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ORTHO-AMINOBENZENETHIOL: A NEW REAGENT
FOR POTENTIOMETRIC TITRATIONS

A DISSERTATION
SUBMITTED TO THE GRADUATE FACULTY
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degree of
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BY
RICHARD SIBLEY MITCHELL
Norman, Oklahoma
1964

ORTHO-AMINOBENZENETHIOL: A NEW REAGENT
FOR POTENTIOMETRIC TITRATIONS

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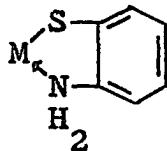
ORTHO-AMINOENZETHIOL: A NEW REAGENT
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CHAPTER I

INTRODUCTION

Organic materials which will combine with metal ions to form ring compounds are becoming increasingly important in inorganic analysis. Chelate compounds have at least one ring which usually consists of five or six atoms. Chelates can be either water soluble or water insoluble. Often the water insoluble organic derivatives of metal ions will be totally unlike typical metal salts in that they have low melting points, are volatile, and dissolve in organic solvents.

The compound o-aminobenzenethiol can be classified as a chelating agent due to the reactive grouping $\text{N}-\text{C}=\text{C}-\text{SH}$. A chelate of o-aminobenzenethiol with a monovalent metal would have the formal structure:



while a bivalent metal would require two molecules of the

reagent. The bond between the metal atom and sulfur would be a covalent bond while the metal-nitrogen bond would be a coordinate covalent bond as indicated by the arrow.

Hofman (8) first reported the preparation of o-aminobenzenethiol by fusing 2-phenylbenzothiazole with potassium hydroxide to form benzoic acid and the thiol. Hofman also reported that the thiol was slowly oxidized to the disulfide by air and rapidly by an oxidizing agent such as ferric chloride. The commercial preparation of o-aminobenzenethiol was reported by C. H. Lumsden (13) in 1930. The compound was prepared by treatment of 2-mercaptobenzothiazole with a solution of sodium hydroxide in a closed vessel at an elevated temperature. Knowles and Watt (10) have described the preparation of the thiol by reduction of benzothiazole with sodium in liquid ammonia and also by reduction with nascent hydrogen generated by the interaction of ammonium bromide with sodium in liquid ammonia, followed by hydrolysis and steam distillation. Lazier and Signaizo (12) have a patent for the production of thiols, including o-aminobenzenethiol, by the hydrogenation of esters of thio acids in the presence of a sulfactive catalyst at elevated temperatures and pressures. The patentees suggest these products as useful intermediates for the manufacture of such products as insecticides, rubber chemicals, dyes, and petroleum additives. Garner (4) reported the preparation of o-aminobenzenethiol by refluxing benzothiazole with an aqueous solution of sodium hydroxide

or potassium hydroxide at atmospheric pressure. The thiol is obtained by acidifying the resulting solution of the sodium or potassium salt. Kinstler and Ebel (9) obtained a 99.6% pure o-aminobenzenethiol by using acetic acid to acidify the mixture obtained by the hydrolysis of benzothiazole with an aqueous caustic solution.

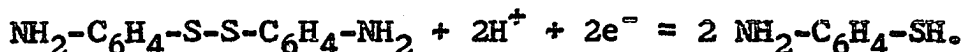
Several metal salts of o-aminobenzenethiol have been reported: lead, by Knowles and Watt (10); zinc, bismuth, mercury, cadmium, iron, gold, and copper by Steiger (15); and nickel and cobalt by Hieber and Bruck (7).

Freiser (3), and Charles and Freiser (2), have determined the dissociation constants of o-aminophenol and o-aminobenzenethiol by potentiometric methods in addition to the stability constants of the chelates of these compounds in a 50% dioxane-water mixture. They report that the chelates of o-aminobenzenethiol are more stable to oxidation despite the fact that the thiol is the more acidic. They cite this as a good indication of the possibility that the strength of the metal-sulfur bond is greater than that of the metal-oxygen bond because of the lower electronegativity of the sulfur and consequent increase in covalent character of the bond. The reactions of o-aminobenzenethiol with several metal ions are described qualitatively and it is suggested that the thiol may be a useful reagent for bismuth.

Hamm (6) has studied the reaction of o-aminobenzene-thiol with thirty-six different ions. In conjunction with

his survey as to the application of the thiol to inorganic analysis, he has used the chelating characteristics of this compound for a spectrophotometric analysis of bismuth, a volumetric analysis of selenium, and a gravimetric analysis of silver.

The compound o-aminobenzenethiol is easily oxidized to bis-(2-aminophenyl-) disulfide. The reverse reaction is also easily accomplished. Mitchell (14) has shown that a reversible electrode is obtained when equilibrium occurs between the two species. This half-cell reaction can be expressed by the following equation:



In an acid solution of pH range from 2.8 to 5.5, the above reaction is reversible and the standard potential for the half cell is $+0.127 \pm .004$ volts.

O-aminobenzenethiol is a bifunctional aromatic compound which is highly reactive. It therefore has many applications as an intermediate in organic reactions. An outline of such applications with an appropriate bibliography may be found in a publication of the American Cyanamid Company (1). The literature related to such applications is outside the scope of this investigation.

The known physical properties of o-aminobenzenethiol are listed in Table I and those for the disulfide in Table II. The data for Table I were obtained at Stamford Research

TABLE I

Physical Properties of O-aminobenzenethiol

Appearance	Colorless liquid*
Molecular Weight (theory)	125.18
Freezing Point	$23 \pm 0.5^{\circ} \text{C}$
Boiling Point	227.2°C
Heat of Vaporization	14.1 kcal
Flash Point (Tagliabue Closed Cup)	$>175^{\circ} \text{F}$ ($>80^{\circ} \text{C}$)
Density	1.168 g/cc at 25°C
Refractive Index	$n_D^{25} = 1.6390$
Viscosity	0.0395 poises at 30°C
Surface Tension	44.5 dynes/cm
Dissociation Constant, K_a (thiol)	1.6×10^{-7}
Dissociation Constant, K_b (amine)	1×10^{-11}
Solubility	
Water	0.7 g/100 cc at 30°C
Heptane	7 g/100 cc at 30°C

The manufacturer advises that o-aminobenzenethiol may cause dermatitis and suggests the use of rubber gloves to avoid skin contact.

* Exposure to air causes rapid yellowing due to oxidation.

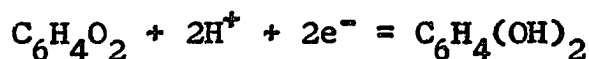
TABLE II

Physical Properties of bis-(2-aminophenyl-) Disulfide

Appearance	Colorless Crystals
Molecular Weight (theory)	248.36
Melting Point	92.5 - 92.7 ⁰ C
Solubility	
Water	Insoluble hot
Toluene	Slightly soluble cold, soluble hot
Alcohol	Soluble hot
Acetone	Soluble hot

Laboratories of the American Cyanamid Company using a redistilled sample of 95% purity.

Many reversible organic oxidation-reduction systems are known. Some are reversible over a very narrow pH range and serve as oxidation-reduction indicators. Glasstone and Hickling (5) state that all quinones and their derivatives together with the corresponding hydroquinones appear to give reversible oxidation-reduction systems. Other organic compounds such as indigo and its sulfonic acids, methylene blue, various indophenols, xanthine and other purine derivatives, azo-compounds and nitrosobenzene will also give a reversible oxidation-reduction system. Of these, the quinone-hydroquinone is the best known. The equation for this half-reaction is:



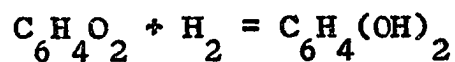
The potential of such a half-cell forming a galvanic cell with the standard hydrogen half-cell can be expressed by the Nernst equation:

$$E = \frac{RT}{nF} \ln K - \frac{RT}{nF} \ln Q .$$

The standard potential, E^0 , is the value obtained when all gases involved in the equilibrium have a fugacity of 1 atmosphere and all dissolved substances have an activity of 1 molal. Thus,

$$E^{\circ} = \frac{RT}{nF} \ln K$$

where K = the equilibrium constant for the reaction



R = the perfect gas law constant

F = number of coulombs per Faraday for the reaction

n = number of electrons involved in the reaction.

The second term in the Nernst equation, involving the quantity Q , accounts for the difference in potential when the species involved are not at unit activity.

The potential of a single electrode cannot be measured. The electrode must be combined with another electrode to form a galvanic cell. The potential of a galvanic cell can be measured and is equal to the algebraic sum of the two separate electrode potentials.

Metal ion analysis with a chelating agent sometimes requires an excess of the chelating material to cause a quantitative reaction. Gravimetric and spectrophotometric procedures can often be applied under this condition.

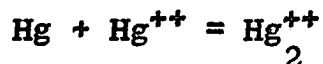
Titrimetric metal ion analysis requires some method of endpoint detection since only an equivalent amount of chelate is to be added. In unbuffered solutions, pH indicator dyes can often be used since many chelating agents release hydrogen ions during chelation of a metal ion; i.e.,



It is often preferable to use buffered solutions for titrations; thus, indicator dyes are required which are sensitive to the metal ion concentration -- just as pH dyes are sensitive to the hydrogen ion indicators.

Laitinen (11) points out that electrode potential measurements are generally not applicable in the case of metal ions. This is because of low exchange current densities. Further, electrode side reactions often lead to "mixed potential phenomena." There is, at present, one electrode which permits potentiometric metal ion titration. The mercury-mercury(II) EDTA complex electrode is suitable as an indicator electrode because:

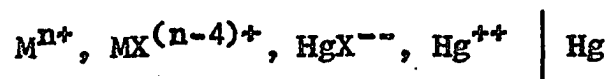
- (a) the electrode has a high exchange current density;
- (b) the equilibrium for the reaction



is very rapid;

- (c) mercury is relatively noble so that the equilibrium potential is not excessively negative despite the stable mercury(II) EDTA complex;
- (d) mixed potential behavior because of hydrogen evolution is prevented by the high hydrogen overpotential of mercury.

Reilley and Schmid (16,17) observed that the mercury-mercury(II) EDTA electrode can be used indirectly as an indicator electrode for some metal ions. When a metal ion-EDTA complex $\text{MX}^{(n-4)+}$ is in equilibrium with mercury and the mercury(II) EDTA complex HgX^{--} , the half-cell



is present. The potential at equilibrium is given by

$$E = E_{Hg^{++}, Hg}^{\circ} + \frac{RT}{2F} \ln \frac{[HgX^{--}]}{[MX^{(n-4)+}]} \frac{K_{MX}}{K_{HgX}} + \frac{RT}{2F} \ln [M^{n+}].$$

During a titration, particularly in the vicinity of the endpoint, the expression

$$E_{Hg^{++}, Hg}^{\circ} + \frac{RT}{2F} \ln \frac{[HgX^{--}]}{[MX^{(n-4)+}]} \frac{K_{MX}}{K_{HgX}}$$

equals a constant. Thus the measured potential of the electrode is a linear function of the metal ion concentration.

CHAPTER II

OBJECTIVES

The objective of this work was to fuse two characteristics of o-aminobenzenethiol into a working arrangement for the quantitative determination of metal ions. The reaction between the thiol and unknown ions might consist of a simple precipitation of a metal (o-amino-) thiophenolate, the formation of a soluble or insoluble chelate, a simple oxidation-reduction reaction, or a combination of a redox mechanism with the subsequent formation of a metal salt. The uniqueness of the analysis would lie in the application of potentiometric procedures to follow the course of a titration in which the potential change at the endpoint and beyond would be entirely due to the titrant itself.

Consequently, the program was broken down into the following subdivisions:

1. Extend the study of the organic electrode through a larger range of pH. This was an attempt to determine if the reaction



would produce a reversible electrode. The pH region in which

the molecular thiol forms a reversible couple with the dimer is restricted to the acid region. Because of the resulting low concentration of thiophenolate ion, many metal chelates will not form.

2. Survey a number of metal ions to determine whether a reaction would occur, the pH at which the reaction would take place, and the resultant change in potential.

3. Develop quantitative titrimetric procedures for the analysis of selected metals with o-aminobenzenethiol using an automatic titrator and determining the equivalence point potentiometrically.

CHAPTER III

THEORY

Mitchell (14) has shown that o-aminobenzenethiol forms a reversible organic electrode in acid media from a pH of 2.8 to 5.5. A plot of potential versus pH for the half-cell reaction



is shown in Figure 1. The linear region shown follows the Nernst equation and has a slope of 0.0587. A least squares treatment of the data yields an intercept at 119 millivolts which corresponds to an E^0 of +0.127 volts. The potential falls off sharply below pH 2.8, presumably due to the protonation of the amine group. Above pH 5.5 the curve again has a change of slope. The acid dissociation constant, K_a , of the thiol is 1.6×10^{-7} . Thus, above pH 5 the amount of ionized thiol becomes significant.

With increased ionization, the amount of molecular thiol in solution will correspondingly decrease. This decrease in concentration will affect the cell potential. Table III shows the results obtained from calculating the electrode potential produced when the total concentration of thiol is

FIGURE 1
CELL POTENTIAL VERSUS pH

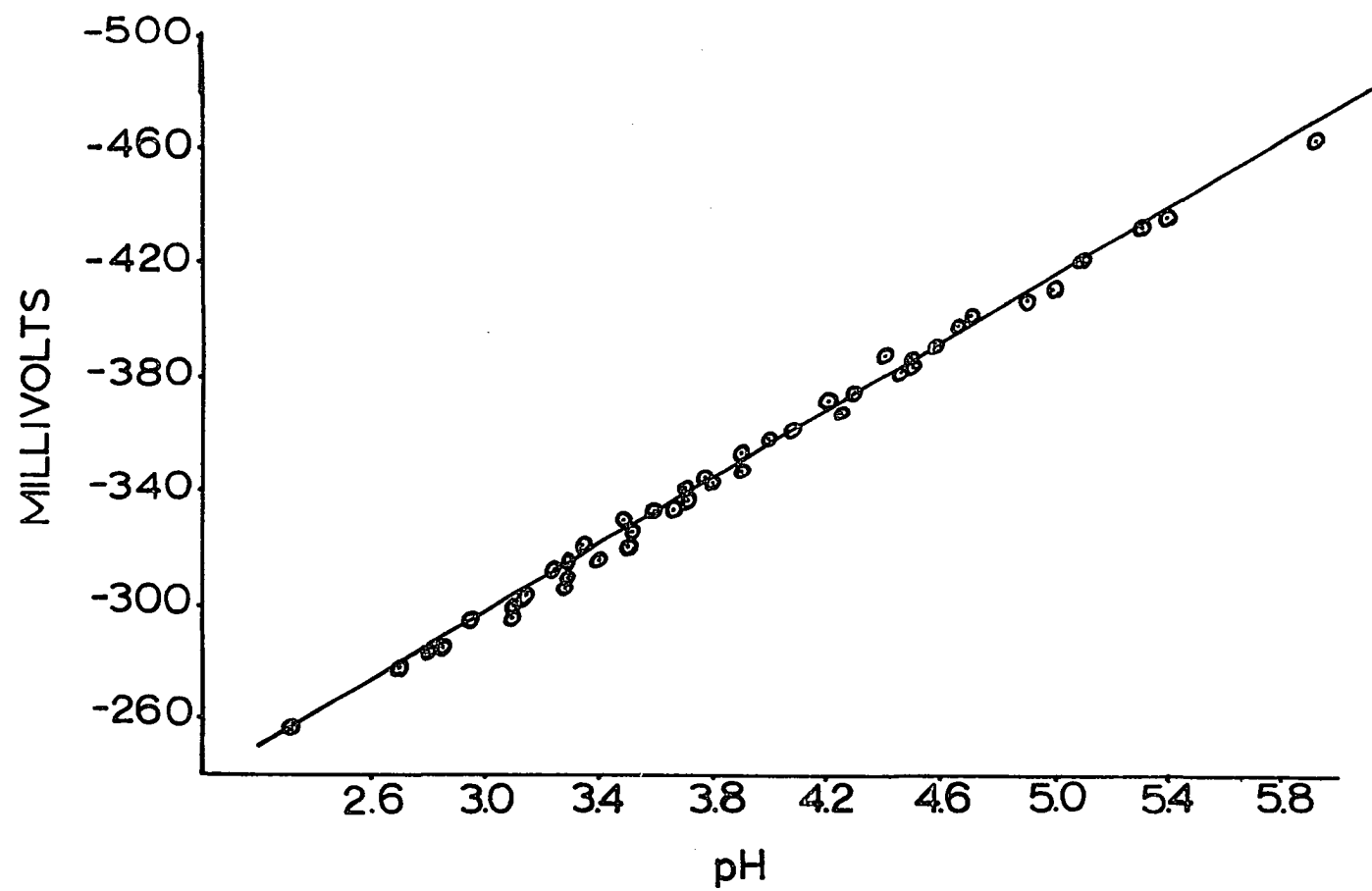


TABLE III

Calculated Electrode Potential

pH	$[H^+]$	$[S^-]$	E_{ce11}
3	10^{-3}	10^{-4}	-59
4	10^{-4}	10^{-4}	-119
5	10^{-5}	10^{-4}	-179
5.5	3.16×10^{-6}	9.5×10^{-5}	-208
6	10^{-6}	8.6×10^{-5}	-235
6.5	3.16×10^{-7}	6.67×10^{-5}	-259
7	10^{-7}	3.85×10^{-5}	-274
7.5	3.16×10^{-8}	1.65×10^{-5}	-282
8	10^{-8}	5.9×10^{-6}	-285
9	10^{-9}	6.2×10^{-7}	-386
10	10^{-10}	6.25×10^{-8}	-287
11	10^{-11}	6.25×10^{-9}	-287

10^{-4} molar and the only electrode process considered is that due to the molecular species. The electrode potential is plotted versus pH in Figure 2. As seen in this figure, there should be two linear regions, below pH 6 and above pH 8. Between these two values, there is a significant change in the ratio of concentrations of the ionized and molecular thiol.

A potential curve similar to Figure 2 should be obtained when only the molecular thiol forms an electrode couple with the disulfide. A second electrode couple may be formed between the ionized thiol and disulfide according to the following reaction:

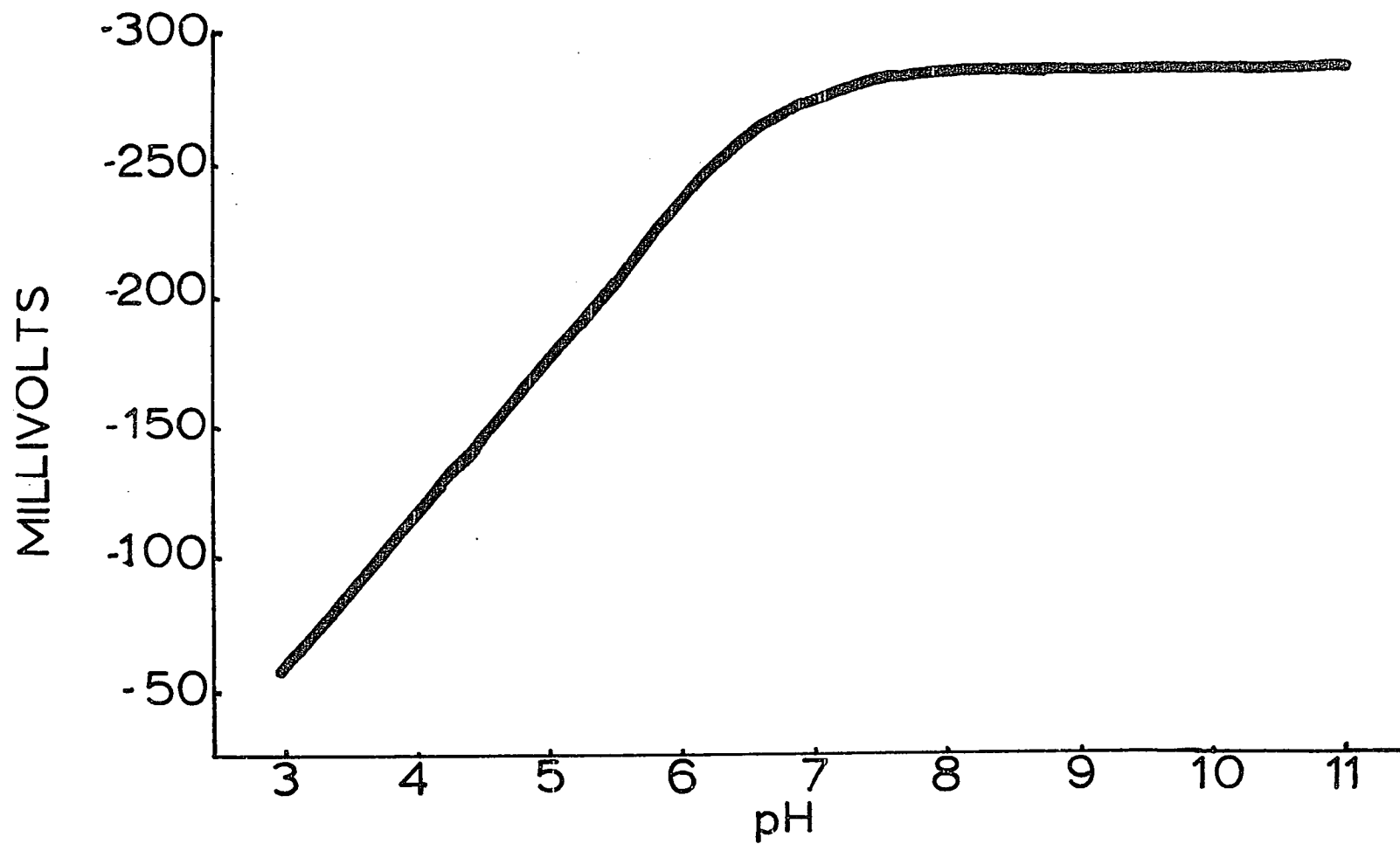


In this event, the observed cell potential would be the sum of the two electrode potentials, both of which will be influenced by changes in concentration. The potential due to the molecular species will be pH dependent and independent of the ionic strength of the solution. The potential due to the ionized species will be independent of pH but dependent upon changes in the ionic strength.

The disulfide is insoluble with the result that the rate of the attainment of solubility equilibrium is slow. The solubility of the molecular thiol is 0.056 moles per liter. The solubility of the salt sodium thiophenolate is much greater than 0.056 molar.

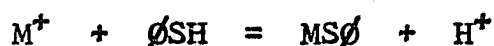
A saturated solution was used to evaluate the half-cell potential of the molecular thiol and disulfide. Because of

FIGURE 2
ELECTRODE POTENTIAL vs pH



the considerably higher solubility of the thiol salt, compared to the free acid, the standard electrode potential is difficult to evaluate. The extent of dissociation of the acid and the activity of the anion will be altered by changes in ionic strength. Thus it will be necessary to know the total thiol concentration, the activity coefficients, and the pH in order to determine the cell potential in alkaline solutions.

The main objective of this work is the potentiometric titration of metal ions using o-aminobenzenethiol as the reagent. For the reaction:



the extent of formation of the metal salt will be dependent upon the hydrogen ion concentration. It is therefore necessary to study the reaction of metal ions with the thiol at various pH values to determine under what conditions, acidic or basic, quantitative reaction occurs. The formation of an insoluble precipitate will not be necessary to make potentiometric titrations feasible, as oxidation-reduction and complex formation could also give titrimetric endpoints.

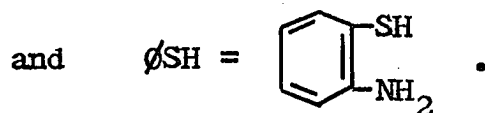
In this problem, it was proposed that o-aminobenzene-thiol be added to a solution of metal ions. The thiol has been shown to form a reversible organic electrode with its dimer, bis-(2-aminophenyl-) disulfide. The disulfide is extremely insoluble. Thus, solutions in contact with thiol

and disulfide will be saturated with respect to the disulfide. The potential observed will be dependent upon the concentration of the thiol.

Before the equivalence point is reached in a metal ion titration, the concentration of thiol will be dependent upon the metal ion concentration and the pH. For buffered systems the pH will remain constant and the dissociation constant of the metal salt may be expressed as follows:

$$K_d' = \frac{[M^+][\phi SH]}{[MS\phi]}$$

where $K_d' = K_d[H^+]$



Therefore,

$$[\phi SH] = K_d' \frac{[MS\phi]}{[M^+]}$$

Further, if the metal salt of the thiol precipitates, the equation may be expressed

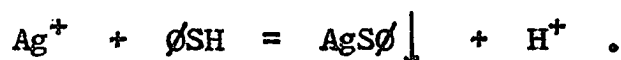
$$[\phi SH] = \frac{K_d''}{[M^+]}$$

where K_d'' represents $K_d'[MS\phi]$, and the thiol concentration is dependent upon the metal ion concentration alone. When two moles of thiol react with a metal ion, the thiol concentration will be given by

$$[\phi SH] = \sqrt{\frac{K_d^n}{[M^{++}]}} .$$

The same type of relationship will be observed whether a chelate or a simple metal salt is formed.

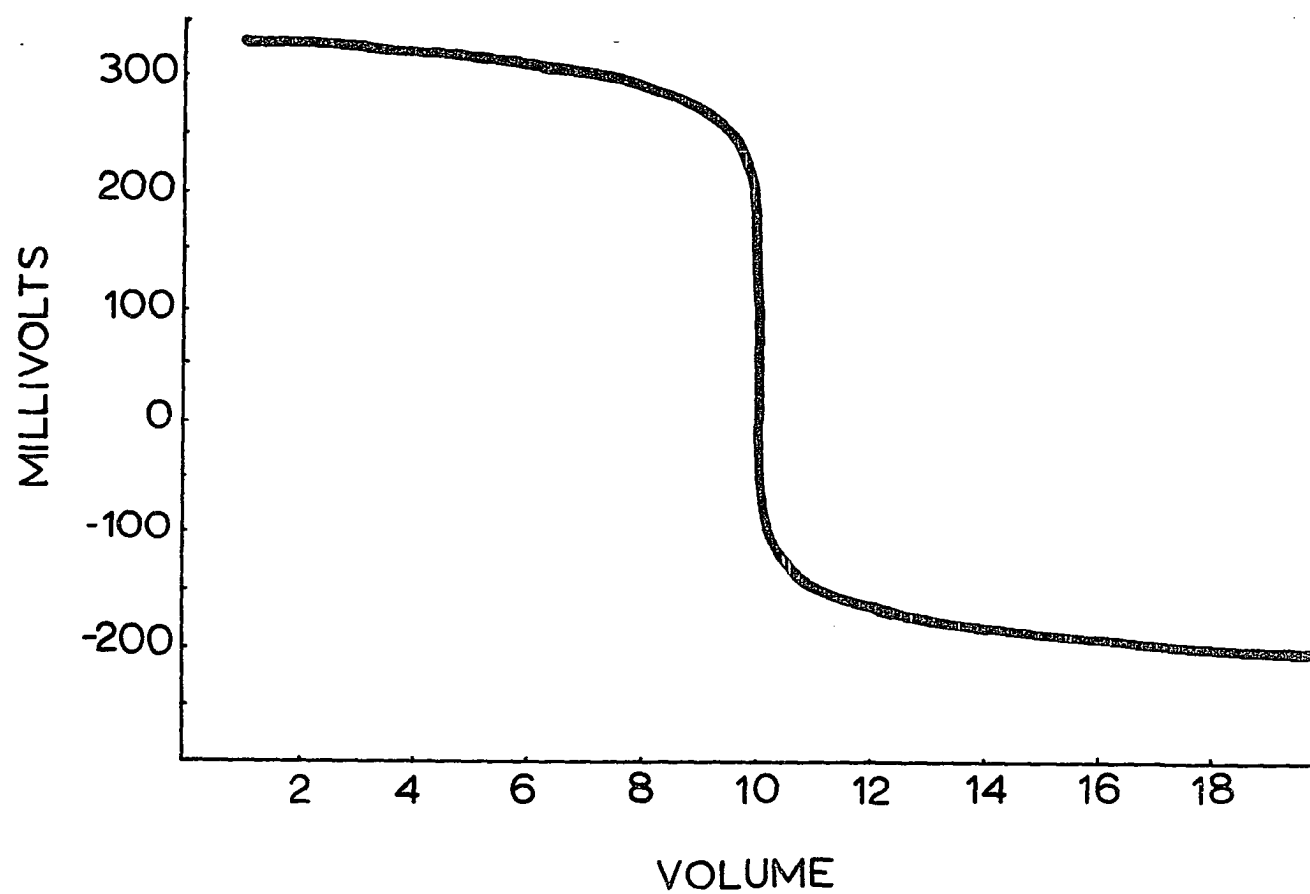
In the titration of silver ion with the thiol, the reaction is 1:1 as follows:



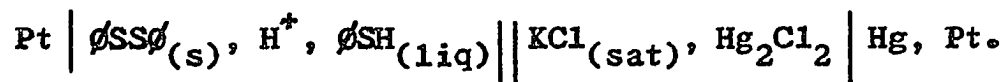
Before the endpoint of the titration, the amount of free thiol will be determined by the solubility product of the precipitate and the excess silver ion remaining in solution. If the K_{sp} is small, the thiol concentration will remain small and relatively constant up to the equivalence point despite the decreasing concentration of silver. Immediately past the equivalence point the thiol concentration will increase greatly and there will be an abrupt change in thiol concentration which will be reflected in the cell potential. Continued addition of thiol past the equivalence point will result in a regular, small increase in thiol concentration and the titration curve will flatten out and approach a constant slope.

Figure 3 is a plot of a theoretical potentiometric titration curve for silver. The calculations were made assuming 50 milliliters of 0.004 molar silver nitrate solution titrated at a pH of 4.00 with a 0.02 molar thiol solution. It was

FIGURE 3
THEORETICAL TITRATION CURVE
for SILVER



assumed that a saturated solution was attained by the time one milliliter of thiol solution had been added. The potential was calculated for the cell



The data for the hypothetical titration are listed in Table IV.

TABLE IV

Data for Theoretical Silver Titration

Vol ϕ_{SH}	$[Ag^+]$	$[\phi_{SH}]$	E_{cell}
0	4×10^{-3}		
1	3.5×10^{-3}	2.9×10^{-12}	.333
2	3.1×10^{-3}	3.2×10^{-12}	.331
3	2.6×10^{-3}	3.8×10^{-12}	.326
4	2.2×10^{-3}	4.5×10^{-12}	.322
5	1.8×10^{-3}	5.6×10^{-12}	.316
6	1.4×10^{-3}	7.1×10^{-12}	.310
7	1.05×10^{-3}	9.5×10^{-12}	.302
8	6.9×10^{-4}	1.5×10^{-11}	.290
9	3.4×10^{-4}	2.9×10^{-11}	.273
9.5	1.7×10^{-4}	5.9×10^{-11}	.255
9.9	3.3×10^{-5}	3×10^{-10}	.212
10.1		5×10^{-5}	-.103
10.5		1.7×10^{-4}	-.133
11		3.3×10^{-4}	-.150
12		6.5×10^{-4}	-.168
13		9.5×10^{-4}	-.178
14		1.25×10^{-3}	-.185
16		1.8×10^{-3}	-.195
18		2.4×10^{-3}	-.202
20		2.9×10^{-3}	-.207

CHAPTER IV

EXPERIMENTAL

Apparatus and Measuring Setup

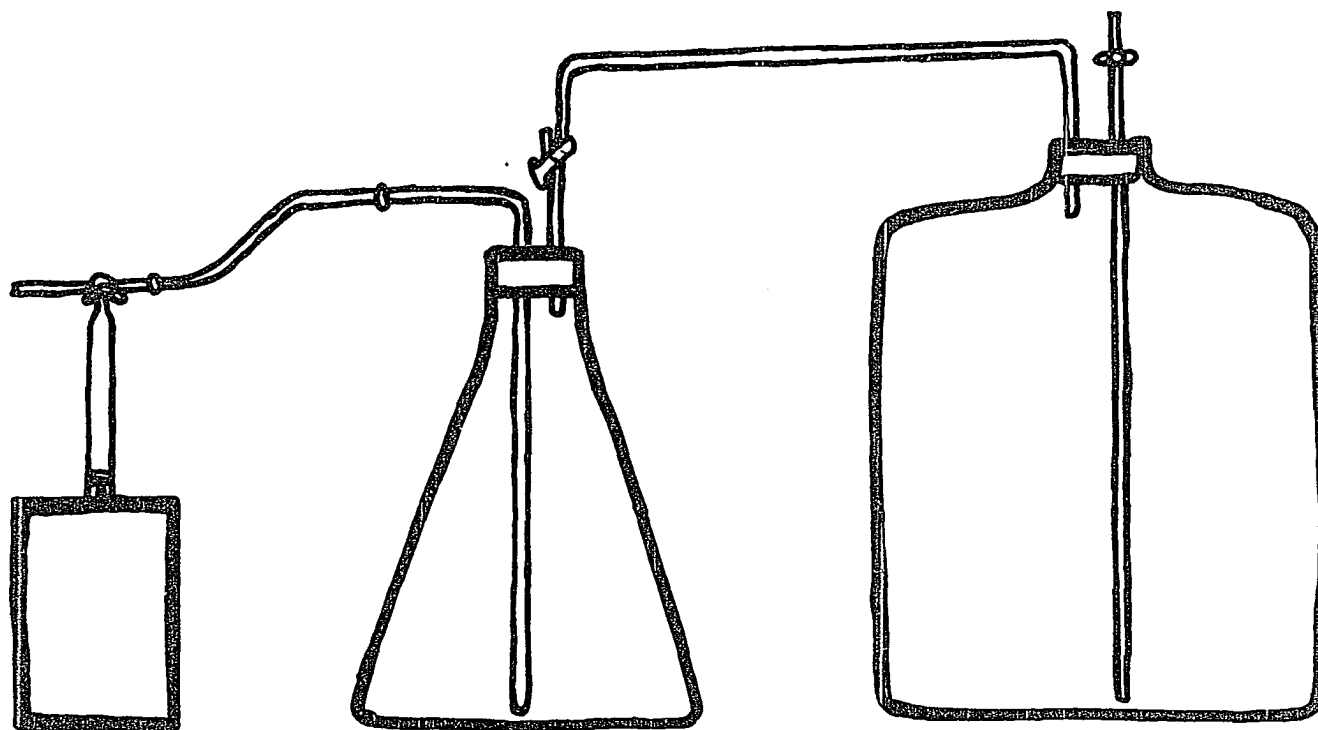
Electrode potentials and pH values were obtained using calomel and platinum electrodes on a Beckman direct reading Zeromatic pH meter.

Potentiometric titrations of metal ions were carried out with the Metrohm E-336 Recording Potentiograph and automatic buret.

The sensitivity of o-aminobenzenethiol to air oxidation required an oxygen-free storage system in order to preserve a standard thiol solution. Figure 4 shows the apparatus which was finally adopted for this purpose. The small container in the center contains the thiol solution. The large container is filled with nitrogen under a small positive pressure. This aided the automatic buret piston when withdrawing titrant from the reservoir and lessened the likelihood of oxygen diffusing into the system and changing the titer.

Electrodes were a Beckman platinum electrode and a Beckman general purpose glass electrode, with a Beckman asbestos fiber calomel electrode used as the reference.

FIGURE 4
THIOL RESERVOIR SYSTEM



Materials and Solutions

The o-aminobenzenethiol and bis-(2-aminophenyl-) disulfide were furnished by the American Cyanamid Company. The o-aminobenzenethiol was approximately 97% pure with the disulfide and water as the principal impurities. The bis-(2-aminophenyl-) disulfide was about 99% pure with water and the thiol as the major impurities.

Reagent grade metal salts and pure metals were used to prepare stock solutions for the analytical studies.

Reagent grade potassium hydrogen phthalate, sodium acetate, ammonium acetate, boric acid, and potassium chloride were used with standardized hydrochloric acid and sodium hydroxide to prepare buffers of known pH for the analytical procedures.

Potential Measurements

In alkaline solution the acid hydrogen of the mercapto group of o-aminobenzenethiol becomes ionized. Thus it was impossible to work with a saturated solution, as was done earlier in acid solution with the thiol when ionization of the mercapto group could be neglected. Therefore, solutions of known thiol concentration and constant ionic strength were used.

Ten milliliters of a thiol solution of known molarity were added to fifty milliliters of one molar potassium chloride solution. The cell potential and pH were measured after constant readings were obtained. The pH was altered

by adding either one molar hydrochloric acid or one molar sodium hydroxide. When the potential remained constant for several minutes, the potential and pH were recorded. All such measurements were made in a solution which had been flushed with nitrogen.

It was observed that the formation of a precipitate occurred rapidly in the alkaline solutions. The precipitate would slowly dissolve when the solution was made acidic. Because of this alteration of the thiol concentration the determination of a meaningful potential for the half-cell combination of ionized and molecular thiol could not be obtained.

Figure 5 is a plot of the data obtained in this portion of the work. The data are listed in Table V. The linear portion of the curve in the acid region confirmed the earlier work. The curve bends about pH 5.5 due to the increasing ionization of the thiol. The data are quite scattered above pH 9. In this region a large amount of precipitate was formed and the variance of the cell potential can be attributed to a variance in thiol concentration.

Ten milliliters of thiol solution were added to 150 milliliters of one molar potassium chloride solution which had been flushed with nitrogen and saturated with the disulfide. The pH and millivoltage were recorded when the readings remained constant for two minutes. The pH was altered using a solution of one molar sodium hydroxide and one molar

FIGURE 5
POTENTIAL vs pH

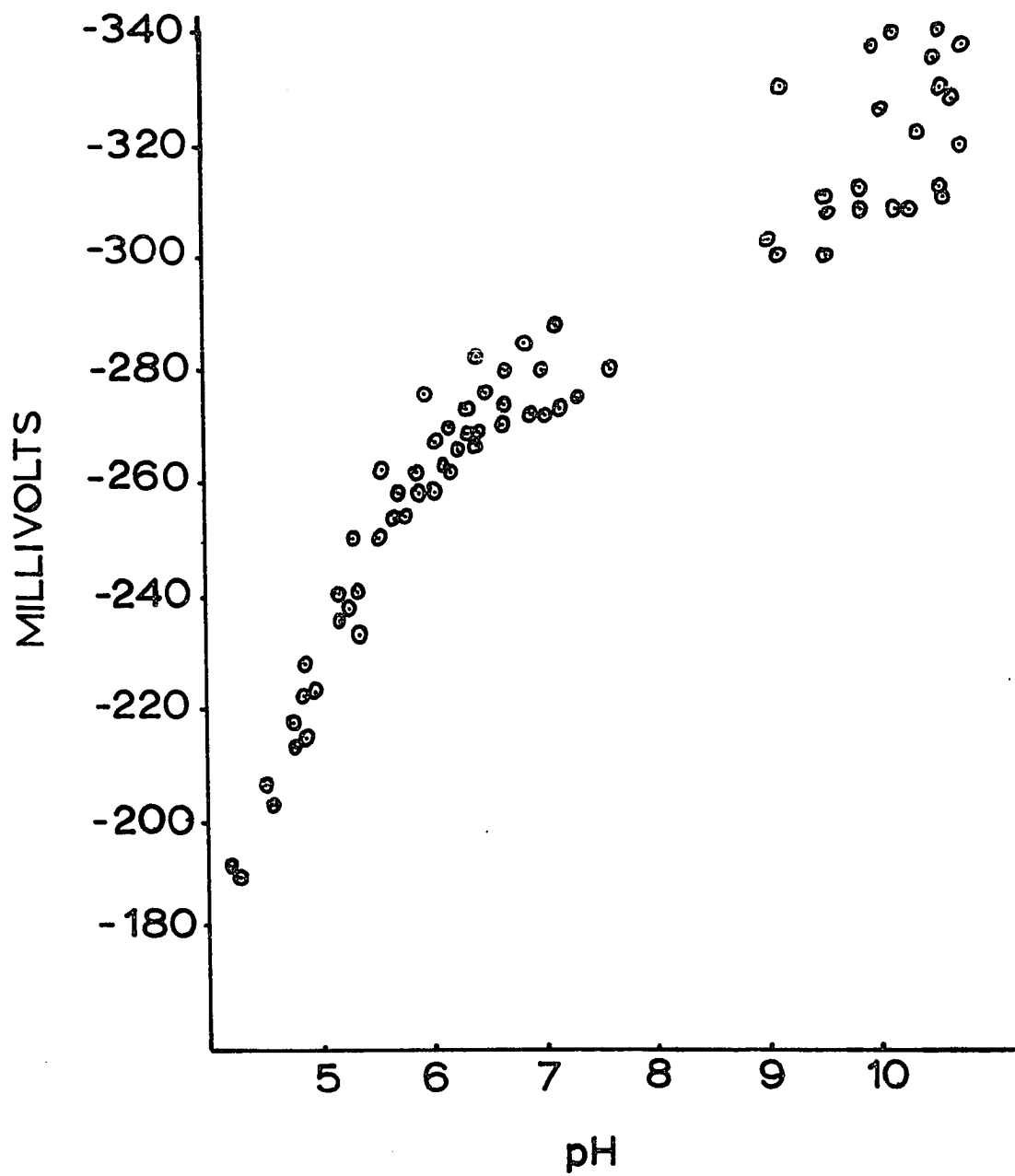


TABLE V

pH Versus Potential Data

pH	mv	pH	mv	pH	mv
4.00	-170	6.00	-240	8.30	-298
4.21	-178	6.00	-276	9.20	-330
4.23	-208	6.20	-263	9.32	-300
4.25	-210	6.22	-260	9.43	-296
4.50	-228	6.42	-268	9.73	-308
4.60	-232	6.46	-282	9.93	-344
4.62	-195	6.63	-263	9.94	-350
4.78	-208	6.60	-280	10.05	-350
4.90	-228	6.80	-273	10.05	-350
4.90	-228	6.82	-288	10.08	-326
4.95	-240	6.85	-285	10.20	-340
5.06	-215	6.90	-285	10.45	-355
5.08	-220	6.95	-256	10.52	-335
5.10	-240	7.07	-288	10.60	-353
5.15	-245	7.10	-258	10.62	-330
5.20	-247	7.13	-267	10.65	-330
5.26	-215	7.24	-260	10.72	-360
5.32	-222	7.42	-292	11.00	-338
5.60	-262	7.60	-263		
5.82	-254	7.70	-293		

potassium chloride. The concentration of thiol was calculated from the relation

$$E_{\text{cell}} = E_{\text{calomel}}^{\circ} - E_{\text{SH,SS}}^{\circ} - 0.059 \text{ pH} - 0.059 \log [\text{SH}]$$

which holds at pH 4 to pH 5. Ignoring dilution and assuming $C_T = C_{\text{SH}} + C_{\text{S}^-} = \text{a constant}$, a working E was calculated from the relation

$$E' = E_{\text{calomel}}^{\circ} - E_{\text{cell}} - 0.059 \log C_T .$$

A plot of E' versus pH is shown in Figure 6. The data shown in Figure 6 were obtained from two studies of neutralization using one molar solutions and one study using a 0.5 molar solution of the sodium hydroxide and potassium chloride. The experimental pH and potential data are listed in columns 1 and 2 of Tables VI, VII and VIII.

Survey of Possible Reactions of Metal Ions with the Thiol

An investigation of several metal ions was conducted to determine if a reaction between the metal ion and the thiol would occur. Evidence of reaction was either a change in potential, the formation of a precipitate, or a change in color. The survey was restricted to the pH values 3, 7, and 9. Table IX lists the ions which were studied. The presence of an "x" indicates that some type of reaction occurred. A dash indicates that no evidence of reaction was observed.

FIGURE 6

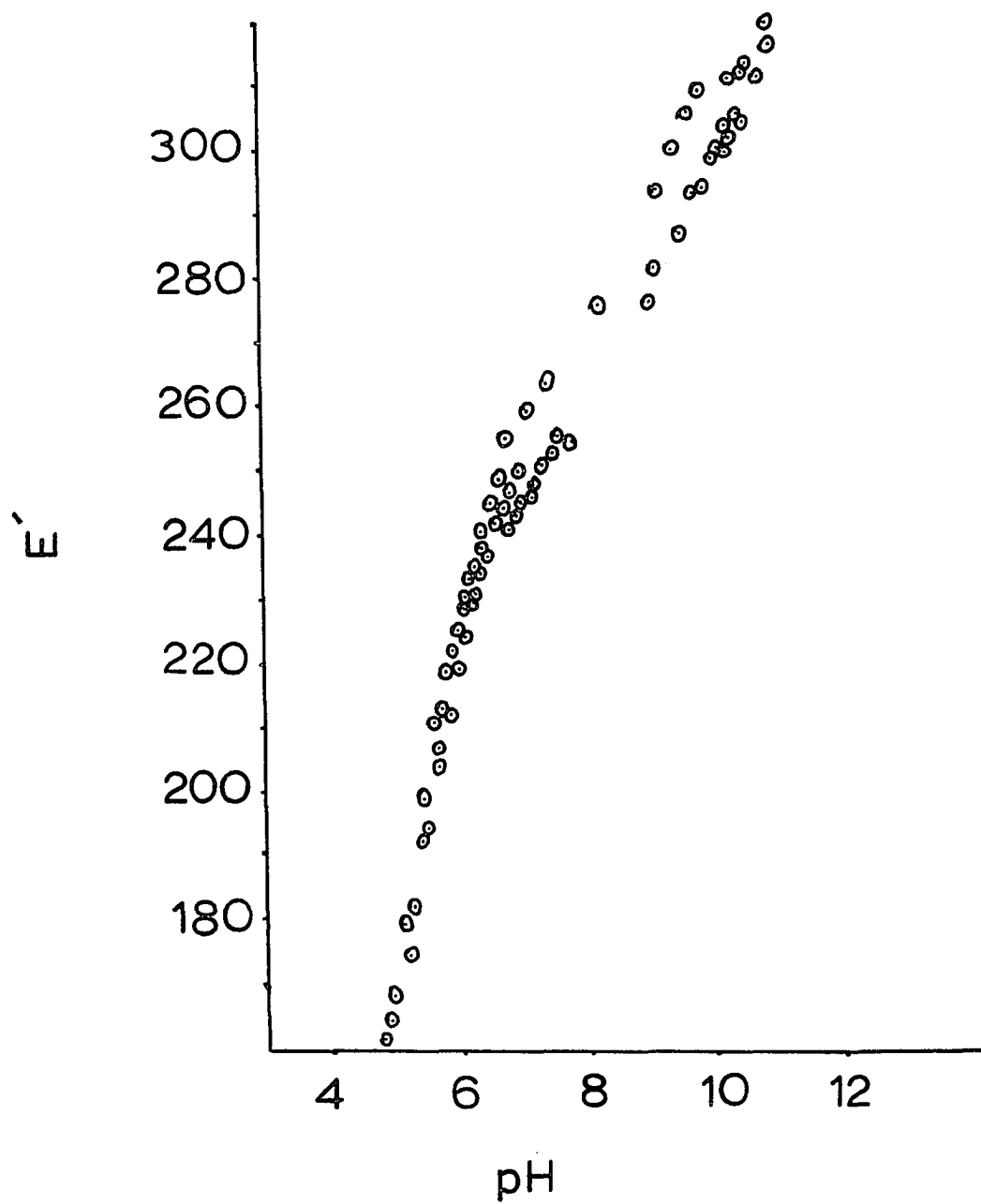
 E' vs pH

TABLE VI

Cell Potentials at Various pH Values
(1 Molar KCl Solution)

pH	mv	0.059 log $[\phi_{SH}]$	E'
3.90	-118	-223	+110
4.06	-123	-228	+115
4.24	-136	-225	+118
4.35	-142	-226	+134
4.50	-150	-227	+142
4.70	-162	-227	+154
4.92	-176	-226	+168
5.20	-190		+182
5.43	-202		+194
5.63	-212		+204
5.78	-220		+212
5.90	-228		+220
6.03	-232		+224
6.14	-238		+230
6.24	-242		+234
6.35	-242		+237
6.48	-250		+242
6.58	-252		+244
6.70	-255		+247
6.88	-258		+250

TABLE VI
(CONTINUED)

pH	mv	0.059 log [ϕ SH]	E°
7.08	-260		+252
7.48	-264		+256
9.00	-290		+282
9.70	-302		+294
9.95	-308		+300
10.10	-310		+302
10.30	-312		+304
10.60	-320		+312
3.70	-100	-229	+ 92

TABLE VII

Cell Potential at Various pH Values

(1 Molar Solution)

pH	mv	0.059 log $[\phi_{SH}]$	E'
4.02	-127	-221	+116
4.12	-132	-222	+121
4.22	-137	-223	+126
4.37	-146	-223	+135
4.55	-157	-223	+146
4.80	-172	-223	+161
5.10	-190		+179
5.38	-210		+199
5.58	-222		+211
5.80	-233		+222
6.00	-240		+229
6.10	-247		+234
6.20	-252		+241
6.34	-256		+245
6.50	-260		+249
6.68	-267		+256
6.92	-271		+260
7.28	-275		+264
8.10	-287		+276
9.00	-305		+294

TABLE VII

(CONTINUED)

pH	mv	0.059 log [ϕ_{SH}]	E'
9.25	-312		+301
9.45	-317		+306
9.68	-321		+310
10.11	-323		+312
10.30	-324		+313
10.70	-332		+321
12.00	-360		+349
3.22	- 73	-227	

TABLE VIII

Cell Potential at Various pH Values
(0.5 Molar Solution)

pH	mv	$0.059 \log [\phi SH]$	E°
4.61	-177	-207	+151
4.87	-190	-209	+164
5.15	-200		+174
5.35	-218		+192
5.53	-230		+204
5.63	-239		+213
5.74	-245		+219
5.90	-251		+225
6.03	-256		+230
6.11	-260		+234
6.26	-263		+237
6.72	-267		+241
6.80	-269		+243
6.86	-270		+244
6.90	-271		+245
7.00	-272		+246
7.10	-274		+248
7.20	-277		+251
7.40	-279		+253
7.69	-280		+254

TABLE VIII
(CONTINUED)

pH	mv	$0.059 \log [\phi SH]$	E'
8.93	-303		+277
9.35	-313		+287
9.58	-320		+294
9.86	-325		+299
10.10	-330		+304
10.40	-340		+314
10.70	-343		+317
11.00	-350		+324

TABLE IX

Metal Ions

Metal Ion		pH 3	pH 7	pH 9
Magnesium	(Mg ⁺²)	-	-	-
Calcium	(Ca ⁺²)	-		
Strontium	(Sr ⁺²)	-	-	-
Barium	(Ba ⁺²)		-	
Yttrium	(Y ⁺³)	-	-	
Lanthanum	(La ⁺³)	-	-	
Titanium	(Ti ⁺⁴)		-	
Zirconium	(Zr ⁺²)	-	x	x
Chromium	(Cr ⁺³)	-	-	-
Molybdenum	(MoO ₄ ⁻²)	x	-	
Tungsten	(WO ₄ ⁻⁻)		-	
Neodymium	(Nd ⁺³)		-	
Uranium	(UO ₂ ⁺⁺)	-	-	
Manganese	(Mn ⁺²)	-	-	-
Iron	(Fe ⁺²)		x	
Iron	(Fe ⁺³)	x		
Ruthenium	(Ru ⁺³)		x	
Cobalt	(Co ⁺²)	-	x	x
Iridium	(Ir ⁺³)		x	
Nickel	(Ni ⁺²)	x	x	x
Palladium	(Pd ⁺²)		-	

TABLE IX
(CONTINUED)

Metal Ion		pH 3	pH 7	pH 9
Palladium	(Pd ⁺⁴)		-	
Platinum	(Pt ⁺⁴)		-	
Copper	(Cu ⁺²)	x	x	x
Silver	(Ag ⁺¹)	x	x	x
Gold	(Au ⁺³)	x	x	x
Zinc	(Zn ⁺²)		x	x
Cadmium	(Cd ⁺²)	x	x	x
Mercury	(Hg ⁺²)	x	x	x
Aluminum	(Al ⁺³)		-	-
Thallium	(Tl ⁺¹)		-	
Tin	(Sn ⁺²)	x	x	
Lead	(Pb ⁺²)	x	x	x
Arsenic	(As ⁺³)	x	x	
Antimony	(Sb ⁺³)	x	x	x
Bismuth	(Bi ⁺³)		x	
Selenium	(Se ⁺⁴)	x	x	
Tellurium	(Te ⁺⁴)		x	

Preparation of Standard Thiol Solutions

The thiol reservoir shown in Figure 4 holds about four liters of solution. Distilled water was saturated with the thiol at room temperature, nitrogen gas being used to mix the two materials and flush oxygen from the solution. The excess thiol was filtered off and the filtrate transferred to the reservoir. Sufficient distilled water was added to nearly fill the reservoir. Nitrogen was passed through the entire system for at least one hour to assure the absence of oxygen. The system was connected to the automatic buret and closed to the atmosphere under a slight positive pressure of nitrogen.

Using this system, it was possible to titrate metal ion solutions with the thiol in the absence of air.

Determination of Silver with Thiol

A standard solution of silver nitrate was prepared by dissolving a known weight of a primary standard salt and diluting to one liter. Known volumes of the standard solutions were pipeted into a titrating vessel, buffer solution added, and the solution titrated with the thiol.

The potentiogram (plot of potential versus volume) of the silver titration when carried out in a borate buffer at pH 9 to 10 was similar to a normal potentiometric titration curve. In solutions of lower pH, two potential changes were observed with the second corresponding to the equivalence point of the titration. The initial potential change was

attributed to slow electrode kinetics.

Figure 7 is a plot of potential data obtained from a silver titration. The recording potentiometer is capable of plotting the derivative of the titration curve, and such a curve is given in Figure 8. The equivalence point of the titration corresponds very well with the point of inflection of the titration curve.

The thiol solution was standardized with standard iodine solution using the starch endpoint. This is the classical procedure for thiol analysis. Table X lists data for the standardization of the iodine solution. The iodine was standardized by titrating 25-milliliter aliquots of a 0.03035 normal solution of arsenious oxide.

Table XI lists the data obtained when the thiol solution was titrated with the iodine solution to the starch endpoint.

A standard silver solution containing 0.7573 grams of silver nitrate per liter was prepared from a primary standard salt. This corresponds to 0.01202 grams of silver per 25 milliliters of solution. Twenty-five milliliter aliquots of this solution were analyzed with the standard thiol solution assuming a 1:1 reaction. Table XII lists the data obtained in this manner.

On the basis of the data listed in Table XII, it was concluded that the titration of silver with thiol is quantitative when carried out in a borate buffer at a pH of 9. Standard silver solutions were employed to standardize all subse-

FIGURE 7
SILVER TITRATION CURVE

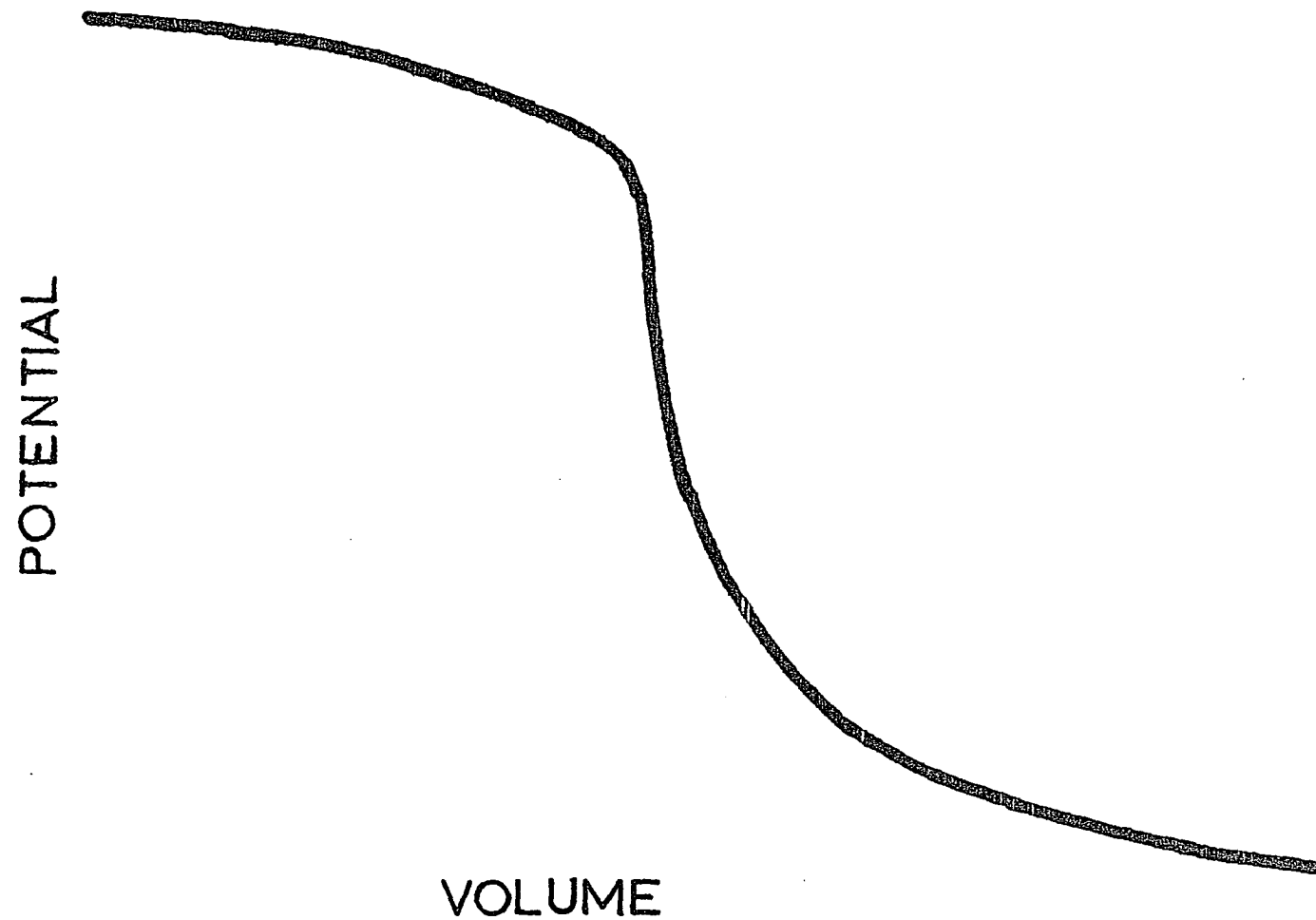
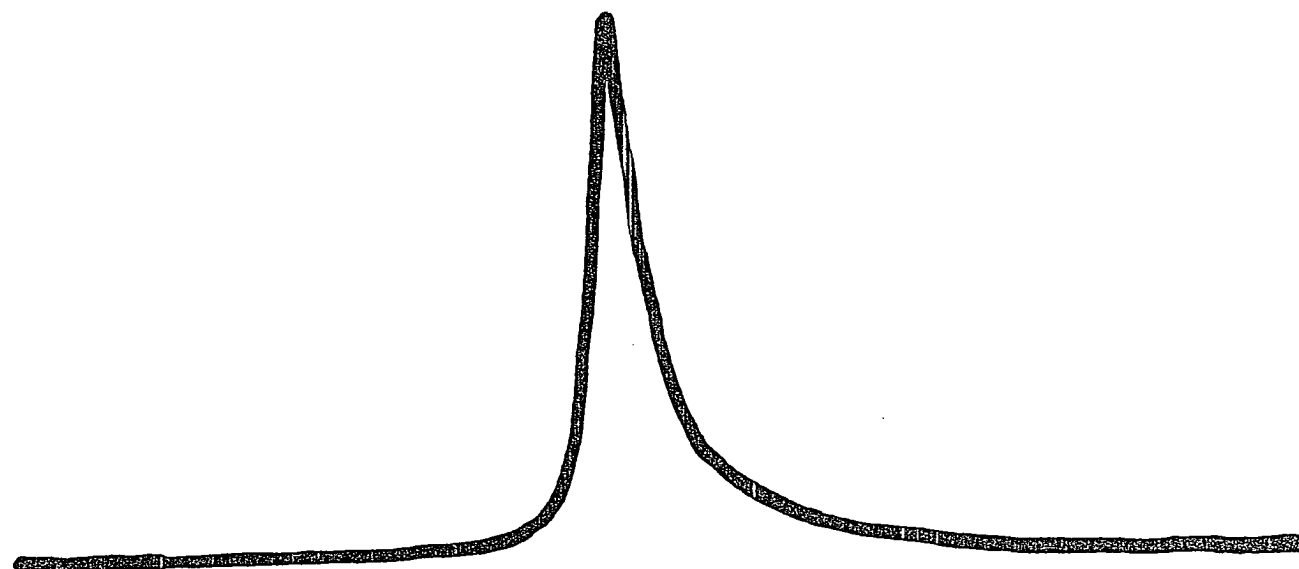


FIGURE 8

DERIVATIVE of a SILVER TITRATION CURVE

POTENTIAL CHANGE



VOLUME

TABLE X

Standardization Data for Iodine Solution

Volume of As_2O_3 Solution	Volume of I_2 Solution	Normality of I_2	Average	Standard Deviation
25 mls	21.30	0.03562		
25 mls	21.31	0.03561	0.03561	0.00002
25 mls	21.32	0.03559		

TABLE XI

Standardization Data for the Thiol Solution

Volume of Thiol Solution	Volume of I ₂	Normality of Thiol	Average	Standard Deviation
25 mls	22.61	0.03221		
25 mls	22.62	0.03222	0.03224	0.00003
25 mls	22.64	0.03225		
25 mls	22.66	0.03228		

TABLE XII

Determination of Silver with Thiol

Volume of Thiol	Weight of Silver (grams/25mls)	Average	Standard Deviation
3.44 mls	0.0120		
3.45 mls	0.0120		
3.45 mls	0.0120		
3.45 mls	0.0120		
3.45 mls	0.0120		
3.45 mls	0.0120		
3.45 mls	0.0120	0.0121	0.0001
3.46 mls	0.0120		
3.47 mls	0.0121		
3.48 mls	0.0121		
3.48 mls	0.0121		
3.48 mls	0.0121		
3.49 mls	0.0121		
3.50 mls	0.0122		

quent thiol solutions.

Determination of Copper with Thiol

A stock solution of copper was prepared by dissolving 3.5270 grams of primary standard copper shot in nitric acid, boiling off the nitrogen oxides, and diluting to one liter. The solution was thus 0.05551 molar in copper ion. Aliquots of this stock solution were titrated at various pH values to determine whether the reaction was quantitative and the ratio of copper ion to thiol. Copper was precipitated with a large potential change from pH 3 to pH 9. Below pH 6, however, the titration did not appear to be quantitative. Two moles of thiol were required for each mole of copper. The best results were obtained in an ammonium acetate buffer at pH 7.

Fifty milliliters of the copper stock solution were diluted to one liter to prepare a 0.00555 normal solution. Twenty-five milliliter aliquots of this solution were titrated and the grams of copper in the original stock solution computed. The correct value was 0.08818 grams. The data from this titration are listed in Table XIII.

The data in Table XIII show that the titration is quantitative for copper under the prescribed conditions. The titration curve is similar to a normal potentiometric titration curve.

Determination of Nickel with Thiol

A solution of nickel ions was prepared by dissolving

TABLE XIII

Determination of Copper with Thiol

Volume of Thiol	Weight of Copper (grams/25mls)	Average	Standard Deviation
4.95	0.0884		
4.95	0.0884		
4.95	0.0884	0.0885	0.0003
4.96	0.0887		
4.97	0.0889		

9.1854 grams of nickel(II) nitrate and diluting to one liter. The solution was 0.03159 molar in nickel(II) ion. A study of this solution indicated that one mole of nickel would react with two moles of thiol quantitatively at pH equal to or greater than 6. Ammonium acetate served as a suitable buffer. Twenty-five milliliters of the stock solution were diluted to 250 milliliters. Twenty-five milliliter aliquots of the diluted solution were titrated with thiol. The thiol normality was 0.03297. The titration data are listed in Table XIV.

A 25 milliliter aliquot of the stock solution should contain 0.04637 grams of nickel if the nickel salt were 100% pure. Thus, the analysis appeared to be quantitative. To establish this, 25 milliliter aliquots of the stock solution were analyzed by a standard gravimetric procedure. The nickel was precipitated and weighed as the salt of dimethylglyoxime. The agreement between titrimetric and gravimetric data shows that the titration is quantitative. The data are listed in Table XV.

Determination of Lead with Thiol

A solution of lead ions was prepared by dissolving 20.9460 grams of lead(II) nitrate and diluting to one liter. The solution was 0.06324 molar in lead(II) ion. A study of this solution showed that one mole of lead would react with two moles of thiol quantitatively at pH values greater than 6. Ammonium acetate served as a suitable buffer. Twenty-

TABLE XIV

Determination of Nickel with Thiol

Volume of Thiol	Weight of Nickel (grams/25mls)	Average	Standard Deviation
4.71	0.0456		
4.75	0.0460		
4.76	0.0461	0.0460	0.0002
4.76	0.0461		

TABLE XV

Determination of Nickel as nickel dimethylglyoximate

Weight of $\text{NiC}_8\text{H}_{14}\text{N}_4\text{O}_4$	Weight of Nickel	Average	Standard Deviation	Average Table XIV	Diff.
0.2259	0.04593				
0.2266	0.04607	0.04602	0.00008	0.0460	-0.00002
0.2266	0.04607				

five milliliters of the stock solution were diluted to 250 milliliters. Twenty-five milliliter aliquots of the diluted solution were titrated with thiol. The thiol normality was 0.03399. The titration data are listed in Table XVI.

A 25 milliliter aliquot of the stock solution should contain 0.3276 grams of lead if the lead salt were 100% pure. Thus the analysis appeared to be quantitative. To confirm the quantitative nature of the titration, 25 milliliter aliquots of the stock solution were analyzed for lead by a standard gravimetric procedure. The lead was precipitated and weighed as lead sulfate. The agreement between titrimetric and gravimetric data shows that the titrimetric procedure is quantitative. The gravimetric data are listed in Table XVII.

Determination of Cadmium with Thiol

A solution of cadmium ions was prepared by dissolving 10.6471 grams of cadmium nitrate and diluting to one liter. The solution was 0.03451 molar in cadmium ions. A study of this solution showed that one mole of cadmium would react with two moles of thiol quantitatively above pH 6. Ammonium acetate served as a suitable buffer. Twenty-five milliliters of the stock solution were diluted to 250 milliliters. Twenty-five milliliter aliquots of the diluted solution were titrated with thiol. The thiol normality was 0.03399. The data for this titration are listed in Table XVIII.

TABLE XVI

Determination of Lead with Thiol

Volume of Thiol	Weight of Lead (grams/25mls)	Average	Standard Deviation
9.15	0.3224		
9.17	0.3231		
9.17	0.3231	0.3232	0.0006
9.18	0.3234		
9.18	0.3234		
9.20	0.3241		

TABLE XVII

Determination of Lead as Lead Sulfate

Weight of PbSO_4	Weight of Lead	Average	Standard Deviation	Average Table XVI	Diff.
0.4757	0.3250				
0.4759	0.3251	0.3254	0.0005	0.3232	-.0022
0.4772	0.3260				

TABLE XVIII

Determination of Cadmium with Thiol

Volume of Thiol	Weight of Cadmium (grams/25mls)	Average	Standard Deviation
5.03	0.0958		
5.04	0.0963		
5.04	0.0963	0.0962	0.0002
5.04	0.0963		
5.04	0.0963		

A 25 milliliter aliquot of this stock solution should contain 0.09698 grams of cadmium if the salt were 100% pure. Thus the analysis seemed quantitative. Twenty-five milliliter aliquots of the stock solution were analyzed by a classical gravimetric procedure as a confirmation of the titration. The cadmium was precipitated as cadmium ammonium phosphate and ignited to the pyrophosphate. The agreement between titrimetric and gravimetric data shows that the thiol analysis is indeed quantitative. The data for the gravimetric analysis are given in Table XIX.

Determination of Zinc with Thiol

A solution of zinc ions was prepared by dissolving 2.3635 grams of reagent grade zinc metal in hydrochloric acid and diluting to one liter. The solution was 0.03600 molar in zinc ions. A study of this solution showed that one mole of zinc reacts with two moles of thiol. The reaction was quantitative above pH 6. Ammonium acetate served as a suitable buffer. Twenty-five milliliters of the stock solution were diluted to 250 milliliters. Twenty-five milliliter aliquots of the diluted solution were titrated with thiol. The normality of the thiol was 0.03399. The data for this titration are listed in Table XX.

A 25 milliliter aliquot of this stock solution should contain 0.05884 grams of zinc. Thus the reaction was quantitative. In order to confirm the analysis, 25 milliliter aliquots of the stock solution were analyzed by a classical

TABLE XIX

Determination of Cadmium as Cadmium Pyrophosphate

Weight of CdP_2O_7	Weight of Cadmium	Average	Standard Deviation	Average Table XVIII	Diff.
0.1714	0.09664				
0.1714	0.09664	0.09666	0.00003	0.0962	-.0004
0.1715	0.09669				

TABLE XX

Determination of Zinc with Thiol

Volume of Thiol	Weight of Zinc (grams/25mls)	Average	Standard Deviation
5.27	0.0585		
5.28	0.0587		
5.30	0.0588	0.0588	0.0002
5.30	0.0588		
5.31	0.0590		
5.31	0.0590		

gravimetric procedure. The zinc was precipitated and weighed as zinc ammonium phosphate. The agreement between titrimetric and gravimetric data shows that the titrimetric procedure is quantitative. The data for the gravimetric determination are given in Table XXI.

Determination of Gold with Thiol

A stock solution of gold was prepared by dissolving 0.2299 grams of primary standard gold in aqua regia and diluting to 250 milliliters. The solution was 0.004668 molar in gold. Aliquots of this stock solution were titrated with standard thiol solutions using several different buffers. The pH ranged from 1 to 9. Although a precipitate was formed and a change of potential noted, the ratio of equivalents of gold to thiol never approached a whole number. Values found ranged from 0.5 to 1.7 in acid and base. These variations apparently result from both an oxidation-reduction and a precipitation reaction.

Determination of Copper in Brass

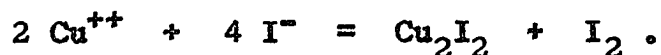
An adaptation of the iodine method for thiol has been applied to an analysis for copper in brass. A brass sample weighing 0.4366 grams was dissolved in concentrated hydrochloric and nitric acids. The solution was boiled to expel oxides of nitrogen, cooled, and diluted to 500 milliliters. Ten-milliliter aliquots of this solution were neutralized with ammonium hydroxide and then buffered to a pH of about

TABLE XXI

Determination of Zinc as Zinc Ammonium Phosphate

Weight of ZnNH_4PO_4	Weight of Zinc (grams/25mls)	Average	Standard Deviation	Average Table XX	Diff.
0.1592	0.05833				
0.1594	0.05840	0.05841	0.00009	0.0588	-0.0004
0.1599	0.05851				

3.5 with ammonium bifluoride. Two grams of potassium iodide were added to reduce the cupric ions to cuprous ions according to the reaction:



Potassium thiocyanate was added to convert the cuprous iodide to cuprous thiocyanate since iodine is absorbed upon cuprous iodide but not upon cuprous thiocyanate. The iodine liberated by the reaction of cupric ion and iodide ion was titrated with standard thiol. The amount of copper was then calculated according to the equation:

$$\% \text{ Cu} = \frac{(\text{volume})(\text{normality})(\text{meq. wt. of Cu})(100)}{\text{Sample weight}}$$

The brass sample used for the analysis was the NBS 37d sample which has a reported value of 70.78% copper. The data for the thiol analysis are shown in Table XXII.

TABLE XXII

Brass Analysis with Thiol

Percent Copper	Average	Standard Deviation
70.0		
70.4		
70.4	70.5	0.4
70.6		
70.6		
71.4		

CHAPTER V

RESULTS AND DISCUSSION

The majority of the metal ion titrations must be carried out at pH values between 5 and 10. Potentiometric titrations depend upon the addition or removal of some species which generates a measurable potential.

Alkaline solutions of known thiol concentration were prepared. The solubility of the salt is so large that the use of a saturated solution is impractical. Potential and pH measurements were made on these solutions. The results of the potential versus pH plot are shown in Figure 5. A precipitate, apparently of the disulfide, formed in the alkaline solutions in every case. This changed the thiol concentration and undoubtedly caused the large scatter in the data observed in the alkaline region. The solutions were kept one molar with potassium chloride to insure a high and relatively constant ionic strength.

The values shown in Figure 6 indicate that the measured potentials are reproducible. The experimental data differ by 20 millivolts in some regions and while they are not sufficiently precise to yield a trustworthy value of E°_{base} for

the half-cell reaction



the data indicate that a pH independent potential exists, which permitted potentiometric titrations to be made within this pH region.

A survey of metal ions was undertaken to determine which of the previously reported metal salts would be sufficiently insoluble to make titrimetric determinations possible. A small quantity of the metal ion under study was placed in the titration vessel and the solution was buffered to the desired pH. The amount of metal ion was restricted to that which would require less than 10 milliliters of the thiol assuming 3 equivalents per mole. Generally a precipitate was formed where potential changes were observed. Iridium was the only metal tested which gave a potential change without forming a precipitate. This could be a reduction to the Ir^{++} ion which is not precipitated by the thiol.

As shown in Table IX, the thiol will react with many metal ions. Reagent grade silver nitrate was examined first for several reasons. It had been shown to be quantitative in a gravimetric procedure (6), and standard stock solutions of known concentration could be prepared directly. It was hoped that the silver titration could quickly be proven quantitative and a procedure for thiol with silver be adopted as the method of standardization since the process with iodine

is laborious and time-consuming.

The data from the silver titration with thiol are given in Table XII. The average of 14 titrations of 25 milliliter aliquots of the stock solution of silver was 0.0121 grams. The computed value on the basis of a weighed amount of silver dissolved and diluted to one liter of solution was 0.01202 grams of silver.

Copper shot was employed to prepare a stock solution for copper determinations. The titration gave a premature endpoint at a pH of 6 or less but an average value of 0.0885 grams of copper per 25 milliliters of stock solution obtained at pH values above 6 is in good agreement with the weight (0.08818 grams) of copper which was taken for analysis.

The silver nitrate and copper metal were sufficiently pure so that no referee analysis was needed. The pH regions at which the titrations were carried out were the lowest pH values for which a smooth titration curve yielding quantitative results could be obtained.

Reagent grade nickel(II) nitrate was used for the titration of nickel ion. At a pH of 7, an average value of 0.0460 grams of nickel per 25 milliliters of stock solution, as given in Table XIV, compares favorably with 0.04637 grams computed from the weight of the salt. The thiol value, however, agrees very well with the value of 0.04602 grams per 25 milliliters which was obtained by a gravimetric analysis with dimethylglyoxime.

Reagent grade lead(II) nitrate was used for the preparation of stock solutions. The value of 0.3232 grams of lead per 25 milliliters of stock solution (Table XVI) agrees favorably with 0.3254 grams (Table XVII) found by analysis for the lead as the sulfate.

A cadmium stock solution was prepared from cadmium nitrate. The precision of the five titrations reported in Table XVIII is very good. The agreement between the thiol analysis of 0.0962 grams of cadmium per 25 milliliters of stock solution and the gravimetric analysis of 0.09666 grams is excellent.

Zinc metal was used to prepare a stock of zinc ion solution. The value of 0.0588 grams of zinc per 25 milliliters of stock solution as shown in Table XX is in excellent agreement with the weight of zinc taken. The value 0.05841 obtained by gravimetric analysis is somewhat low, but does confirm that the titration is quantitative.

A titration of gold could not be made reproducible. Precipitate formation occurred and potential changes ranging from 200 to 500 millivolts were observed in the range of pH 1 to 8. The ratio of gold to thiol varied from 0.5 to 1.7, apparently due to more than one reaction.

The Metrohm B 336 Potentiograph used in this work had a 10-milliliter buret. Rather than make the errors in volume measurement due to refilling the buret midway through the titration, metal ion concentrations were restricted to those

requiring less than 10 milliliters of thiol for the titration. A larger buret would increase the precision of the individual titrations by decreasing the percentage uncertainty in the volume measurement.

The potential curves plotted by the potentiograph indicate only the potential change and not the specific voltage of the cell at any single point. Because of this lack, silver ion was titrated potentiometrically point by point and the measured potential plotted versus pH in order to compare experimental and theoretical curves.

Figure 9 shows the titration curve obtained by titrating 25 milliliters of silver nitrate solution at pH 4.15 with standard thiol using a potassium acid phthalate buffer. The titration data are recorded in Table XXIII. It should be noted that while there are two inflections in the titration curve, the second represents the endpoint. The broken line in Figure 9 represents the course of the theoretical titration curve after the endpoint where it is thiol dependent. The calculation was based upon the thiol concentration and the previously determined value of $E^{\circ} = +0.127$ volts. The experimental and theoretical curves shown in Figure 9 are in good agreement. The difference between the two curves is less than 12 millivolts.

Figure 10 shows the experimental titration curve obtained by titrating 50 milliliters of silver nitrate solution at pH 9.7 with standard thiol using an ammonium borate buffer.

FIGURE 9
SILVER TITRATION
pH 4.15

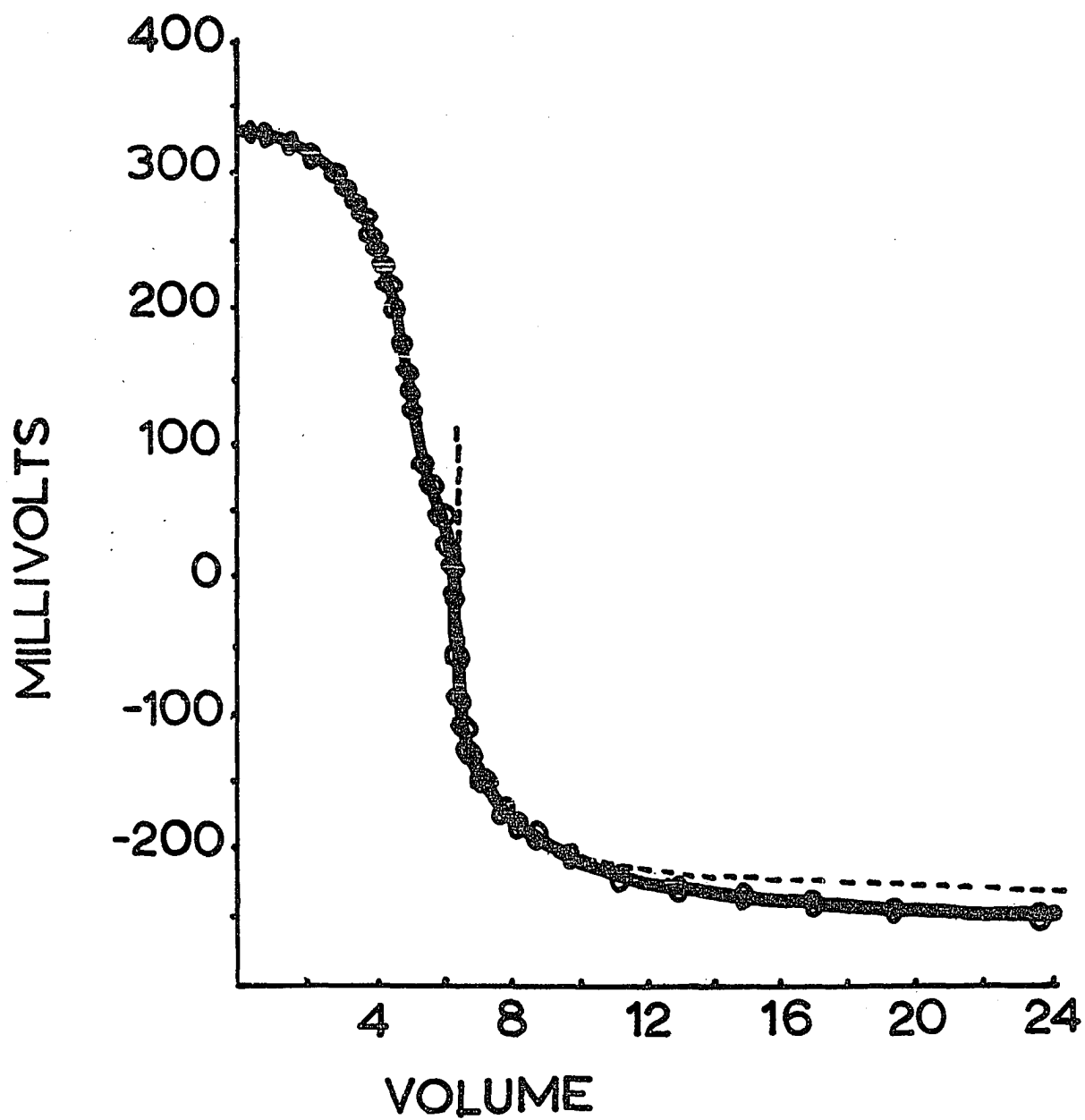
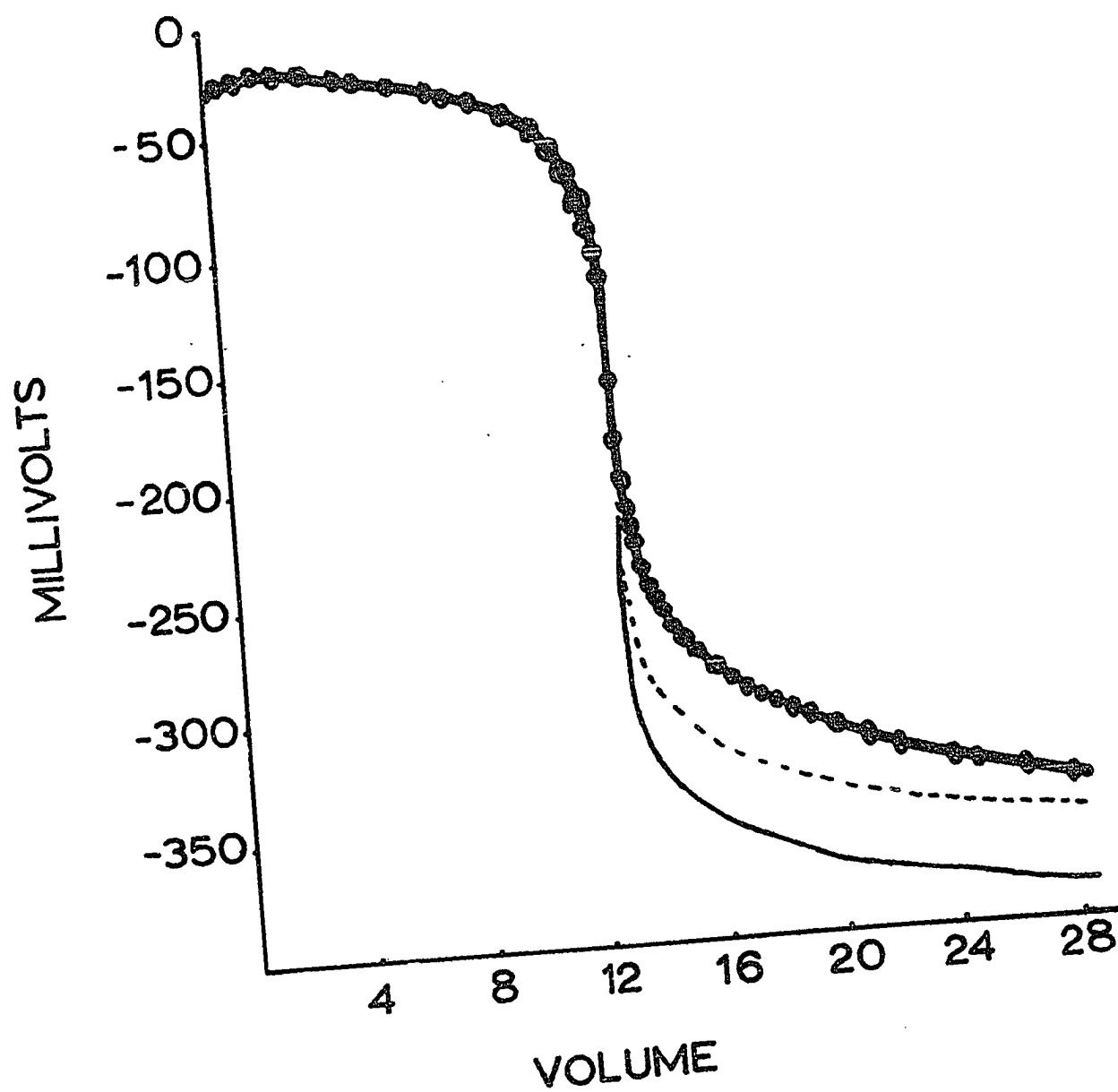


TABLE XXIII
Silver Titration Data (pH 4.15)

mls	mv	mls	mv	mls	mv
0.0	332	4.2	230	6.2	25
0.5	328	4.3	222	6.3	10
1.0	325	4.4	216	6.4	- 10
1.5	320	4.5	210	6.5	- 60
2.0	312	4.6	200	6.6	- 90
2.2	310	4.7	188	6.7	-110
2.5	305	4.8	170	6.8	-125
2.7	300	4.9	162	6.9	-136
3.0	292	5.0	145	7.0	-145
3.1	290	5.1	125	7.2	-155
3.2	288	5.2	112	7.5	-168
3.3	282	5.3	103	8.0	-180
3.4	280	5.4	92	8.5	-190
3.5	275	5.5	82	9.0	-198
3.6	270	5.6	85	10.0	-210
3.7	262	5.7	72	11.0	-218
3.8	258	5.8	62	13.0	-228
3.9	252	5.9	54	15.0	-235
4.0	245	6.0	45	17.0	-240
4.1	238	6.1	36	20.0	-248

FIGURE 10
SILVER TITRATION
pH 9.7



The titration data are recorded in Table XXIV. It should be observed that the premature change in potential observed at lower pH values (Figure 9) does not appear in the titration curve at pH 9.7. The smooth line in Figure 10 represents a theoretical curve calculated using a formal E of +0.292 volts estimated from the potential versus pH data shown in Figure 6. The poor agreement can be charged to the error in the arbitrarily chosen value for E, a lack of attainment of electrode equilibrium, and non-correction for the activity of the thiol ion.

The contribution of the activity coefficient of the ionized thiol can be estimated from the relation:

$$- \log f_{\pm} = A Z_A Z_B (I)^{\frac{1}{2}} = 0.5 Z_A Z_B (I)^{\frac{1}{2}}$$

where Z_A and Z_B represent the ionic charges

$$I = \frac{1}{2} \sum c_i z_i^2$$

c_i = concentration of the i^{th} ion

Z_i = ionic charge of the i^{th} ion

A calculation shows that the activity coefficient will move the theoretical curve 33 millivolts in the positive direction. The dashed curve of Figure 10 shows this correction. The new curve varies from 10 to 30 millivolts from the experimental curve. It should be noted that the major variance occurs just past the equivalence point. The theoretical and experimental curves are in closer agreement after more than 10 milliliters of excess thiol solution have been added. Thus, after a con-

TABLE XXIV
Silver Titration Data (pH 9.70)

mls	mv	mls	mv	mls	mv
0.0	-28	12.3	- 88	14.6	-267
1.0	-23	12.4	- 90	14.8	-270
2.0	-22	12.5	- 92	15.0	-273
3.0	-22	12.6	- 92	15.2	-276
4.0	-23	12.7	- 98	15.4	-278
5.0	-25	12.8	-105	15.6	-281
6.0	-29	12.9	-115	15.8	-284
7.0	-31	13.0	-160	16.0	-286
8.0	-35	13.1	-188	16.5	-290
9.0	-40	13.2	-203	17.0	-295
10.0	-44	13.3	-215	17.5	-299
11.0	-50	13.4	-222	18.0	-300
11.2	-51	13.5	-230	18.5	-304
11.4	-55	13.6	-235	19.0	-308
11.6	-58	13.7	-240	20.0	-312
11.8	-65	13.8	-245	21.0	-320
11.9	-73	13.9	-250	22.0	-322
12.0	-80	14.0	-252	24.0	-330
12.1	-82	14.2	-258	26.0	-333
12.2	-85	14.4	-260	28.0	-340

sideration of activity effects is included, experimental and theoretical curves for the silver titration in Figure 10 are in reasonable agreement.

CHAPTER VI

CONCLUSIONS

Many metal ions react with o-aminobenzenethiol, some of them quantitatively. The formation constant is dependent upon the hydrogen ion activity. As a result, the majority of the reactions occur in neutral and alkaline pH regions.

The standard potential for the equilibrium of the ionized species of o-aminobenzenethiol with bis-(2-aminophenyl-) disulfide could not be determined. However, it has been shown that a reproducible potential can be obtained upon addition of thiol solution to an alkaline solution. Further, this potential is dependent upon the thiol concentration of the solution.

The reaction of o-aminobenzenethiol with silver, copper, cadmium, zinc, lead, and nickel is quantitative. It has been shown that a titrimetric analysis of these metal ions is possible, using a potentiometric method to follow the course of titration.

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