

# 8-Hydroxyquinaldine as an Analytical Reagent

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8-Hydroxyquinaldine is a more selective reagent than 8-hydroxyquinoline because it does not precipitate aluminum. Separations of zinc from magnesium, from aluminum, and from magnesium and aluminum are given. The precipitates of the zinc and the magnesium complex salts may be either weighed or determined volumetrically by bromination. Aluminum may be determined in the filtrate of the zinc determination by adding 8-hydroxyquinoline. The effect of the pH upon the completeness of precipitation of the 8-hydroxyquinaldine complexes of cupric, zinc, ferric, and magnesium ions has been studied. Complete directions for an improved method of preparing 8-hydroxyquinaldine are given.

MANY derivatives of 8-hydroxyquinoline, "oxine", have been prepared and their analytical uses have been investigated (7). Most of these derivatives have been 5-, 7- or 5,7-substitution products. Although several 2-substituted derivatives are known, apparently only one, 2-phenyl-8-hydroxyquinoline-4-carboxylic acid, has been tested for analytical purposes (1). Since the 2-methyl-8-hydroxyquinoline or 8-hydroxyquinaldine has been known for some time (2) and is one of the simplest 2-substituted derivatives, the authors choose to investigate it first.

As compared to 8-hydroxyquinoline, 8-hydroxyquinaldine exhibits some important differences in behavior. Probably because of its increased size, it is a more selective reagent. If size of the molecule is a determining factor, the larger molecule might be expected not to react with the smaller ions because of the difficulty in grouping three large molecules around the small ion. If the complex is formed, it might be less stable. This is supported by the fact that 8-hydroxyquinaldine does not react with aluminum ions, one of the smallest trivalent ions (3) with which 8-hydroxyquinoline reacts, and the 8-hydroxyquinaldine complex with ferric ion is precipitated completely only in a much less acid solution than that required by 8-hydroxyquinoline.

## REAGENTS

**2-METHYL-8-HYDROXYQUINOLINE.** The original method of Doebner and v. Miller (2) was modified as suggested by Kochendoerfer (5). Fifty-five grams (0.50 mole) of *o*-aminophenol and 25 grams (0.18 mole) of *o*-nitrophenol were dissolved in 100 grams of 12 *N* hydrochloric acid in a three-necked flask fitted with reflux condenser, mechanical stirrer, and dropping funnel. Forty grams (0.57 mole) of crotonaldehyde were added with stirring over a period of about 45 minutes. The mixture was heated on the steam bath for 6 hours with continual stirring and was then allowed to stand overnight. The excess *o*-nitrophenol was removed by steam-distillation from the acid solution. Fourteen grams of *o*-nitrophenol were recovered.

The residue was nearly neutralized with 6 *N* sodium hydroxide solution and then saturated with sodium carbonate and steam-distilled. The yield of crude 8-hydroxyquinaldine was 24 to 32 grams or 30 to 40%.

Five grams of the crude material were distilled under reduced pressure (water pump) in a sublimation tube and 4.9 grams of light red material were obtained. The 8-hydroxyquinaldine (4.9 grams) was crystallized from a mixture of 20 ml. of 95% ethyl alcohol plus 10 ml. of water and 4.1 grams of a slightly yellow product were obtained, m.p. = 69° C. This product is pure enough for analytical use but was recrystallized once again for the authors' experiments: m.p. = 72° C. (literature, 2, 74° C.) Some crude material can be recovered from the mother liquors.

The reagent solution is prepared by dissolving 5 grams of 8-hydroxyquinaldine in 12 grams of glacial acetic acid and diluting to 100 ml. with water. An alcoholic solution is prepared by dissolving 5 grams in 100 ml. of 95% ethyl alcohol. Alcoholic solutions of the reagent turn dark in 1 to 2 days and should be freshly prepared. An acetic acid solution is stable for a week or longer.

**STANDARD SOLUTIONS.** Standard solutions of iron, copper,

and zinc were prepared by dissolving weighed samples of the pure metals in acid and diluting to volume in a volumetric flask. Copper was dissolved in nitric acid and evaporated with sulfuric acid to obtain the sulfate. Iron was dissolved in sulfuric acid and oxidized to the ferric state with nitric acid, the excess of which was later evaporated off. Zinc was dissolved in hydrochloric acid.

A standard solution of magnesium sulfate was prepared by dissolving a weighed amount of c.p. magnesium sulfate heptahydrate in a measured amount of water. The solution was further standardized by gravimetric precipitation of the magnesium as magnesium ammonium phosphate and ignition to the pyrophosphate and by precipitation of the 8-hydroxyquinoline salt.

A standard solution of aluminum ion was prepared by dissolving c.p. potassium alum in a measured amount of water.

**STANDARD POTASSIUM BROMATE SOLUTION.** A standard potassium bromate solution, approximately 0.1 *N*, was prepared by dissolving a weighed amount of c.p. potassium bromate, dried at 110° C., in water and diluting to the mark in a volumetric flask. It was further standardized against Bureau of Standards arsenious oxide, using methyl orange as indicator.

**STANDARD SODIUM THIOSULFATE SOLUTION.** c.p. sodium thiosulfate was dissolved in distilled water to make an approximately 0.05 *N* solution, which was standardized against the potassium bromate solution.

**AMMONIUM ACETATE SOLUTION, 2 *N*.** This was prepared by dissolving 154 grams of c.p. ammonium acetate in water and diluting to 1 liter.

## QUALITATIVE REACTIONS OF 8-HYDROXYQUINALDINE

Qualitative tests were performed upon most of the common ions as listed below. In acetic acid-acetate buffered solutions, 8-hydroxyquinaldine forms precipitates with Bi<sup>+++</sup>, Cd<sup>++</sup>, Cr<sup>+++</sup>, Co<sup>++</sup>, Cu<sup>++</sup>, Fe<sup>++</sup>, Fe<sup>+++</sup>, Mn<sup>++</sup>, Ni<sup>++</sup>, Ag<sup>+</sup>, TiO<sup>++</sup>, Zn<sup>++</sup>, MoO<sub>4</sub><sup>--</sup>, WO<sub>4</sub><sup>--</sup>, and VO<sub>3</sub><sup>-</sup>. It does not form a precipitate with Be<sup>++</sup>, Al<sup>+++</sup>, Ca<sup>++</sup>, Sr<sup>++</sup>, Ba<sup>++</sup>, Pb<sup>++</sup>, Mg<sup>++</sup>, K<sup>+</sup>, Na<sup>+</sup>, or NH<sub>4</sub><sup>+</sup>. It does not precipitate Bi<sup>+++</sup> or Sn<sup>++++</sup> in tartrate solutions.

In ammoniacal solutions, the ions precipitated in acetic acid-acetate solutions, with the exception of MoO<sub>4</sub><sup>--</sup>, WO<sub>4</sub><sup>--</sup>, and small amounts of VO<sub>3</sub><sup>-</sup>, are precipitated and, in addition, Pb<sup>++</sup>, Mg<sup>++</sup>, Ca<sup>++</sup>, and Sr<sup>++</sup>. Aluminum ions are still not precipitated. Tartrate was added to the solution to prevent the precipitation of aluminum hydroxide.

## EFFECT OF pH UPON PRECIPITATION OF ZINC, COPPER, IRON, AND MAGNESIUM

Zinc, cupric, ferric, and magnesium ions were selected for further study as probably the most important and representative ions which are precipitated by 8-hydroxyquinaldine.

A definite amount, 24.99 ml., of the standard solution of one of the four ions, containing, respectively, 0.05121 gram of zinc, 0.05028 gram of copper, 0.04965 gram of iron, or 0.02558 gram of magnesium, was taken for precipitation. An excess of 1 to 2 ml. of 5% 8-hydroxyquinaldine in 2 *N* acetic acid was added and the total volume brought to about 200 ml. with distilled water. The solution was heated to 60° to 80° C. and 2 *N* ammonium acetate solution was added until the desired pH, as determined by means of a glass electrode, was reached. The precipitate was filtered through a Gooch crucible and dried at 120° to 130° C. for at least 3 hours and weighed. The per cent precipitated is plotted against the pH in Figure 1.

According to Figure 1 it appears probable that cupric, ferric, or zinc ions could be separated from magnesium. The separation of each of these ions from aluminum is also a possibility with this reagent. The ferric complex with 8-hydroxyquinaldine requires a considerably higher pH for complete precipitation than the corresponding 8-hydroxyquinoline complex (4, 6).

## RECOMMENDED PROCEDURES

Zinc can be separated from aluminum and magnesium ions by precipitation in acetic acid-acetate solutions with 8-hydroxyquinoline. The zinc can be determined gravimetrically by weighing the precipitate or volumetrically by bromination. If aluminum is present, tartrate is added to prevent precipitation of any basic aluminum salts.

Magnesium can be determined in the filtrate from the zinc determination, if no aluminum is present, by raising the pH to 9.3 or higher. When tartrates and a high concentration of ammonium salts are present (when aluminum is present) the magnesium-8-hydroxyquinoline complex precipitates so slowly that the method is useless. Calcium ions interfere in the magnesium determination in amounts over 2 or 3 mg. and should be previously removed.

Aluminum can be determined after removal of the zinc by adding 8-hydroxyquinoline.

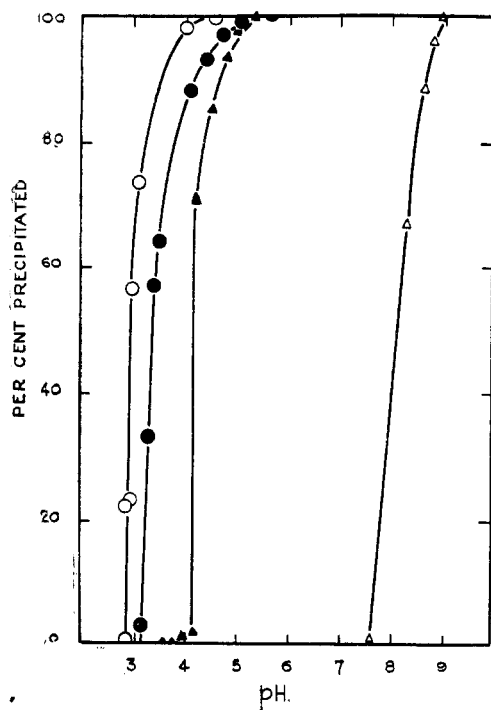


Figure 1. Effect of pH upon Precipitation of 8-Hydroxyquinoline Complexes

○ Cupric  
● Ferric  
△ Magnesium  
▲ Zinc

It is advantageous to use an alcoholic solution of 8-hydroxyquinoline for the volumetric determination of magnesium and an alcoholic solution may be employed in the zinc determination. The reagent is more soluble in the presence of alcohol and is not coprecipitated in the alkaline solutions. No trouble is experienced in the gravimetric determinations and when using acid solutions. The coprecipitated reagent is volatile at 130° C. The magnesium and zinc salts are soluble in hot 95% alcohol and the solubility in water is undoubtedly slightly increased by the presence of alcohol; therefore only the required amount of reagent should be employed. The presence of an excess of reagent is indicated by a yellow filtrate. If the supernatant liquid is not yellow, more reagent should be added.

**PROCEDURE FOR ZINC.** If aluminum is present add 1 gram of ammonium tartrate to the clear, slightly acid solution. Add 2 ml. of 5% 8-hydroxyquinoline solution in 2*N* acetic acid for every 10 mg. of zinc present, dilute the solution to about 200 ml., and heat to 60° to 80° C. Neutralize the excess acid by adding dilute (1 to 5) ammonium hydroxide drop by drop until the zinc

Table I. Determination of Zinc, Magnesium, and Aluminum

Zn Taken Gram	Zn Found Gram	Mg Taken Gram	Mg Found Gram	Al Taken Gram	Al Found Gram
Gravimetric results					
0.0512	0.0515	...	...	0.0500	0.0500
0.0512	0.0512	...	...	0.0500	0.0500
0.0510	0.0513	...	...	0.0100	0.0100
0.0510	0.0509	...	...	0.0100	0.0103
0.0510	0.0513	0.0287	0.0285	...	...
0.0510	0.0513	0.0115	0.0112	...	...
0.0205	0.0202	0.0115	...	0.0248	...
0.0109	0.0103	0.0115	...	0.0248	...
0.0020	0.0018	0.0287	...	0.0250	...
Volumetric results					
0.0512	0.0510	0.0256	0.0256	...	...
0.0512	0.0516	0.0287	0.0286	...	...
0.0205	0.0208	0.0256	0.0254	...	...
0.0040	0.0044	0.0287	0.0286	...	...
0.0040	0.0042	0.0287	0.0286	...	...
0.0510	0.0518	0.0287	...	0.0250	...
0.0510	0.0507	0.0287	...	0.0250	...
0.0206	0.0204	0.0287	...	0.0250	...
0.0010	0.0013	0.0287	...	0.0100	...
0.0010	0.0013	0.0287	...	0.0100	...

complex salt which forms on the addition of each drop just redissolves on stirring. Add 45 ml. of 2*N* ammonium acetate slowly and with stirring. The pH should be at least 5.5. Allow the solution to stand for 10 to 20 minutes before filtering through a Gooch or filtering crucible if the precipitate is to be weighed or through a filter paper if the precipitate is to be determined volumetrically. If the amount of zinc is low and the amount of aluminum and magnesium is high, allow the solution to stand several hours before filtering. Wash well with hot water. If the precipitate is to be weighed, dry it at 130° to 140° C. for at least 2 hours.

To determine the zinc volumetrically, dissolve the washed precipitate with 30 ml. of hot 1 to 2 hydrochloric acid and wash thoroughly with hot 1 to 3 hydrochloric acid and then with hot water. Moisten the paper with a few drops of concentrated hydrochloric acid before the final two washings with water in order to ensure the complete solution and removal of all zinc complex salt. If the amount of zinc is small and the amount of aluminum and magnesium is large, reprecipitate the zinc as described above. Use only 1 to 2 ml. of the 8-hydroxyquinoline reagent for the reprecipitation.

Dissolve the second precipitate in 30 ml. of hot 1 to 3 hydrochloric acid, wash the paper thoroughly with hydrochloric acid and hot water as before, and add 3 grams of potassium bromide to the filtrate. Dilute the solution to about 150 ml. and add a few drops of methyl red indicator. Run in standard 0.1*N* potassium bromate solution from a buret until there is an excess present as shown by the bleaching of the indicator. Add 5 ml. of bromate solution in excess. Add 3 grams of potassium iodide, stir until dissolved, and back-titrate with standard sodium thiosulfate solution using a 2% starch solution as indicator.

If no aluminum is present and no tartrate has been added, the proper pH for the precipitation of zinc can be attained by adding dilute ammonium hydroxide until a white precipitate of zinc hydroxide appears. Redissolve the zinc hydroxide with a drop of acetic acid. Add 2 ml. of the acetic acid solution of 8-hydroxyquinoline for each 10 mg. of zinc present and then 2 to 3 drops of concentrated ammonium hydroxide. The pH should be at least 5.5. This procedure eliminates the high concentration of ammonium salts and makes it easier to reach the required pH for the precipitation of magnesium. If ammonium acetate is used, the least amount possible should be added.

**PROCEDURE FOR MAGNESIUM.** If aluminum was not present and tartrates were not added when zinc was precipitated, the filtrate from the zinc determination can be used for the determination of magnesium. Add 3 ml. of acetic acid solution of 8-hydroxyquinoline for every 10 mg. of magnesium present (if the determination is to be carried out volumetrically, use an alcoholic solution of the reagent) and add concentrated ammonium hydroxide until the pH is at least 9.3 or until no further precipitate forms. Digest the solution at 60° to 80° C. for 20 minutes and filter through a Gooch or filtering crucible if the magnesium is to be determined gravimetrically or through a paper filter if the determination is to be completed volumetrically. Wash with hot water, dry the precipitate at 130° to 140° C., and weigh for a gravimetric determination.

The precipitate may be dissolved in hydrochloric acid and titrated with potassium bromate according to the procedure outlined above for the volumetric determination of zinc.

**PROCEDURE FOR ALUMINUM.** After the zinc has been removed, aluminum may be precipitated from the filtrate by adding 8-

hydroxyquinoline. Warm the filtrate to 60° to 80° C. and add 40 ml. of a 2.5% solution of 8-hydroxyquinoline in 7.5% acetic acid and then 10 ml. of 2 N ammonium acetate. Allow the precipitate to digest 10 to 20 minutes and filter through a Gooch or filtering crucible. Wash with hot water and dry at 130° to 140° C. for at least 2 hours. The precipitate may also be determined volumetrically as described above for zinc.

Results of several typical analyses are given in Table I.

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## Determining Phytin Phosphorus Stoichiometric Relation of Iron and Phosphorus in Ferric Phytate

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A stoichiometric relationship between phosphorus and iron in ferric phytate with an atomic ratio of 6P/4Fe was found to exist when phytic acid was precipitated with a sufficient excess of ferric chloride in the presence of sodium sulfate. On the basis of this finding, a method was developed for the determination of phytin phosphorus in corn grain.

THE determination of phytin phosphorus by the method of Heubner and Stadler (4) is based on the titration of phytic acid with standard ferric chloride solution with the formation of ferric phytate, in the presence of ammonium thiocyanate indicator. The titration is carried out in the presence of 0.6% hydrochloric acid. The end point, shown by the reddish brown ferric thiocyanate, is indefinite and is taken arbitrarily as the point at which the color persists for 5 minutes. It is evident that the nature of ferric phytate and particularly the ratio of iron to phosphorus in it are of vital importance in the evaluation and use of this method.

The gravimetric ratio of phosphorus to iron in Heubner and Stadler's method is 1.19. This factor has been confirmed by Rather (5). By using Starkenstein's (6) and Anderson's (1, 2) formulas for phytic acid, corresponding to  $C_6H_8O_6[PO(OH)_2]_3 \cdot 3H_2O$  and  $C_6H_8O_6[PO(OH)_2]_4$ , respectively, it may be calculated that the factor, 1.19, represents the addition of 2.8 moles of iron to 1 mole of phytic acid—that is, the gravimetric ratio of 6P/2.8Fe is 1.19. From these formulas it may also be observed that there are 12 hydrogen atoms which theoretically may be replaced by 4 moles of ferric iron. This means, therefore, that the Heubner-Stadler end point does not represent complete saturation of the phytic acid with ferric iron, but that it is rather an intermediate point in the saturation process which is reproducible with a fair degree of accuracy.

The idea of completely saturating phytic acid with iron occurred to the writer as a possible method of determining phytin phosphorus. The data from this investigation, presented in this paper, indicate that 1 mole of phytic acid (inositol hexaphosphoric acid) under proper conditions will add 4 moles of ferric iron.

In this case the relationship of phosphorus to iron in tetra-ferric phytate is 6 moles of the former to 4 of the latter. This atomic ratio, 6P/4Fe, corresponds to the gravimetric factor, 0.833. This relation places iron and phosphorus on a chemical equivalent basis in the molecule and obviates the necessity of using an empirical factor. The empirical formula of this com-

pound is believed to be  $C_6H_8O_{24}P_6Fe_4 \cdot 3H_2O$ . However, in view of the polyvalence of both phytate and ferric ions, it is unlikely that any such molecules as above formulated are formed. The probability is very great that the respective ions unite in positions that may be termed "out of phase", with the result that a polymeric type of precipitate is formed with no definite molecular boundaries. The gradual rather than stepwise loss of reactivity with the decrease of replaceable hydrogen on approaching the Heubner and Stadler end point, points to this conclusion as well as the absence of a definite end point. This conclusion is also supported by the nonintegral atomic ratio of 6P/2.8Fe in the precipitate formed at the end point chosen by Heubner and Stadler.

In studying the relationship of phosphorus and iron in ferric phytate, two sources of phytic acid were used—namely, calcium phytate and corn grain extract.

The calcium phytate was obtained from the Soil Biology Department. It was shaken with a large excess of distilled water to dissolve any soluble fractions which might be present. It was then filtered, washed with additional water, then alcohol, and dried at 100° C. for 30 hours. This substance contained 16.09% total phosphorus and from its reaction with iron corresponded to the formula  $C_6H_8O_{24}P_6Ca_6 \cdot 3H_2O + 12H_2O$ . The data in Table I were secured with this material according to the procedure given for the corn grain extract.

The remainder of the data in the paper were secured on phytic acid freshly extracted from corn grain. The freshly ground corn was extracted with 1.2% hydrochloric acid, containing 10% by weight of sodium sulfate, for 2 hours on the shaking machine. The ratio of grain to solvent was 1 gram to 20 ml. The acid ex-

Table I. Phosphorus-Iron Ratios in Ferric Phytate Precipitate

(As influenced by iron-phosphorus ratio in the precipitating mixture. Precipitation from acidified calcium phytate)

In Precipitating Mixture			In Precipitate		
P, Mg.	Fe, Mg.	Multiple of theoretical ratio, 4Fe/6P	Fe, Mg.	P/Fe	Atomic ratio
4.18	8.05	1.6	4.18	1.19 <sup>a</sup>	6P:2.80Fe <sup>a</sup>
4.18	10.04	2.0	4.54	0.921	6P:3.33Fe
4.18	10.04	2.0	4.33	0.965	6P:3.62Fe
4.18	12.05	2.4	4.78	0.874	6P:3.45Fe
4.18	12.05	2.4	4.67	0.895	6P:3.81Fe
4.18	17.31	3.4	4.99	0.838	6P:3.72Fe
4.18	17.31	3.4	4.77	0.876	6P:3.98Fe
4.18	43.27	8.6	5.02	0.833	6P:3.80Fe
					6P:4.00Fe

<sup>a</sup> Values which correspond with Heubner-Stadler end point; not experimental.