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SOME APPLICATIONS OF o-AMINOBENZENETHIOL
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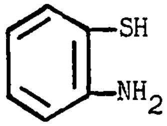
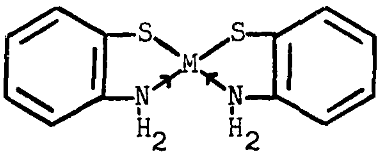
CHAPTER I

INTRODUCTION AND LITERATURE SURVEY

The compound o-aminobenzenethiol, 

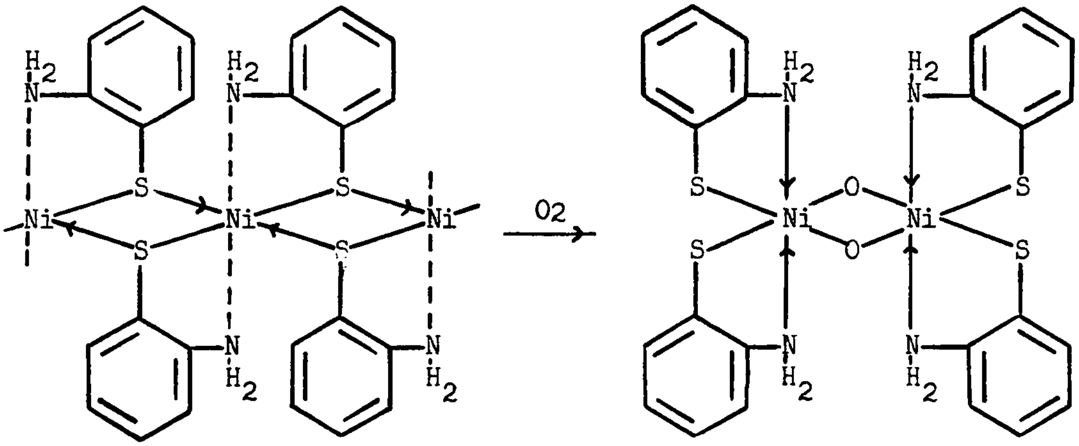
, possesses the reactive grouping, N-C=C-SH, capable of forming five-membered, ringed, chelate compounds with metals. Chelate compounds are ring compounds with coordinate valence in the ring; they are named from the Greek word which means "crab's claw" (43). Organic compounds which act as chelating agents form derivatives with metals, some of which are water-soluble. However, a number of the derivatives are quite unlike salts, being low-melting and volatile, but slightly water-soluble (giving non-conducting solutions), and soluble in hydrocarbons. A compound of o-aminobenzenethiol with a bivalent metal would theoretically have the structure:



Two links, shown by the arrows, are coordinate, the electrons at these points having been donated by the nitrogen atoms. The stability and "organic" nature of such compounds is partly attributable to the size of the rings, five- and six-membered rings being most stable.

Preparation of o-aminobenzenethiol (o-aminothiophenol) was described as early as 1930 when C. H. Lumsden (29) reported that 2-mercaptobenzothiazole is hydrolyzed to o-aminobenzenethiol upon treatment with a 5 to 40 per cent solution of sodium hydroxide at an elevated temperature in a closed vessel. Knowles and Watt (27) have described the preparation of o-aminobenzenethiol by reduction of benzothiazole with sodium metal in liquid ammonia followed by hydrolysis and then by steam distillation. These authors also state that when the residual aqueous solution obtained above is acidified with acetic acid and treated with lead(II) acetate a double salt is precipitated which has the composition $C_6H_7NSPb(CH_3COO)_2$. Ballard and Winkler (5) have a patent covering the production of thiophenolic compounds, including o-aminobenzenethiol, by treatment of the corresponding phenolic compounds with hydrogen sulfide in the presence of a metal oxide catalyst at an elevated temperature and superatmospheric pressures. The patentees suggest that the thiophenols produced find use as additives to lubricating oils, intermediates in organic syntheses, insecticides, fungicides, etc.

Precipitations of metal salts of o-aminobenzenethiol have been described: for lead by Knowles and Watt (27), see above, and Bauer and Burschkies (6); for zinc, bismuth, mercury, cadmium, iron, gold and copper by Steiger (39, 40); for palladium and platinum by Livingston (28); and for nickel and cobalt by Hieber and Brück (18, 19, 20). Hieber and Brück have investigated the significance of a nickel(IV) complex for the formation of nickel carbonyl, and have investigated the oxidation products of cobalt(II) and nickel(II) complexes of o-aminobenzenethiol. Hieber and Bruck state that a chocolate-colored cobalt(II) complex is oxidized by air to a green-blue cobalt(III) complex, and that yellow, amorphous nickel(II)-o-aminothiophenolate, in strongly basic solutions, is oxidized by air to a deep blue, crystalline, dioxo-nickel(IV) compound according to the following scheme:



Nickel(II)-o-Aminothiophenolate Dioxo-Nickel(IV) Compound

Freiser (15), and Charles and Freiser (11), by potentiometric techniques, have determined the acid dissociation constants of o-aminophenol and o-aminobenzenethiol and the stability constants of the chelates of these reagents with some common divalent metals. They have found that the chelates of o-aminobenzenethiol are more stable than those of o-aminophenol, despite the greater acidity of the thiol. This is attributed to the probably greater covalent character of the metal-sulfur bond than that of the metal-oxygen bond. The reactions of o-aminobenzenethiol with copper(II), nickel(II), cobalt(II), bismuth(III), zinc(II), mercury(II), cadmium(II), silver(I) and iron(III) are described qualitatively. It is suggested that o-aminobenzenethiol may be a useful reagent for bismuth. Irving and Williams (26) have included o-aminobenzenethiol in their discussions of some factors controlling the selectivity of organic reagents. o-Aminobenzenethiol, since it is a highly reactive, bifunctional, aromatic compound, has, of course, many applications as an intermediate in purely organic chemistry. The literature covering these applications is outside the scope of this investigation, but the reader who is interested will find an excellent outline of these reactions and a brief bibliography in a publication of American Cyanamid Company (1).

The physical properties of o-aminobenzenethiol listed in Table 1 were determined at the Stamford Research Laboratories of American Cyanamid Company using a redistilled sample of 95 per cent purity. The manufacturer advises that caution should be observed in handling the reagent as severe dermatitis may result from skin contact.

The work and data outlined in the previous pages and in Table 1 give all the information that has been found concerning the reactions of o-aminobenzenethiol with metal ions. Freiser, and Freiser and Charles, by pointing out the high order of stability of the metal chelates of this reagent and by observing the slight solubility of these chelates, encourage the hope that this reagent may be useful in quantitative inorganic analysis. However, none of the workers quoted above has explored the application of o-aminobenzenethiol to inorganic analysis. This paper presents the results of some investigations aimed at quantitative determinations through use of the reagent.

TABLE 1.—Physical properties of o-aminobenzenethiol

Property		Description or Measure
Appearance		Colorless liquid, but exposure to air causes rapid yellowing due to oxidation
Molecular Weight (theory)		125.18
Freezing Point		23±0.5 °C
Boiling Point (760 mm. Hg)		227.2 °C, some decomposition above 180 °C
Heat of Vaporization		14.1 kcal.
Flash Point (Tagliabue Closed Cup)		>175 °F (>80 °C)
Density		1.168 g./cc. at 25 °C 1.164 g./cc. at 30 °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)		1.0×10^{-11}
Solubility:	Water	0.7 g./ml. at 30 °C
	Heptane	7.0 g./ml. at 30 °C

o-Aminobenzenethiol is completely miscible at 30 °C with acetone, carbon tetrachloride, dioxane, ethanol, ethyl acetate and xylene

CHAPTER II

PRELIMINARY WORK

Preparation of Metal Ion Test Solutions

To permit a study of the reactions of a wide range of elements, solutions of thirty-six different ions were prepared. The ions dissolved included common valence forms of most of the true metals and, in addition, ions of some elements with little or no metallic character. Analytical grade salts were used without purification. None of the salts was dried before weighing, since so many solutions were to be prepared, and since, at first, only qualitative information was to be sought. Each solution was prepared and stored in a 250 ml. volumetric flask fitted with a one-hole rubber stopper holding a 5 ml. transfer pipet (the pipet was capped when not in use). Enough metal salt was dissolved to make each solution 0.2 N in the metal ion. Thus each 5 ml. aliquot of a solution contained 0.001 equivalent of metal ion; this made it convenient to calculate the amount of a given reagent theoretically required to react completely with the metal in an aliquot portion. Common acids or bases were used as required to effect solution. The ionic forms involved, the actual salts used, the nature of the solvent, the color of the solutions, the weight of salt taken, and the weight of metal ion calculated as present in a 5 ml. aliquot are listed for each

TABLE 2.—Composition of metal ion test solutions

Ion	Salt	Solvents Other Than Water ml./250 ml.	Color of the Solution	Weight of Salt g./250 ml.	Weight of Metal in Aliquot g./5 ml.
B(III)	H_3BO_3	10 ml. HCl	Colorless	1.0305	0.0036
Mg(II)	Metal	10 ml. HCl	Colorless	0.6080	0.0122
Al(III)	Metal	12 ml. HCl	Colorless	0.4495	0.0090
Si(IV)	$Na_2SiO_3 \cdot 9H_2O$	--	Colorless	3.5525	0.0070
Ca(II)	$CaCO_3$	10 ml. HCl	Colorless	2.5025	0.0200
Ti(IV)	TiO_2	(5 g. $K_2S_2O_7$) (20 ml. H_2SO_4) (6 ml. 30% H_2O_2)	Orange-red	0.9990	0.0120
V(V)	NH_4VO_3	5 ml. H_2SO_4	Deep yellow	1.1700	0.0102
Cr(VI)	$K_2Cr_2O_7$	--	Deep orange	1.2258	0.0087
Mn(VII)	$KMnO_4$	--	Deep purple	1.1290	0.0079
Fe(III)	$Fe_2(SO_4)_3$	10 ml. HCl	Deep yellow	3.3323	0.0186
Fe(II)	$FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$	1 ml. HCl	Pale yellow	9.8040	0.0279
Co(II)	$CoCl_2 \cdot 6H_2O$	--	Deep pink	5.9490	0.0295
Ni(II)	$Ni(CH_3COO)_2 \cdot 4H_2O$	--	Green	6.2155	0.0294
Cu(II)	CuO	20 ml. HCl	Blue-green	1.9895	0.0318
Cu(I)	CuCl	40 ml. HCl	Gray-green	4.9515	0.0635
Zn(II)	Metal	15 ml. HCl	Colorless	1.6345	0.0327
As(III)	As_2O_3	--	Colorless	1.6488	0.0250
Se(VI)	$Na_2SeO_4 \cdot 10H_2O$	--	Colorless	3.0760	0.0132
Se(IV)	$Na_2SeO_3 \cdot 5H_2O$	--	Colorless	3.2880	0.0197
Sr(II)	$Sr(NO_3)_2$	--	Colorless	5.2965	0.0438
Zr(IV)	$ZrO(NO_3)_2 \cdot 2H_2O$	15 ml. H_2SO_4	Colorless	1.9905	0.0228
Mo(VI)	$(NH_4)_2MoO_4$	(5 ml. HNO_3) (10 ml. NH_4OH)	Colorless	1.6335	0.0160
Ag(I)	$AgNO_3$	1 ml. HNO_3	Colorless	8.4945	0.1079
Cd(II)	$CdCO_3$	(15 ml. HCl) (5 ml. HNO_3)	Colorless	4.3100	0.0562
Sn(II)	$SnCl_2 \cdot 2H_2O$	85 ml. HCl	Colorless	5.6415	0.0594
Sb(III)	$KSbC_4H_4O_7 \cdot 1/2H_2O$	--	Colorless	5.5655	0.0406
Te(IV)	K_2TeO_3	15 ml. HCl	Colorless	3.1725	0.0319
Ba(II)	$BaCl_2 \cdot 2H_2O$	--	Colorless	6.1075	0.0687
Ce(IV)	$Ce(SO_4)_2$	(10 ml. HCl) (15 ml. H_2SO_4) (50 ml. HNO_3)	Pale yellow	4.1530	0.0350
W(VI)	$Na_2WO_4 \cdot 2H_2O$	--	Colorless	2.7495	0.0307
Hg(II)	$HgCl_2$	--	Colorless	6.7880	0.1003
Hg(I)	$HgNO_3 \cdot H_2O$	15 ml. HNO_3	Colorless	14.0315	0.2006
Pb(II)	$Pb(NO_3)_2$	--	Colorless	8.2805	0.1036
Bi(III)	Metal	(15 ml. HCl) (5 ml. HNO_3)	Colorless	3.4835	0.0677
Th(IV)	$Th(NO_3)_4 \cdot 4H_2O$	--	Colorless	6.9030	0.0580
U(VI)	$UO_2(NO_3)_2 \cdot 6H_2O$	5 ml. HNO_3	Deep yellow	4.1855	0.0397

solution in Table 2.

Reactions of Test Solutions with Reagents Other Than o-Aminobenzenethiol

Although the principal purpose of this research was to be an investigation of the reactions of metal ions with o-aminobenzenethiol, considerable work was done in which aliquot portions of each metal ion test solution were reacted with more common precipitating agents including ammonium hydroxide, sodium carbonate, ammonium oxalate and 8-hydroxyquinoline. This work was done to gain familiarity with reactions of many individual metal ions which might later prove useful in making separations from complex solutions. All operations and measurements were done carefully, but the work was only semi-quantitative in that the test solutions were not standardized and techniques were not adapted to conform to the peculiarities of singular ions.

Reactions with Ammonium Hydroxide

For these experiments a 5 ml. aliquot of each metal ion solution (containing 0.001 equivalent of metal ion) was diluted to 100 ml. with distilled water. Five milliliters of concentrated hydrochloric acid was added to each diluted solution. Each solution was then heated to boiling and neutralized while hot with 1:1 ammonium hydroxide solution until a faint odor of ammonia could be detected. Effects observed upon addition of the hydrochloric acid, and upon neutralization with ammonia are listed in Table 3. It is interesting to note that from the thirty-six solutions only twelve hydrous oxide precipitates were obtained, of which, six, precipitates of aluminum, zirconium, cerium, lead, bismuth, and thorium,

TABLE 3.--Reactions with ammonium hydroxide

Ion	Effect upon Addition of HCl	Effect upon Neutralization with NH_4OH
B(III)	None	None
Mg(II)	None	None
Al(III)	None	Gray-white floc
Si(IV)	None	None
Ca(II)	None	None
Ti(IV)	None	Pale Yellow floc
V(V)	None	Colorless solution became rather dark yellow but faded to colorless again
Cr(VI)	None	Yellow color faded somewhat
Mn(VII)	Dark brown curd	Dirty brown precipitate
Fe(III)	Yellow color darkened upon boiling	Rust-red floc
Fe(II)	None	Brownish-black floc
Co(II)	None	Pink color deepened somewhat
Ni(II)	None	Greenish-yellow color changed to blue
Cu(II)	Slight intensification of blue color	Greenish-blue solution changed to deep blue
Cu(I)	Slight intensification of blue color	Greenish-blue solution changed to deep blue
Zn(II)	None	None
As(III)	None	None
Se(VI)	None	None
Se(IV)	None	None
Sr(II)	None	None
Zr(IV)	None	Silvery white floc
Mo(VI)	None	None
Ag(I)	White AgCl separated	Precipitate coagulated
Cd(II)	None	None
Sn(II)	None	Voluminous yellow-white floc
Sb(III)	White SbOCl separated but redissolved upon mixing	None
Te(IV)	None	None
Ba(II)	None	None
Ce(IV)	None	None
W(VI)	Colorless solution became milky	Precipitate redissolved
Hg(II)	None	None
Hg(I)	White Hg_2Cl_2 separated; precipitate coagulated upon boiling	Part of the precipitate reduced to metallic mercury--gray cast
Pb(II)	None	White precipitate
Th(IV)	None	White floc
U(VI)	None	Bright yellow floc

were white. These precipitates were filtered on a fast paper, washed with one per cent ammonium chloride solution, ignited over a burner at about 1,000 °C, cooled and weighed. It was assumed that each ignitate was a normal oxide and the corresponding weight of metal was calculated in each case. These weights are listed together with those obtained by other reactions (to facilitate comparisons) in Table 9. In addition to the hydrous oxides there were obtained, of course, the white silver chloride and white mercurous chloride precipitates; the silver chloride precipitate coagulated upon neutralization with ammonia and may have been partially or almost completely converted to the hydroxide. These two precipitates were discarded.

Reactions with Sodium Carbonate

For these experiments thirty-six 100 ml. portions of five per cent sodium carbonate were boiled and then a 5 ml. aliquot of one metal ion solution was added to each hot solution. In cases in which the metal ion solution to be added was acid, a calculated excess of sodium carbonate was added before addition of the metal ion solution so that the final concentration of unreacted carbonate in the hot solution would be approximately five per cent. The solutions of sodium carbonate were, of course, colorless and water-clear before the addition of the metal ion solutions. Observed effects for all metal ions tested are shown in Tables 4 and 9. Of the thirty-six solutions tested, twenty-one gave permanent precipitates either as hydrous oxides, insoluble carbonates, or slightly soluble compounds. These precipitates were not filtered, but all precipitates and solutions were reserved for use in the next experi-

TABLE 4.--Reactions with sodium carbonate

Ion	Effect upon Addition of the Metal Ion Solution to Hot 5% Na_2CO_3 Solution
B(III)	None
Mg(II)	A small amount of silvery white floc was formed. $Mg(OH)_2$?
Al(III)	None
Si(IV)	None
Ca(II)	Granular white precipitate formed
Ti(IV)	Violet-gray floc formed which changed to buff color in four days
V(V)	Colorless solution became dark yellow but faded rapidly to colorless again
Cr(VI)	Clear bright yellow solution formed
Mn(VII)	Purple permanganate solution formed
Fe(III)	Reddish brown precipitate, lighter color than the ammonia precipitate, formed
Fe(II)	Same reaction as for the Fe(III) ion
Co(II)	Dark blue floc formed which changed to a green color in four days
Ni(II)	Pale pastel green floc formed
Cu(II)	Pale green floc formed which rapidly darkened to a dark brown color
Cu(I)	Chartreuse floc formed which slowly became dark green, almost black after four days
Zn(II)	Silvery white floc formed
As(III)	None
Se(VI)	None
Se(IV)	None
Sr(II)	Rather fine white precipitate formed
Zr(IV)	None
Mo(VI)	None
Ag(I)	Yellow floc formed which rapidly became a brownish-black and then chartreuse after four days. Ag_2CO_3?
Cd(II)	Fine white precipitate and suspension formed
Sn(II)	A white floc formed which redissolved to give a colorless solution
Sb(III)	A small amount of very fine white precipitate formed
Te(IV)	A fine white solid separated but redissolved to give a clear solution
Ba(II)	Fine white precipitate and suspension formed
Ce(IV)	A white floc formed which redissolved to give a yellow solution from which a fine light colored precipitate separated
W(VI)	None
Hg(II)	Finely divided bright orange precipitate formed
Hg(I)	Finely divided buff precipitate formed
Pb(II)	Finely divided white solid separated
Bi(III)	Curdy white precipitate and suspension formed
Th(IV)	Silvery white floc formed
U(VI)	Pale yellow solution formed

ments.

Reactions with Ammonium Oxalate

For these experiments, the sodium carbonate solutions reserved from the previous experiments were first treated with sufficient acid to neutralize the base and give 5 per cent free acid. The silver and mercury(I) solutions were acidified with nitric acid, the other solutions with hydrochloric acid. The vanadium solution was the only solution which showed an unusual reaction upon acidification; this colorless solution assumed a deep yellow color near the neutral point and then faded to colorless again as acidification was completed. All solutions were sparkling clear after acidification.

Five milliliters of a 4 per cent solution of ammonium oxalate was now added to each acid solution. The thorium solution gave a milky white precipitate immediately upon addition of the oxalate solution; no other metal gave a precipitate with ammonium oxalate in strongly acid solution. The cerium solution faded from a pale yellow color to colorless upon addition of the oxalate solution.

After addition of the oxalate solution each metal ion solution was neutralized with 1:1 ammonium hydroxide solution to a pH of about 8.0 as measured with an indicator paper. The effects observed are recorded in Table 5. Of the thirty-six solutions thus treated twelve gave definite precipitates upon neutralization, and a few others gave slight turbidities or delayed partial precipitations. Twelve precipitates were filtered, washed, ignited to the oxides, and weighed. The weights of metal calculated from the oxides are listed in Table 9.

TABLE 5.--Reactions with ammonium oxalate

Ion	Effect upon Neutralizing the Metal-Oxalate Solutions
B(III)	None
Mg(II)	None
Al(III)	Silver white floc formed
Si(IV)	None
Ca(II)	Fine-grained white precipitate formed
Ti(IV)	Pale yellow floc formed
V(V)	None
Cr(VI)	None
Mn(VII)	No immediate effect, but a slight brownish turbidity developed slowly
Fe(III)	Light brown floc
Fe(II)	Light brown floc
Co(II)	Pink color of the solution deepened somewhat
Ni(II)	Color of the solution changed from almost colorless to pale blue
Cu(II)	Greenish blue solution changed to dark blue
Cu(I)	Greenish blue solution changed to dark blue
Zn(II)	None
As(III)	None
Se(VI)	None
Se(IV)	None
Sr(II)	Very small amount of fine white precipitate formed
Zr(IV)	Silvery white floc formed
Mo(VI)	None
Ag(I)	None
Cd(II)	None
Sn(II)	Silvery white floc formed
Sb(III)	No immediate effect but a small amount of fine white precipitate formed within two hours
Te(IV)	None
Ba(II)	None
Ce(IV)	White floc formed
W(VI)	None
Hg(II)	Fine white precipitate formed
Hg(I)	Delayed precipitation of a small amount of fine white precipitate
Pb(II)	Fine white precipitate formed
Bi(III)	White floc formed
Th(IV)	Fine white precipitate formed in strong acid persisted upon neutralization
U(VI)	None

Reactions with 8-Hydroxyquinoline

For these experiments a 5 ml. aliquot of each metal ion solution was diluted to 100 ml. with distilled water. To each dilute solution was then added, in order, 5 ml. of concentrated acid (the silver and mercury(I) solutions were acidified with nitric acid, the other solutions with hydrochloric acid), 5 ml. of 8-hydroxyquinoline solution (5 g. of 8-hydroxyquinoline per 100 ml. of 2 N acetic acid), and finally sufficient 1:1 ammonium hydroxide solution to give a strongly basic solution. Effects observed upon neutralization are listed in Table 6. Of the thirty-six solutions tested, twenty-six gave definite precipitates. Tin, antimony, and tungsten gave partial precipitations. All twenty-nine precipitates were filtered, washed, ignited to the oxides, and weighed. The weights of metal calculated from these oxides are listed in Table 9. However, some quite low weights are not indicative of the degree of completeness of precipitation of the metal-oxines, for some, such as copper-oxine, were quite volatile and were lost during ignition.

TABLE 6.--Reactions with 8-hydroxyquinoline

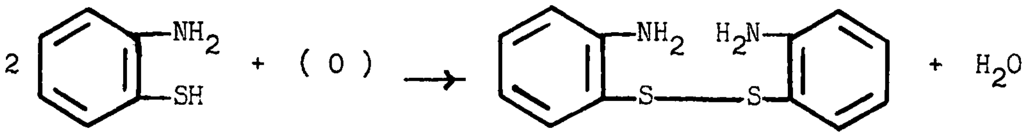
Ion	Effect upon Adding Excess Ammonium Hydroxide to the Metal-Oxine Solutions
B(III)	Some light colored precipitate separated at the neutral point but it immediately redissolved--may have been merely oxine
Mg(II)	Pale yellow, finely divided precipitate formed
Al(III)	Pale yellow curd formed
Si(IV)	Same as Boron, see above
Ca(II)	Pale yellow, finely divided precipitate formed
Ti(IV)	Pale yellow, finely divided precipitate formed
V(V)	Below pH 5 a dark green almost black precipitate separated and then redissolved; above pH 7 a permanent brownish-yellow precipitate formed
Cr(VI)	Upon addition of the oxine the solution developed a reddish-brown color; and upon neutralization a dark brown precipitate formed
Mn(VII)	Upon addition of the oxine the purple solution changed to yellow; upon neutralization a green floc formed
Fe(III)	(Both Fe(III) and Fe(II) ions gave an inky black precipitate which)
Fe(II)	(redissolved below pH 7 to give a green solution but was permanent) (above pH 7)
Co(II)	Orange curd formed
Ni(II)	Pale green curd formed
Cu(II)	Pale green curd formed
Cu(I)	Pale green curd formed
Zn(II)	Pale yellow curd formed
As(III)	Same as Boron, see above
Se(VI)	Same as Boron, see above
Se(IV)	Same as Boron, see above
Sr(II)	No precipitate below pH 7 but a fine white granular precipitate formed gradually within a few minutes after excess base added
Zr(IV)	Pale greenish-yellow floc formed
Mo(VI)	Pale yellow precipitate formed
Ag(I)	Greenish-yellow precipitate formed at pH 7; color changed to dark brown with excess base
Cd(II)	Pale yellow curd formed
Sn(II)	Turbid solution formed
Sb(III)	Pale yellow solution
Te(IV)	Same as Boron, see above
Ba(II)	No precipitate
Ce(IV)	Orange floc formed which changed in color to a pale brown
W(VI)	Pale precipitate formed in 5% HCl which redissolved at pH 7
Hg(II)	Pale yellow precipitate formed
Hg(I)	Finely divided orange-yellow precipitate formed
Pb(II)	Pale yellow curd formed
Bi(III)	Yellow curd formed
Th(IV)	Orange-yellow curd formed
U(VI)	Dark orange precipitate formed

Reactions of Test Solutions with o-Aminobenzenethiol

Reactions in Hydrochloric Acid Solutions

To obtain a comprehensive picture of the reactions of o-aminobenzenethiol with metals this reagent was used in experiments with the thirty-six metal ion solutions described in Table 2 and also with a 0.2 N solution of gold(III) prepared by diluting 6.57 g. of chloroauric acid, $HAuCl_4 \cdot 3H_2O$, to 250 ml. with distilled water. Two series of experiments were done with solutions prepared in dilute hydrochloric acid. In the first series of experiments 5 ml. of each metal ion test solution (except the silver solution and the mercury(I) solution) was diluted to 100 ml. with five per cent hydrochloric acid. A "blank" solution consisting of 100 ml. of five per cent hydrochloric acid containing no metal ion was also prepared and subsequently treated in the same way as were the other solutions. To each dilute solution 10 drops of o-aminobenzenethiol was added. Ten drops of o-aminobenzenethiol weigh about 0.250 g., and this weight corresponds to 0.002 of an equivalent of the thiol. After the addition of the thiol the solutions were stirred and neutralized slowly with 1:1 ammonium hydroxide solution. The pH of incipient precipitation, about pH 3 for many of the metal ions, was checked roughly with an indicator paper, but each solution was neutralized to a final pH of 7.0 to 8.0. The solutions were allowed to stand for about 48 hours; then the following observations were made.

The blank solution which had shown a pale yellow turbidity, immediately upon neutralization to a pH of about 3.0, now had long (¼ to 1 inch) pale yellowish-green needles. These needles are assumed to be the disulfide of the thiol since o-aminobenzenethiol is converted slowly by atmospheric oxygen to bis (2-aminophenyl) disulfide (22), a solid which melts at 92.5 to 92.7 °C and is insoluble in water (2).



The needles obtained in the blank solution were filtered on fritted glass crucibles, washed with water and dried. The precipitate, after it had been further dried at 100 °C for one hour, weighed 0.1718 g., and, after it had been further dried at 240 °C, weighed 0.1685 g. (as compared to an estimated 0.250 g. of o-aminobenzenethiol taken). The dried precipitate showed evidence of melting and decomposition.

Solutions of the following metals apparently had no precipitate other than the needles noticed in the blank solution: magnesium, calcium, barium, boron, silicon, tungsten and strontium. These solutions were discarded.

The other solutions gave precipitates; the most distinctive precipitate was that from the bismuth solution which was a bright orange color. Precipitates of those metals which have stable oxides were filtered through paper, washed with water, ignited at 1,000 °C, cooled, and weighed; but the results were not good. Low values were obtained for the oxides of manganese, titanium, and iron by ignition of the precipitates obtained through the neutralization of the metal-aminobenzenethiol solutions, whereas by use of ammonia alone one may precipitate these metals quantitatively as hydrous oxides that can be ignited without loss. It is not known whether the low values result from incomplete precipitation or from volatilization during the ignition. A few precipitates (those from aluminum, zirconium, cerium, thorium, and uranium) apparently did give fairly satisfactory values for the oxides by this method, but for all these cases equally satisfactory results can be obtained by use of ammonia alone.

Other precipitates were filtered on fritted glass crucibles, washed with water, dried for one hour at 100 °C, cooled and weighed. The weights of metal calculated from the dried precipitates thus treated were all too high compared to the amount of metal taken, which fact is not surprising since the blank solution, as mentioned above, gave considerable precipitate that persisted up to 240 °C. Most of these precipitates showed evidence of melting and decomposition from this treatment.

In the second series of experiments the conditions of the experiments were more carefully controlled. For these experiments 5 ml. of each metal ion test solution was diluted to 50 ml. with five per cent hydrochloric acid. To each dilute metal ion solution 50 ml. of a freshly prepared, filtered solution containing 20 drops of o-aminobenzenethiol in five per cent hydrochloric acid was added slowly with constant stirring. Each acid solution was then neutralized to a pH of approximately 2.2 by adding 1:1 ammonium hydroxide solution drop-wise while measuring the pH with a Model H Beckman pH meter. The effects observed upon addition of o-aminobenzenethiol to the acid solution, the pH of incipient precipitation, the final pH, and the appearance of precipitates obtained upon neutralization are recorded in Table 7. Many of these precipitates were filtered on fritted glass, washed with water, dried at a moderate tem-

TABLE 7.--Reactions with o-aminobenezenethiol in hydrochloric acid solutions

Ion	Effect upon Adding o-Aminobenzenethiol to an Acid Solution of the Metal Ion	Effect upon Neutralizing with NH_4OH		
		pH Turbid	pH Final	Precipitate Observed
B(III)	None	2.2	2.2	Pale yellow turbidity**
Mg(II)	None	2.2	2.2	Pale yellow turbidity**
Al(III)	None	2.2	2.2	Pale yellow turbidity**
Si(IV)	None	2.2	2.2	Pale yellow turbidity**
Ca(II)	None	2.2	2.2	Pale yellow turbidity**
Ti(IV)	Orange faded to almost colorless*	1.2	2.4	Dense pale yellow curd
V(V)	Pale yellow changed to pale green	2.0	2.2	Pale yellow turbidity**
Cr(VI)	Deep yellow changed to gray-green	2.1	2.4	Grayish-cream precipitate
Mn(VII)	Purple changed to turbid brown	1.8	2.4	Dirty yellow precipitate
Fe(III)	Deep yellow faded to colorless	1.9	2.5	Pale yellow precipitate
Fe(II)	Pale yellow faded to colorless	1.9	2.7	Pale yellow precipitate
Co(II)	Pink color faded	0.7	3.0	Chocolate brown precipitate that changed to blue
Ni(II)	Pale green color faded somewhat	0.4	2.2	Greenish-yellow floc
Cu(II)	Blue color changed to yellow	2.1	2.3	Pale yellow precipitate
Cu(I)	White turbidity appeared	---	---	White floc--no NH_4OH added
Zn(II)	None	2.0	2.3	Voluminous white floc
As(III)	Colorless changed to pale yellow	1.1	1.3	White floc that redissolved
Se(VI)	Brick-red precipitate	---	---	No NH_4OH added
Se(IV)	Brick-red precipitate	---	---	No NH_4OH added
Sr(II)	None	2.2	2.3	Pale yellow turbidity**
Zr(IV)	None	2.2	2.3	White floc
Mo(VI)	Colorless changed to clear brown	1.0	2.3	Brownish-black precipitate
Ag(I)	Curdy AgCl coagulated to a floc	---	---	No NH_4OH added
Cd(II)	None	2.5	3.0	White curd
Sn(II)	Colorless changed to yellow	1.5	2.0	Pale yellow curd
Sb(III)	Colorless changed to pale yellow	1.4	1.8	Yellow precipitate
Te(IV)	Finely divided black precipitate	---	---	No NH_4OH added
Ba(II)	None	2.2	2.2	Pale yellow turbidity**
Ce(IV)	None	2.2	3.6	Fine white precipitate
W(VI)	None--white turbidity in HCl	---	---	No NH_4OH added
Hg(II)	Short white needles	---	---	No NH_4OH added
Hg(I)	Did not try in HCl solution	---	---	Did not try in HCl solution
Pb(II)	Small amount of white precipitate	0.5	3.5	Green-yellow curd
Bi(III)	Colorless changed to deep yellow	1.6	2.2	Bright orange floc
Th(IV)	None	2.0	5.5	Pale yellow precipitate
U(VI)	Yellow color faded	2.2	2.2	Pale yellow turbidity**
None***	Colorless changed to pale yellow	2.2	2.5	Pale yellow turbidity**

* References are to changes in the colors of clear solutions unless the appearance of a precipitate is specifically mentioned.

**A precipitate described as a "Pale yellow turbidity" is thought to indicate separation of o-aminobenzenethiol without any precipitation of the metal.

*** This solution originally consisted merely of 5% HCl used as a "blank."

perature (room temperature to 100 °C), and the weight of metal contained in each was calculated. It was assumed that each dried precipitate contained one equivalent of metal for each mole of o-aminobenzenethiol. These weights are recorded in Table 9.

Reactions in Nitric Acid Solutions

The experiments conducted in hydrochloric acid solutions had demonstrated that o-aminobenzenethiol has significant reducing power in this solvent. To see whether the same reactions would prevail in an oxidizing solvent, and to have a solvent suitable for testing silver and mercury(I) ions, a series of experiments was performed exactly as was the second series in hydrochloric acid, except that the aliquots of the metal ion test solutions and the o-aminobenzenethiol were dissolved in five per cent nitric rather than in five per cent hydrochloric acid. The effects observed upon addition of o-aminobenzenethiol to the acid solution, the pH of incipient precipitation, the final pH, and the appearance of precipitates obtained upon neutralization are recorded in Table 8. Many of these precipitates were filtered on fritted glass, washed with water, dried, and the weight of metal contained in each was calculated. These weights are recorded in Table 9.

Summary of the Results from the Reactions of Test Solutions with o-Aminobenzenethiol

Examination of the data recorded in Tables 7 and 8 reveals that the most distinctive color change (without precipitation) that is obtained upon addition of o-aminobenzenethiol to five per cent acid solutions is the change from colorless to a clear deep yellow color that

TABLE 8.--Reactions with o-aminobenzenethiol in nitric acid solutions

Ion	Effect upon Adding o-Aminobenzenethiol to an Acid Solution of the Metal Ion	Effect upon Neutralizing with NH_4OH		
		pH Turbid	pH Final	Precipitate Observed
B(III)	None	2.2	2.2	Pale yellow turbidity**
Mg(II)	None	2.2	2.2	Pale yellow turbidity**
Al(III)	None	2.2	2.2	Pale yellow turbidity**
Si(IV)	None	2.2	2.2	Pale yellow turbidity**
Ca(II)	None	2.2	2.2	Pale yellow turbidity**
Ti(IV)	Yellow color faded somewhat*	1.3	2.1	Pale yellow floc
V(V)	Colorless changed to pale blue	2.1	2.4	Pale yellow precipitate
Cr(VI)	Yellow changed to gray-green	1.3	2.3	Pale yellow precipitate
Mn(VII)	Purple changed to turbid brown	---	---	No NH_4OH added
Fe(III)	None	1.8	2.3	Pale yellow precipitate
Fe(II)	None	1.5	1.9	Pale yellow precipitate
Co(II)	Pink color deepened	0.2	2.0	Gray-green floc
Ni(II)	Pale green changed to pale blue	0.1	1.5	Pale yellow floc
Cu(II)	Black precipitate that turned white	---	---	No NH_4OH added
Cu(I)	Black precipitate that turned white	---	---	No NH_4OH added
Zn(II)	None	1.6	1.9	Dense white floc
As(III)	None	1.2	1.3	Fine white floc
Se(VI)	Brick-red precipitate	---	---	No NH_4OH added
Se(IV)	Brick-red precipitate	---	---	No NH_4OH added
Sr(II)	None	2.3	2.4	Pale yellow turbidity**
Zr(IV)	None	1.0	2.6	Pale yellow floc
Mo(VI)	Colorless changed to pink	1.5	2.2	Green-brown floc
Ag(I)	Immediate white floc	---	---	No NH_4OH added
Cd(II)	None	2.3	2.7	White curd
Sn(II)	Colorless changed to pale yellow	1.3	1.5	Bright yellow floc
Sb(III)	None	1.4	1.4	Bright yellow floc
Te(IV)	Fine black precipitate	---	---	No NH_4OH added
Ba(II)	None	2.2	2.3	Pale yellow turbidity**
Ce(IV)	None	2.3	2.8	Pale yellow precipitate
W(VI)	None--acid caused turbidity	---	---	No NH_4OH added
Hg(II)	None	2.1	2.6	Pale yellow precipitate
Hg(I)	Fibrous gray-white needles	---	---	No NH_4OH added
Pb(II)	None	2.3	2.9	Canary yellow precipitate
Bi(III)	Colorless changed to deep yellow	1.6	2.0	Bright orange floc
Th(IV)	None	2.3	3.0	Pale yellow precipitate
U(VI)	None	2.2	2.2	Pale yellow turbidity**
Au(III)	Coppery crystalline precipitate	---	---	No NH_4OH added
None***	None	2.6	3.3	Pale yellow turbidity**

* References are to changes in the colors of clear solutions unless the appearance of a precipitate is specifically mentioned.

** A precipitate described as a "Pale yellow turbidity" is thought to indicate separation of o-aminobenzenethiol without any precipitation of the metal.

***This solution originally consisted merely of 5% HNO_3 used as a "blank."

occurs in solutions of the bismuth ion. This effect has been used to develop a colorimetric method for the quantitative determination of bismuth in solution as described in Chapter III. Tables 7 and 8 also reveal that dilute acid solutions of bismuth when treated with o-aminobenzenethiol and then neutralized to a pH of about 2.0 yield a unique bright orange precipitate. Investigations of the possibilities for qualitative and quantitative gravimetric determinations of bismuth by use of this precipitate are also described in Chapter III.

Interesting precipitations, listed in both Tables 7 and 8, that occur upon the addition of the thiol to acid solutions include: (1) the immediate precipitation of a dark brick-red solid, elemental selenium metal, from both the selenate and the selenite solution, and (2) the somewhat slower precipitation of black tellurium metal from its solution. A brief investigation of the possibilities for use of these precipitation reactions for gravimetric determinations of selenium and tellurium is described in Chapter IV.

Another precipitation reaction involving o-aminobenzenethiol that has been revealed by these preliminary tests and that has stimulated further investigation is that of silver from five per cent nitric acid solutions. Results that have been obtained by use of the thiol for the quantitative gravimetric determination of silver are described in Chapter V.

As shown in Table 8, the mercury(I) ion is also precipitated by o-aminobenzenethiol from five per cent nitric acid solutions. The precipitate obtained has a very interesting appearance; it consists of gray-white fibrous needles about one-quarter inch long which mat upon the

TABLE 9.--Weight of metal found with different precipitating agents

Ion	Precipitating Agents and Weight of Metal Found							
	NH_4OH	Na_2CO_3	$(NH_4)_2C_2O_4$	Oxine	ABT in HCl***		ABT in HNO_3****	
	grams	grams	grams	grams	Final pH	grams	Final pH	grams
B(III)								
Mg(II)		*		0.0117				
Al(III)	0.0085		0.0095	0.0086				
Si(IV)								
Ca(II)		*	0.0263	0.0144				
Ti(IV)	0.0156	*	0.0163	0.0004**	2.4	0.0154	2.1	0.0172
V(V)				0.0013**			2.4	0.0095
Cr(VI)				0.0051			2.3	0.0089
Mn(VII)	0.0074	*		0.0075			<1.0	0.0000**
Fe(III)	0.0136	*	0.0155	0.0135	2.5	0.0153	2.3	0.0189
Fe(II)	0.0278	*	0.0321	0.0272	2.7	0.0166	1.9	0.0188
Co(II)		*		0.0267	3.0	0.0370	2.0	0.0332
Ni(II)		*		0.0234	2.2	0.0335	1.5	0.0198
Cu(II)		*		0.0283			<1.0	0.0304
Cu(I)		*		0.0599	<1.0	0.0754	<1.0	0.2310
Zn(II)		*		0.0321	2.3	0.0225	1.9	0.0361
As(III)							1.3	0.0197
Se(VI)					<1.0	*	<1.0	0.0200
Se(IV)					<1.0	0.0347	<1.0	0.0336
Sr(II)		*						
Zr(IV)	0.0195		0.0193	0.0196	2.3	0.0036	2.6	0.0299
Mo(VI)				0.0030	2.3	0.0142	2.2	0.0352
Ag(I)		*		0.0131**			<1.0	0.1066
Cd(II)		*		0.0417	3.0	0.0650	2.6	0.0743
Sn(II)	0.0552		0.0662	0.0207	2.0	0.0526	1.5	0.0564
Sb(III)		*		0.0047	1.8	0.0407	1.5	0.0389
Te(IV)					<1.0	0.0194	<1.0	0.0163
Ba(II)		*						
Ce(IV)	0.0235		0.0303	0.0241			2.8	0.0283
W(VI)				0.0238			<1.0	0.0278
Hg(II)		*	0.0057**	0.0007**	<1.0	0.0555	2.6	0.1323
Hg(I)		*		0.0000**			<1.0	0.1100
Pb(II)	0.0724	*	0.0991	0.0986	2.5	0.1262	2.9	0.1416
Bi(III)	0.0602	*	0.0692	0.0669	2.2	0.0650	2.0	0.1023
Th(IV)	0.0582	*	0.0457	0.0587			3.0	0.0334
U(VI)	0.0422			0.0445			2.2	0.0204

* A definite precipitate was obtained, but it was not separated and weighed.

** The precipitate volatilized upon ignition.

*** o-Aminobenzenethiol in 5% hydrochloric acid solution.

****o-Aminobenzenethiol in 5% nitric acid solution.

filter very much like asbestos fibers. This reaction was not investigated further.

Other ions precipitated by o-aminobenzenethiol in five per cent acid solutions include those of copper and gold. The white copper precipitate, while stable in acid solution, darkened to a bluish black upon contact with water or air, and furthermore dissolved somewhat in neutral water washes. Gold, if present in solution, would be more readily separated by reduction to the metal by common reagents. No attempt, therefore, was made to develop these reactions for use in analyses for copper or gold, but the reactions receive consideration in Chapter V because they interfere in the gravimetric determination of silver.

Examination of the results listed in Table 9 shows that a great many other metals may be quantitatively precipitated by o-aminobenzenethiol from acid solutions that have been partially neutralized. However, so many of these metals precipitate at or near the same pH, pH 2, that separations of specific elements would be difficult. Furthermore, most of the precipitates have no distinctive color; colors vary from white through pale yellows and greens to a fairly bright clear yellow found in precipitates of antimony and tin. No further use was made of these reactions.

CHAPTER III

DETERMINATION OF BISMUTH

Results obtained in preliminary work indicated the desirability of investigating further the possibilities for determination of bismuth with o-aminobenzenethiol. These investigations, covering colorimetric, qualitative, and gravimetric experiments, are described in this chapter. The development of a colorimetric method, which seems most promising, is discussed first.

Colorimetric Determination of Bismuth

Two colorimetric methods for the determination of bismuth are well established. Small amounts of bismuth, such as 0.05 to 0.5 mg. may be determined by colorimetric comparison of the yellow to amber color obtained by treatment with potassium iodide in dilute nitric acid solution with that produced in a standard solution (21, 34). Interfering substances include copper and trivalent iron that react to give iodine, certain members of the arsenic group which also give colored solutions, and colored salts such as nickel nitrate in sufficient concentration to tint the solution. Lead causes no trouble unless it is present in large amount, for the yellow iodide can be filtered off before the test is made; large amounts of lead iodide may carry down bismuth. A saturated solution of sulfur dioxide may be used to destroy the color due to free iodine. A cinchonine potassium iodide colorimetric method that may be considered a variation of the above method is described by Scott (34). Presumably the same interferences are met.

Somewhat larger amounts of bismuth, such as 0.1 to 4 mg. can be determined photometrically in dilute nitric acid solution by adding thiourea and noting the transmission of the yellow-colored complex compound at approximately 425 mμ (21, 3, 7). Antimony, palladium, osmium and ruthenium also give colored complexes with thiourea in acid solution (45). Hydrofluoric acid prevents the formation of a colored antimony compound; silver, mercury, lead, copper, cadmium and zinc give white precipitates when present in appreciable amounts but no precipitates or colors in dilute solutions; iron in excess of 0.1 mg. per 50 ml. of solution must be removed or reduced to the ferrous state (30). Selenium and tellurium interfere (44).

In the present paper is described the evolution of a method by which amounts of bismuth such as 0.1 to 10 mg. can be determined photometrically in dilute mineral acid solution by adding o-aminobenzenethiol and noting the absorption of the yellow-colored complex compound at approximately 425 mμ. As detailed below, the interferences parallel somewhat those listed in the above methods, but, of course, there is no interference from iodine, and the presence of relatively large quantities of iron and some other metal ions can be tolerated.

Apparatus

The following instruments were used:

Model DU Beckman Spectrophotometer

AC Model Fisher Electrophotometer equipped with a 425 mμ filter and 3/4 x 3 inch cells

Model H Beckman pH Meter.

Reagents

Analytical grade reagents were used.

o-Aminobenzenethiol. The sample of liquid reagent furnished by American Cyanamid Company, New York, was used without purification. The manufacturer advises that caution should be observed in handling the reagent as severe dermatitis may result from contact (1).

Metal ion solutions for preliminary tests. For each metal tested sufficient metal or metal salt was dissolved to give 100 ml. of a solution approximately 0.001 N in metal ion and 0.6 N in an appropriate mineral acid.

Metal ion solutions for interference tests. For each metal tested sufficient metal or metal salt was dissolved to give one gram of metal per 100 ml. of solution. If acids other than perchloric were used for solution, the excess acid was evaporated off. The dissolved salts were then diluted to 100 ml. with 0.6 N perchloric acid. These stock solutions contained 10,000 ppm of the dissolved metal. Weaker solutions were prepared as desired by dilution with 0.6 N perchloric acid. Perchloric acid was used because it keeps more of the metals to be tested in solution in the presence of o-aminobenzenethiol than does any other common acid.

Stock solution of bismuth, 10,000 ppm. Exactly 1.0000 g. of bismuth metal was dissolved by boiling with concentrated hydrochloric acid to which concentrated nitric acid was added dropwise. The solution was evaporated to a moist paste. The paste was dissolved and diluted to exactly 100 ml. with the desired 0.6 N acid solution.

Stock solution of bismuth, 100 ppm. One milliliter of the 10,000 ppm solution was diluted to exactly 100 ml. with the desired 0.6 N acid solution. Weaker solutions of bismuth were made by similar dilutions of the 100 ppm solution.

Hydrochloric acid, 0.6 N solution. Each 5 ml. of concentrated hydrochloric acid was diluted to 100 ml. with distilled water.

Perchloric acid, 0.6 N solution. Each 5 ml. of 70-72% perchloric acid was diluted to 100 ml. with distilled water.

Nitric acid, 0.6 N solution. Each 3.9 ml. of concentrated nitric acid was diluted to 100 ml. with distilled water.

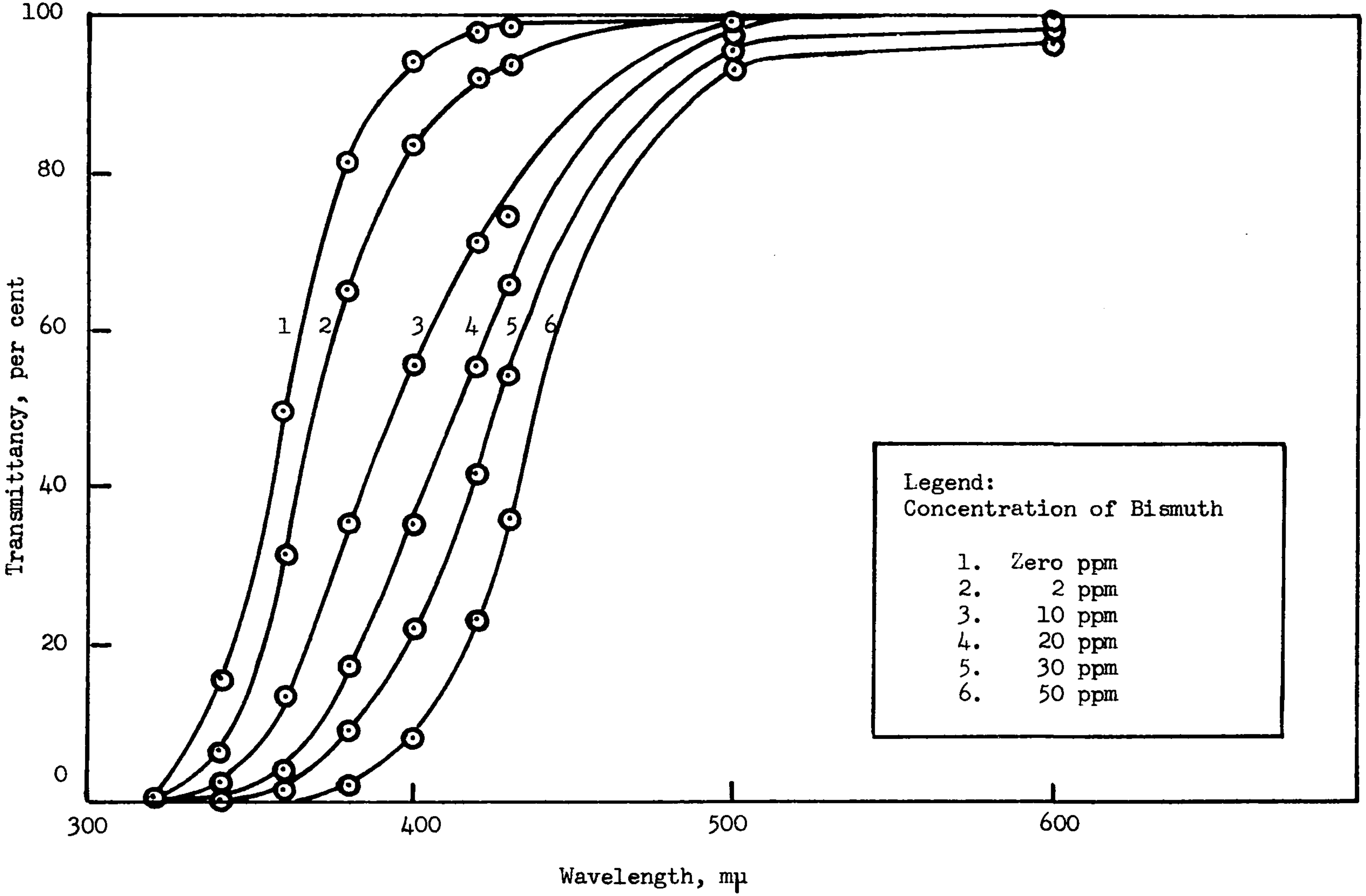
Measurements with the Model DU Beckman Spectrophotometer

As described in Chapter II, preliminary qualitative tests demonstrated that bismuth solutions, upon addition of o-aminobenzenethiol, develop a yellow color of a much greater intensity than is developed by a solution with a like concentration of any other of the thirty-six ions tested. Further qualitative tests indicated that the depth of color developed in the bismuth solutions is proportional to the concentration of bismuth. Measurements were then made on the Model DU Beckman Spectrophotometer to determine whether there was a wavelength, or range of wavelengths, at which these measurements for a desired series of concentrations of bismuth in dilute acid solutions would show the desirable characteristics of: (1) maximum absorption, (2) no steep rise or fall in the curve, and (3) 25 to 65 per cent transmittancy. For these measurements a series of solutions was prepared, each solution of which was 0.6 N in nitric acid and contained 10 drops of o-aminobenzenethiol per 100 ml. Respective solutions contained zero, 2, 10, 20, 30, or 50 ppm bismuth. The transmittancy of the resulting yellow-colored solutions was measured on the spectrophotometer, according to the manufacturer's instructions, for each solution at each of the following wavelengths: 320, 340, 360, 380, 400, 420, 430, 500, and 600 mµ. The results plotted in Figure 1 demonstrate that there is no preferred wavelength or range.

Variation of Color with Bismuth Concentration

The curves obtained with the spectrophotometer, Figure 1, rise steeply in the range (of transmittancy and of bismuth concentrations) at which it is desirable to make measurements. Since, therefore, a small error in selection of the wavelength gives a relatively large difference in the reading obtained with these solutions, it seemed advisable to use an instrument that does not require precise repetition of a chosen wavelength setting. For this reason subsequent measurements were made using an electrophotometer with a 425 mµ filter. Measurements were first made to establish quantitatively that the depth of color of a solution of the bismuth-o-aminobenzenethiol complex in dilute acid is proportional to the concentration of bismuth in solution. For these measurements three series of solutions were prepared, one series each in 0.6 N nitric acid,

FIG. 1.—Variation of transmittancy with wavelength for solutions of the bismuth-o-aminobenzenethiol complex

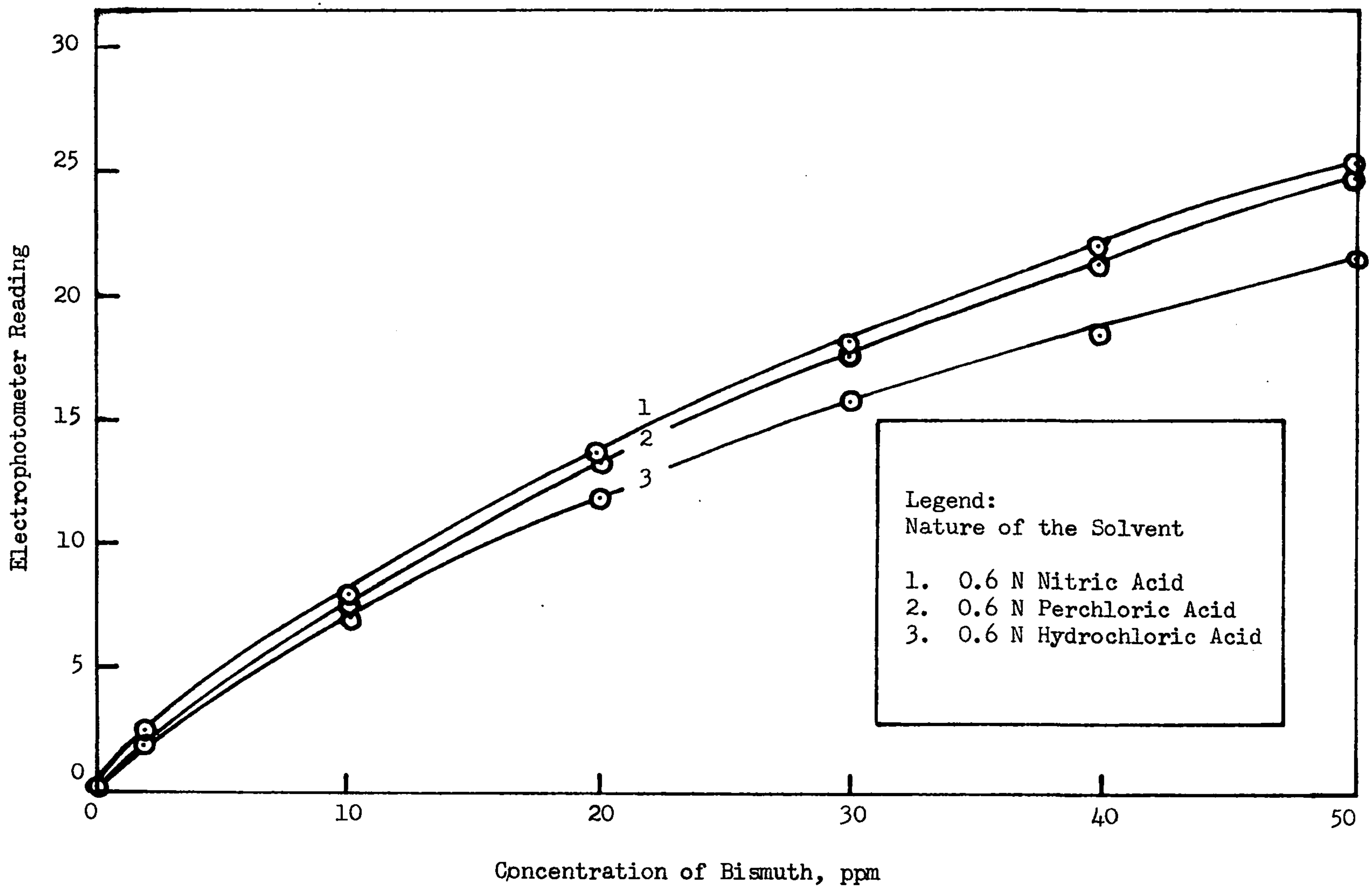


0.6 N perchloric acid and 0.6 N hydrochloric acid. Each series contained solutions with, respectively, zero, 2, 10, 20, 30, 40 or 50 ppm bismuth. All solutions contained 10 drops of o-aminobenzenethiol per 100 ml. Preliminary adjustments of the electrophotometer were made according to the manufacturer's instructions. A cell filled with distilled water was placed in the instrument and the upper "A" scale was adjusted to give a reading of zero. Readings were taken from the "A" scale for each solution of the bismuth-o-aminobenzenethiol complex. Results for solutions containing up to 50 ppm bismuth are shown in Figure 2. The color of a hydrochloric acid solution containing 100 ppm bismuth was measured, and it gave a reading of 33.2. This reading is not shown, but, if plotted, it would fall upon a smooth extension of Curve 3 of Figure 2. It is thought that colors for even higher concentrations can be measured if desired. Qualitative tests indicate that dilute phosphoric and sulfuric acid solutions will give similar results. However, the color of solutions containing the bismuth-o-aminobenzenethiol complex is not at all proportional to the concentration of the bismuth in the presence of organic acids such as acetic, tartaric, or citric acid, nor in the presence of organic solvents such as carbon tetrachloride, heptane, xylene, alcohol, pyrrolidone or dioxane.

Variation of Color with Time

The readings plotted in Figure 2 were made immediately (0 to 10 minutes) after the solutions were prepared. For a given solution there was some variation of the reading with time. Using the same apparatus, reagents and procedures as in the preceding section, measurements were

FIG. 2.--Variation of color with bismuth concentration for solutions of the bismuth-o-aminobenzenethiol complex



made at intervals of one hour, 24 hours, and 7 days from the time of preparation of the solutions. Results for the nitric acid solutions only are shown in Table 10; since variations were of a similar nature and magnitude for the three series. As shown in the table the variations are not significant if the readings are taken within an hour and are hardly greater at the end of 24 hours. However, after a few days the colors may change in an erratic fashion, so that, for instance, as shown in the right-hand column of the table, the solution with 50 ppm is of a lighter hue than the solution with 40 ppm bismuth.

TABLE 10.--Variation of color with time for solutions of the bismuth-o-aminobenzenethiol complex

Concentration of Bismuth	Interval between the Time of Preparation of the Solution and the Time of Measurement of Color			
ppm	0-10 minutes	1 hour	24 hours	7 days
0	0.4	0.4	0.4	2.6
2	2.6	2.5	2.7	6.4
10	8.2	8.3	8.3	9.3
20	13.9	14.5	14.5	14.2
30	18.6	18.9	18.9	14.2
40	22.4	22.5	22.8	24.6
50	25.7	26.0	26.0	15.3

Variation of Color with the o-Aminobenzenethiol Concentration

To test the effect of the concentration of o-aminobenzenethiol upon the color of solutions of the bismuth-o-aminobenzenethiol complex a series of solutions was prepared in which the concentration of o-aminobenzenethiol was varied from zero to 50 drops per 100 ml. of solution.

Each solution of the series contained 10 ppm bismuth and 5 ml. of concentrated hydrochloric acid per 100 ml. of solution. The color of each solution was measured using the apparatus and procedures described above. Results for solutions containing zero to 25 drops of o-aminobenzenethiol per 100 ml. are shown as Curve 1, Figure 3. A solution with 50 drops of o-aminobenzenethiol per 100 ml. gave a reading of 12.6, which could be plotted to form a smooth extension of Curve 1.

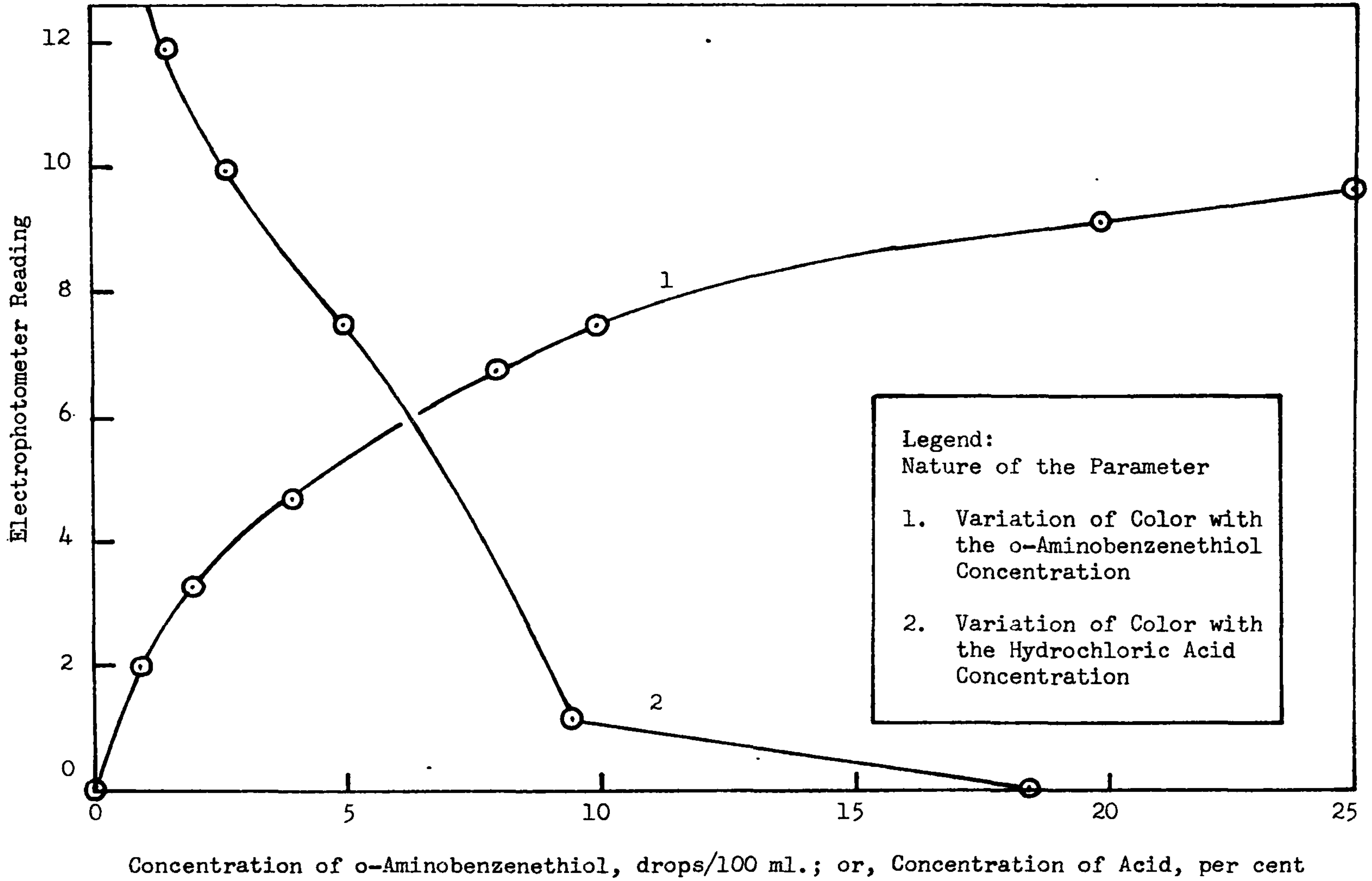
Variation of Color with Acid Concentration

To test the effect of acid concentration upon the color of solutions of the bismuth-o-aminobenzenethiol complex a series of hydrochloric acid solutions was prepared in which the per cent of acid in the solutions was varied from 0.5 to 18.5 per cent. Each solution of the series contained 10 ppm bismuth and 10 drops of o-aminobenzenethiol per 100 ml. The color of each solution was measured using the apparatus and procedures described above. Results are shown as Curve 2, Figure 3.

Color Measurements at Higher pH Values and Higher o-Aminobenzenethiol Concentrations

The curves plotted in Figure 3 for solutions containing 10 ppm bismuth show that the yellow color of these solutions was intensified both by lowering the concentration of acid (to give a higher pH value) and by increasing the concentration of o-aminobenzenethiol. The curves plotted in Figure 2, on the other hand, show that the color is sufficient to permit reasonably accurate measurements for solutions in which the concentration of bismuth is as low as two parts per million when the concentration of acid is 4 to 5 per cent (0.6 N, pH $<$ 1.0) and the con-

FIG. 3.--Variation of color with the o-aminobenzenethiol concentration or with acid concentration for solutions of the bismuth-o-aminobenzenethiol complex

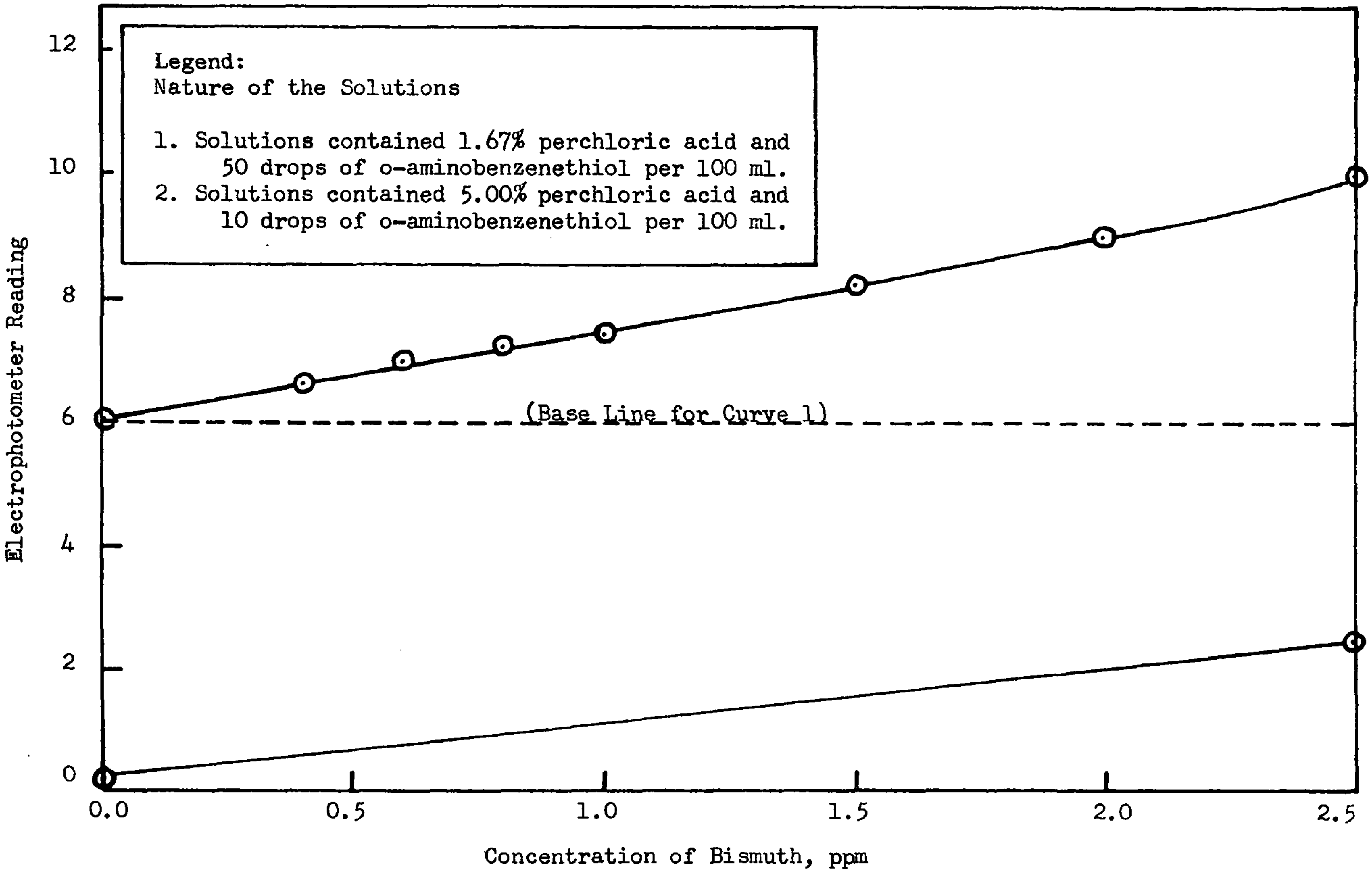


centration of o-aminobenzenethiol is 10 drops per 100 ml. For lower concentrations of bismuth a more intense color is desirable. Therefore, a series of solutions was prepared in which the concentration of bismuth was varied from zero to 2.5 ppm, but each solution contained 1.67 per cent of perchloric acid (pH of 1.5) and 50 drops of o-aminobenzenethiol per 100 ml. The color of each solution was measured as before and the results are shown as Curve 1 in Figure 4. Curve 2 in Figure 4 is an expanded portion of the perchloric acid solution curve from Figure 2, presented here for comparison. These two curves show that the expected benefit is almost lost because solutions with no bismuth have sufficient color to give a reading of 6.0 at the higher pH value and higher concentration of o-aminobenzenethiol.

Effects of Foreign Metal Ions and Other Interferences

All of the preceding measurements were made upon solutions that contained no metal ions other than bismuth. Some alloys and ores of bismuth are listed in Table 11 to show the kinds (and amounts where known) of other metal ions that would commonly be obtained with bismuth in solutions prepared for analysis. Bismuth, in solution with o-aminobenzenethiol, gives the deepest yellow color of any of the metals listed in Table 11. However, some of the other metals do give a yellow color and some have colors other than yellow which augment the light absorption readings given at 425 mµ by the electrophotometer. To test the extent of the interferences that might result from the presence of these metals solutions were prepared which contained varying amounts of bismuth and also varying amounts of the selected foreign ion in 5 per cent per-

FIG. 4.--Color measurements at higher pH values and higher o-aminobenzenethiol concentrations



chloric acid containing 10 drops of o-aminobenzenethiol per 100 ml., and their light absorption at 425 mμ was measured on the electrophotometer.

TABLE 11.--Composition of some bismuth alloys and ores

Metals Present	Type of Material and Per Cent of Each Metal Present					
	NBS No. 53b Lead-Base Bearing Metal (31)	NBS No. 54b Tin-Base Bearing Metal (32)	NBS No. 431 Tin Metal (33)	Wood's Metal (25)	Rose's Metal (25)	Ores (35)
Bismuth	0.075	0.029	0.020	50.0	50.0	*
Lead	84.35	1.81	0.19	25.0	25.0	*
Antimony	10.28	7.39	0.19			
Tin	5.06	87.48	99.115	12.5	12.5	
Copper	0.209	3.19	0.19			*
Arsenic	0.042	0.052	0.17			*
Nickel	0.006		0.038			
Silver	0.003	0.029	0.015			
Iron	0.002	0.028				
Zinc			0.014			*
Cadmium			0.020	12.5		
Aluminum	0.0007	<0.001				
Molybdenum) Vanadium) Selenium) Tellurium)						*

* May be present in variable amounts.

In addition to the metals listed in Table 11 solutions of sodium ion and of ammonium ion were prepared and checked. Also, a deepening of the color that results when dilute acid solutions containing only bismuth are filtered through paper before the addition of o-aminobenzenethiol was measured on the photometer.

Readings obtained for solutions of each metal alone, with metal concentrations up to as high as 1,000 ppm, are plotted in Figure 5.

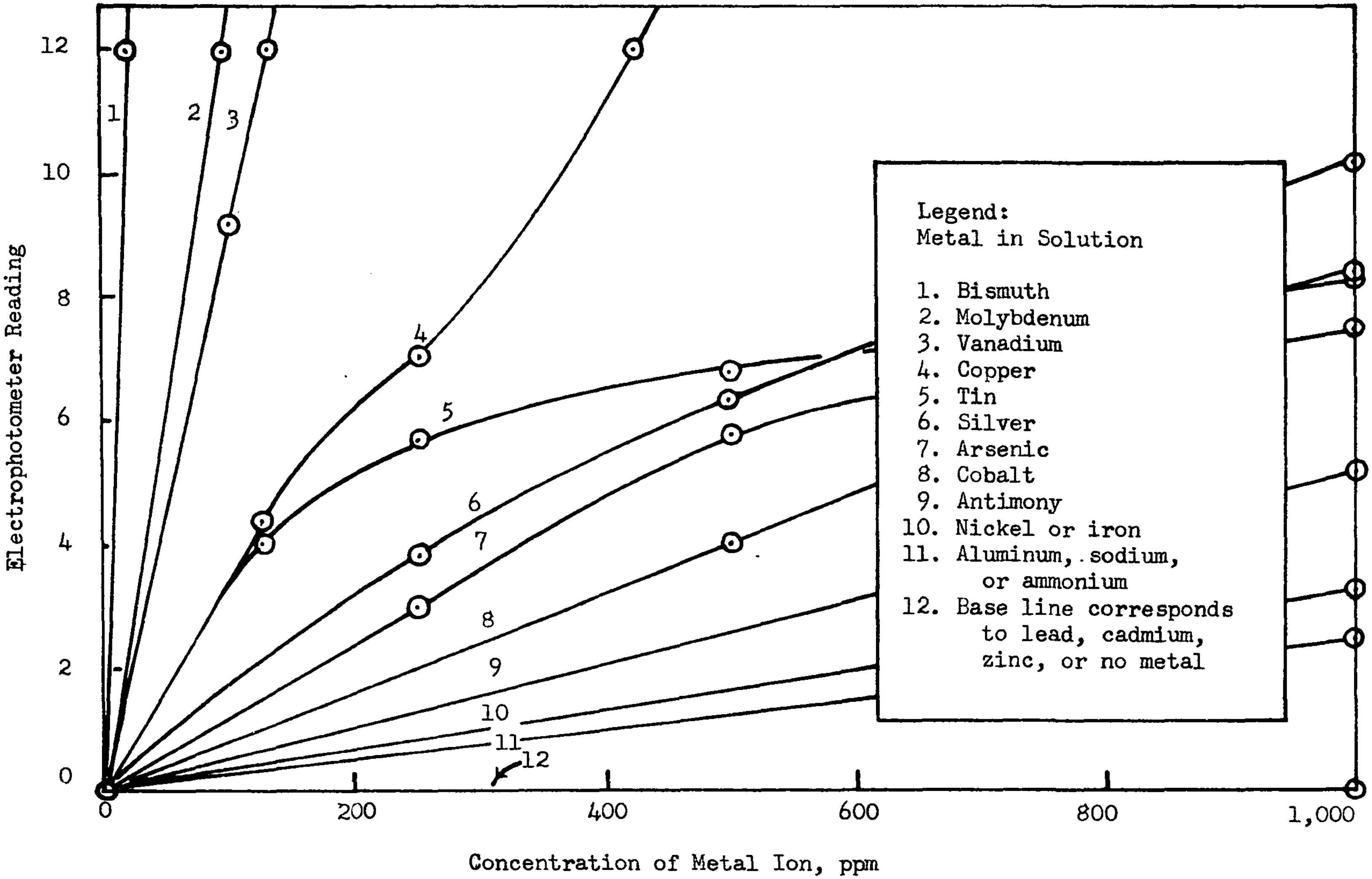
These curves allow a ready comparison of the relative amount of absorption for solutions of the other metals compared to those of bismuth.

Readings obtained for a series of solutions containing bismuth plus varying concentrations of one other metal are plotted in Figures 6 to 15.

To allow comparison of the relative effects of the different metals one curve each from Figures 6 to 15 is plotted in Figure 16. Curves showing the effects of 1,000 ppm of lead, cadmium, zinc, aluminum, sodium, or ammonium ion, and the effect of filtration through paper upon the bismuth-o-aminobenzenethiol color are also shown in Figure 16.

These experiments have revealed that selenium is reduced and precipitated as red selenium metal and that tellurium is reduced and precipitated as black tellurium metal from 5 per cent acid solutions (HCl, $HClO_4$, or HNO_3) by o-aminobenzenethiol. These metals can be filtered off to leave essentially colorless solutions so that they will not interfere in the colorimetric determination of bismuth unless present in amounts large enough to reduce materially the concentration of o-aminobenzenethiol in solution. Molybdenum, vanadium, and copper all give serious interference at rather moderate concentrations. Molybdenum is not soluble in concentrations much above 250 ppm but precipitates as a very dark blue-black solid from 5 per cent perchloric acid solutions containing o-aminobenzenethiol. Furthermore, once precipitated, this blue-black solid does not redissolve upon dilution but remains as a suspension at concentrations as low as 25 ppm molybdenum. However, if a molybdenum solution is diluted before the addition of o-aminobenzenethiol, clear deep yellow solutions are obtained for 250 ppm and less of molybdenum. Vanadium is very similar to molybdenum in its reactions and under the same conditions is insoluble, giving a very dark blue-black solid, at concentrations much above 500 ppm vanadium. The vanadium solutions are greenish-yellow. The copper(II) ion (the only copper ion tried in perchloric acid) is not soluble in concentrations much above 500 ppm copper but precipitates as a gray floc from 5 per cent perchloric acid solutions containing o-aminobenzenethiol. Copper is evidently even less soluble, in the presence of o-aminobenzenethiol, in 5 per cent nitric acid solutions containing some hydrochloric acid; both copper(II) and copper(I) ions give white precipitates under these conditions. Within the range of its solubility copper gives rather deep yellow solutions in perchloric acid. As shown in Figure 5, tin is unusual in that the intensity of the yellow color produced rises rapidly with increasing metal concentration at rather low concentrations of tin and then levels off. Of the other ions that give yellow-colored complexes, silver and arsenic give moderately strong colors in perchloric acid solutions, while iron and antimony give very weak colors. Silver and monovalent mercury are insoluble in dilute nitric acid solutions containing o-aminobenzenethiol; the former giving a white floc and the latter grayish white fibers resembling asbestos. Antimony is more likely to interfere by separating, upon standing, to give a turbid solution. Nickel and cobalt do not yield yellow solutions with o-aminobenzenethiol, but the characteristic green and pink of their respective solutions interfere. Cadmium, lead, zinc, aluminum, sodium and the ammonium ion give essentially colorless solutions with o-aminobenzenethiol and do not interfere with the color of the bismuth complex.

FIG. 5.--Color readings obtained for solutions of several different metal-o-aminobenzenethiol complexes



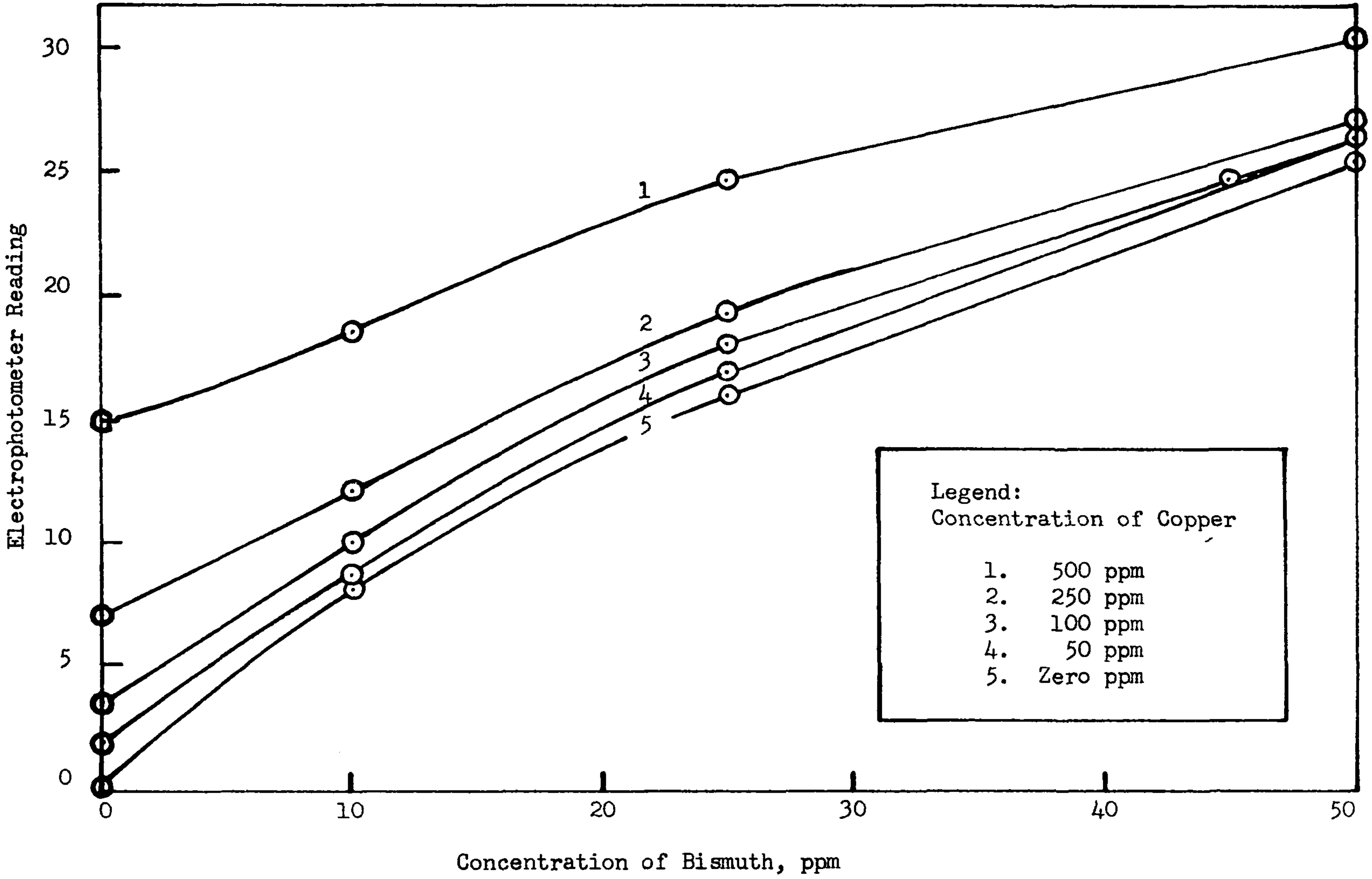


FIG. 6.--Color readings obtained for solutions containing the o-aminobenzenethiol complexes of bismuth and of copper

FIG. 7.--Color readings obtained for solutions containing the o-aminobenzenethiol complexes of bismuth and of iron

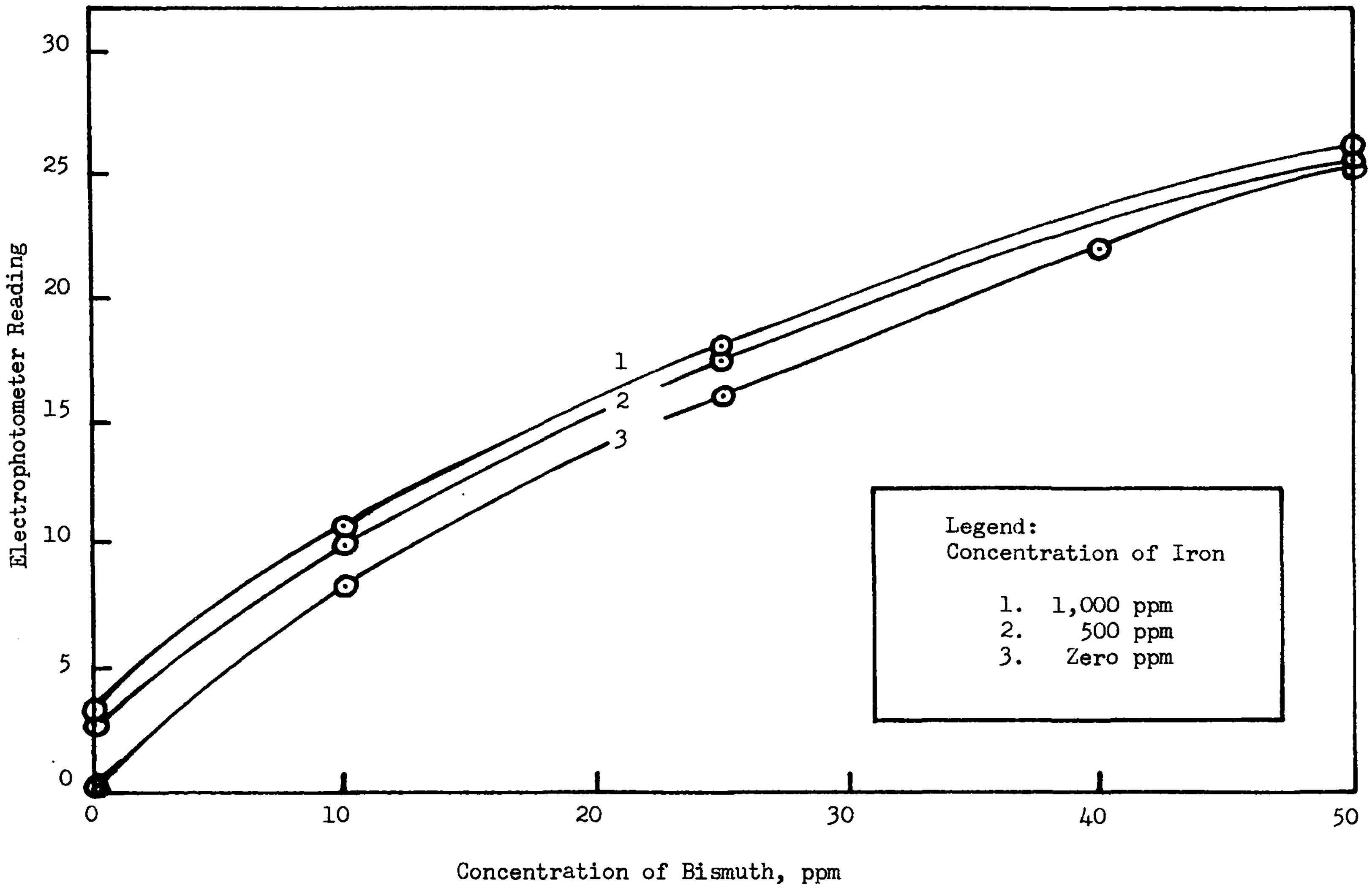


FIG. 8.--Color readings obtained for solutions containing the o-aminobenzenethiol complexes of bismuth and of nickel

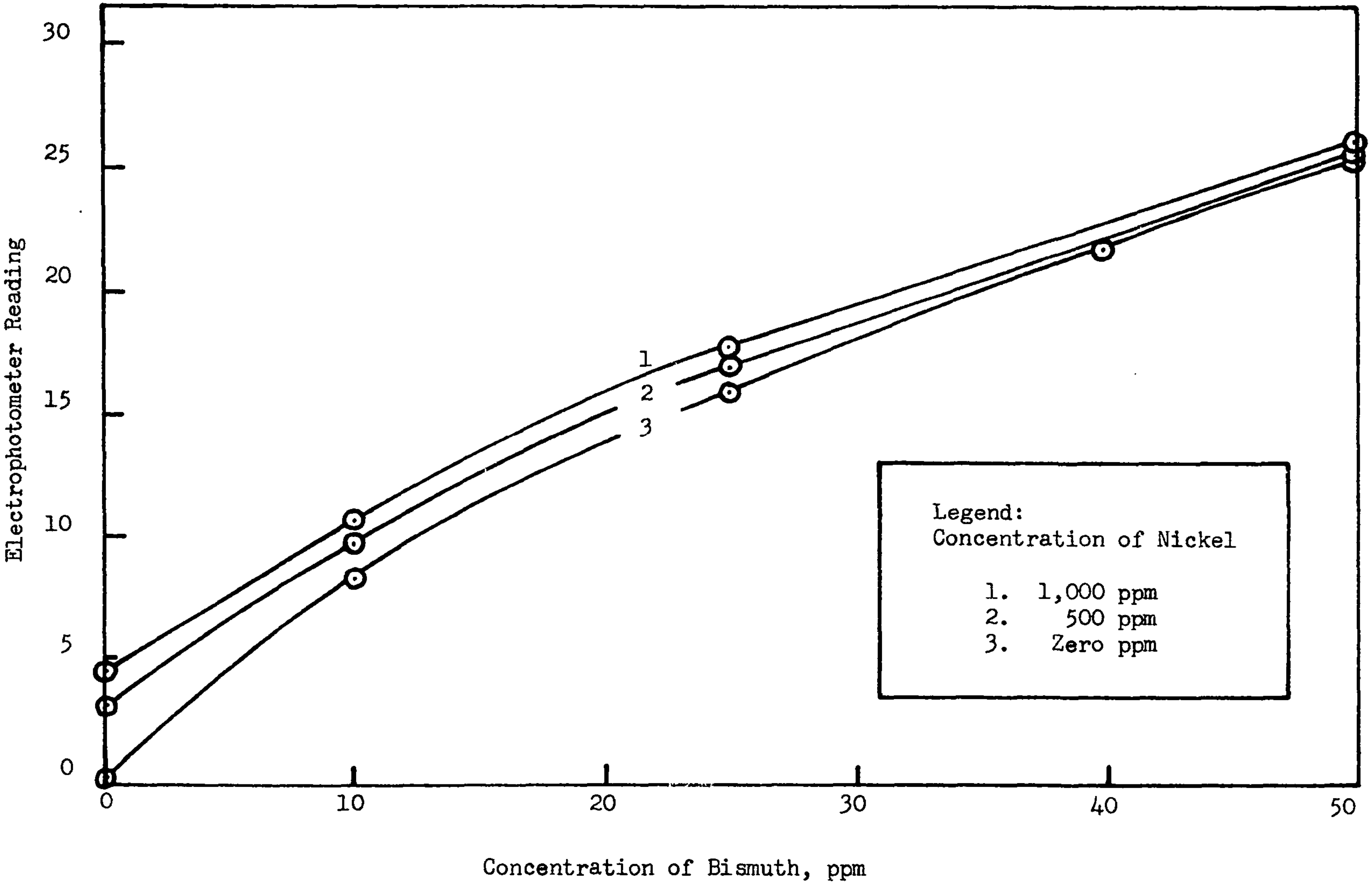


FIG. 9.—Color readings obtained for solutions containing the o-aminobenzenethiol complexes of bismuth and of molybdenum

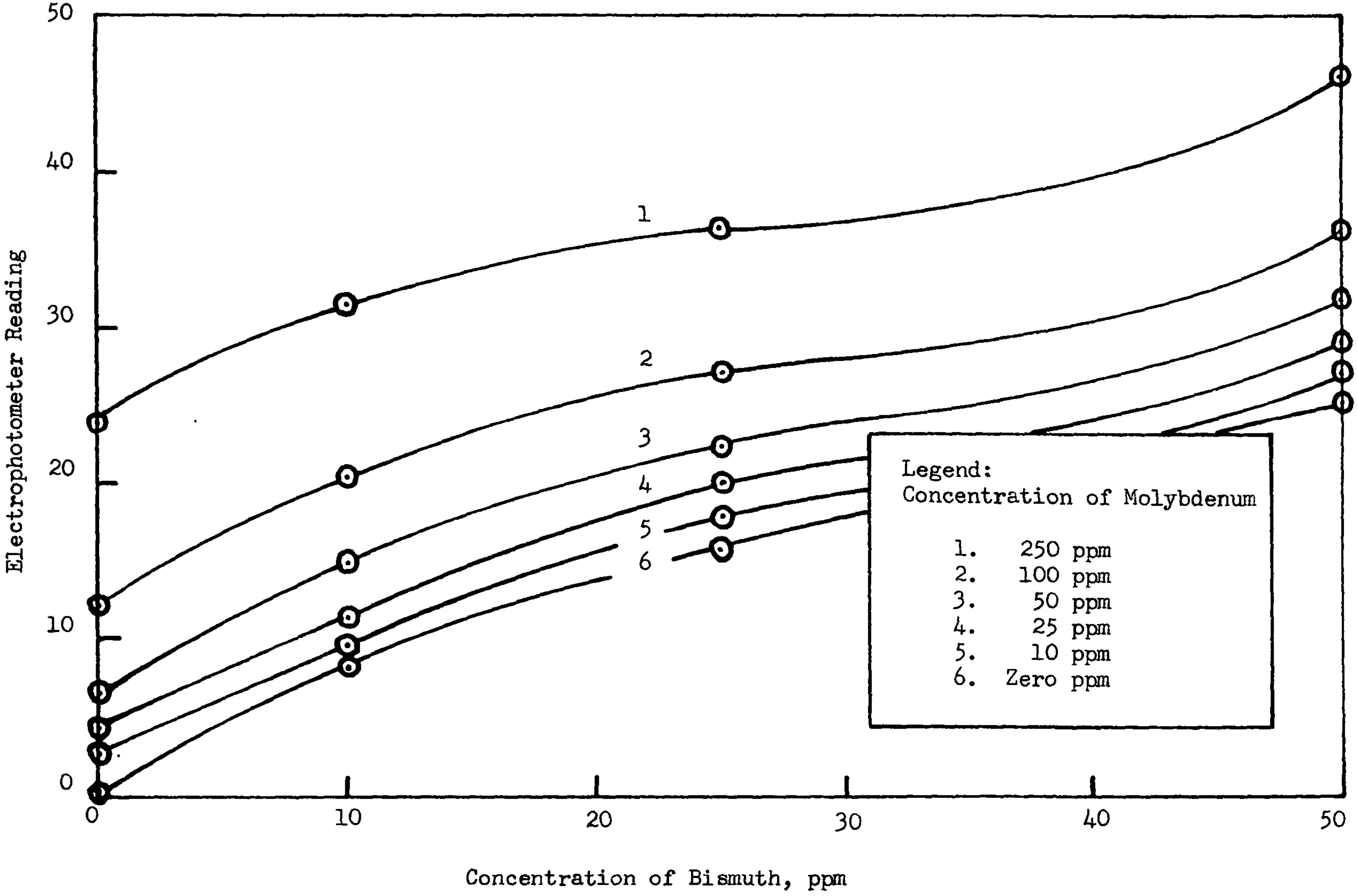


FIG. 10.--Color readings obtained for solutions containing the o-aminobenzenethiol complexes of bismuth and of arsenic

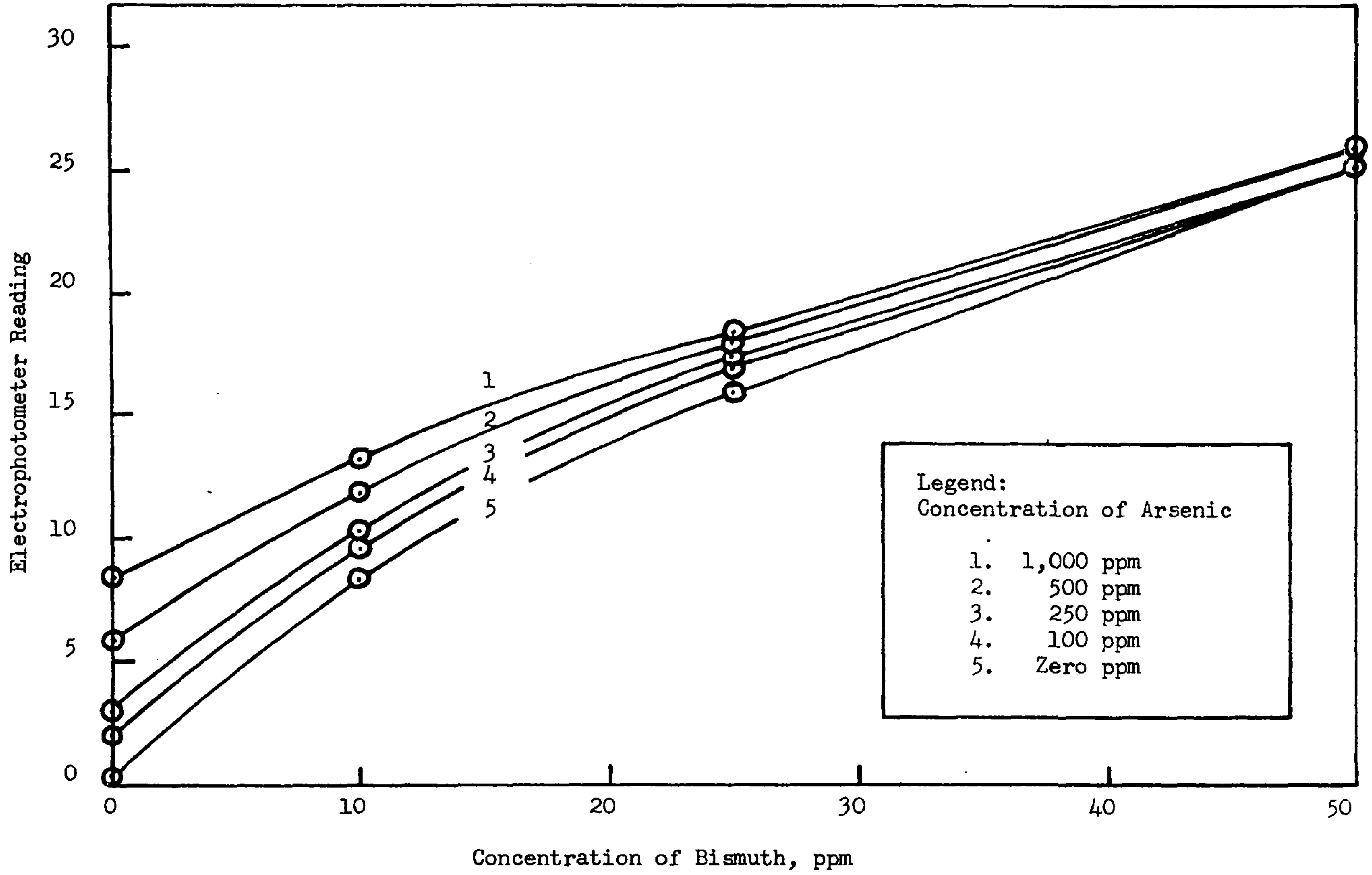


FIG. 11.--Color readings obtained for solutions containing the o-aminobenzenethiol complexes of bismuth and of silver

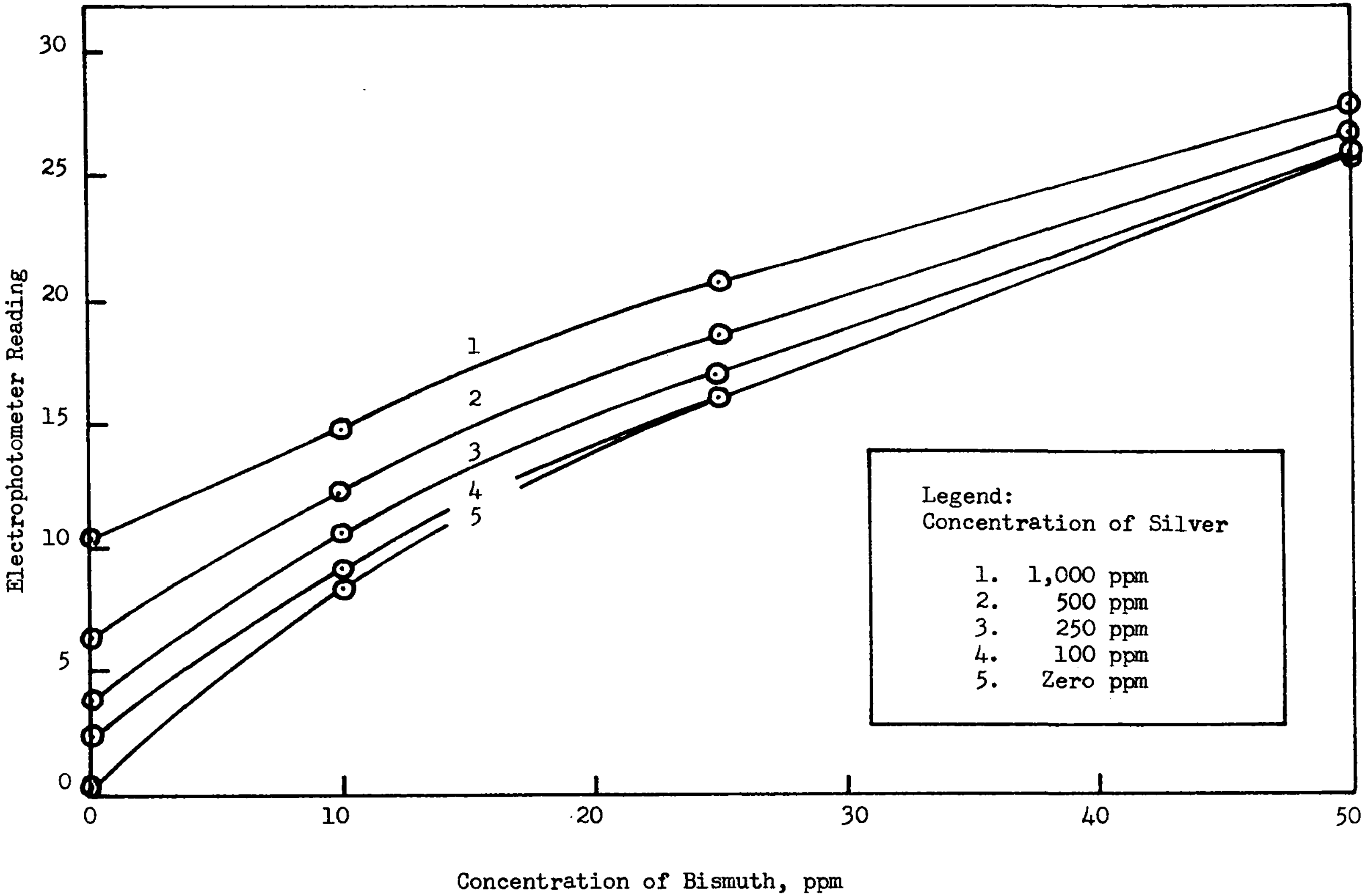


FIG. 12.--Color readings obtained for solutions containing the o-aminobenzenethiol complexes of bismuth and of antimony

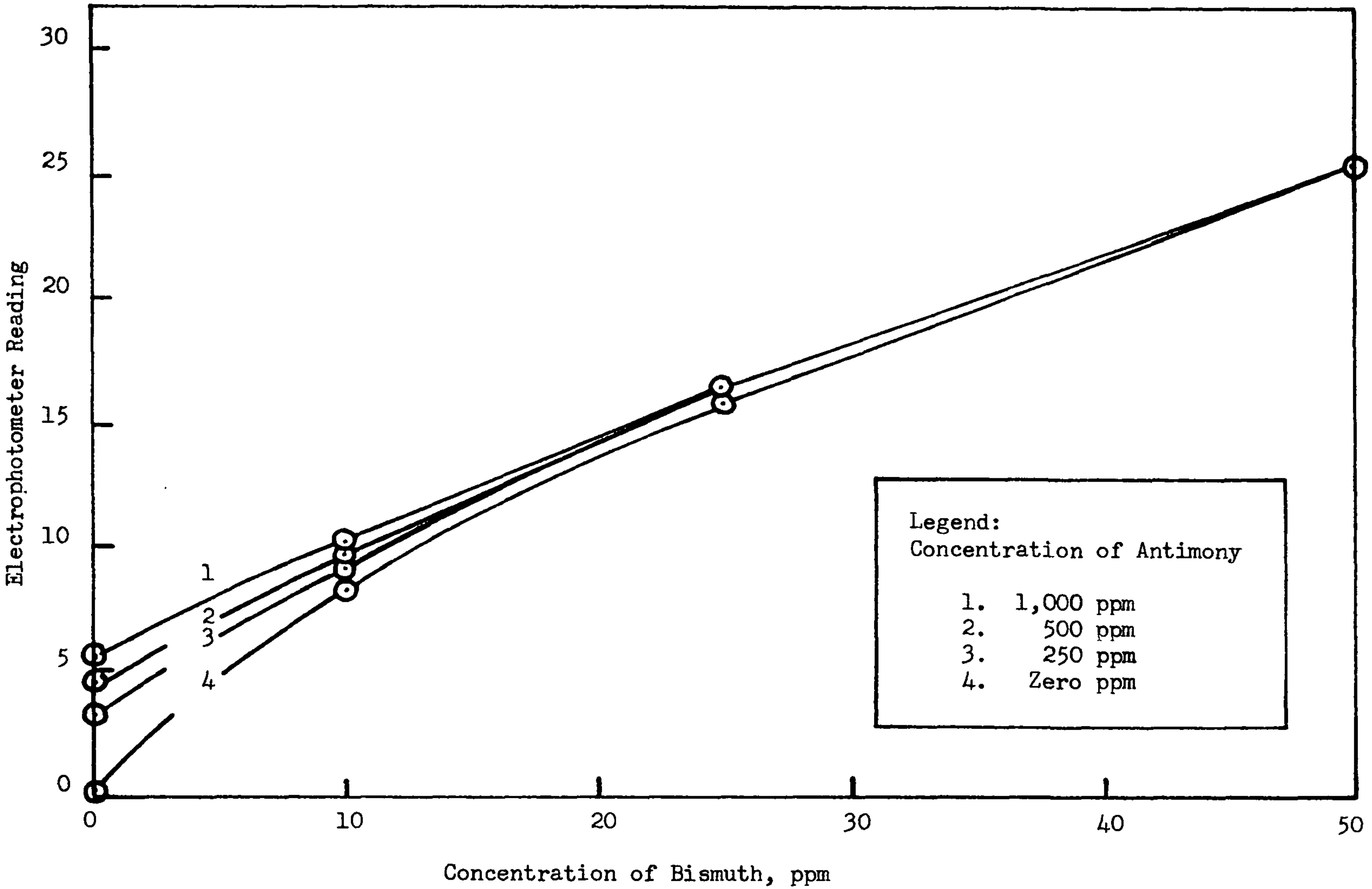


FIG. 13.---Color readings obtained for solutions containing the o-aminobenzenethiol complexes of bismuth and of tin

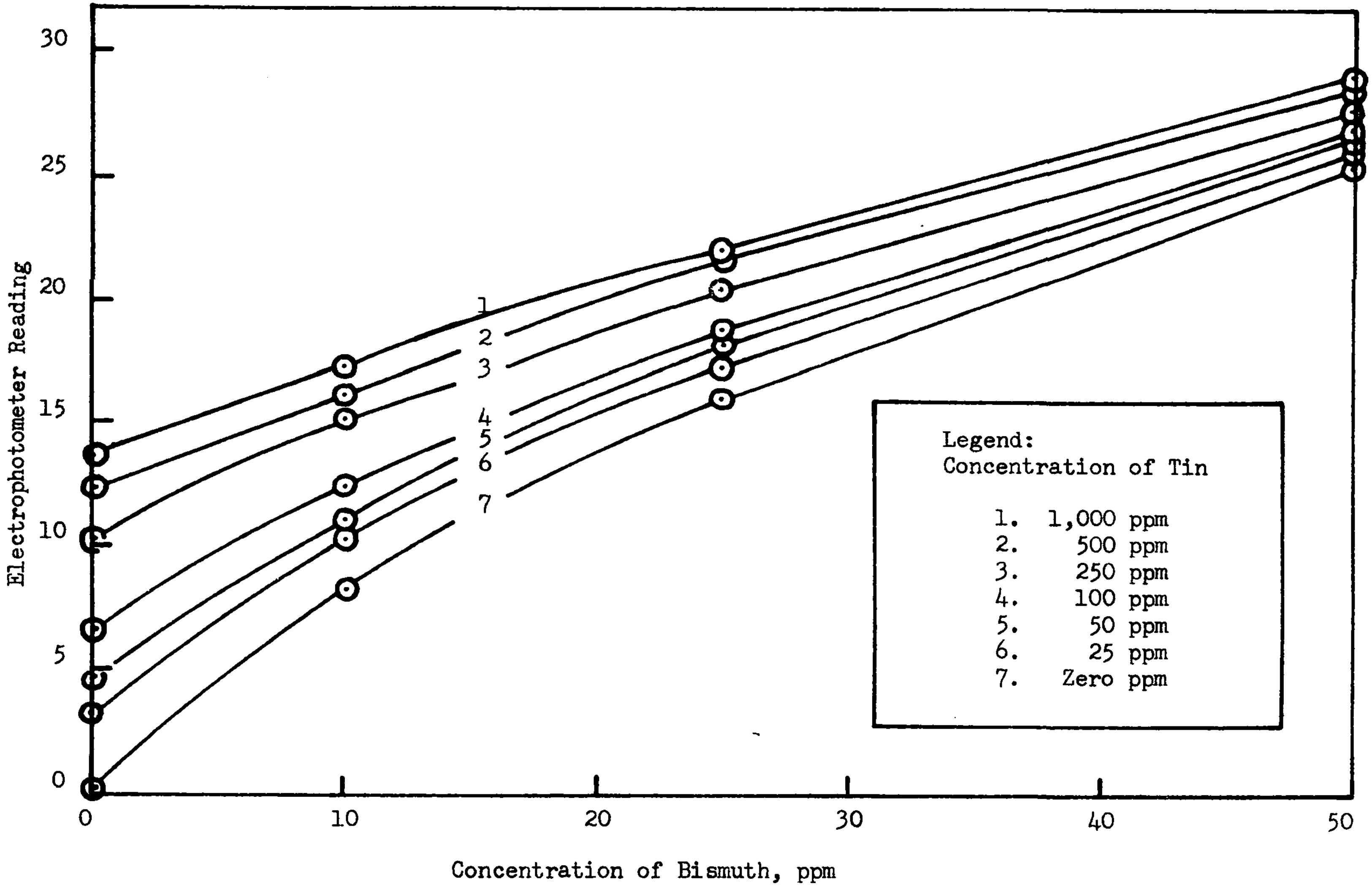


FIG. 14.--Color readings obtained for solutions containing the o-aminobenzenethiol complexes of bismuth and of cobalt

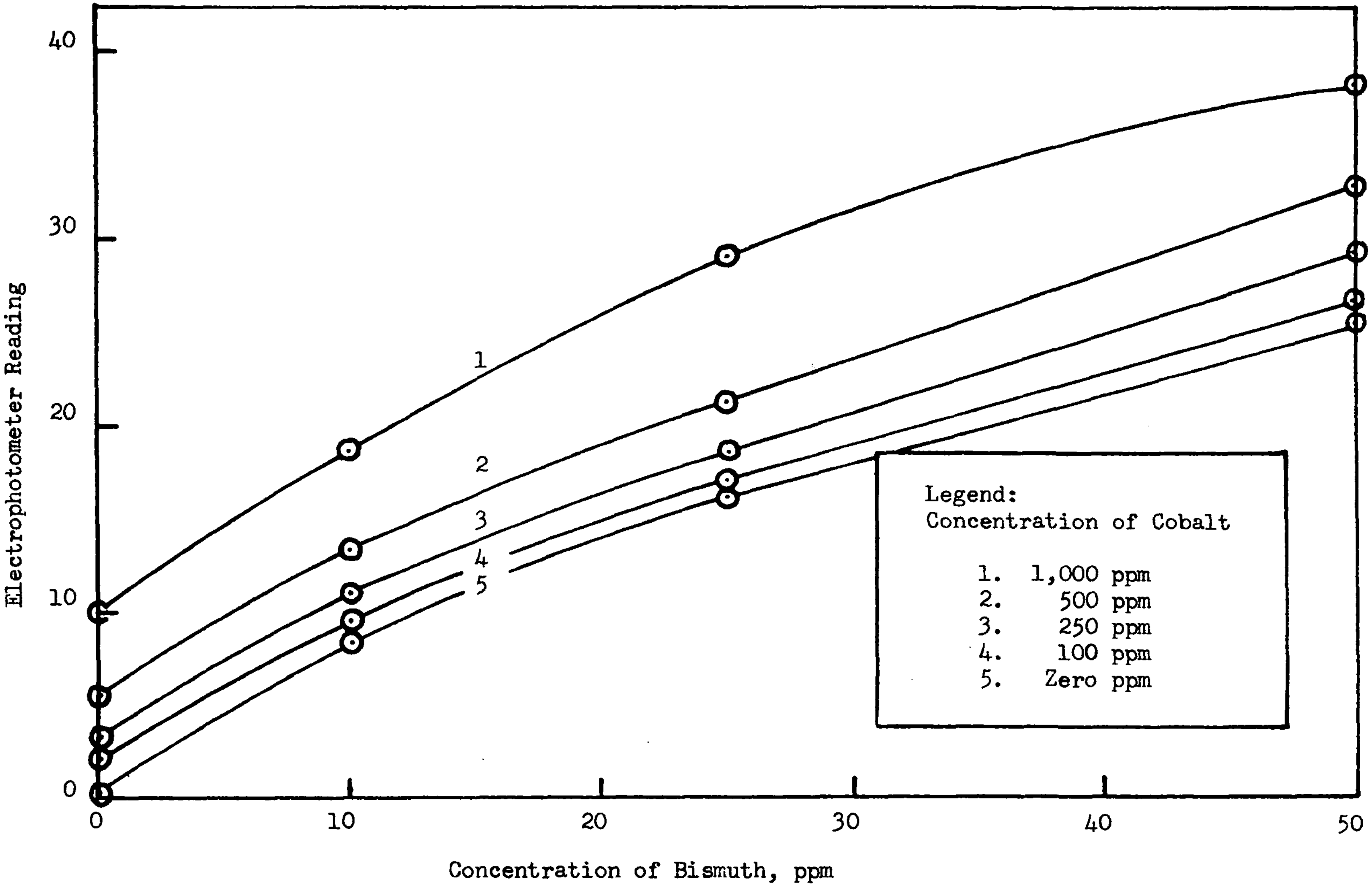


FIG. 15.--Color readings obtained for solutions containing the o-aminobenzenethiol complexes of bismuth and of vanadium

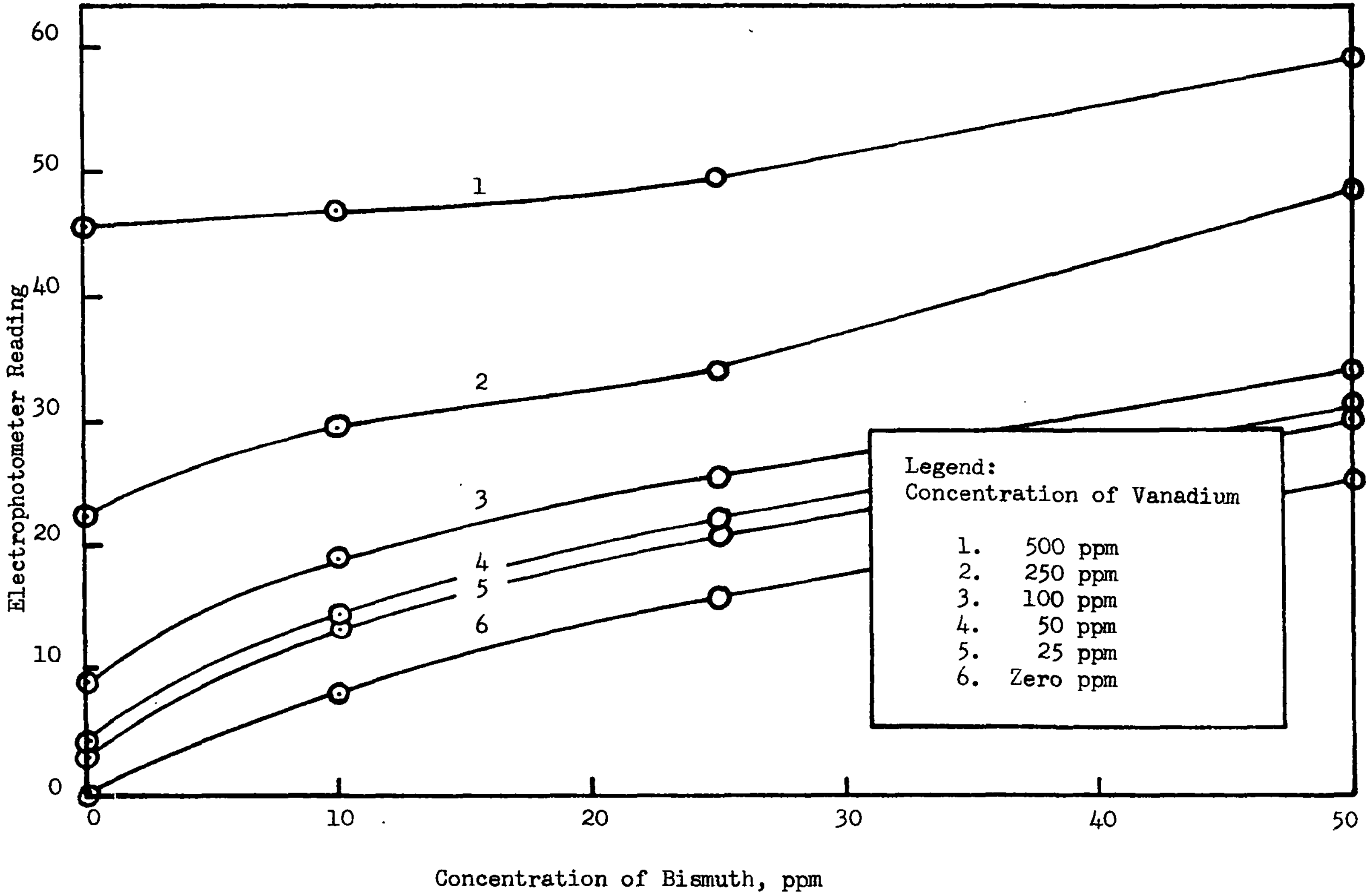
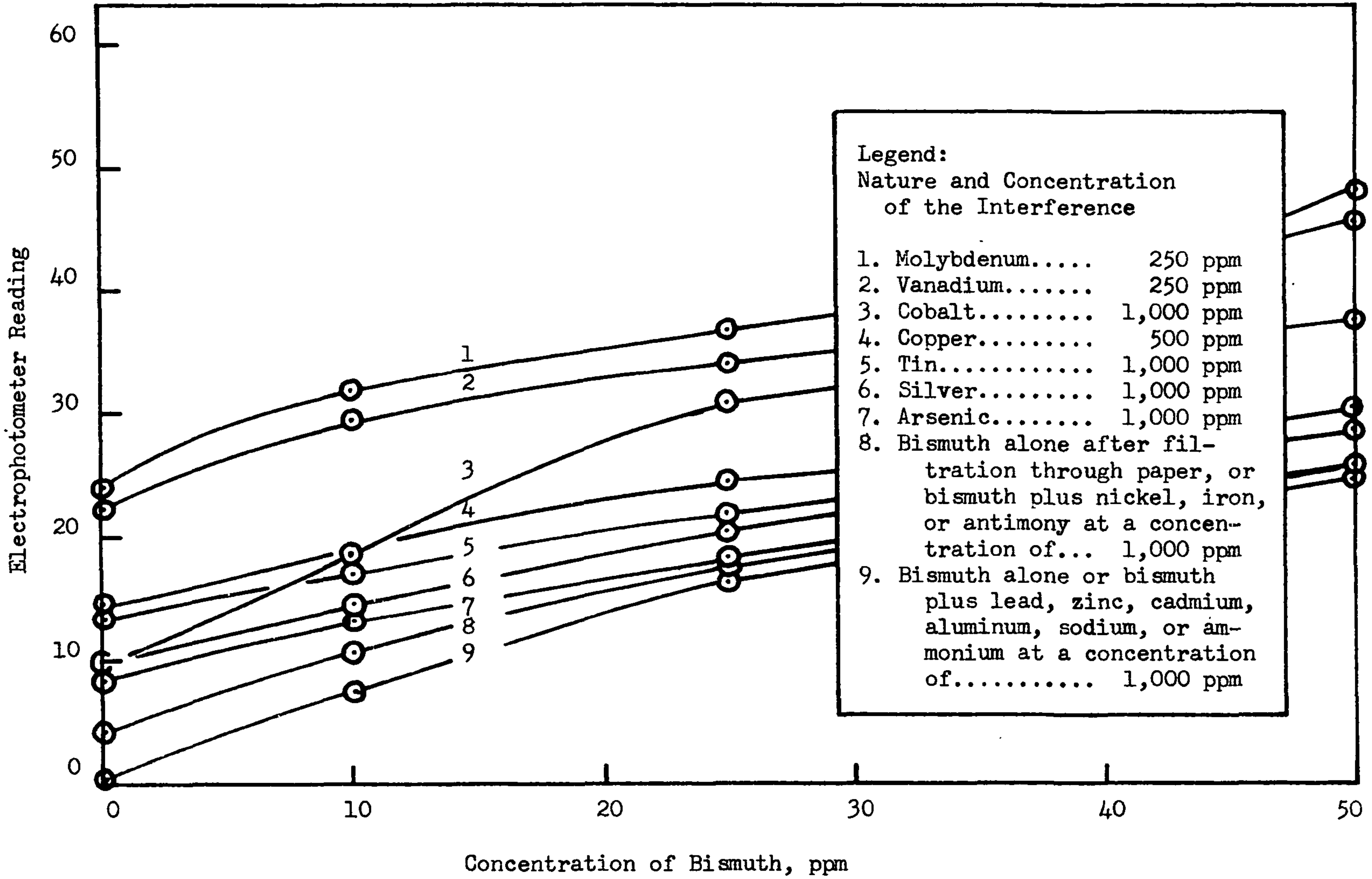


FIG. 16.--Color readings obtained for solutions of the bismuth-o-aminobenzenethiol complex in the presence of selected different interferences



Analysis of Alloys, NBS Sample 53b

The National Bureau of Standards samples of bearing metals present real tests for any methods of analysis for bismuth. NBS Standard Sample 53b Lead-Base Bearing Metal contains only 0.075% bismuth alloyed with 84.35% lead, 10.28% antimony, 5.06% tin, 0.209% copper, 0.042% arsenic, 0.006% nickel, 0.003% silver, 0.002% iron and 0.0007% aluminum. Duplicate samples of this alloy were dissolved and analyzed for bismuth as follows: A 1.0000 g. sample of alloy was boiled for a few minutes with 3 ml. of concentrated nitric acid in a beaker covered with a close-fitting watch glass. Fifteen milliliters of water was added and the solution was again boiled for a few minutes until dissolving action had apparently ceased and the residue was black. Three milliliters of concentrated hydrochloric acid was added to the boiling hot solution which was again boiled for a few minutes until the black residue was dissolved and completely replaced by a white salt. The watch glass was then raised on glass hooks and the turbid solution was evaporated to a moist white paste. The white paste was diluted to about 25 ml. with 0.6 N nitric acid solution. The solution was filtered through Whatman No. 42 paper that had been previously washed with 50 ml. of distilled water and then with 50 ml. of 0.6 N nitric acid solution. The residue in the beaker and on the paper was washed with about 5 ml. of 0.6 N nitric acid and then discarded. Five drops of o-aminobenzenethiol were added to the filtrate. The filtrate was diluted to exactly 50 ml., and mixed well, and its color was measured immediately on the electrophotometer. It is imperative that the color readings for these solutions be taken immediately since the solutions become turbid within a very short time after the addition of the o-aminobenzenethiol, perhaps from separation of the rather large amount of antimony that is present. Readings for the duplicate samples agreed precisely. At the same time aliquots of a concentrated stock solution of dissolved bismuth of volumes sufficient to give concentrations of 10 and 20 ppm bismuth, respectively, upon dilution to 50 ml., were first diluted to about 25 ml. with 0.6 N nitric acid. Each 25 ml. solution was then filtered, treated with o-aminobenzenethiol and finally diluted to 50 ml. and mixed exactly as for the alloy solution. The color of these standard solutions was also measured on the electrophotometer. The readings for the alloy solutions and the standard solutions were compared; a straight line relationship was assumed. The per cent bismuth found is shown in Table 12.

Analysis of Alloys, NBS Sample 54b

NBS Standard Sample 54b Tin-Base Bearing Metal contains only 0.029% bismuth alloyed with 87.48% tin, 7.39% antimony, 3.19% copper, 1.81% lead, 0.052% arsenic, 0.028% iron, 0.029% silver and less than 0.001% aluminum. Duplicate samples of this alloy were dissolved and analyzed for bismuth as follows: a 1.0000 g. sample of alloy was boiled for a few minutes with 3 ml. of concentrated hydrochloric acid in a covered beaker. Fifteen milliliters of water was added and the solution was boiled for a few minutes until dissolving action had apparently ceased and the residue was black. Three milliliters of concentrated nitric acid was added to the boiling hot solution which was again boiled for a few minutes until the black residue was dissolved and completely replaced by a bluish-white salt in a turbid pale blue solution. Note that the order of addition of the two acids used is reversed from that for solution of sample 53b. This turbid solution was evaporated to a moist paste, diluted to 15 ml. with 0.6 N nitric acid and filtered as above. The filtrate at this point was a clear bluish-green typical of acidic copper solutions. When three drops of o-aminobenzenethiol were added to the filtrate, a gray precipitate of copper was obtained which apparently used up all of the o-aminobenzenethiol while still leaving enough copper in solution to maintain the bluish-green color. The solution was again filtered; 5 crops more of o-aminobenzenethiol were added and again a precipitate of copper (now a creamy white in color) was obtained. The solution was filtered for a third time to give a clear yellow filtrate. This filtrate was diluted to 25 ml. with 0.6 N nitric acid and mixed well, and its color was measured on the electrophotometer. Readings for the duplicate samples agreed precisely. The readings for these alloy solutions were compared with those for the standard solutions described for alloy 53b. The per cent bismuth found is shown in Table 12.

Analysis of Alloys, Wood's Metal

A synthetic solution was prepared which corresponded to a solution of Wood's Metal and contained 50 ppm bismuth, 25 ppm lead, 12.5 ppm tin and 12.5 ppm cadmium in 0.6 N nitric acid. The color developed in this solution upon the addition of 10 drops of o-aminobenzenethiol per 100 ml. was measured upon the electrophotometer and compared with the color developed by standard solutions. The standard solutions were prepared by diluting aliquots of a concentrated bismuth solution with 0.6 N nitric acid to give solutions containing 40, 50, and 60 ppm bismuth and

10 drops of o-aminobenzenethiol per 100 ml. The per cent bismuth found is shown in Table 12.

TABLE 12.--Use of o-aminobenzenethiol in colorimetric analysis for bismuth in alloys

Alloy Analyzed	Bismuth Present per cent	Bismuth Found per cent
NBS 53b	0.075	0.090
NBS 54b	0.029	0.036
Wood's Metal	50.0	51.0

Analysis of Alloys, Discussion

It is realized that the procedures used above are oversimplified, and that the results obtained cannot, therefore, be considered accurate. However, the fact that values near the correct ones were obtained with excellent precision by these simplified procedures, which use one gram or less of sample, is encouraging. For comparison, one analyst for the National Bureau of Standards (32) obtained a value of 0.031% bismuth (versus the 0.036% listed in Table 13) in NBS sample 54b by using a 10 g. sample, separating the bismuth by internal electrolysis (13), dissolving the deposit and determining the bismuth as BiOCl. As applied to alloys of this type it is thought that the procedures presented in this paper should be modified as follows to give nearly correct results: (1) tin should be separated as metastannic acid by digestion with nitric acid prior to the addition of o-aminobenzenethiol; (2) copper, if present in excess of 500 ppm, may be separated by adding excess o-aminobenzenethiol to precipitate the copper and then filtering. However, the standard solutions to be used for comparison should each contain a like amount of copper and should be treated with the same amount of o-aminobenzenethiol and filtered. If copper is present in a concentration less than 500 ppm, it may be desirable to add excess copper to insure precipitation. The same considerations would apply to molybdenum and vanadium, if present. (3) As in all colorimetric methods, best results will be obtained if the kinds and concentrations of those metal ions that give serious interference are approximately the same in the standard solutions used for color comparison as in the solutions being analyzed. (4) Standard solutions should be treated with o-aminobenzenethiol and their colors measured at the same time as for the solutions being analyzed, since the reagent itself deepens in color (from air oxidation) throughout its shelf life. Calibration curves prepared long in advance cannot be used for color comparisons.

Qualitative Determination of Bismuth

An acid solution containing rather large amounts of bismuth and a few drops of o-aminobenzenethiol upon neutralization to a pH of 1.6 or higher yields a bright orange flocculent precipitate. This precipitation test is quite characteristic for bismuth, but it is not sensitive to small concentrations.

Apparatus

Circles of filter paper or a white porcelain spot plate together with several droppers and several small beakers were used.

Reagents

Bismuth solution. Solutions with varying concentrations of bismuth in approximately 5 per cent acid were prepared (perchloric acid solutions were used).

o-Aminobenzenethiol solution. A solution containing 100 drops of o-aminobenzenethiol per 100 ml. of 5 per cent acid was prepared.

Sodium hydroxide, 20% solution. Each 20 grams of sodium hydroxide pellets was dissolved in 100 ml. of distilled water.

Ammonium hydroxide, 1:1 solution. One volume of concentrated ammonium hydroxide was diluted with one volume of distilled water.

Chromatographic Procedure

To a circle of filter paper were added in order: one drop of bismuth solution, one drop of o-aminobenzenethiol solution and one drop of 1:1 ammonium hydroxide solution. By this method an orange precipitate can be detected for a concentration as low as 500 ppm bismuth through comparison with a standard spot, but a concentration of 1,000 ppm bismuth is required for positive identification.

Spot Plate Procedure

To a well in the spot plate were added in order: one drop of bismuth solution, one drop of ammonium hydroxide solution and one drop of o-aminobenzenethiol solution. This method is superior to the chromatographic method in that a few small flecks of orange precipitate can be detected with a solution that contains only 100 ppm bismuth, but a concentration of 500 ppm bismuth is required for positive identification.

The separation of the orange floc is more distinct if the ammonia is added ahead of the o-aminobenzenethiol. The test works less well when the 20 per cent sodium hydroxide solution is substituted for the ammonia solution.

Procedure in the Presence of Copper

The dark precipitates given by rather large amounts of copper (and a few other ions) upon addition of o-aminobenzenethiol to a solution may hide the orange precipitate given by bismuth if the above procedures are used without modification. In the presence of copper it was found better to add the o-aminobenzenethiol solution to the solution being tested, preferably in a spot plate, ahead of the ammonia solution. When the drop of o-aminobenzenethiol is added gently, without stirring, to the center of the test solution, a dark precipitate of copper will form at once, and if bismuth is also present this will appear as a bright yellow liquid ring around the outside of the dark precipitate. If now a drop of the ammonia solution is added carefully at the edge of the well the orange precipitate characteristic of bismuth will form outside the dark precipitate. Alternantly, one can lay a strip of filter paper in the solution after adding the o-aminobenzenethiol and then add a drop of the ammonia solution to the filter paper; the paper filters the bismuth solution away from the dark precipitate and permits the orange to show.

Although not sensitive, this test is so simple and definite that it is thought that it may be used in introductory courses in qualitative analysis where the concentration of metal ions in "unknown" and "test" solutions are often within the range of 1,000 to 10,000 ppm (1 to 10 mg. of metal ion per milliliter of solution).

Gravimetric Determination of Bismuth

Our experiments indicate that the precipitation of bismuth as an orange floc obtained by partial neutralization of dilute acid solutions of the bismuth-o-aminobenzenethiol complex is not quantitative.

Apparatus

A Model H Beckman pH Meter was used to control the neutralization.

Reagents

o-Aminobenzenethiol. The undiluted reagent described previously was used.

Concentrated stock solution of bismuth. Approximately 3.4835 g. of bismuth metal was dissolved by boiling with 15 ml. of hydrochloric acid and 5 ml. of nitric acid and then diluted to 250 ml. Weaker solutions were prepared as desired by dilution.

Ammonium hydroxide, 1:1 solution. One volume of concentrated ammonium hydroxide was diluted with one volume of distilled water.

Sodium hydroxide, 20% solution. Each 20 grams of sodium hydroxide was dissolved in 100 ml. of distilled water.

Ammonium carbonate. The dry salt was used.

Precipitations with a Moderate Excess of o-Aminobenzenethiol

Many of the following precipitations involve approximately 0.0697 g. or 0.001 equivalent of bismuth(III) ion. Preliminary experiments showed that 5 drops of o-aminobenzenethiol weigh 0.125 g. which constitutes 0.001 equivalent of this reagent. In these experiments 10 to 20 drops, or a one to three-fold excess, of o-aminobenzenethiol were used. In general precipitations were made by adding 10 drops of o-aminobenzenethiol per 100 ml. of bismuth solution and then neutralizing to a pH of 1.9 to 2.0 with one of the basic solutions listed above. After precipitation the solutions were left to stand for a period of time, varying from one hour to overnight, and then filtered. Some solutions were filtered through weighed, glass, porous-bottomed, filter crucibles and washed with water that had been adjusted to a pH of 2.0 with perchloric acid. The precipitates caught on glass were either dried at room temperature in an evacuated dessicator or dried in an oven at 100 °C. In either case, these precipitates were cooled and weighed as $Bi(-SC_6H_4-NH_2)_3$. Other solutions were filtered through paper of medium texture. These precipitates and papers were then ignited in an electric furnace, cooled, and weighed as Bi_2O_3. Variations in conditions and final results are shown in Table 13.

Conventional precipitations as the subcarbonate or hydroxide were made, according to directions in Scott (36), to serve as a standard of comparison. For these precipitations the bismuth solutions were diluted to about 300 ml. and dilute ammonia was added cautiously until a faint turbidity was obtained and then one gram of dry ammonium carbonate was added. The solutions were heated to boiling, the precipitates filtered off, washed with hot water, ignited at 750 °C, cooled and weighed as Bi_2O_3. These results also are listed (first entry) in Table 13.

The following observations are made concerning the results listed in Table 13. The reagent, o-aminobenzenethiol, separates when a solution containing it alone is neutralized to about pH 2.5, and quite probably some of the reagent is carried down at lower pH values when a metal is precipitated in its presence. Moreover, any excess reagent thus precipitated is not appreciably volatilized at temperatures as high as 240 °C. It is thought, therefore, that the weights of all precipitates dried at 30 and 100 °C include excess o-aminobenzenethiol and also, perhaps, some water (and/or acid) of constitution. Also, all of the solutions used contain some chloride since hydrochloric acid was used in dissolving the bismuth metal, and it is thought that any neutralization beyond that required for precipitation of the bismuth-o-aminobenzenethiol complex (pH of 1.9 to 2.0) serves to promote the formation of BiOCl. The presence of BiOCl could explain the high weights calculated from some of the precipitates ignited at 750 °C, for the oxychloride is fairly stable at this temperature. Scott (37) states that the determination of bismuth as the oxide requires the absence of hydrochloric or sulfuric acid from the solution of the element, since either of these acids invariably contaminates the final product. Results indicate that sodium hydroxide may precipitate the bismuth complex more completely than does ammonia but that a sodium complex that is difficult to wash out may contaminate the precipitate. At best, however, precipitation with o-aminobenzenethiol affords no separation of bismuth from other metal ions, as most metals, if precipitated at all with o-aminobenzenethiol, are precipitated at or near pH 2.0.

TABLE 13.—Precipitation of bismuth

Solvent	Precipitating Agents		Weight of Bismuth Taken	Weight of Bismuth Found at the Indicated Drying or Ignition Temperature	
	o-Amino-benzenethiol drops/100 ml.	Others	grams	deg.C	grams
5% HNO_3	None	NH_4OH & $(NH_4)_2CO_3$	0.0677	750	0.0671, 0.0678 0.0677, 0.0677
5% HNO_3	10	NaOH	0.0677	100	0.1023
5% HNO_3	10	NH_4OH	0.0677	750	0.0628, 0.0758
5% HCl	10	NH_4OH	0.0677	100	0.2286
				750	0.0667, 0.0471, 0.0514, 0.0770, 0.0772
5% H_2SO_4	10	NH_4OH	0.0677	750	0.0588, 0.0781
5% H_3PO_4	10	NH_4OH	0.0677	750	0.0727, 0.0602, 0.0623, 0.0772, 0.0768
5% HOAc	10	NH_4OH	0.0677	750	0.0538
5% $HClO_4$	10	NH_4OH	0.0677	750	0.0695, 0.0703, 0.0673, 0.0657, 0.0672, 0.0698, 0.0761, 0.0773
5% $HClO_4$	20	NH_4OH	0.1000	750	0.0920
			0.0500	750	0.0482
			0.0100	750	0.0057
			0.0050	750	0.0003
			0.0010	750	0.0000
			0.0005	750	0.0000
5% $HClO_4$	20	NaOH	0.1000	750	0.1089, 0.1102
			0.0500	750	0.0525, 0.0523, 0.0583
			0.0100	750	0.0170, 0.0090, 0.0175
			0.0050	750	0.0077
			0.0030	750	0.0044, 0.0063
			0.0010	750	0.0016, 0.0029, 0.0028
			0.0005	750	0.0002, 0.0055, 0.0062
			0.0500	30*	0.0662, 0.0717
			0.0100	30*	0.0217, 0.0291
			0.0030	30*	0.0086, 0.0197
			0.0010	30*	0.0073, 0.0061
			0.0005	30*	0.0052, 0.0086

* Dried in a dessicator under vacuum.

Precipitations with a Large Excess of o-Aminobenzenethiol

An additional experiment was done to find whether a large excess of o-aminobenzenethiol would insure complete precipitation of bismuth from weakly acid solutions. Five solutions were prepared, each of which contained 0.0677 g. of bismuth in 100 ml. of 0.6 N perchloric acid. To one solution 10 drops of o-aminobenzenethiol were added, to another 20 drops, then 50 drops, then 100 drops, and finally to one solution, 10 ml., equivalent to 300 drops of reagent, were added. Each solution was then neutralized to a pH of 1.9 to 2.0 with ammonium hydroxide solution. The precipitate, if any, was filtered on paper, washed with water, ignited to the oxide, Bi_2O_3, at 750 °C, cooled and weighed. The solution to which 10 ml. of o-aminobenzenethiol was added did not give a precipitate, except for a very slight turbidity, but the bismuth apparently collected in the excess undissolved o-aminobenzenethiol to give a reddish oil on the bottom of the beaker. Results are shown in Table 14. The trend is unmistakable; excess o-aminobenzenethiol hinders rather than aids the precipitation of bismuth.

TABLE 14.--Effect of excess o-aminobenzenethiol upon the precipitation of bismuth

Concentration of o-Aminobenzenethiol drops/100 ml.	Weight of Metal Taken grams	Weight of Metal Found grams	Deviation grams
10	0.0677	0.0717	+ 0.0040
20	0.0677	0.0677	0.0000
50	0.0677	0.0650	- 0.0027
100	0.0677	0.0557	- 0.0120
300	0.0677	0.0	- 0.0677

Summary

The reagent o-aminobenzenethiol reacts with bismuth in dilute acid solutions to yield a complex compound. When this complex is formed in dilute acid solutions whose pH is less than 1.5, a bright yellow color is developed. The depth of this color is proportional to the concentration of bismuth in the solution and can be used as a basis for a colorimetric determination of bismuth. When an acid solution containing an appreciable amount of the dissolved complex is neutralized to a pH greater than 1.5, a unique, bright orange floc separates out; the precipitate is quite characteristic and may be useful as a qualitative test for bismuth, but the test is not sensitive for small concentrations. The precipitation of bismuth with o-aminobenzenethiol in weakly acid solutions apparently is not quantitative.

CHAPTER IV

DETERMINATION OF SELENIUM AND TELLURIUM

Selenium and tellurium are closely related to sulfur in their chemical behavior; both are to be regarded as nonmetals although tellurium resembles the metals in some characteristics. The important oxidation states of sulfur, selenium and tellurium are the -2, +4, and +6 states. The importance of the negative oxidation state rapidly drops off with increase in atomic number within the series. As is the case with sulfur, several forms of selenium are known. In addition to two red (monoclinic) and a gray (hexagonal) form, there have been reported several forms of amorphous selenium (both red and black). The gray form (and presumably also the amorphous forms) of selenium consists of "zigzag" chains of bound selenium atoms, but one of the red forms has been shown to contain Se_8 "rings." The gray form of selenium has become especially important in recent years; the sharp increase in its electrical conductivity upon exposure to light makes it a valuable material for use in photoconductive cells.

As stated in Gould (16), "Elemental sulfur is both a better oxidizing agent and a better reducing agent than elemental selenium." This means that selenious acid, H_2SeO_3, is more easily reduced to the elemental selenium than is H_2SO_3 to elemental sulfur, but H_2SeO_3 is much less easily oxidized to the selenate state than is H_2SO_3 to the sulfate state. Similarly, compounds of hexavalent selenium are much more easily reduced than analagous compounds of either hexavalent sulfur or hexavalent tellurium. The practical analytical application of these relationships is that SO_2 gas is commonly used to reduce the soluble ionic radicals of both selenium and tellurium to acid-insoluble elemental forms of these "metals." Preliminary work outlined in Chapter II indicated that o-aminobenzenethiol has a reducing action similar to that of SO_2 gas upon the ionic radicals of selenium and tellurium. The following experiments were made to find whether quantitative determinations of selenium and tellurium may be made with this new reagent.

Gravimetric Determination of Selenium

Selenium is usually weighed as the element after it has been precipitated by reduction in strong acid solution with either sulfur dioxide or hydroxylamine. The use of other reducing agents such as $FeSO_4$, $TiCl_3$, H_3PO_3, $SnCl_2$, or metals is not satisfactory for more or less occlusion takes place (22).

Reagents

Stock solution of selenium, 0.2 N. The solution of sodium selenite, $Na_2SeO_3 \cdot 5H_2O$, prepared for preliminary work as described in Table 2 was used. This solution consisted of 3.2880 g. of the salt dissolved and diluted to 250 ml. with distilled water. Preliminary work indicated that the solution contains approximately 0.0340 g. of selenium per 5 ml. aliquot. Weaker solutions of selenium were prepared by dilution of aliquots of this stock solution with solutions containing desired concentrations of hydrochloric acid.

Solution of SO_2 gas, saturated. Sulfur dioxide gas, obtained by heating a flask containing 10 g. of sodium sulfite in 250 ml. of water while sulfuric acid was being added drop by drop, was discharged below the surface into 300 ml. of concentrated hydrochloric acid for several minutes.

o-Aminobenzenethiol solutions. The liquid reagent described above was added in the amount of 20 drops of thiol per 100 ml. of solution to a solution containing a desired concentration of hydrochloric acid. This solution was then stirred and filtered through a tight paper. The solution was prepared fresh just before each precipitation experiment.

Hydrochloric acid, 5% solutions, etc. The 5 per cent hydrochloric acid solution was prepared by diluting 5 ml. of concentrated acid to 100 ml. with distilled water. Solutions of other concentrations were prepared in a similar manner.

Standardization of the Stock Solution of Selenium

To determine accurately the amount of selenium present in the stock solution of selenium a series of determinations was made by the accepted method using sulfur dioxide gas (22, 38). The series of selenium solutions used in these determinations consisted of three pairs of solutions. The pairs contained respectively, 0.25, 1.25, and 5.0 ml. of the stock solution diluted to 50 ml. with cold concentrated hydrochloric acid. The solutions were cooled in ice water. To each solution was added 50 ml. of the cool concentrated acid that had been saturated with sulfur dioxide. The solution was allowed to stand until the red selenium subsided, after which it was filtered through a weighed fritted glass crucible and washed thoroughly, first with concentrated hydrochloric acid, then with cold water, next with alcohol to displace the water, and finally with ether. The red selenium was dried for 3 to 4 hours at room temperature to remove the ether and then one and a half hours at 120 to 130 °C, cooled, and weighed as selenium. The results obtained are shown in Table 15.

TABLE 15.--Precipitation of selenium with sulfur dioxide

Volume of Stock Solution Taken ml.	Weight of Selenium Found grams	Accepted Value for Weight of Selenium grams
0.25	0.0016, 0.0015	0.0016
1.25	0.0080, 0.0080	0.0080
5.00	0.0316, 0.0321	0.0320

Precipitation of Selenium with o-Aminobenzenethiol

Effect of acid concentration. Several experiments were conducted to determine whether the precipitation of selenium through reduction by o-aminobenzenethiol in strong acid solution can be quantitative and at the same time to determine the effect of the acid concentration upon the precipitation. In these experiments the concentration of hydrochloric acid used for solution of the selenium and of the o-aminobenzenethiol was varied from 5 to 100 per cent. Otherwise, the conditions for all experiments were essentially the same. All precipitations were made at room temperature. For each experiment precipitation was made as follows:

A series of replicate solutions of selenium was prepared. Each set of replicates contained a different concentration of selenium, but all solutions of the series were diluted to 50 ml. with a solution containing the same predetermined concentration of hydrochloric acid. To each solution was added, slowly with stirring, 50 ml. of solution containing 20 drops of o-aminobenzenethiol per 100 ml. and the same concentration of hydrochloric acid as was present in the selenium solution. Each solution was allowed to stand overnight, filtered through a weighed fritted glass crucible and washed thoroughly first with hydrochloric acid of the same concentration as was used in the precipitation, then with cold water, next with alcohol to displace the water and finally with ether. The red selenium was dried for a few minutes at room temperature to remove the ether and then one and a half hours at 120 to 130 °C, cooled, and weighed as selenium. The results obtained are shown in Table 16. The figures in the table show that in 5 per cent acid solutions containing 0.0320 g. of selenium per 100 ml. the occlusion may cause an increase of as much as 10 per cent in the weight of the precipitate. On the other hand the completeness of precipitation falls off rapidly when the concentration of acid is greater than 20 per cent. There is some decomposition of o-aminobenzenethiol in concentrated (100 per cent) hydrochloric acid, and the resulting solution is a pale blue color. Precipitations from solutions containing from 10 to 20 per cent hydrochloric acid are fairly satisfactory for the range of selenium concentration that was tested.

TABLE 16.--Effect of acid concentration upon the precipitation of selenium with o-aminobenzenethiol

Concentration of Hydrochloric Acid per cent	Weight of Selenium Taken grams	Weight of Selenium Found grams	Deviation (average) grams
5	0.0016	0.0014, 0.0015	-0.0001
	0.0080	0.0077, 0.0078	-0.0002
	0.0320	0.0347, 0.0358	+0.0033
10	0.0016	0.0011, 0.0011	-0.0005
	0.0080	0.0075, 0.0076	-0.0004
	0.0320	0.0312, 0.0318	-0.0005
20	0.0016	0.0013, 0.0015	-0.0002
	0.0080	0.0077, 0.0078	-0.0002
	0.0096	0.0089, 0.0092	-0.0005
	0.0320	0.0307, 0.0317 0.0317, 0.0320	-0.0005
30	0.0016	0.0008, 0.0008	-0.0008
	0.0080	0.0072, 0.0073	-0.0007
	0.0320	0.0316, 0.0316	-0.0004
100	0.0016	0.0000, 0.0000	-0.0016
	0.0080	0.0000, 0.0000	-0.0080
	0.0320	0.0154, 0.0074	-0.0206

Effect of digestion time. To test the effect of the time allowed for "digestion" or "aging" of the selenium precipitate upon the completeness of precipitation and upon the interference from occlusion, additional experiments were conducted. In these experiments selenium was precipitated from 5 per cent and from 30 per cent acid solutions exactly as above; in one case, at each acid concentration, the precipitates were allowed to digest at room temperature for three hours, and in the other case the precipitates were allowed to digest at room temperature overnight (about 20 hours). The results are shown in Table 17.

The results shown in the table for the precipitations from 5 per cent acid solutions indicate that the time allowed for digestion has little influence upon the extent of occlusion observed for the 0.0320 g. samples of selenium. The results for the precipitations from 30 per cent acid solutions indicate that the longer digestion time is highly favorable to more complete precipitation.

TABLE 17.--Effect of digestion time upon the precipitation of selenium with o-aminobenzenethiol

Concentration of Hydrochloric Acid	Digestion Time	Weight of Selenium Taken	Weight of Selenium Found	Deviation (average)
per cent	hours	grams	grams	grams
5	3	0.0003	0.0001, 0.0002	-0.0001
		0.0016	0.0013, 0.0013	-0.0003
		0.0080	0.0075, 0.0075	-0.0005
		0.0320	0.0347, 0.0361	+0.0034
	20	0.0016	0.0014, 0.0015	-0.0001
		0.0080	0.0077, 0.0078	-0.0002
		0.0320	0.0347, 0.0358	+0.0033
30	3	0.0016	0.0006, 0.0006	-0.0010
		0.0080	0.0068, 0.0068	-0.0012
		0.0320	0.0278, 0.0291	-0.0035
	20	0.0016	0.0008, 0.0008	-0.0008
		0.0080	0.0072, 0.0073	-0.0007
		0.0320	0.0316, 0.0316	-0.0004

Summary of results. The results shown in the above tables indicate that precipitation of selenium by o-aminobenzenethiol may be fairly satisfactory as to both precision and accuracy in solutions that contain 10 to 20 per cent of hydrochloric acid, and such precipitation may be worthy of more extensive investigation. However, the results indicate that precipitation is not as complete as might be desired. Also, the fact that an overnight digestion period is necessary to approach complete precipitation places the o-aminobenzenethiol precipitation at a disadvantage as compared to the accepted precipitation with sulfur dioxide which requires perhaps thirty minutes for complete reduction and flocculation of the selenium. Finally, the fact that precipitation of selenium with o-aminobenzenethiol fails in concentrated (100 per cent) acid apparently does not allow the usual separation of selenium from tellurium. Therefore no further investigations of this reaction were made.

Volumetric Determination of Selenium

At the point at which the o-aminobenzenethiol solutions were added slowly to the selenium solutions in the experiments described just above it was observed that the selenium solutions developed a clear yellow color immediately upon contact with the o-aminobenzenethiol solutions. Furthermore, the color persisted for a shorter time in those solutions that contained but little selenium than for those solutions that contained more selenium. Then, at a time just before precipitation was to begin, these yellow solutions faded rather suddenly to colorless. The following very brief experiment was conducted to see whether the disappearance of the yellow color would indicate the addition of a quantity of o-aminobenzenethiol proportional to the quantity of selenium in a solution being treated.

For this experiment a small amount of selenium solution, remaining from the precipitation experiments described above, which contained 0.0320 g. of selenium per 100 ml. of 5 per cent hydrochloric acid solution was divided and treated as follows: From a buret, one 10 ml. and two 5 ml. portions of the selenium solution were measured into separate beakers. Each portion was diluted to 50 ml. with 5 per cent hydrochloric acid and then titrated with an o-aminobenzenethiol solution containing 20 drops of the thiol per 100 m. of 5 per cent hydrochloric acid. The sudden disappearance of the yellow color was taken as the end-point of the titration. As shown in Table 18, a definite and precise proportionality of thiol to selenium is reflected by the titration results. No further work was done, however, as it is suspected that tellurium which is often associated with selenium will give similar results, and it is known that many metals, see Figures 6 to 16 in Chapter III, give yellow colors with o-aminobenzenethiol that do not fade under the conditions of the above titration. Also, it is realized that the fading of a yellow color is not easily detected by all persons. The work is, nevertheless, thought to be worthy of mention as it may offer possibilities for control work upon solutions containing selenium only.

TABLE 18.—Titration of selenium with o-aminobenzenethiol

Original Volume of Selenium Solution ml.	Weight of Selenium Taken grams	Volume of o-Aminobenzenethiol Solution ml.	Weight of Selenium per Volume of Thiol Solution grams/ml.
10	0.0032	5.5	0.00058
5	0.0016	2.7	0.00059
5	0.0016	2.75	0.00058

Gravimetric Determination of Tellurium

As shown by results recorded in Tables 7, 8 and 9 of Chapter II, there is a possibility that tellurium may be quantitatively reduced and separated from its solutions through reaction with o-aminobenzenethiol. However, since the gravimetric determination of tellurium normally follows the prior separation and gravimetric determination of selenium and since the possibilities for such separation and determination of selenium with o-aminobenzenethiol have not been fully investigaged, no further trials were made with tellurium.

CHAPTER V

DETERMINATION OF SILVER

Gravimetric Determination of Silver

The outstanding separation of silver is that based on the precipitation of its chloride in dilute nitric acid solution. Substances that interfere are lead, palladium, mercury(I), copper and thallium which form insoluble chlorides, cyanides and thiosulfates which dissolve silver chloride, compounds such as bismuth and antimony that hydrolyze in the dilute acid solution that is necessary for the complete precipitation of the silver, and organic matter which sometimes prevents proper coagulation of the chloride. The solubility of silver chloride in dilute nitric acid solution containing a small excess of the chloride ion is very slight and can be disregarded in ordinary analyses. The solubility of silver chloride is, however, appreciable in hot or cold water, in strong solutions of hydrochloric or nitric acid, or in solutions containing excessive amounts of chlorides or nitrates of the alkalies or alkaline earths. Silver chloride is prone to occlude substances, even sodium chloride or silver nitrate. In all the analytical operations the silver chloride must be protected from light as much as possible.

Preliminary work described in Chapter II demonstrated that precipitation of silver with o-aminobenzenethiol might offer some advantages. Silver is precipitated by this reagent from 5 per cent nitric acid solutions as a white floc that is readily filterable and is apparently more stable towards light than is silver chloride. The possibilities offered by this precipitation reaction for the gravimetric determination of silver have been investigated as described below.

Reagents

Analytical grade reagents were used.

Stock solution of silver, 0.2 N. 8.4945 g. of silver nitrate was dissolved and diluted to 250 ml. with distilled water containing 1 per cent by volume of concentrated nitric acid. Weaker solutions were prepared as required by dilution with a chosen solvent.

Tin(II) solution, 0.2 N. For this solution, 5.6415 g. of stannous chloride, $SnCl_2 \cdot 2H_2O$, was dissolved and diluted to 250 ml. in such a manner that the final solution contained 85 ml. of concentrated hydrochloric acid.

Gold(III) solution, 0.2 N. For this solution, 6.57 g. of chloroauric acid, $HAuCl_4 \cdot 3H_2O$, was dissolved and diluted to 250 ml. with distilled water.

Other metal ion solutions, 0.2 N. It was desired, where possible, to test the precipitation reactions of o-aminobenzenethiol and the pertinent metals in 5 per cent nitric acid solutions free of chloride. Therefore, except for the tin and gold solutions described above, solutions of the desired metal ions were prepared as follows: Sufficient metal or metal salt other than the metal chloride was dissolved in 5 per cent nitric acid to give 250 ml. of a solution approximately 0.2 N in metal ion. Such solutions were prepared from the following metals and salts: $CdCO_3$, $Co(NO_3)_2 \cdot 6H_2O$, copper turnings, $Fe(NO_3)_3 \cdot 9H_2O$, HgO, $ZnCO_3$ and $Ni(NO_3)_2 \cdot 6H_2O$.

Nitric acid, 5% solution. Each 5 ml. of concentrated nitric acid was diluted to 100 ml. with distilled water.

Hydrochloric acid, 0.2 N solution, etc. Each 1.6 ml. of concentrated acid was diluted to 100 ml. with distilled water. For a 0.01 N solution each 5 ml. of 0.2 N solution was diluted to 100 ml.

o-Aminobenzenethiol solutions. In most cases solutions were prepared in 5 per cent nitric acid, but different solvents were used in a few places as described in the text below. In any case, 20 drops, or some other desired quantity, of the liquid o-aminobenzenethiol described previously was added per 100 ml. of solution. This solution was stirred and filtered through a tight paper. The solution was prepared fresh just before each precipitation experiment.

Alcohol. The alcohol used for washing precipitates was 95 per cent ethyl alcohol, not denatured.

Ether. The ether used for washing precipitates was ethyl ether solvent, not anhydrous.

Organic solvents. The organic solvents used for testing the solubility of the precipitates included the alcohol and ether described above and a good grade of each of the following solvents: acetone, carbon tetrachloride, 1,4-dioxane, ethyl acetate, heptane, xylene, and 2-pyrrolidone.

EDTA solution, 1.0 N. 47 g. of the disodium salt of ethylenediaminetetraacetate (EDTA) was moistened with 100 ml. of distilled water. Enough concentrated ammonium hydroxide (about 30 ml.) was added to dissolve the salt, and the resulting slightly turbid solution was filtered and then diluted to 250 ml. with distilled water.

Oxine solution, 0.4 N. 25 g. of 8-hydroxyquinoline (oxine) was dissolved in 60 ml. of concentrated acetic acid and then diluted to 500 ml. with distilled water.

Salicylaldoxime, 1% solution. 1 g. of salicylaldoxime was dissolved in 5 ml. of alochol, which was then poured slowly with stirring into 95 ml. of water at 86 °C.

Standardization of the Stock Solution of Silver

To determine accurately the amount of silver present in the stock solution, a duplicate set of determinations was made by precipitation of silver chloride (23). For each determination a 5 ml. aliquot of the stock solution was diluted to 200 ml. with one per cent nitric acid. The solution was heated to 70 °C, and 0.2 N hydrochloric acid was added slowly with constant stirring until no further precipitation was produced. The solution was warmed until the precipitate settled, left to cool to 25 to 30 °C, and then the supernatant liquid was tested with 1 or 2 drops of the 0.2 N hydrochloric acid solution to make sure that precipitation was complete. The solution was allowed to stand in a dark cabinet overnight and then filtered through a weighed fritted glass crucible. The precipitate was washed by decantation with 0.01 N hydrochloric acid and then transferred to the crucible. The crucible and contents were dried first at 100 °C and then at 130 to 150 °C, cooled in a dessicator, and weighed as AgCl. Each precipitate weighed precisely 0.1410 g., and was equivalent to 0.1060 g. of silver.

Precipitation of Silver Alone with o-Aminobenzenethiol

Effect of the drying temperature. Four duplicate sets of silver solutions were treated in the first experiments designed to find whether accurate determinations of silver can be made by precipitation of the silver with o-aminobenzenethiol in 5 per cent nitric acid. For the duplicate sets, aliquot volumes of the stock solution containing 0.0010, 0.0053, 0.0265, or 0.1060 g. of silver, respectively, were diluted to 50 ml. with 5 per cent nitric acid. To each cold solution 50 ml. of 5 per cent nitric acid containing 20 drops of o-aminobenzenethiol per 100 ml. was added slowly with stirring. The solution and white flocculent precipitate were allowed to stand overnight and then filtered under vacuum through a weighed fritted glass crucible. The beaker and precipitate were washed twice by decantation with cold 5 per cent nitric acid and then the precipitate was transferred to the crucible. The beaker was then policed and washed with cold water three times; the washings were transferred to the crucible, and the crucible was sucked dry. The crucible and precipitate were placed in a dessicator. A vacuum was drawn on the dessicator, and the precipitate was allowed to dry at room temperature overnight and then weighed. It was assumed that the composition of the precipitate is represented by the formula $Ag(-SC_6H_4NH_2)$, and, therefore, the weight of the precipitate was multiplied by the factor 0.0465 to find the weight of silver present. Results are shown in Table 19.

After this first weighing, the above precipitates were placed in an oven and dried at 105 °C for one and a half hours, cooled, and weighed. The weight of silver was calculated as above. Results after this treatment are also shown in Table 19.

TABLE 19.--Effect of the drying temperature upon the weight of silver-o-aminobenzenethiol precipitates

Drying Temperature °C	Weight of Silver Taken grams	Weight of Silver Found grams	Deviation (average) grams
30	0.0010	0.0008, 0.0009	-0.0001
	0.0053	0.0054, 0.0054	+0.0001
	0.0265	0.0323, 0.0268	+0.0031
	0.1060	0.1475, 0.1490	+0.0423
105	0.0010	0.0008, 0.0009	-0.0001
	0.0053	0.0054, 0.0054	+0.0001
	0.0265	0.0287, 0.0265	+0.0011
	0.1060	0.1436, 0.1366	+0.0351

As shown in the table, good results were not obtained by either of the above treatments. However, it is thought that the large positive error observed for the larger samples results from the presence of excess o-aminobenzenethiol that was not completely washed from the precipitates by the cold wash solutions used. This suspicion is supported in part by the fact that the larger precipitates, which were much too heavy, developed dark brown spots, indicative of the decomposition of organic material, upon drying at room temperature in the evacuated dessicator. Later heating at 105 °C did not add appreciably to this darkening effect. Also, precipitates that were near the correct weight after drying at room temperature in the evacuated dessicator lost hardly any weight upon further drying at 105 °C. It is thought, therefore, that if the silver-o-aminobenzenethiol precipitate has been washed clean of foreign material it can be dried at room temperature under a vacuum or at 105 °C, whichever is desired.

Effect of the washing procedure. The above experiments demonstrated that large quantities of the silver-o-aminobenzenethiol precipitate cannot be washed free of foreign matter by using cold dilute acid followed by cold water. Values from the above experiments that were obtained for precipitates dried at 105 °C (Table 19) are also listed in Table 20 to allow ready comparison with the values obtained in the following experiments.

For the next experiments two duplicate sets of silver solutions were prepared. The duplicate solutions contained 0.0010 and 0.1060 g. of silver respectively. Each solution was treated exactly as were the solutions in the preceding section up to the point at which the precipitate retained by the fritted glass crucible was to be washed. Each precipitate was then washed once with cold 5 per cent nitric acid, twice with cold 2.5 per cent nitric acid, four times with cold water, twice with cold alcohol and once with cold ether. The precipitate was then dried at 105 °C for one and a half hours, cooled and weighed. The weights of silver found by these experiments are shown in Table 20. Again, the precipitates from the larger samples have not been washed free of foreign matter. The more extensive washing has helped considerably, however, as evidenced by the more nearly correct weights obtained and by the fact that the white precipitates did not develop brown spots upon heating (precipitates did take on a pale gray cast).

After the precipitates from the above experiments had been weighed, those from the 0.1060 g. samples were washed further: twice with hot 5 per cent nitric acid, twice with hot 2.5 per cent nitric acid, four times with hot water, five times with hot alcohol, and once with cold ether. The precipitates were then dried at 105 °C for one and a half hours, cooled and reweighed. The weights of silver found after this treatment are also shown in Table 20, and they reveal that the accuracy of the determination was considerably improved by use of the hot wash solutions.

Finally, the above experiments were repeated with two important variations: (1) the solutions of silver that had been diluted to 50 ml. each were heated to 90 to 100 °C before the o-aminobenzenethiol solutions were added, and (2) the precipitates were washed with hot solutions as described in the last paragraph above. These experiments were first conducted with duplicate sets of solutions containing 0.0010 and 0.1060 g., respectively, of silver. When it was found that the results were good for these first experiments, additional experiments were conducted in the same manner using duplicate sets of solutions containing 0.0005, 0.0010, 0.0053, 0.0265, 0.0530 and 0.1060 g., respectively, of silver. Results for all experiments are listed in Table 20. These results demonstrate that acceptable determinations of silver may be made by these last procedures if the solutions to be analyzed contain only silver.

Effect of the temperature of precipitation. Observations made during the previous precipitations and comparisons of the final results obtained from the precipitations, as listed in Table 20, indicate that heating the silver solution before the addition of the o-aminobenzenethiol solution does not cause the precipitation to be significantly more or less rapid, nor more or less complete. However, it did appear that precipitates obtained from the hot solutions were more dense and more readily filterable than those obtained from cold solutions. Heating of the silver solution is therefore recommended.

TABLE 20.--Effect of the washing procedure in the determination of silver with o-aminobenzenethiol

Wash Solutions Used	Weight of Silver Taken grams	Weight of Silver Found grams	Deviation (average) grams
Cold 5% HNO_3 and water	0.0010	0.0008, 0.0009	-0.0001
	0.0053	0.0054, 0.0054	+0.0001
	0.0265	0.0287, 0.0265	+0.0011
	0.1060	0.1436, 0.1366	+0.0351
Cold 5% HNO_3, 2.5% HNO_3, water, alcohol, and ether	0.0010	0.0009, 0.0010	0.0000
	0.1060	0.1125, 0.1155	+0.0080
Above cold solvents followed by: hot 5% HNO_3, 2.5% HNO_3, water, alcohol, and cold ether	0.1060	0.1062, 0.1079	+0.0011
Hot 5% HNO_3, 2.5% HNO_3, water, alcohol, and cold ether	0.0005	0.0003, 0.0003	-0.0002
	0.0010	0.0007, 0.0007, 0.0007, 0.0007	-0.0003
	0.0053	0.0049, 0.0050	-0.0003
	0.0265	0.0264, 0.0265	0.0000
	0.0530	0.0525, 0.0527	-0.0004
	0.1060	0.1062, 0.1062, 0.1066, 0.1066	+0.0004

It was also observed that precipitations of the larger samples that were allowed to procede without stirring caused the formation of a white "gel" that "set" to the shape of the beaker. This gel was easily broken up with a stirring rod, and it did not re-form after it had been broken. However, it appears that there would be less likelihood of occluding foreign matter if the silver solution were stirred for a few minutes after the addition of the o-aminobenzenethiol solution. Precipitates from smaller samples (0.0005 to 0.0010 g. of silver), although they appeared white while in solution, always had a tan color on the filter. This effect did not lead to high results.

Effect of digestion time. Observations made during these precipitations revealed that the 0.0265, 0.0530 and 0.1060 g. samples of silver separated immediately, and perhaps completely, when the o-aminobenzenethiol solutions were added. The 0.0053 g. samples separated within 30 minutes. The 0.0005 and 0.0010 g. samples gave only a slight turbidity within six hours after addition of the thiol, but these samples gave definite flocs after standing overnight. It therefore seems advisable to let all solutions stand overnight after addition of the thiol before the solutions are filtered.

Effect of the nitric acid concentration. One experiment was done to see whether silver can be quantitatively precipitated by o-aminobenzenethiol from solutions containing more than 5 per cent of nitric acid. For this experiment two solutions, each containing 0.0265 g. of silver in 50 ml. of 10 per cent nitric acid, were prepared. These solutions of silver were heated to about 90 °C, and the silver was precipitated by the addition of o-aminobenzenethiol in 10 per cent nitric acid solutions. The precipitates were then digested, filtered, washed with hot solvents, dried at 105 °C, cooled, and weighed as described above.

Values of 0.0264 and 0.0271 g. of silver were obtained, and the average deviation was thus a positive 0.0003 g. Therefore, it seems that, if required, silver can be satisfactorily precipitated from 10 per cent nitric acid by o-aminobenzenethiol.

Effects from the presence of hydrochloric acid. In an investigation of the determination of silver with 1,2,3-benzotriazol by Cheng (12) it was observed that the presence of chloride ion does not interfere. The determination no doubt enjoys this immunity because precipitations are made in ammoniacal solutions in which silver chloride is freely soluble. It was not expected that precipitations of silver in the presence of chloride ion by o-aminobenzenethiol could have the same freedom from contamination by silver chloride if the precipitations were made in 5 to 10 per cent nitric acid. However, qualitative tests indicated that the fine curdy precipitate of silver chloride that forms first when dilute hydrochloric acid is added to a silver solution is to a great extent replaced by a voluminous white floc when o-aminobenzenethiol is added to the solution. Two experiments were therefore tried to see whether the presence of hydrochloric acid can be tolerated in precipitations by the thiol. For one experiment duplicate solutions each containing 0.0265 g. of silver in 50 ml. of 5 per cent hydrochloric acid were each heated to about 90 °C and then treated with 50 ml. of 5 per cent hydrochloric acid containing 20 drops of o-aminobenzenethiol per 100 ml. and left to stand overnight. For the second experiment duplicate solutions each containing 0.0265 g. of silver in 50 ml. of "mixed acid" (2.5 per cent nitric acid, 2.5 per cent hydrochloric acid) were each heated to 90 °C and then treated with 50 ml. of the same mixed acid containing 10 drops of o-aminobenzenethiol and left overnight. After standing overnight, all four solutions were filtered and washed according to the accepted procedure with hot 5 per cent nitric acid, etc. The precipitates were dried for one and a half hours at 105 °C, cooled and weighed. It was assumed that there was no silver chloride present, that the composition of the precipitates corresponded to the formula $Ag(-SC_6H_4NH_2)$, and the weight of silver was calculated. The results listed in Table 21 indicate that there is some contamination by silver chloride, but that the effects might be tolerated if the per cent of hydrochloric acid present in the solutions is less than 2.5 per cent.

TABLE 21.--Effect of hydrochloric acid upon the silver-o-aminobenzenethiol precipitation

Hydrochloric Acid Present per cent	Weight of Silver Taken grams	Weight of Silver Found grams	Deviation (average) grams
5% HCl only	0.0265	0.0245, 0.0248	-0.0018
2.5% HCl and 2.5% HNO_3	0.0265	0.0254, 0.0266	-0.0005

<u>Solubility of the silver precipitate in organic solvents.</u> For these experiments some of the silver-o-aminobenzenethiol compound that had been precipitated from nitric acid and subsequently filtered and dried at 105 °C was first ground to a powder, and about 0.1 g. of the powdered material was added to each of several small clean dry beakers. To each of the beakers was then added about 10 ml. of one of the following organic solvents: alcohcl, ether, acetone, carbon tetrachloride,

heptane, 1,4-dioxane, ethyl acetate, xylene, and 2-pyrrolidone. The solvents were stirred frequently and were observed for a period of several hours, but the precipitate was apparently entirely insoluble in all of the solvents except 2-pyrrolidone. Even in 2-pyrrolidone the precipitate did not give a clear solution but formed a turbid brownish-yellow suspension.

Recommended procedure. Consideration of the effects observed in the preceding experiments led to the adoption of the following procedure in subsequent precipitations of silver-o-aminobenzenethiol: The solution containing 1 to 100 mg. of silver per 50 ml. of 5 to 10 per cent nitric acid is heated to about 90 °C. To the hot solution which should contain no more than 100 mg. of the metal is added 50 ml. of cold o-aminobenzenethiol solution that has been prepared as described under "Reagents." The solution and precipitate are allowed to stand overnight and then filtered under vacuum on a weighed fritted glass crucible. The precipitate that remains in the beaker is washed twice by decantation with approximately 10 ml. portions of hot 5 per cent nitric acid, and twice with like portions of hot 2.5 per cent nitric acid. The remaining precipitate is washed from the beaker into the crucible with a stream of hot water from a wash bottle. The beaker is twice washed with hot water and scrubbed with a policeman, and the washings are transferred to the crucible. The precipitate on the crucible is washed once again with hot water and sucked dry. The precipitate is then washed five times with hot alochol. In the first alcohol wash the crucible is filled with the liquid and sucked dry; in the subsequent washes only enough alcohol is added each time to cover the precipitate to a depth of 1/8 to 1/4 of an inch. Finally, the crucible is filled once with cold ether and sucked dry. The crucible is left in the open at room temperature for a few minutes to allow any excess ether to evaporate and then is dried for 1 to 2 hours at 105 °C, cooled and weighed. The weight of the precipitate is multiplied by the factor 0.465 to calculate the weight of silver that it contains.

Composition of Some Silver Alloys

The preceding precipitations were made from solutions that contained no metal ions other than silver. Some alloys of silver are listed in Table 22 to show the kinds and the relative amounts of other metals that would commonly be obtained with silver in solutions prepared for analysis (17).

TABLE 22.--Composition of some silver alloys

Metals Present	Type of Material and Per Cent of Each Metal Present					
	Gold Solder	Standard Cadmium Silver	Silver Solder	Gray Gold	Platinum Substitute	Platinum Substitute
Silver	55	92.5	40	0.0- 8.6	70	70
Copper	29	5.75	14			
Gold	12			86.0		
Zinc	5.5		6			
Iron				5.7-17.0		
Cobalt					5	
Nickel						5
Cadmium		1.75				
Tin			40			
Platinum					25	
Palladium						25

No tests were made to determine the interferences that might be caused by presence of the less common elements, platinum and palladium, in solutions to be treated with o-aminobenzenethiol. Although no alloy was found listed that contained silver together with mercury, still a solution of the mercury(II) ion was tested to see whether it interferes with the silver determination. The reactions of the mercury(II) ion were investigated because preliminary work outlined in Chapter II indicated that the mercury(I) ion is precipitated by o-aminobenzenethiol from 5 per cent nitric acid solutions, but that the mercury(II) ion is not. At least three types of experiments were conducted with solutions of mercury(II) and of every other metal, except platinum and palladium, listed in Table 23: (1) A 5 per cent nitric acid solution of each metal alone was treated with o-aminobenzenethiol. (2) A solution of each metal together with silver was treated in the same manner, and (3) A solution of several of the metals together with silver was treated in the same manner. Gold and copper, both of which give serious interference, were given special attention, and experiments involving these metals are discussed first.

Efforts to Eliminate Interference by Gold

Even a brief survey reveals that gold and/or copper appear in many, many alloys with silver. But, as revealed by preliminary work outlined in Chapter II, both gold and copper, as well as silver, are precipitated by o-aminobenzenethiol from 5 per cent acid solutions. Special efforts have therefore been made to eliminate interference by these two metals. Experiments involving gold are discussed immediately below, and experiments involving copper are discussed in the next major section.

Solubility of the gold-o-aminobenzenethiol precipitate in organic solvents. There is a strong possibility that disintegration of silver alloys by use of nitric acid alone would not dissolve gold that might be present but would allow this element to settle out in a form that could be separated by filtration before the addition of o-aminobenzenethiol. In case gold is obtained in solution with silver there are three possible means of separation: (1) The gold might be caused to remain in solution as a soluble complex while the silver was precipitated by the thiol. (2) The gold alone might be precipitated by a selective reaction and filtered off, and (3) The gold and silver might be precipitated together with o-aminobenzenethiol, filtered off, and then one of the two metal complexes might be dissolved away from the mixture by a selective solvent. The third possibility was investigated first.

As discussed in the next to the last paragraph of the previous section, the silver-o-aminobenzenethiol precipitate is insoluble in most organic solvents. Trials were next made to see whether the gold-o-aminobenzenethiol precipitate might be soluble enough in one of these solvents to allow its separation from the silver complex. For these trials some of the gold o-aminobenzenethiol compound that had been precipitated from 5 per cent nitric acid and subsequently filtered and dried at room temperature, was first ground to a powder, and about 0.1 g. of the powdered material was added to each of several small clean dry beakers. To each of the beakers was then added about 10 ml. of one of the following organic solvents: alcohol, ether, acetone, carbon tetrachloride, heptane, 1,4-dioxane, ethyl acetate, xylene, and 2-pyrrolidone. The solvents were stirred frequently and observed for a period of several hours. The gold complex apparently dissolved in the pyrrolidone, and remained in solution when the pyrrolidone was diluted 15 to 1 with water, but, since the silver complex is somewhat soluble in this reagent, there is no basis for separation. The gold complex gave a turbid, white suspension in acetone and was apparently completely insoluble in all of the other solvents.

Effect of EDTA. The disodium salt of ethylenediaminetetraacetate (EDTA) forms soluble complexes with many metals and thus prevents these metals from undergoing their normal precipitation reactions. However, this salt, when tried under several widely different sets of conditions, did not prevent precipitation of gold by o-aminobenzenethiol.

Effect of oxine. Some metals can be separated from each other by use of the reagent 8-hydroxyquinoline (oxine) at a selected pH. Experiments revealed that gold begins to precipitate in the presence of this reagent at a pH of less than one but is not completely precipitated until the pH reaches 5 to 7. Silver in the presence of the reagent begins to precipitate at a pH of 2.4. The reagent thus affords no separation of these metals.

Effect of common reducing agents. Finally, experiments were conducted which indicated that the best separations of gold from silver may be made by use of common reducing agents to reduce the former to the metal. The metallic gold is, of course, insoluble in any single mineral acid. Since the gold solution that was available contained chloride, this solution was not combined with a silver solution, but parallel series of experiments were conducted using gold solutions in one case and silver solutions in the other. It is thought, however, that the good results that were obtained in these experiments could be duplicated for a chloride-free solution that contained both gold and silver. Four reducing agents, solutions of Na_2SO_3, $FeSO_4$, $(NH_4)_2C_2O_4$, and hydrazine hydrate, were used in these experiments. For the experiments with gold, four solutions were prepared which each contained 5 ml. of approximately 0.2 N gold(III) solution in 50 ml. of 5 per cent nitric acid. For the experiments with silver, four solutions were prepared each of which contained 0.0265 g. of silver in 50 ml. of 5 per cent nitric acid. To one gold solution and to one silver solution 25 ml. of 5 per cent nitric acid solution containing 0.5 g. of Na_2SO_3 was added; to another pair of solutions 25 ml. of 5 per cent nitric acid solution containing 0.5 g. of $FeSO_4$ was added; to another pair of solutions 10 ml. of a water solution containing 0.4 g. of $(NH_4)_2C_2O_4$ was added; and to the last pair of solutions 2 ml. of a water solution containing 0.08 g. of hydrazine hydrate was added.

Gold metal separated immediately from its cold solutions to which Na_2SO_3, $FeSO_4$, or hydrazine hydrate was added; these solutions were not heated. Gold metal separated from the solution to which $(NH_4)_2C_2O_4$ was added only after the solution had been boiled; boiling was continued for about 15 minutes. Each silver solution was treated exactly like its counterpart gold solution, but no precipitate separated from any solution. After one hour the gold solutions were filtered through weighed fritted glass crucibles. The precipitates were weighed and counted as gold metal. The results are shown in Table 23.

To each of the four filtrates from the gold precipitates and to each of the four silver solutions was then added 50 ml. of 5 per cent nitric acid which contained 20 drops of o-aminobenzenethiol per 100 ml. of solution. The gold filtrates remained clear through this treatment, whereas all silver solutions developed the characteristic white floc. All solutions were left to stand overnight. After standing overnight all gold filtrates were still free of any precipitate and were discarded.

After standing overnight the silver solution to which Na_2SO_3 and o-aminobenzenethiol had been added contained a finely divided black precipitate that appeared to be elemental silver (in place of the white floc that had formed when o-aminobenzenethiol was first added). The other silver solutions still contained the white floc characteristic of the silver-o-aminobenzenethiol complex. All silver solutions were filtered, and the precipitates were treated according to the recommended procedure. The weights of silver calculated by multiplying the weights of the precipitates by the factor 0.465 are shown in Table 23.

TABLE 23.--Use of reducing agents ahead of o-aminobenzenethiol in gold and in silver solutions

Reducing Agent Used	Weight of Gold Found grams	Weight of Silver Taken grams	Weight of Silver Found grams	Deviation (for Silver) grams
Na_2SO_3	0.0467	0.0265	0.0149	-0.0116
$FeSO_4$	0.0471	0.0265	0.0271	+0.0006
$(NH_4)_2C_2O_4$	0.0475	0.0265	0.0269	+0.0004
$(H_2N)_2 \cdot xH_2O$	0.0495	0.0265	0.0270	+0.0005

The following observations are made concerning the results of these experiments: Although the gold solutions had not been standardized, the fact that the agreement among the weights of gold obtained by use of the four different reducing agents is good and the fact that no precipitates were obtained when o-aminobenzenethiol was added to the filtrates from the gold indicate that the gold was completely removed by each of the four reagents. The gold obtained by use of the hydrazine hydrate was slow to filter, and it was not washed as much as the other precipitates. This, no doubt, explains the higher weight of gold found by this experiment. The Na_2SO_3, however, is apparently too strong a reducing agent to use in conjunction with o-aminobenzenethiol for determination of silver. Evidently $FeSO_4$, $(NH_4)_2C_2O_4$, or hydrazine hydrate solutions can be used to separate gold from silver without any bad effects upon the subsequent precipitation of silver by o-aminobenzenethiol. This would, of course, be true only for chloride-free solutions.

Efforts to Eliminate Interference by Copper

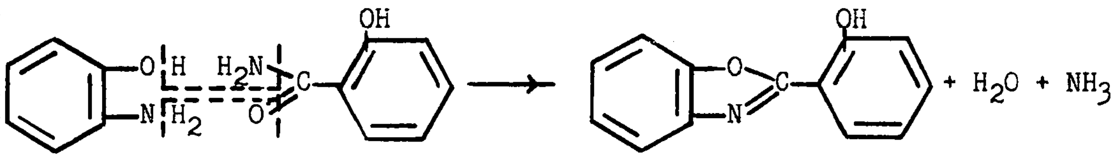
Effect of EDTA. As with gold, the disodium salt of ethylenediaminetetraacetate was tried under several widely different sets of conditions, and it did not prevent precipitation of copper by o-aminobenzenethiol.

Effect of Oxine. Experiments revealed that copper is not completely precipitated by 8-hydroxyquinoline below a pH of 2.7. Silver in the presence of the reagent begins to precipitate at a pH of 2.4. The reagent thus affords no separation of these metals.

Effect of Salicylaldoxime. Information was found to the effect that copper is completely precipitated by salizylaldoxime at a pH of

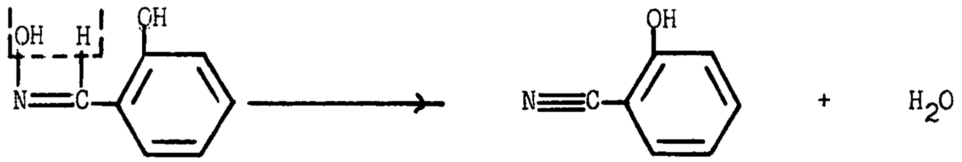
2.6, whereas silver does not begin to precipitate with this reagent at any pH below 6.3 (4, 8, 12). This reaction was tried, and it did, indeed, give a precise and complete separation of copper from silver in a solution containing both. However, when the filtrate from the copper-salicylaldoxime precipitate was treated with o-aminobenzenethiol, the thiol reacted with excess salicylaldoxime to give a new reagent, insoluble in the 5 per cent nitric acid, and otherwise quite different in its chemical properties from either salicylaldoxime or o-aminobenzenethiol. The insoluble compound thus obtained apparently included the silver that had been present in the solution, and it was stable towards the hot acid and hot water washes, but it was readily soluble in both alcohol and ether. The presence of a new compound in this case was also indicated by the fact that when precipitation was carried out in a hot solution the flocculent precipitate obtained was at first a deep purplish-red color which then faded to a cream or orange color. The shade of color finally obtained evidently depended upon the extent to which the salicylaldoxime solution was heated before the o-aminobenzenethiol was added. However, a salicylaldoxime solution containing silver that was not heated gave the same color changes from purplish-red to pale orange. A further experiment revealed that a solution of salicylaldoxime in a 5 per cent nitric acid solution that contains no copper, silver, or other metal ion, yields a white flocculent precipitate when treated with a 5 per cent nitric acid solution of o-aminobenzenethiol.

No investigation was made of the physical and chemical properties of the acid-insoluble organic compound obtained by this reaction, and its structure is therefore unknown. However, by an analogy with an equation given by Walter and Freiser (41) for the preparation of 2(o-hydroxyphenyl)benzoxazole:



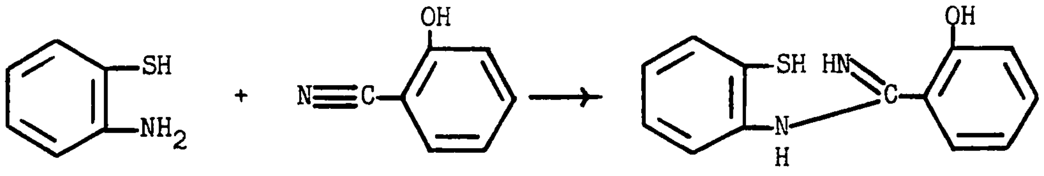
o-Aminophenol Salicylamide 2(o-hydroxyphenyl)benzoxazole

it is supposed that the compound might be 2(o-hydroxyphenyl)benzothiazole. Dr. A. J. Weinheimer (42) has postulated that the thiazole could be formed under the conditions outlined above through the following series of reactions: (1) The salicylaldoxime is first dehydrated in the presence of the 5 per cent nitric acid to yield the nitrile:



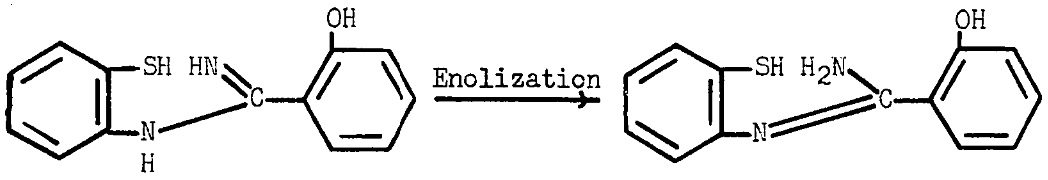
Salicylaldoxime Salicylnitrile

(2) The nitrile group may then react with the amine group of o-aminobenzenethiol to first form a single bond between the nitrile carbon and the amine nitrogen:

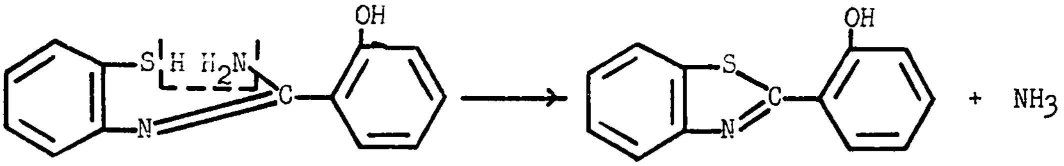


o-Aminobenzenethiol Salicylnitrile

(3) At this stage ammonia might be split out to form the benzothiazole at once, but for the sake of closer analogy to the model reaction quoted above, it is assumed that the product of equation (2) enolizes:



(4) Finally, ammonia splits out from the product of reaction (3) to yield 2(o-hydroxyphenyl)benzothiazole:



2(o-hydroxyphenyl)benzothiazole

Furthermore, formation of benzothiazoles by reactions similar to those postulated are recorded in the literature. Bogert and Stull (10) mention syntheses of benzothiazoles by condensation of o-amino-phenyl-mercaptans and acyl halides, anhydrides, or aldehydes, and Bogert and Corbitt (9) have prepared 2(o-hydroxyphenyl)benzothiazole by reaction of zinc-o-aminothiophenolate with salicylaldehyde.

Summary. After the unsuccessful tests with ethylenediaminetetraacetate, 8-hydroxyquinoline, and salicylaldoxime, efforts to separate copper from silver prior to precipitation of the silver with o-aminobenzenethiol were abandoned. The fact that interference by copper cannot, as yet, be eliminated constitutes a serious limitation upon the method, but there are alloys of silver that do not contain copper and do contain several other metals. The interferences, if any, from metals other than copper and gold were investigated next.

Precipitations of Metals Other than Silver with o-Aminobenzenethiol

For these experiments aliquot volumes that contained about 0.05 g. of metal were taken for each of several metal solutions. These aliquot volumes were diluted to 50 ml. with 5 per cent nitric acid, heated to 90 to 100 °C, treated with 50 ml. of 5 per cent nitric acid containing 20 drops of o-aminobenzenethiol, and left to stand overnight. The metals tested and the results observed for each are listed in Table 24. As shown in the table, only gold and copper gave a weighable amount of precipitate.

TABLE 24.--Precipitations of metals other than silver with o-aminobenzenethiol

Ion	Precipitate Observed, If Any
Cd(II)	No Precipitate
Co(II)	No Precipitate
Fe(III)	No Precipitate
Ni(II)	No Precipitate
Zn(II)	No Precipitate
Sn(II)	No Precipitate
Hg(II)	Minute amount of fine white precipitate*
Cu(II)	White crystalline precipitate
Au(III)	Cream crystalline precipitate

* The amount of precipitate is considered to be so small as to be unweighable. The precipitate may result from the presence of some mercury(I) ion or from some other impurity.

Precipitations of Silver in the Presence of Other Metals with o-Aminobenzenethiol

Two series of experiments were conducted to investigate interferences that occur when silver is precipitated in the presence of other metals by o-aminobenzenethiol. In one series of experiments solutions containing silver and only one of the other metals to be tested were treated according to the "recommended procedure" (page 88) for determining silver. The results for these experiments are shown in Table 25.

It is thought that the somewhat low weight of silver found for the solution containing tin results from interference from the hydrochloric acid introduced with the tin solution rather than from the tin. The solution containing mercury(II) gave a pale gray precipitate. It is thought that this precipitate contains some metallic silver formed by reaction with some mercury(I) ion which may have been present as an impurity or may have been formed by some reduction of mercury(II) by the o-aminobenzenethiol. However, only the solutions containing copper and gold showed serious deviations.

TABLE 25.--Precipitations of silver in the presence of one other metal with o-aminobenzenethiol

Weight of Silver Taken	Other Metal Taken		Weight of Silver Found	Deviation
grams	ionic form	grams	grams	grams
0.0265	Cd(II)	0.0562	0.0267	+0.0002
0.0265	Co(II)	0.0590	0.0267	+0.0002
0.0265	Zn(II)	0.0654	0.0265	0.0000
0.0265	Fe(III)	0.0558	0.0267	+0.0002
0.0265	Hg(II)	0.0501	0.0263	-0.0002
0.0265	Ni(II)	0.0588	0.0267	+0.0002
0.0265	Sn(II)	0.0594	0.0251	-0.0014
0.0265	Cu(II)	0.0636	0.0673	+0.0408
0.0265	Au(III)	0.0471	0.0651	+0.0386

For the other series of experiments, solutions containing silver and some combination of the other metals were treated in the same manner as in the preceding experiments. Results for these experiments are shown in Table 26.

TABLE 26.--Precipitations of silver in the presence of a combination of other metals with o-aminobenzenethiol

Weight of Silver Taken grams	Other Metals Taken (about 0.05 g. each) ionic forms	Weight of Silver Found grams	Deviation grams
0.0265	Cd(II), Co(II), Fe(III), Ni(II), Zn(II), Sn(II)	0.0233	-0.0032
0.0265	Cd(II), Co(II), Fe(III), Ni(II), Zn(II), Sn(II), Hg(II)	0.0251	-0.0014
0.0265	Cd(II), Co(II), Fe(III), Ni(II), Zn(II)	0.0268	+0.0003

As shown in the table, the solution that contained tin and the one that contained both tin and mercury gave somewhat low results, probably for the same reasons that are suggested for the simpler experiments above. The solution that contained neither tin nor mercury gave an almost perfect value for the amount of silver present.

This concludes the work to be done with o-aminobenzenethiol for this project. The work has always been interesting, and the results have been encouraging. It is hoped that others can extend and improve the applications of this intriguing reagent.

CHAPTER VI

SUMMARY

Introduction and Literature Survey. Preparation of o-aminobenzenethiol was described at least as early as 1930. Since that time some study of this compound has been made in work of a general nature that sought to establish some factors controlling the selectivity of organic reagents, and several metal salts of the reagent have been prepared. This paper presents the results of some investigations aimed at quantitative determinations of metal ions in complex mixtures by use of the reagent.

Preliminary Work. Solutions of thirty-six different ions were prepared and treated with various common reagents and with o-aminobenzenethiol to establish which elements might be determined.

Determination of Bismuth. The reagent o-aminobenzenethiol reacts with bismuth in dilute acid solutions to yield a complex compound. When this complex is formed in dilute acid solutions whose pH is less than 1.5, a bright yellow color is developed the intensity of which is proportional to the concentration of bismuth in solution. Photoelectric measurement of this yellow color was used to develop an analytical procedure for the determination of bismuth. Interferences were investigated, and several alloys were analyzed.

When an acid solution containing an appreciable amount of dissolved bismuth-o-aminobenzenethiol complex is neutralized to a pH greater than 1.5, a unique, bright orange floc separates out. It was established that this precipitate is quite characteristic and may be useful as a qualitative test for bismuth, but the test is not sensitive for small concentrations. It was established that precipitation with o-aminobenzenethiol is not suitable for quantitative gravimetric determination of bismuth.

Determination of Selenium and Tellurium. It was found that o-aminobenzenethiol reduces soluble ionic radicals of both selenium and tellurium to acid-insoluble elemental forms of these elements. It was established that the reaction with selenium may be used for semi-quantitative gravimetric determination of this element. Only a qualitative study was made of the reaction with tellurium. Also, a brief investigation was made of a volumetric determination of selenium based upon the appearance, and then the disappearance, of a yellow color that occurs when selenium solutions are titrated with o-aminobenzenethiol.

Determination of Silver. It was established that silver may be determined by its quantitative gravimetric precipitation in 5 per cent nitric acid with o-aminobenzenethiol. Gold and copper interfere.

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