THE USE OF 8-HYDROXYQUINOLINE AS A PRECIPITANT OF THE CATIONS WITH SPECIAL REFERENCE TO THE DETERMINATION OF ALUMINUM

by

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THE USE OF 8-HYDROXYQUINOLINE AS A PRECIPITANT OF THE CATIONS WITH SPECIAL REFERENCE TO THE DETERMINATION OF ALUMINUM

I. INTRODUCTION: PURPOSE OF THE INVESTIGATION

The qualitative or quantitative separation of the iron-group metals by precipitation as hydroxides is open to certain disadvantages. In an alkaline solution manganese is readily oxidized by the air and may be precipitated as the dioxide. The precipitated hydroxides may also be contaminated by other metals as a result of adsorption on the surface of the gelatinous hydrated oxides of the iron-group metals, and, further, by chemical combination with aluminum hydroxide. In the latter case, compounds similar to the spinels are formed as a result of the amphoteric character of aluminum oxide. The metal beryllium, which occurs extensively in East Tennessee and in other localities, and which is invariably associated with aluminum, is similar to the latter in chemical as well as in physical properties. Consequently, the separation of the metal from aluminum for either qualitative or quantitative purposes is difficult.[1] Another difficulty in the determination of aluminum by precipitation as hydroxide is that organic matter interferes by combination with the aluminum to form complexes or by forming the adsorption compounds known as "lakes".

It has been reported by Berg[2] and others that under certain conditions 8-Hydroxyquinoline, C_9H_6ONH, called "oxine", will precipitate aluminum. Is is the purpose of this investigation to study this reagent

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1. Kolthoff and Sandell: "A Rapid Method for the Separation of Aluminum and Beryllium", J. Am. Chem. Soc., 50, 1900 (1928).
2. Berg: "New Methods for the Determination and Separation of Metals with the Aid of 8-hydroxyquinoline", Z. Anal. Chem., 71, 321-331 (1927); Chem. Abstracts, 21, 3849 (1927)

more fully as a precipitant of aluminum. In particular, it is sought to determine which of the metals are precipitated by the new reagent, and the conditions under which the reagent may be utilized for the separation of aluminum from beryllium and other metals.

II. THE WORK OF PREVIOUS INVESTIGATORS

A. Preparation of the Reagent. The oxine is soluble in water, alcohol, alkalies, and acids. The acetic acid solution recommended by the Bureau of Standards[3] is prepared as follows: 2.5 g. of 8-hydroxyquinoline are triturated with 5 cc. of glacial acetic acid. This is poured into 100 cc. of water at 60° and the solution cooled. If necessary the solution is filtered also. One cc. of this solution is equivalent to 2.9 mg. of alumina. The alcoholic solution is made up by dissolving 2 g. of the oxine in 100 cc. of water to which has been added several drops of ammonia.

B. Properties of the Precipitated Metal Compounds; Their Consideration for Purposes of Qualitative Estimation. With the exception of the metals whose oxides are volatile, the metal-compounds of 8-hydroxyquinoline may be ignited and the metal weighed as the oxide. When the metal-hydroxyquinoline compound is to be weighed as such it is important to note that whereas most of these compounds are hydrated, some lose their water of hydration easily while others do not. However, a more convenient method is to determine the oxine volumetrically. This is done as follows: Dissolve the oxine precipitate in 8-10 % HCl and add a little 1 % indigo carmine solution as an indicator. Add an excess of standard $KBrO_3$-KBr solution, and then some 20 % KI solution, and titrate the liberated iodine with standard thiosulfate[4]. Titration of this kind will be referred to as iodometric in the succeesing pages.

Another method of volumetric procedure is based on the fact that 2

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3. Lundell and Knowles: "Use of 8-Hydroxyquinoline in Separations of Aluminum", U. S. Bur. Stds. Jour. Research, 3, 90-6 (1929).
4. Hahn and Hartlieb: "Methods of Precipitation with 8-Hydroxyquinoline", Z. Anal.Chem., 71, 225-235 (1929); Chem. Abstracts, 21, 2632 (1927).

mols of acid are liberated when a bivalent cation is precipitated with oxine, and 3 mols of acid are liberated when a tervalent cation is precipitated. The liberated acid can be titrated with standard NaOH with phenol red or a-naphtholphthalein as indicator[5]. The objection to this procedure is that the precipitate carries down with it some of the base and indicator. It is advisable to filter off the precipitate, or to allow it to settle and to take an aliquot part of the supernatant liquid and titrate the liberated acid.

C. Methods of Precipitation by Previous Investigators. 1. Precipitation of Aluminum. Aluminum has been shown by Berg[6] to be completely precipitated as $(C_9H_6ON)_3Al$ by 8-hydroxyquinoline in slightly acid or ammoniacal solutions. After drying at 110° it may be weighed as such, or it may be ignited to the oxide, Al_2O_3, by ignition under a cover of oxalic acid[7]. Also, it may be determined volumetrically with the $KBrO_3$- KBr procedure. A third method is to dissolve the precipitate while on the filter paper with HNO_3, then again precipitate the aluminum in the filtrate with NH_4OH, and ignite the precipitate to the oxide. By the usual methods, organic matter interferes with the determination of aluminum[8], but by the oxine method, organic matter does not interfere. This is also true of other cations whose salts are easily hydrolyzed.

2. Separation of Aluminum and Beryllium. Berg, Hahn, and Kolthoff[9] worked out a method for the separation of aluminum and beryllium. They used a solution of oxine in water made slightly acid with acetic acid

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5. Ibid.
6. Berg: "New Methods for the Determination and Separation of Metals with the Aid of 8-hydroxyquinoline", Z. Anal. Chem., 71, 321-331 (1927); (Chem. Abstracts, 21, 3849 (1927)).
7. Ibid.
8. Ibid.
9. Kolthoff and Sandell: "A Rapid Method for the Separation of Aluminum and Beryllium", J. Am. Chem. Soc., 150, 1900 (1928).

acid and containing ammonium acetate. The aluminum was precipitated quantitatively as $(C_9H_6ON)_3Al$. Under these conditions beryllium was not precipitated. At first a 5 % solution of oxine in 95 % alcohol was used in precipitating the aluminum, but Kolthoff found the results to be 0.4 % low. These experimenters confirmed his results and then found the low values to be due to the solubility of the aluminum-oxine in warm, dilute alcoholic solution in which the precipitation was made. Then the possibility of using an acetic acid solution was explored for the precipitation of aluminum and other metals. The advantages claimed for the acid solution over the alcoholic solution were that the former was more stable -- capable of being kept for many weeks without change -- and that it gave more accurate results because it gave a more complete precipitation. The solution containing the aluminum salt was made slightly acid with acetic acid and then warmed to 50-60° and treated with an excess of the oxine reagent. A solution of 2 N ammonium acetate was slowly added until a permanent precipitate was obtained, and then 20-25 cc. excess added. After permitting the precipitate to settle, the solution was filtered on a Gooch crucible. The precipitate was washed with cold water and dried at 110°. The composition of the residue was $(C_9H_6ON)_3Al$ which represents 11.10 % Al_2O_3. If ferric iron is present, it is precipitated with the aluminum. There is a slight solubility of aluminum-oxide in water which is increased by the presence of beryllium salts. But an excess of the oxine reduces the solubility of the precipitate.

3. Separation of Aluminum and Phosphorus. The separation of aluminum and phosphorus is carried out with an ammoniacal solution of 8-hydroxquinoline. An excess of the oxine in acetic acid solution is

added to the slightly acid solution containing small amounts of aluminum and phosphorus. Then ammonium hydroxide (5 cc. of NH_4OH to 100 cc. of water) is added until the solution is alkaline. The mixture is heated to 60-70° and the precipitate digested until it coagulates. Then it is cooled by ice water and filtered through a tight filter. The precipitate is washed with cold NH_4OH (1:40) containing 25 cc. of the oxine. The precipitate is dissolved in HNO_3-H_2SO_4 and in the filtrate the aluminum is precipitated with NH_4OH and ignited to the oxide[10].

4. Separation of Aluminum and Vanadium. When aluminum is in the presence of vanadium, the vanadium is oxidized to a higher valency with H_2O_2 by adding 10-15 cc. of 3 % peroxide. The oxine reagent is then added and the procedure as outlined for the phosphorus separation is followed.

5. Separation of Aluminum and Arsenic, etc. The separation of aluminum from arsenic, fluorine, and boron is accomplished as in the procedure for phosphorus. Tantalum, columbium, titanium, and molybdenum are oxidized to their higher valencies with H_2O_2 as in the procedure with vanadium[11].

6. Separation of Aluminum and Uranium. In the presence of uranium, the slightly acid solution is carefully neutralized with $(NH_4)_2CO_3$, and an excess of 2.5 cc of the ammonium carbonate solution added for every 100 cc. of the aluminum solution. The solution is then heated gently to 50°, avoiding great effervescence; it is then filtered and the precipitate treated as in procedure 3.[12]

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10. Lundell and Knowles: "Use of 8-Hydroxyquinoline in Separations of Aluminum", U. S. Bur. Stds. Jour. Research, 3, (1929).
11. Ibid.
12. Ibid.

7. Separation of Aluminum and Bismuth. In acetic acid or ammoniacal tartrate solutions of bismuth, the addition of 8-hydroxyquinoline gives an orange-yellow crystalline precipitate of $Bi(C_9H_6ON)_3 . H_2O$, in which form it can be weighed after drying at 105°. The precipitate becomes anhydrous after long heating at 130-140°. The solution in which precipitation takes place must be at a temperature of 60-70° when the oxine is added. A saturated solution of oxine in acetone or alcohol should be used as a precipitant. Also, the precipitate can be titrated iodometrically[13]. Since bismuth gives a precipitate with the oxine, it will be necessary to separate bismuth from aluminum by means of some other reagent. A convenient method of separation is to precipitate the bismuth as Bi_2S_3 by passing H_2S into an acid solution of the metals.

8. Separation of Aluminum and Iron. Iron is separated from aluminum by first adding oxalic, malonic, tartaric, or salicylic acid which form complexes with these metals and then, when the concentration of the organic acid has been properly adjusted, adding the oxine reagent. Iron will be precipitated while the aluminum remains in solution. In 100 cc. of a solution containing 3 g. of ammonium acetate, 3-4 g. of ammonium tartrate and 15-20 % acetic acid, the precipitate of 0.05 g. of iron in the presence of 0.10 g. of aluminum can be accomplished at 50° by the dropwise addition of the oxine reagent to the well-stirred solution. After filtering, the excess oxine can be determined by the iodometric method, and in an aliquot part, the aluminum can be determined in ammoniacal solution. Excellent results were obtained with malonic acid[14].

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13. Berg: "Separation and Determination of Metals with the aid of 8-hydroxyquinoline", Z. Anal. Chem., 72, 177-179 (1927); Chem. Ab. 22,1929 (1928).
14. Berg: "New Method for Determination and Separation of Metals with the aid of o-hydroxyquinoline", Z. Anal. Chem., 76, 191-204, (1929); Chem. Abstracts, 23, 1588 (1929).

This reagent may be employed for the testing of impurities of iron and aluminum in phosphoric acid and alkali phosphate solutions. The advantage of the oxine over NH_4OH is that the former will give the precipitate in a clear solution, whereas the latter will not[15].

9. Precipitation of Copper, Zinc, Cadmium, and Magnesium. The low solubility of the compounds of copper, zinc, and cadmium with the oxine permits the separation of these elements from magnesium. The same principle permits the separation of copper and cadmium, since the latter is not precipitated when the acetic acid content is increased.[16]

Magnesium differs from these metals in that it does not give a precipitate in acetic acid solutions, but does give a precipitate in ammoniacal and caustic solutions.[16] In a sodium acetate solution only 0.008 mg. of copper in 5 cc. of solution may be detected and less than 0.02 mg. in 5 cc. of a solution which has been treated with 0.5 cc. of a saturated sodium tartrate solution. To obtain a precipitate with the reagent in either case add 0.5 cc. of 2 N NaOH. The copper precipitate has the composition of $Cu(C_9H_6ON)_2$ and contains 18.13 % copper. It can be dried and weighed or it may be dissolved in HCl and determined iodometrically. The precipitation in acetic acid solutions is as follows: To a solution containing 0.12 g. of copper or less in 100 cc., add 5 g. of sodium acetate and acetic acid to make the concentration 10 %. Heat to about 60° and add dropwise a slight excess of a 2 % oxine solution in alcohol. Gradually raise the temperature to 90°. Filter and wash with water. Dry at 110° or dissolve in HCl and determine the excess oxine

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16. Berg: "New Method for the Determination and Separation of Metals with the Aid of o-hydroxyquinoline", Z. Anal. Chem., 70, 341-347 (1927).
15. Lundell and Knowles: "Use of 8-Hydroxyquinoline in Separations of Aluminum", U. S. Bur. Stds. Jour. Research, 3, 90-6(1929).

iodometrically. For the precipitation of copper in NaOH solution, add 3.5 g. of tartaric acid to the copper solution, neutralize with 20 % NaOH, adding 15 cc. of 2 N NaOH in excess and continue as in the presence of acetic acid[17].

Tervalent iron and bismuth, quadrivalent tin, and quinquevalent antimony all interfere with the iodometric determination of copper. By precipitating in alkaline solutions with oxine, pure copper precipitates were obtained which gave good results with the iodometric titration; the greatest error corresponding to 2 % of the total copper present. The separation of copper from zinc in this manner proved unsuccessful[18].

Oxine gives a greenish yellow, crystalline precipitate with magnesium ions in an ammoniacal or caustic alkali solution containing ammonium tartrate. The precipitate is much more sensitive than the customary form of $MgNH_4PO_4$. In ammoniacal solution, magnesium is precipitated by oxine in the presence of K, Li, Na, Ca, Sr, and Ba if certain precautions are taken. In NaOH solutions containing tartrate, the magnesium precipitate carries down with it copper, zinc, cadmium, and ferric iron. The magnesium precipitate is very soluble in acids so that a very dilute acid solution prevents its formation. When dried at 105°, the formula corresponds to $Mg(C_9H_6ON)_2 \cdot 2\ H_2O$, but it becomes anhydrous at 130-140°. It can be weighed in either form however. The precipitate can also be ignited to the oxide after the quinoline complex has been destroyed by heating with anhydrous oxalic acid.[19]

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17. Berg: "New Method for the Determination and Separation of the Metals with the Aid of 8-Hydroxyquinoline", Z. Anal. Chem., 70, 341-347 (1927); Chem. Abstracts, 21, 1738 (1927).
18. Ibid.
19. Berg: "New Way for Determination and Separation with the Aid of 8-hydroxyquinoline", Z. Anal. Chem., 71, 171-185 (1927); Chem. Abstracts, 21, 2631 (1927).

Zinc precipitations were carried out in tartrate solutions, in acetic acid solutions, and also in KCN solutions. The precipitate corresponds to $Zn(C_9H_6ON)_2 \cdot 2\ H_2O$ when dried at room temperature in a desiccator. When dried at 100° it contains 1.5 mols of water; when dried at 120-130° it is anhydrous. Molecular weight determinations show that when the precipitate is dissolved in naphthalene, the normal molecular weight is obtained if two mols of water of crystallization are present, but that when the anhydrous salt is used, the molecular weight is twice that corresponding to the simplest formula. As much as 0.5 % of acetic acid suffices to prevent the precipitation of the magnesium compound, whereas precipitation of zinc is completely accomplished in the presence of 7 % acetic acid. Zinc cannot be separated from copper and cadmium by oxine, but from the other cations the separation is easy, although a double precipitation is sometimes necessary.[20]

10. Precipitation of Lead. Lead may be precipitated by oxine in a solution having a pH value of 8.5 - 9.5. As a reagent, the aqueous solution of the oxine is preferable to the alcoholic solution. The precipitate is best formed in a hot solution, but it should be allowed to stand overnight in a cool place to insure complete precipitation. The precipitate should be washed with as little water as possible, because of its appreciable solubility. It is dried to constant weight at 105°.[21]

11. Precipitation of Iron and Its Separation from Other Cations. A 3-4 % solution of the oxine in alcohol or a 4 % solution in acetate solution is used in the precipitation of the cation, ferric iron. In

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20. Berg: "New Method for the Determination and Separation of Metals with the Aid of o-hydroxyquinoline", Z. Anal. Chem., 71, 171-185 ('27).
21. Marsson and Haase: "Determination of Lead with 8-hydroxyquinoline", Chem Ztg., 52, 974-975 (1928); Chem. Abstracts, 23, 1077 (1929).

the latter case, 4 g. of oxine is dissolved in 8-10 cc. of acetic acid and the solution diluted to 100 cc. Iron in the presence of even 25 % acetic acid or sodium acetate is precipitated quantitatively as $Fe(C_9H_6ON)_3$. It is weighed as such after drying at 120°, or it may be ignited to the oxide, Fe_2O_3, or after dissolving in HCl it can be determined iodometrically.[22]

For the separation of iron from the alkali earths, the iron can be precipitated as described under the separation of aluminum and iron, and in the filtrate, magnesium can be determined by precipitating with oxine in ammoniacal solution. Calcium can be precipitated as oxalate; strontium and barium as sulfates. Similarly, iron can be separated from beryllium. To separate iron from manganese, it has been found best to precipitate iron in the cold in a 10 % acetic acid solution containing considerable acetate, and then to precipitate the manganese in ammoniacal solution.[23]

12. The Precipitation of Manganese. The $Mn(C_9H_6ON)_2$ is very sensitive to acids, in this respect being similar to magnesium. It can be separated from zinc and cadmium in much the same way as magnesium is separated from these cations. The zinc forms a precipitate with oxine at acid concentrations in which the pH is less than 5, while manganese requires a higher pH value.[24] The manganese forms a dull-yellow precipitate of $Mn(C_9H_6ON)_2 \cdot 2\,H_2O$ in neutral or faintly acid solutions. The precipitate is not sufficiently stable to lend itself to direct drying and weighing, but it can be ignited with oxalic acid to the oxide. Titration

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22. Berg: "New Method for Determinarion and Separation of Metals with the Aid of o-hydroxyquinoline", Z. Anal. Chem., 76, 191-204 (1929); (Chem. Abstracts, 23, 1588 (1929)).
23. Ibid.
24. Ibid.

of the excess oxine also gives good results.

13. Precipitation and Separation of Titanium from other Cations. The 8-hydroxyquinoline gives a crystalline precipitate of $TiO(C_9H_6ON)_2 \cdot 2\ H_2O$ when as little as 0.017 mg. of titanium is present in 5 cc. of a solution containing acetic acid, sodium acetate, or tartrate, or in 5 cc. of ammonium tartrate solution. It is weighed as such after drying at 110°. Strong ignition converts it to TiO_2. It may also be determined iodometrically.[25] Berg and Teitelbaum [25] state that titanium may be separated from other elements in the following ways: (1) By the addition of NaOH and an alkali tartrate which prevents the precipitation of titanium, but which permits the precipitation of copper, cadmium, zinc, and magnesium, and (2) by the addition of acetic acid which prevents the precipitation of calcium, strontium, barium, magnesium, and the alkalies, but which permits the precipitation of titanium. If malonic acid is also present, the aluminum is held in solution.

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25. Berg and Teitelbaum: "Determination and Separation of Titanium with Oxine", Z. Anal. Chem., 81, 1-8 (1930); Chem. Abstracts, 24, 4479 (1930).

III. THE NATURE OF THE METAL-OXINE COMPOUNDS

A. Constitution. The formation of insoluble compounds when certain organic dyes are added to metallic salts has been recognized in the dyeing industry for many years. Such compounds are called "lakes". The process of mordanting is dependent upon this formation. Aluminum compounds have been used quite extensively for this purpose.

Insoluble bodies having large surfaces may take up a dye by adsorption on the surface. The gelatinous hydroxides, or hydrated oxides, of the aluminum-group metals have large surfaces and they readily remove many dyes from solution by adsorption. This is analogous to the removal of color and odor from solutions by means of charcoal.

In the case of 8-hydroxyquinoline, however, the reactions in which it takes part as a precipitant for metals is double decomposition or metathesis, the H in the OH group being replaced by the metal of the inorganic salt. Just as alizarin, $C_6H_4(CO)_2\ C_6H_2(OH)_2$, forms the insoluble compound $C_6H_4(CO)_2\ C_6H_2O_2Ca$ with a calcium salt, so 8-hydroxyquinoline C_9H_6NOH forms the insoluble compound $(C_9H_6ON)_3Al$ with an aluminum salt. Such salts are usually hydrates and they lose their water of hydration when heated, some at moderately low temperatures, others only at rather high temperatures.

B. Color. Colors of the oxine precipitates. In his examination of the color of the oxine precipitates, Fox[26] has arrived at the conclusion that "the color of the salts is not due to any alteration of the structure of the molecule".

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26. Fox: "Salts of 8-Hydroxyquinoline", J. Chem. Soc., 99, 119-123 (1911).

IV. EXPERIMENTAL PROCEDURE

Solutions of the soluble salts of the common metals and some of the rare earths were made up of approximately 1 % strength. These solutions were placed in 50 cc. bottles, stoppered, and labeled. The 8-hydroxyquinoline solution was prepared in two ways. One solution was prepared according to the directions given by the Bureau of Standards as described under A of Chapter II. The other was prepared by dissolving about 1/2 gram of the oxine in about 50 cc. of water to which had been added several drops of concentrated NH_4OH. Thus, one solution was acid, the other slightly alkaline. The pH of the salt solutions used was determined roughly by testing them with litmus paper.

A series of test tubes were thoroughly cleaned and placed in racks. About 5 cc. of each of the solutions to be tested were placed in a test tube and the acetic acid-oxine reagent then added dropwise and the effects observed. In case a precipitate was formed, an excess of the reagent was added and heated to coagulate the precipitate. Then the precipitate was divided between 5 test tubes and the effect of the acids, HCl, HNO_3, H_2SO_4, and of the bases NaOH and NH_4OH on the precipitate were observed. The results of these observations are recorded in Table I. When no precipitate was formed by the acid-oxine, the slightly alkaline reagent was tried, and its effect on the salt observed. The effect of the ammoniacal reagent was tried in some cases even when a precipitate was formed with the acid reagent. The effect of the alkalies and acids on the reagent was also noted, and the behavior of the reagent on evaporation.

Table I

Precipitation of Cations with 8-Hydroxyquinoline

No.	Salt	Conc. %	pH of Soln. 7	7	7	Precipitate	Effect with Reagents HNO_3	H_2SO_4	HCl	NaOH	NH_4OH	Comments
1.	$Al(Cl)_3$	1	x			Yellow $Al(C_9H_6ON)_3$	Sol	Sol	Sol	Ins	Ins	Ppt.is very fine. Boiling coagulates
2.	$AgNO_3$	1	x			White AgC_9H_6ON	Sol	Sol	Sol	Sol	Sol	Sirup-like mixture of ppt. and sol.
3.	$Mg(NO_3)_2$	1		x		Yellow Ppt.	Sol	Sol	Sol	Ins	Ins	Ppt.is formed from water sol.of oxine
4.	$CdSO_4$	1	x			None	Sol	Sol	Sol	Ins	Ins	Yel.ppt.obtained by H_2Osol.of oxine.
5.	$Cr(NO_3)_3$	1	x			None						A yellow cloudiness is obtained with H_2Osol. Disappears on heating.
6.	$SrCl_2.6H_2O$	1	x			None						
7.	Ir	?	x			Turns green						No effect on heating.
8.	$TiCl_4$	1	x			Brownish green, $TiO(C_9H_6ON)_2.2\ H_3O$	Sol	Sol	Sol			Light flocculent ppt. Coagulates somewhat on boiling.
9.	Li_2CO_3	1			x	Fibrous ppt. White	Sol	Sol	Sol	Ins	Sol	Gel.is formed. Redissolves on dil.
10.	$Pb(NO_3)_2$	1	x			None						
11.	$Mn(NO_3)_2$	1	x			Yel.ppt. $Mn(C_9H_6ON)_2$	Sol	Sol	Sol			Cloudiness. Disappears on boiling. Slight yellow ppt. is formed.
12.	$(NH_4)_2VO_4$	1	x			Dark green ppt.	Sol	Sol	Sol	Sol	Sol	The ppt. is heavy (thick).
13.	RbCl	1		x								
14.	SbOCl	1	x			Green to brown	Ins	Ins	Ins	Ins	Ins	The ppt.forms slowly as it cools.
15.	$Na_2HAs\ O_3$	1			x							
16.	H_2WO_4	1			x	White	*	*	*	Sol	Sol	Alk.oxine gives a white,fibrous ppt.
17.	$NiSO_4$	1	x			Yellow	Sol	Sol	Sol	Sol	Sol	Much precipitate.
18.	$Be(NO_3)_2$	1	x									No ppt.with alk. or acid-oxines.
19.	$CuSO_4.5H_2O$	1	x			Green ppt.	Sol	Sol	Sol	Ins	Ins	Flocculent
20.	$Fe(NO_3)_3$	1	x				Sol	Sol	Sol	Ins	Ins	

* Yellow precipitate left.

Table I, continued

Precipitation of Cations with 8-Hydroxyquinoline

No.	Salt	Conc. %	pH of Soln. <7	7	>7	Precipitate	Effect with Reagents HNO_3	H_2SO_4	HCl	NaOH	NH_4OH	Comments
21.	$Hg(NO_3)_2$	1	x			Orange-yellow ppt. with alk-oxine	Sol	Sol	Sol	Ins	Ins	Green sol. obtained on boiling with alk-oxine mixture.
22.	$Bi(NO_3)_3.5\ H_2O$		x									Clear amber sol. when hot with alk-oxine; cloudy, when cold.
23.	$BaCl_2$	1	x			White ppt.with alk-oxine	Sol	Ins	Sol	Ins	Ins	
24.	$Ca(NO_3)_2$	1	x									
25.	$CoCl_2$*	1	x									
26.	$SnCl_2$	1	x			Yel.ppt.with alk-oxine	Sol	Sol	Sol	Sol	Ins	
27.	[illegible]	1	x									
27.	$HgNO_3$		x			In alk-oxine, reddish-brown ppt.	Sol	Sol	Y.P	*	*	A beautiful red. ppt. forms slowly.
28.	$ZnCl_2$		x			Yel. ppt. in alk-oxine sol. Yel. ppt. in acid. ox.	Sol	Sol	Sol	Ins	Ins	
29.	$FeSO_4$		x			Red-brown ppt. in acid-oxine.	Sol	Sol	Sol	Ins	Ins	

* Brownish yellow precipitates.

V. OBSERVATIONS

The oxine is a white solid of prismatic crystals. Its solutions in both acids and bases was yellow to amber colored. This color was not affected by heating or evaporation, but the oxine was completely volatile. HCl, H_2SO_4, and NH_4OH had no effect on it. NaOH formed a yellow precipitate which was soluble in excess of the reagent. HNO_3 produced a deep amber solution, the color of which was due to NO_2 fumes formed by the decomposition of the acid.

Nearly all of the common metals are precipitates by 8-hydroxyquinoline, some only in alkaline solution, but most of them in acid solution. This may be observed by an examination of the data in Table I. The precipitates of silver, lithium tungsten, and barium are white. Those of copper and vanadium are green, that of titanium, brownish green. Mercurous mercury gave a beautiful red precipitate which formed slowly. The aluminum, magnesium, cadmium, manganese, nickel, mercuric mercury, calcium, tin, and the base sensitive sodium precipitates are yellow. The ferrous iron and antimony gave reddish brown precipitates. The iridium and ferric iron solutions turned green on the addition of the oxine. The salts of lead, chromium, bismuth, and ferric iron became cloudy (yellow) with oxine, but they gave no positive precipitate even after boiling. The cloudiness due to chromium and bismuth disappeared on heating, but reappeared on cooling. Neither arsenic nor cobalt gave precipitates. The conduct of the last five cations was not what was to be expected because other experimenters obtained precipitates with these cations. The beryllium salt gave no precipitate in acid or alkali solutions. The aluminum was precipitated in both acid and alkaline solutions of the 8-hydroxyquinoline or oxine.

VI. CONCLUSIONS

Aluminum can be precipitated by acid or alkaline-oxine solutions. In acid solution, this metal can be separated from magnesium, cadmium, chromium, strontium iridium, rubidium, beryllium, barium, calcium, and sodium. The oxine of aluminum can readily be distinguished from the precipitated oxines of silver, titanium, lithium, vanadium, antimony, tungsten, copper, barium, mercurous mercury, and ferrous iton by its color. In alkaline solution, aluminum can be distinguished by its color from the oxine precipitated of tungsten, barium, and mercurous mercury. In the alkaline solution of oxine aluminum can be separated from strontium, iridium, lithium, antimony, tungsten, beryllium, ferric iron, barium, cobalt, mercurous mercury, and ferrous iron. The precipitation of the oxine compound of aluminum is especially to be recommended when this metal is associated with beryllium.

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VIII. APPROVAL

The foregoing thesis is hereby approved as a creditable study of an engineering subject, carried out and presented in a manner sufficiently satisfactory to warrant its acceptance as a prerequisite to the degree for which it has been submitted. It is to be understood that by this approval the undersigned does not necessarily endorse or approve any statement made, opinions expressed, or conclusions drawn therein, but approves the thesis only for the purpose for which it is submitted.

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