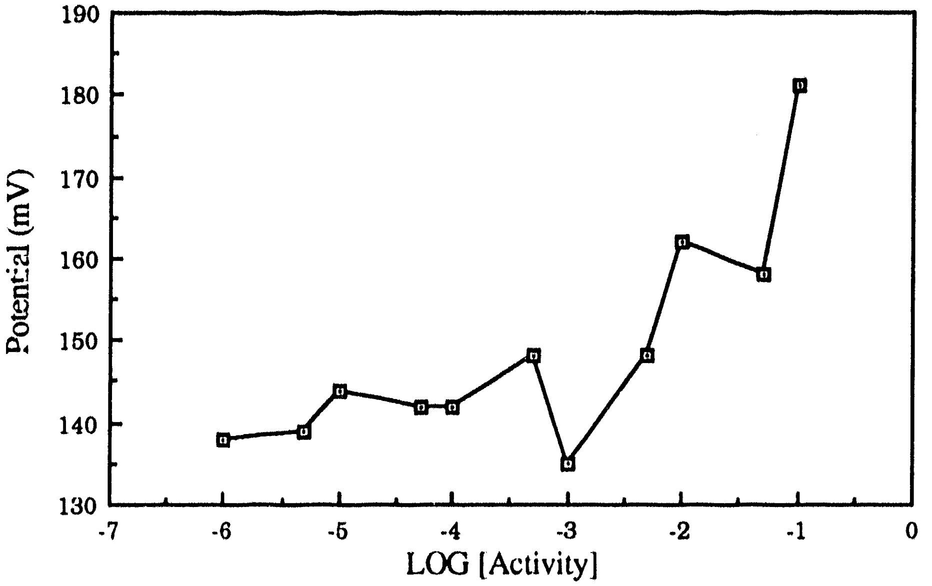


Figure A.35. Linear Portion of Tartaric Acid Calibration #3.

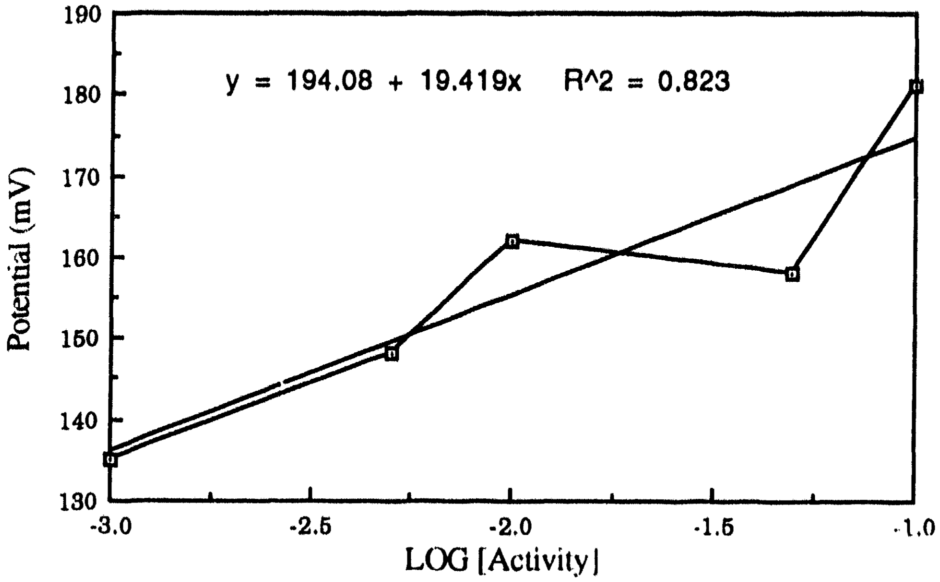


Table A.I. EDTA Calibration Data - Calibration #1

Concentration (M)	Electrode #2 (mV)	Electrode #3 (mV)	Electrode #4 (mV)	Average (mV)
10^{-1}	-116	-108	-100	-108
$10^{-1.3}$	-125	-119	-128	-124
10^{-2}	-154	-155	-159	-156
$10^{-2.3}$	-162	-171	-168	-167
10^{-3}	-200	-192	-193	-195
$10^{-3.3}$	-201	-190	-197	-196
10^{-4}	-158	-162	-160	-160
$10^{-4.3}$	-149	-158	-152	-153
10^{-5}	-132	-133	-125	-130
$10^{-5.3}$	-124	-139	-121	-128
10^{-6}	-112	-118	-109	-113

Table A.II. EDTA Calibration Data - Calibration #2

Concentration (M)	Electrode #2 (mV)	Electrode #3 (mV)	Electrode #4 (mV)	Average (mV)
10^{-1}	-19	-25	-25	-23
$10^{-1.3}$	-40	-42	-44	-42
10^{-2}	-77	-71	-80	-76
$10^{-2.3}$	-93	-89	-88	-90
10^{-3}	-119	-119	-120	-120
$10^{-3.3}$	-124	-123	-119	-122
10^{-4}	-90	-83	-85	-86
$10^{-4.3}$	-48	-51	-54	-51
10^{-5}	-43	-39	-41	-41
$10^{-5.3}$	-31	-38	-36	-35
10^{-6}	-18	-30	-24	-24

Table A.III. EDTA Calibration Data - Calibration #3

Concentration (M)	Electrode #2 (mV)	Electrode #3 (mV)	Electrode #4 (mV)	Average (mV)
10^{-1}	-27	-30	-33	-30
$10^{-1.3}$	-42	-41	-40	-41
10^{-2}	-80	-81	-73	-78
$10^{-2.3}$	-85	-88	-85	-86
10^{-3}	-115	-110	-111	-112
$10^{-3.3}$	-108	-105	-108	-107
10^{-4}	-72	-77	-73	-74
$10^{-4.3}$	-73	-74	-72	-73
10^{-5}	-51	-46	-50	-49
$10^{-5.3}$	-35	-36	-40	-37
10^{-6}	-9	-11	-16	-12

Table A.IV. NTA Calibration Data - Calibration #1

Concentration (M)	Electrode #1 (mV)	Electrode #2 (mV)	Electrode #3 (mV)	Average (mV)
10^{-1}	215	202	204	207
$10^{-1.3}$	201	192	192	195
10^{-2}	171	168	165	168
$10^{-2.3}$	153	149	142	148
10^{-3}	131	125	113	123
$10^{-3.3}$	112	107	111	110
10^{-4}	163	152	162	159
$10^{-4.3}$	155	150	160	155
10^{-5}	178	177	185	180
$10^{-5.3}$	178	170	174	174
10^{-6}	184	177	167	176

Table A.V. NTA Calibration Data - Calibration #2

Concentration (M)	Electrode #1 (mV)	Electrode #2 (mV)	Electrode #3 (mV)	Average (mV)
10^{-1}	208	205	199	204
$10^{-1.3}$	202	198	200	200
10^{-2}	155	149	149	151
$10^{-2.3}$	136	138	134	136
10^{-3}	111	110	103	108
$10^{-3.3}$	102	96	99	99
10^{-4}	151	151	154	152
$10^{-4.3}$	162	164	151	159
10^{-5}	178	172	172	174
$10^{-5.3}$	180	171	171	174
10^{-6}	181	173	183	179

Table A.VI. NTA Calibration Data - Calibration #3

Concentration (M)	Electrode #1 (mV)	Electrode #2 (mV)	Electrode #3 (mV)	Average (mV)
10^{-1}	210	204	201	205
$10^{-1.3}$	205	197	195	199
10^{-2}	168	168	171	169
$10^{-2.3}$	147	146	139	144
10^{-3}	125	119	122	122
$10^{-3.3}$	118	110	105	111
10^{-4}	165	162	165	164
$10^{-4.3}$	161	159	151	157
10^{-5}	177	178	200	185
$10^{-5.3}$	180	179	184	181
10^{-6}	190	182	183	185

Table A.VII. Citric Acid Calibration Data - Calibration #1

Concentration (M)	Electrode #1 (mV)	Electrode #3 (mV)	Electrode #4 (mV)	Average (mV)
10^{-1}	124	134	126	128
$10^{-1.3}$	120	129	126	125
10^{-2}	110	104	98	104
$10^{-2.3}$	100	99	95	98
10^{-3}	85	83	93	87
$10^{-3.3}$	82	80	75	79
10^{-4}	69	75	72	72
$10^{-4.3}$	83	86	80	83
10^{-5}	102	99	96	99
$10^{-5.3}$	109	109	100	106
10^{-6}	109	107	105	107

Table A.VIII. Citric Acid Calibration Data - Calibration #2

Concentration (M)	Electrode #1 (mV)	Electrode #3 (mV)	Electrode #4 (mV)	Average (mV)
10^{-1}	144	151	158	151
$10^{-1.3}$	142	135	152	143
10^{-2}	130	117	122	123
$10^{-2.3}$	122	112	114	117
10^{-3}	120	109	110	113
$10^{-3.3}$	103	105	98	102
10^{-4}	93	93	87	91
$10^{-4.3}$	110	108	104	107
10^{-5}	119	114	115	116
$10^{-5.3}$	119	115	120	118
10^{-6}	126	125	133	128

Table A.IX. Citric Acid Calibration Data - Calibration #3

Concentration (M)	Electrode #1 (mV)	Electrode #3 (mV)	Electrode #4 (mV)	Average (mV)
10^{-1}	139	141	149	143
$10^{-1.3}$	125	130	135	130
10^{-2}	110	114	109	111
$10^{-2.3}$	106	108	104	106
10^{-3}	101	90	95	89
$10^{-3.3}$	74	82	84	80
10^{-4}	76	77	81	78
$10^{-4.3}$	92	88	93	91
10^{-5}	101	94	102	99
$10^{-5.3}$	110	108	109	109
10^{-6}	110	108	109	108

Table A.X. Oxalic Acid Calibration Data - Calibration #1

Concentration (M)	Electrode #1 (mV)	Electrode #2 (mV)	Electrode #3 (mV)	Average (mV)
10^{-1}	195	190	194	193
$10^{-1.3}$	205	193	193	197
10^{-2}	200	189	190	193
$10^{-2.3}$	203	187	210	200
10^{-3}	197	187	186	190
$10^{-3.3}$	180	180	171	177
10^{-4}	163	164	156	161
$10^{-4.3}$	161	150	148	153
10^{-5}	132	129	129	130
$10^{-5.3}$	123	117	117	119
10^{-6}	127	118	115	120

Table A.XI. Oxalic Acid Calibration Data - Calibration #2

Concentration (M)	Electrode #1 (mV)	Electrode #2 (mV)	Electrode #3 (mV)	Average (mV)
10^{-1}	200	211	195	202
$10^{-1.3}$	215	210	211	212
10^{-2}	216	208	203	209
$10^{-2.3}$	205	204	200	203
10^{-3}	198	200	199	199
$10^{-3.3}$	197	200	203	200
10^{-4}	185	185	176	182
$10^{-4.3}$	180	176	181	179
10^{-5}	160	160	169	163
$10^{-5.3}$	140	134	126	133
10^{-6}	132	126	141	133

Table A.XII. Oxalic Acid Calibration Data - Calibration #3

Concentration (M)	Electrode #1 (mV)	Electrode #2 (mV)	Electrode #3 (mV)	Average (mV)
10^{-1}	214	216	215	215
$10^{-1.3}$	217	215	210	214
10^{-2}	207	212	208	209
$10^{-2.3}$	204	217	209	210
10^{-3}	202	197	195	198
$10^{-3.3}$	200	195	199	198
10^{-4}	180	177	189	182
$10^{-4.3}$	179	179	182	180
10^{-5}	158	152	149	153
$10^{-5.3}$	139	140	144	141
10^{-6}	129	150	141	140

Table A.XIII. Tartaric Acid Calibration Data - Calibration #1

Concentration (M)	Electrode #1 (mV)	Electrode #2 (mV)	Electrode #3 (mV)	Average (mV)
10^{-1}	155	142	144	147
$10^{-1.3}$	156	125	148	143
10^{-2}	147	128	139	138
$10^{-2.3}$	140	124	129	131
10^{-3}	115	110	108	111
$10^{-3.3}$	114	116	94	108
10^{-4}	110	115	111	112
$10^{-4.3}$	115	119	111	115
10^{-5}	112	122	117	117
$10^{-5.3}$	108	124	119	117
10^{-6}	108	137	121	122

Table A.XIV. Tartaric Acid Calibration Data - Calibration #2

Concentration (M)	Electrode #1 (mV)	Electrode #2 (mV)	Electrode #3 (mV)	Average (mV)
10^{-1}	150	140	127	139
$10^{-1.3}$	142	139	130	137
10^{-2}	125	133	111	123
$10^{-2.3}$	122	130	120	124
10^{-3}	108	122	103	111
$10^{-3.3}$	117	124	113	118
10^{-4}	111	120	120	117
$10^{-4.3}$	113	114	124	117
10^{-5}	112	110	123	115
$10^{-5.3}$	108	111	123	114
10^{-6}	109	119	120	116

Table A.XV. Tartaric Acid Calibration Data - Calibration #3

Concentration (M)	Electrode #1 (mV)	Electrode #2 (mV)	Electrode #3 (mV)	Average (mV)
10^{-1}	185	177	181	181
$10^{-1.3}$	160	172	142	158
10^{-2}	159	157	170	162
$10^{-2.3}$	151	150	143	148
10^{-3}	140	136	129	135
$10^{-3.3}$	142	151	151	148
10^{-4}	142	150	134	142
$10^{-4.3}$	139	156	131	142
10^{-5}	138	157	137	144
$10^{-5.3}$	140	137	140	139
10^{-6}	137	135	142	138

APPENDIX [illegible]

Electrode-Cement Data

Figure B.1. EDTA Two Point Calibration Used for Electrode-Cement Test.

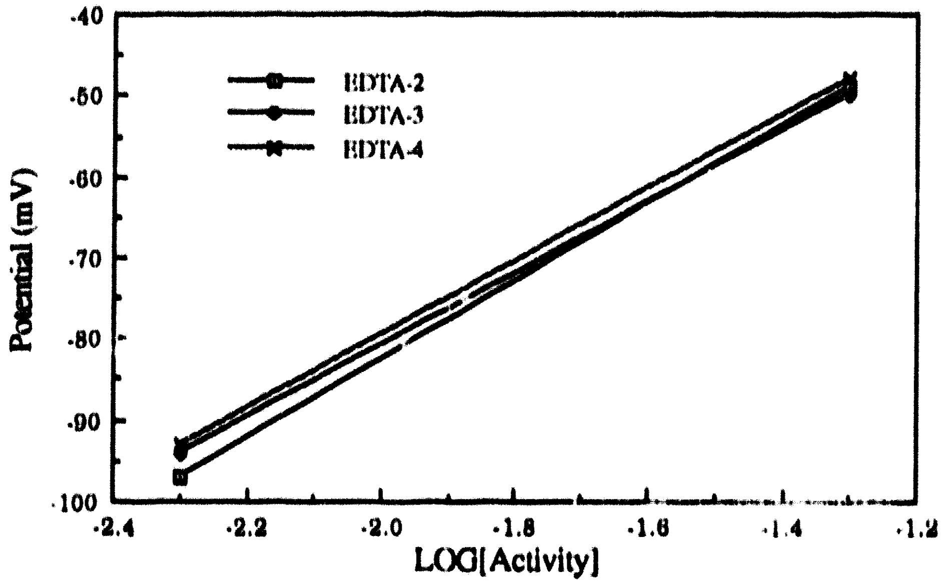


Figure B.2. Two Point Calibration of EDTA Electrode #2.

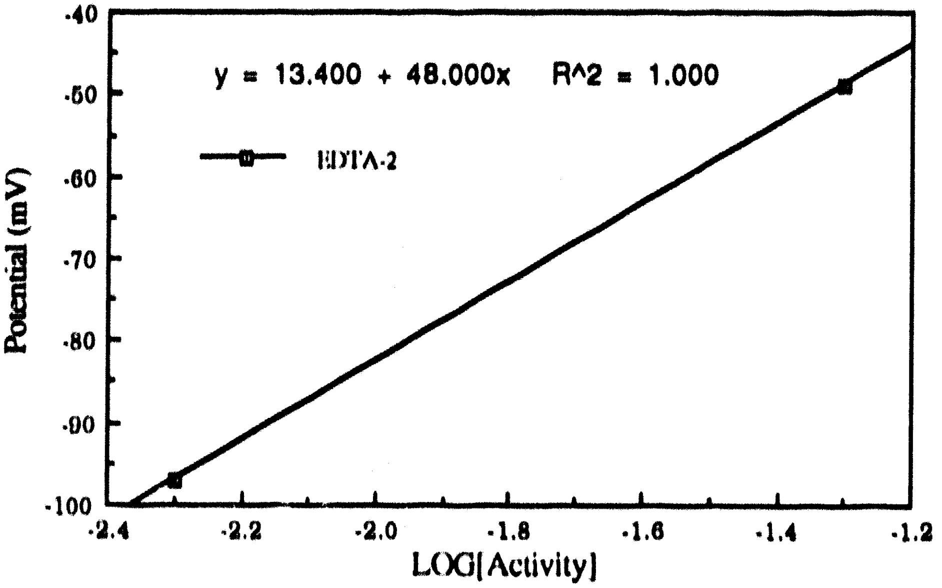


Figure B.3. Two Point Calibration of EDTA Electrode #3.

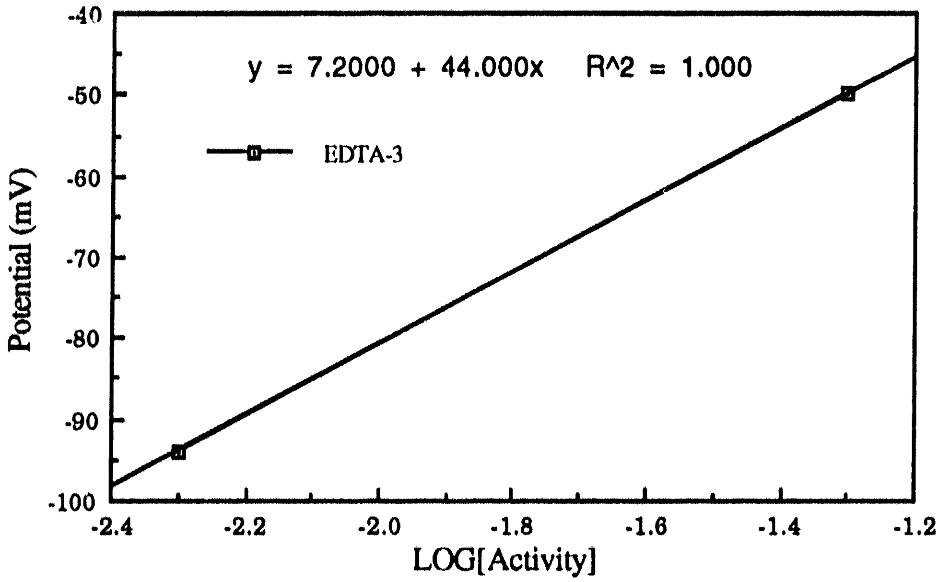


Figure B.4. Two Point Calibration of EDTA Electrode #4.

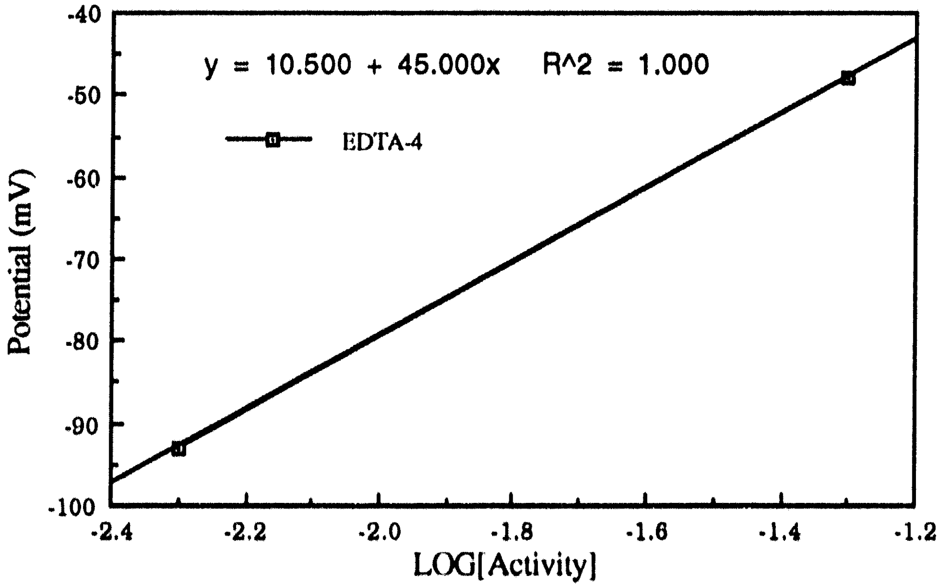


Figure B.5. Comparison of Cement Sample Data Using EDTA Electrode #2.

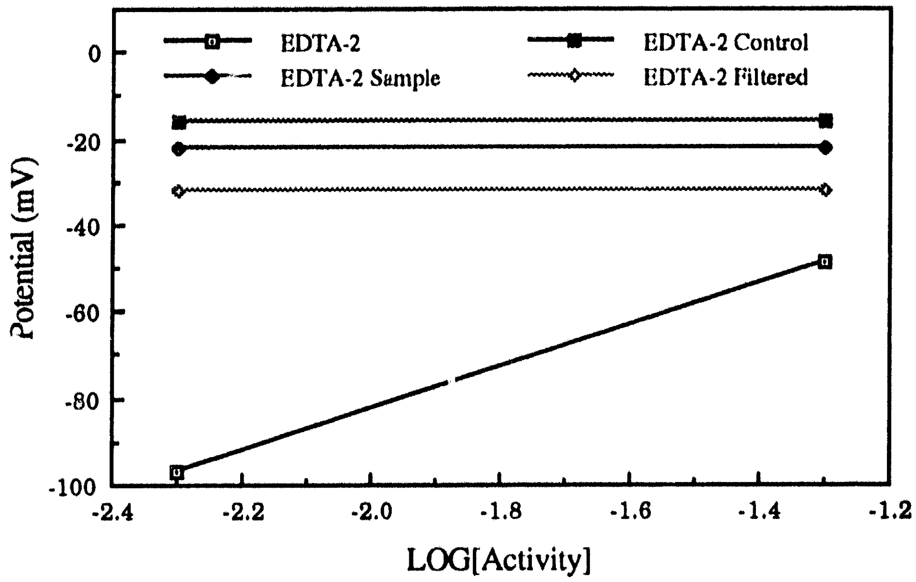


Figure B.6. Comparison of Cement Sample Data Using EDTA Electrode #3.

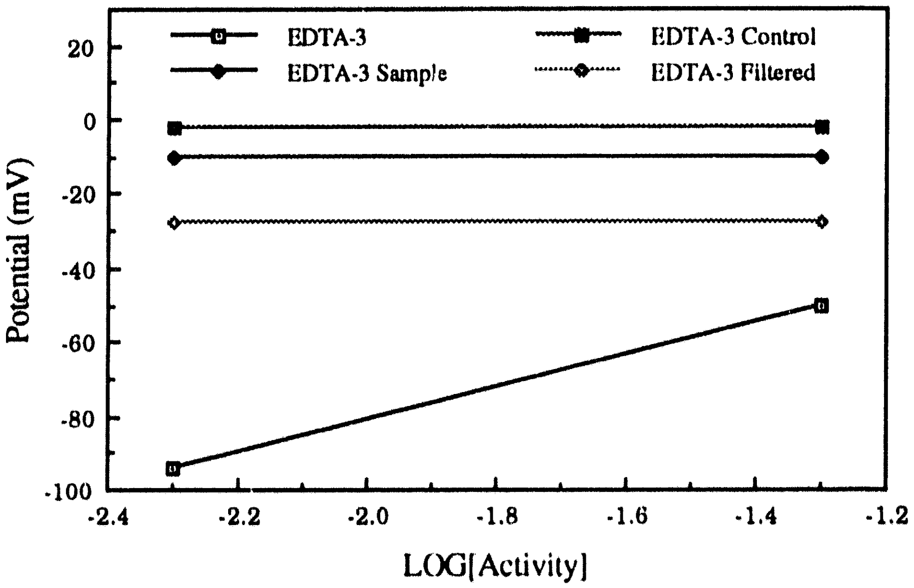


Figure B.7. Comparison of Cement Sample Data Using EDTA Electrode #4.

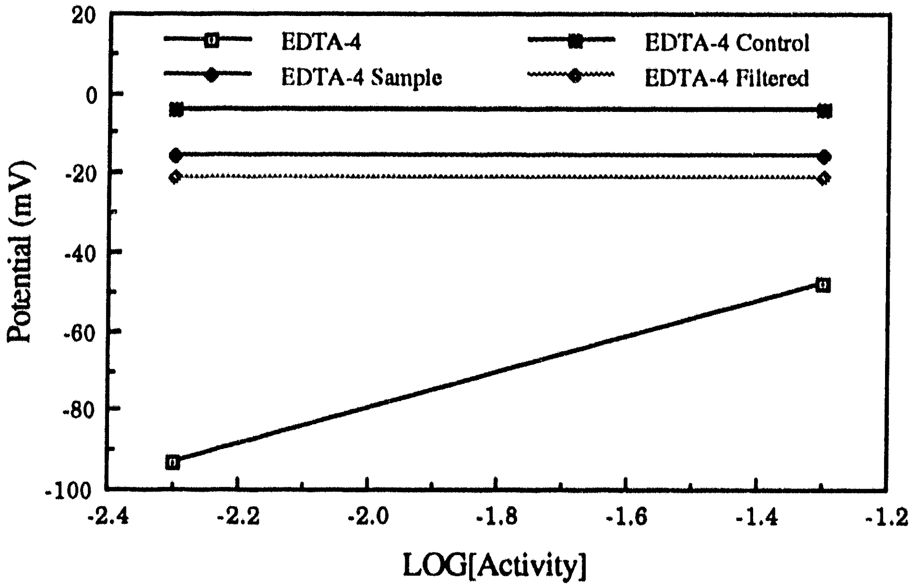


Figure B.8. NTA Two Point Calibration
Used for Electrode-Cement Test.

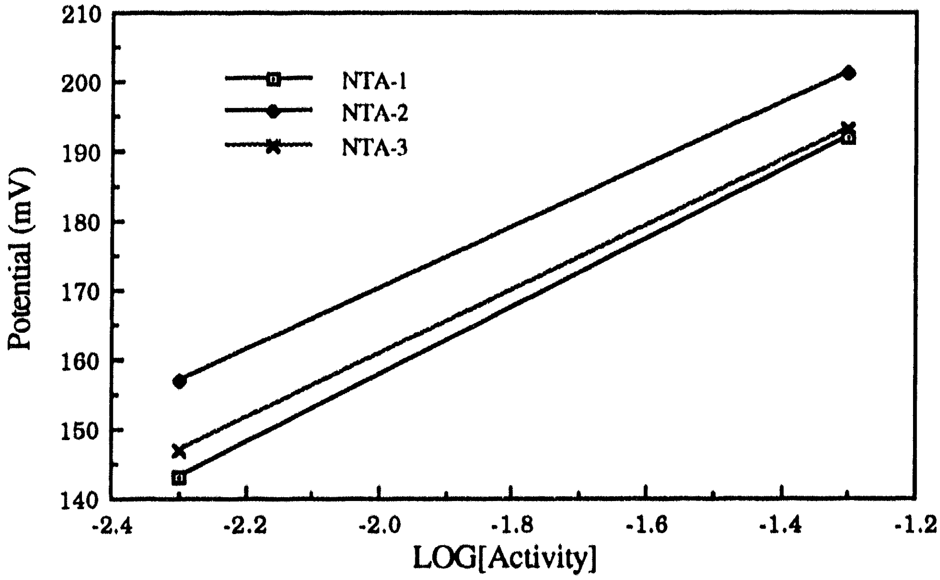


Figure B.9. Two Point Calibration of NTA Electrode #1.

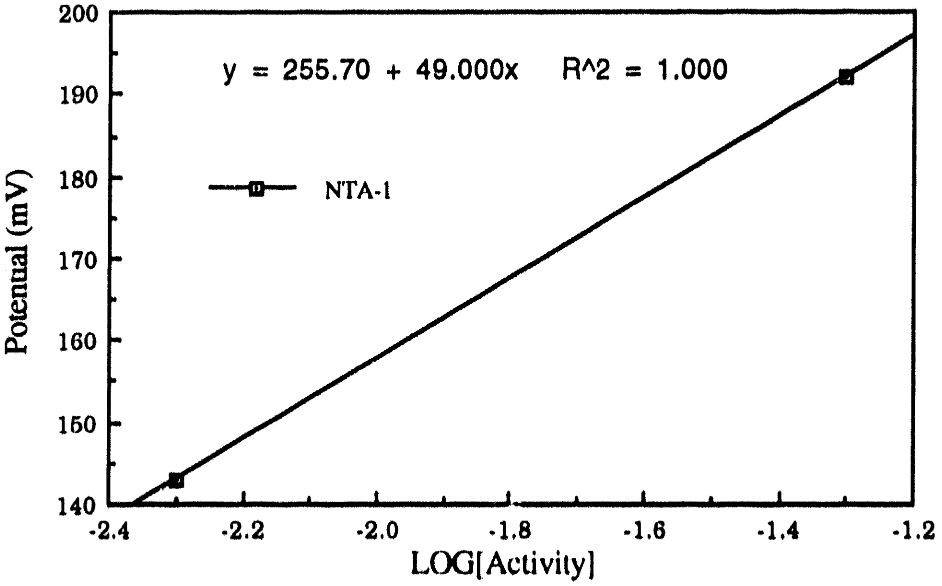


Figure B.10. Two Point Calibration of NTA Electrode #2.

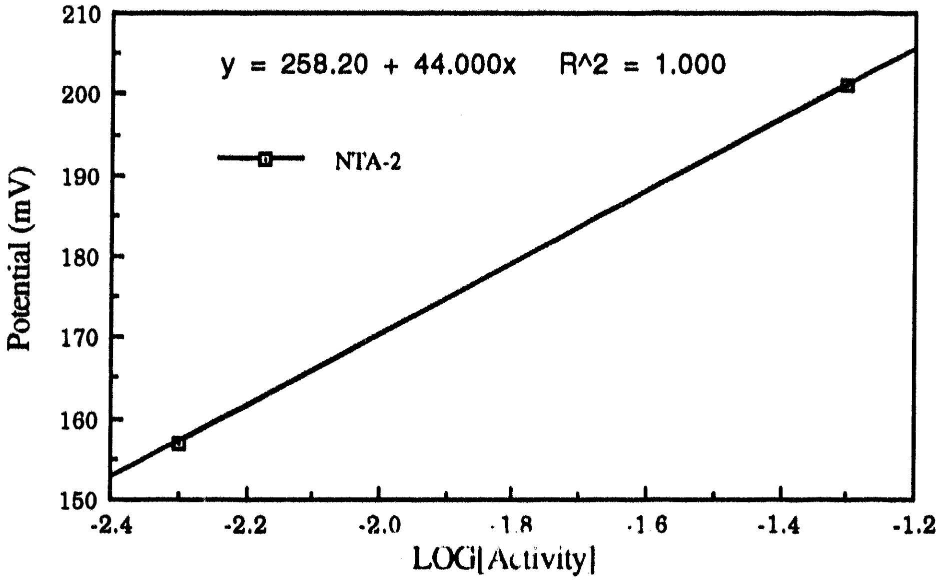


Figure B.11. Two Point Calibration of NTA Electrode #3.

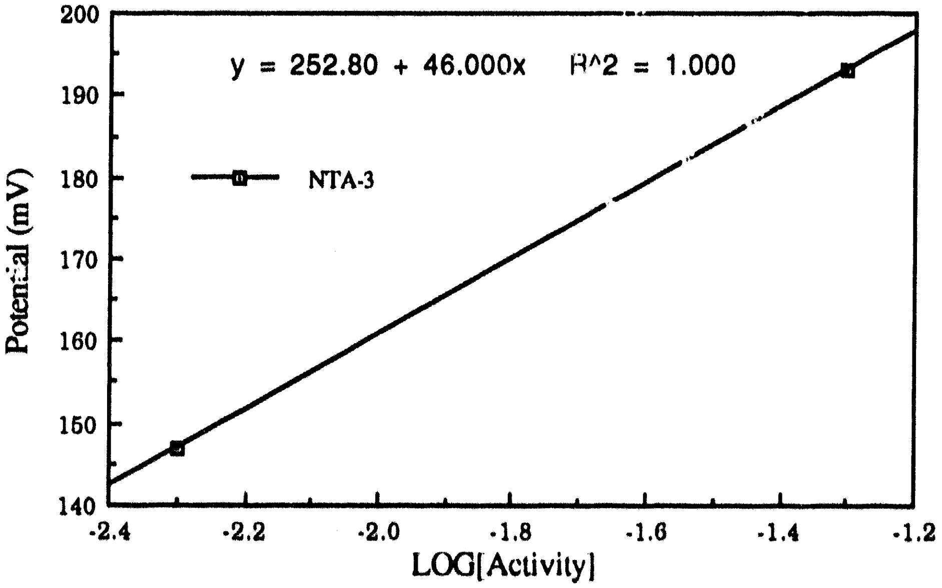


Figure B.12. Comparison of Cement Sample Data Using NTA Electrode #1.

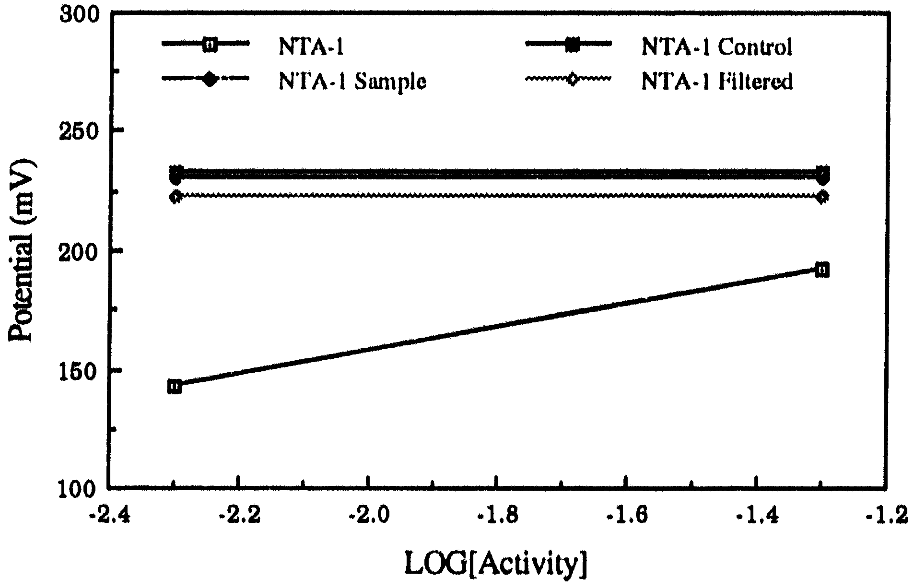


Figure B.13. Comparison of Cement Sample Data Using NTA Electrode #2.

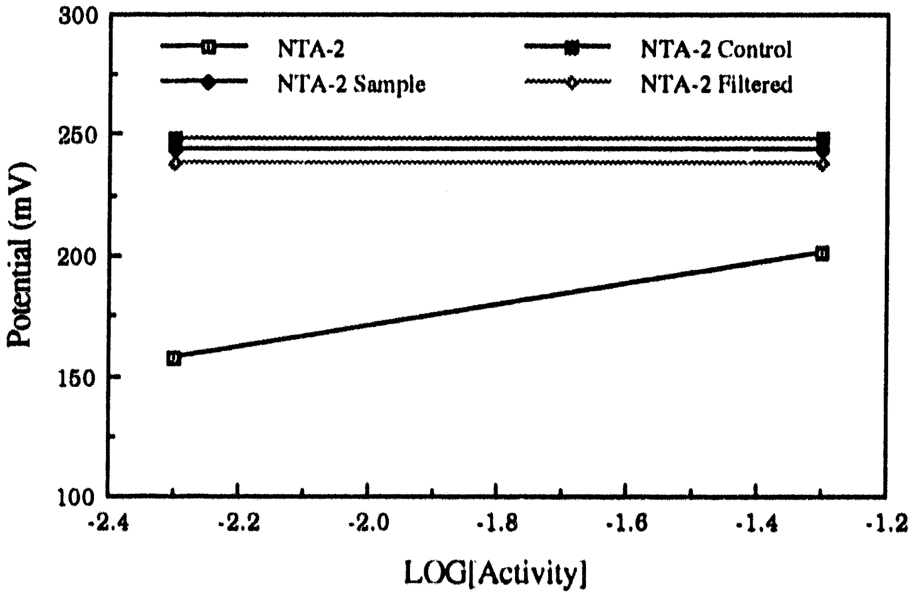


Figure B.14. Comparison of Cement Sample Data Using NTA Electrode #3.

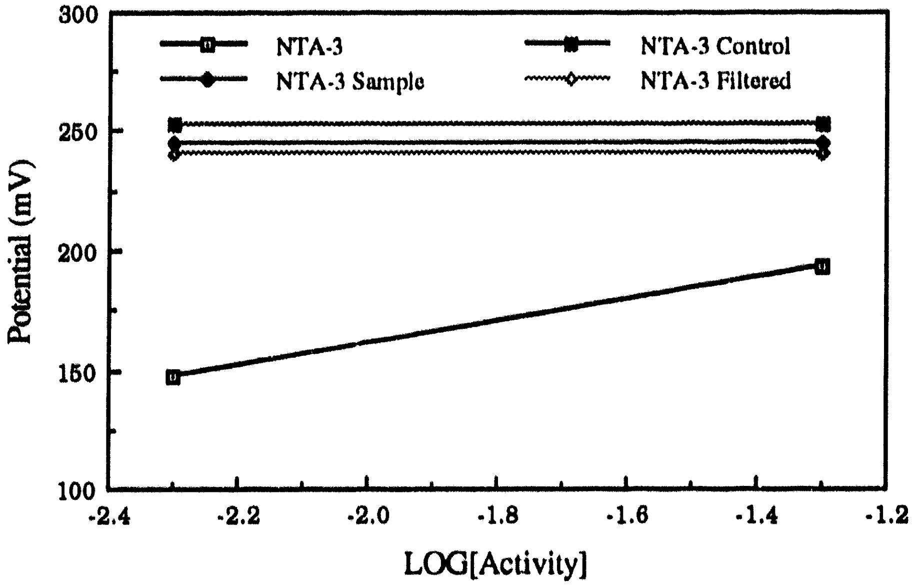


Table B.I. Electrode-Cement Test Data

Electrode	Two Point Cal 0.05 M (mV)	0.005 M (mV)	EDTA/ Cement (mV)	Control (mV)	Filtered (mV)
EDTA					
#2	-49.0	-97.0	-22.0	-16.0	-32.0
#3	-50.0	-94.0	-10.0	-2.0	-28.0
#4	-48.0	-93.0	-16.0	-4.0	-21.0
NTA					
#1	192.0	143.0	230.0	233.0	238.0
#2	201.0	157.0	244.0	248.0	238.0
#3	193.0	147.0	245.0	253.0	240.0

REFERENCES

1. Ayres, J. A. Editor. *Decontamination of Nuclear Reactors and Equipment.* New York: The Ronald Press Company., 1970.

2. Bailey, P. L. *Analysis with Ion-Selective Electrodes.* 2nd Edition. London: Heyden & Sons, LTD., 1980.

3. Bell, C. F. *Principles and Applications of Metal Chelation.* Oxford: Clarendon Press., 1977.

4. Castellan, G. W. *Physical Chemistry.* 3rd Edition. Reading, Massachusetts: Addison-Wesley Publishing Company., 1983.

5. Covington, A. K. *Ion-Selective Electrode Methodology.* Boca Raton: CRC Press, Inc., 1979.

6. Danesi, P. R., R. Chiarizia and G. Scibona. "A Simple Purification Method for the Liquid Cation Exchanger Dinonylnaphthalene Sulfonic Acid (DNNSA)." *Journal of Inorganic Nuclear Chemistry.* Vol. 35., 1973.

7. Ferrara, D. *Detection of Phenothiazines Using Coated Wire Ion-Selective Electrodes.* M. S. Thesis. University of Arizona., 1986. E9791 1986 318.

8. Levine, W. G. *The Chelation of Heavy Metals.* Oxford: Pergamon Press., 1979.

9. Lindsay, W. L. *Chemical Equilibria in Soils.* New York: John Wiley & Sons., 1979.

10. Martin, C. R. and H. Freiser. "Coated-Wire Ion Selective Electrodes and Their Application to the Teaching Laboratory." *Journal of Chemical Education.* Vol. 57. No. 7., July 1980.

11. Martin, C. R. and H. Freiser. "Response Characteristics of Ion Selective Electrodes Based on Dinonylnaphthalenesulfonic Acid." *Analytical Chemistry.* Vol. 52. No. 3., March 1980.

12. Means, J. L. and C. A. Alexander. *The Environmental Geochemistry of Chelating Agents and Radionuclide-Chelate Complexes.* DE84010690. Battelle-Columbus Laboratories, 1980.

13. Morrison, R. T. and R. N. Boyd. *Organic Chemistry.* 3rd Edition. Boston: Allyn and Bacon, Inc., 1973.

14. Swanson, J. L. *Organic Complexant-Enhanced Mobility of Toxic Elements in Low-Level Wastes.* NUREG/CR-4660. Pacific Northwest Laboratory., 1986.

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