3-Hydroxy-1,3-diphenyltriazine as a Reagent for Copper(II), Palladium(II), and Nickel(II) and 3-Hydroxy-1-p-chlorophenyl-3-phenyltriazine for Titanium(IV)

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Below pH 3, 3-hydroxy-1,3-diphenyltriazine is a highly selective reagent for the gravimetric estimation of copper(II) and its separation from a large number of elements by direct weighing. It is superior to salicylaldoxime and α-benzoinoxime, and is useful for estimating palladium(II) in the presence of other members of the platinum group. At higher pH, it can be used for estimating nickel(II). The chloro-substituted derivative, 3-hydroxy-1-p-chlorophenyl-3-phenyltriazine, forms a bright orange complex with titanium(IV), which is stable toward heat and can be used for estimating titanium(IV).

IN AN earlier communication (11) the use of 3-hydroxy-1,3-diphenyltriazine (N-phenyl-N-phenylazohydroxylamine) for the estimation of palladium(II) and its separation from various elements was reported and its extremely high specificity toward copper(II) was indicated. This paper describes its use for the gravimetric determination of copper(II) by direct weighing and its separation from a large number of foreign ions. Separation of palladium(II) from rhodium(IV), ruthenium(III), iridium (III), thorium(IV), tin(IV), lead(II), titanium(IV), molybdate, tungstate, fluoride, and phosphate is also included.

At somewhat higher pH (4.5 to 7.0) the reagent precipitates nickel(II) quantitatively, and can be used for its estimation and separation from various elements. As at that pH some other elements are also partially precipitated, the use of the reagent for precipitating nickel is not so specific as for copper(II) and palladium(II).

As in the case of palladium(II), the reagent is particularly suitable for the estimation of copper(II) and its separation from various elements. In reproducibility of results, specificity, stability of the complex toward heat and acid, and insolubility in water and fairly concentrated solutions of alcohol, the reagent, in the opinion of the authors, is superior to all the copper reagents described in the literature, including salicylaldoxime (4) and α-benzoinoxime (5). Azzalin, Shik, Chambers, and others (1, 3, 7, 9, 12) pointed out some serious limitations of these two reagents, which do not apply to 3-hydroxy-1,3-diphenyltriazine. Unlike other copper reagents, it works on the acidic side, where pH is adjusted with mineral acid; consequently, it has much better specificity. The fact that the excess of the reagent is completely hydrolyzed into water-soluble products (pH 2 to 3.5), and can thus be easily eliminated from the reaction mixture without affecting the complex, offers this compound all the advantages of a water-soluble reagent. Its factor (0.1303) is more favorable than those of salicylaldoxime (0.1895) and α-benzoinoxime (0.2202).

3-Hydroxy-1,3-diphenyltriazine introduces an entirely new group of complex-forming organic reagents, which does not appear to have been described earlier. Its cost of production is very low, as it is prepared from common laboratory chemicals like nitrobenzene and aniline.

The mechanism of hydrolysis of the reagent has been examined. It is initially converted to phenylhydroxylamine and benzenediazonium salt, which subsequently form p-aminophenol and phenol, respectively.

It was found that 3-hydroxy-1,3-diphenyltriazine precipitated titanium(IV) quantitatively. The titanium complex, however, was substantially soluble when the concentration of alcohol in the reaction medium was above 5%. It decomposed if the medium was heated above 55° C. and was therefore unsuitable for analytical purposes. However, most of these drawbacks were eliminated in the chloro-substituted derivative, 3-hydroxy-1-p-chlorophenyl-3-phenyltriazine,
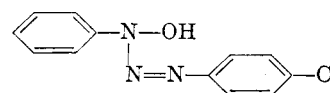
which precipitates titanium(IV) quantitatively as a bright orange complex, which is stable at 100° C. in the aqueous-acidic reaction medium, so that the excess of the alcohol used during estimation may be removed by direct heating on a water bath. The o-chloro analog, which was examined simultaneously, was unsuitable, as the complexes formed by it were not granular and were comparatively less stable.

With this reagent titanium(IV) can be estimated as such or in the presence of various other elements, including a large amount of aluminum. The titanium complex, however, is not of definite composition and has to be ignited to titanium dioxide before weighing. 3-Hydroxy-1-p-chlorophenyl-3-phenyltriazine compares well with other titanium reagents (2, 7, 8, 10) and is superior to the related compounds N-nitrosophenylhydroxylamine (cupferron) (6) and N-benzoylphenylhydroxylamine (8), the titanium complexes of which are unstable even at 25° C. Like the parent compound, 3-hydroxy-1,3-diphenyltriazine, it forms precipitates with other elements under similar pH conditions. The complexes in this case are comparatively more stable, but the reagent offered no special advantage in the estimation of copper(II), palladium(II), and nickel(II), as the excess of the reagent could not be removed easily either by hydrolysis or by washing with alcohol.

REAGENTS AND APPARATUS

Preparation of Reagents. The preparation and spectral characteristics of the parent reagent, 3-hydroxy-1,3-diphenyltriazine, have been described (11). The chloro derivative was prepared by following the same procedure but using an equivalent amount of p-chloroaniline in place of aniline. Thus, 12.7 grams of p-chloroaniline after diazotization and coupling with 11 grams of phenylhydroxylamine in the usual way, followed by two crystallizations from alcohol, gave 11 grams of 3-hydroxy-1-p-chlorophenyl-3-phenyltriazine; its melting point was 140°–140.5° C. with decomposition. The reagent is stable toward heat, light, and air and can be preserved indefinitely. Analysis. Found: C, 58.47; H, 4.15; N, 17.08; Cl, 15.70%. $C_{12}H_{10}N_3Cl$ requires: C, 58.26; H, 4.07; N, 16.97; Cl, 14.32%.

Spectral characteristics in alcoholic solution are: $\lambda_{max.}$ 235, 281, and 350 mμ; log ϵ = 3.9911, 3.8743, and 4.1833, respectively.

Standard Copper(II), Titanium(IV), and Palladium(II) Solutions. Copper solution was prepared by dissolving copper sulfate

analytical reagent. In special cases where the sulfate ions interfered, copper acetate was used. The amount of copper in the solution was determined by standard methods. For the titanium solution 1 gram of titanium dioxide was fused with 10 grams of potassium pyrosulfate for about 10 minutes. The melt was cooled, extracted with 200 ml. of 6% (w./v.) sulfuric acid, and diluted to 1 liter. The amount of titanium present was estimated as dioxide in the conventional way. Palladium(II) solution was prepared and standardized as described earlier.

Buffering Solutions. Hydrochloric acid, $1N$, and 10% (w./v.) solutions of sodium acetate and sodium potassium tartrate were used. On a few special occasions glacial acetic and $1N$ sulfuric acid were used for copper and palladium instead of hydrochloric acid.

Reagent Solutions. Solutions of the parent reagent [1% (w./v.)] in 95% ethyl alcohol and the chloro reagent in methanol were used.

Other Solutions and Apparatus. Reagent grade soluble salts of various elements as described were used. Ashless filter paper No. 40 and sintered crucibles Nos. 2 and 3 were used for collecting the precipitates and platinum crucibles were used for ignition. Macro- and semimicro Mettler balances were used for weighing. Beckman pH meter Model H-2 was used for pH measurements and Beckman quartz spectrophotometer Model DU for taking absorption spectra.

PROPERTIES OF COMPLEXES

The copper complex is a chocolate-brown substance, very stable toward heat and moderate concentrations of acid. It is very granular and can be filtered easily even in the hot state through sintered crucible No. 2. It is very soluble in benzene, chloroform, and carbon tetrachloride, fairly soluble in ether and acetone, and only slightly soluble in alcohol. It can be crystallized from acetone in the form of silky brown needles; its melting point is 193°. It shows no sign of decomposition before melting and can be dried to a constant weight at 120° to 130° C. in about 30 minutes. It corresponds to the molecular formula $(C_{12}H_{10}N_3O)_2Cu$ and can be represented as a possible chelate as shown below:
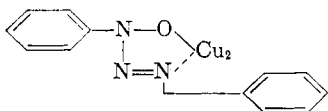
Analysis showed N, 17.76%. $(C_{12}H_{10}N_3O)_2Cu$ requires N, 17.21%. Spectral characteristics in alcoholic solution are: $\lambda_{max.}$ 247, 283, and 362 mμ; log ϵ = 4.5634, 4.1324, and 4.5720, respectively.

The deep yellow nickel complex had similar properties. It could be crystallized from acetone as bright yellow needles, melting point 209° C. Analysis showed N, 17.76%. $(C_{12}H_{10}N_3O)_2Ni$ requires N, 17.39%.

Spectral characteristics in alcoholic solution are $\lambda_{max.}$ 248, 320, and 410 mμ; log ϵ = 4.4545, 4.3910, and 4.1988, respectively.

The titanium complex is also a bright orange substance, very soluble in chloroform, benzene, and acetone and only fairly soluble in methanol and ethyl alcohol. It is very stable toward heat in aqueous acidic medium but decomposes at 105° to 110° C. when heated in a dry state. It can be crystallized from alcohol as bright yellow crystals; melting point 146°. Analysis showed that it was not of definite composition.

Effect of pH. Effect of pH on palladium precipitation has been described. Copper(II) was completely precipitated between pH 1.9 and 7.0, when only a slight excess of the reagent was used. Results were checked gravimetrically as well as by spot tests, using rubeanic acid. Most of the estimations were carried out between pH 2.3 and 3.0 to facilitate the hydrolysis of the reagent and to increase specificity. Titanium(IV) is quantitatively precipitated by the reagent between pH 1.6 and 2.8. Prolonged heating (over 1 hour) of the complex at lower pH slightly decomposes it. At higher pH, the complex is not very granular and shows signs of hydrolysis. The optimum pH was found to be between 2.2 and 2.5 and most of the determinations were carried out at pH 2.3. The complex formed under these conditions is

very granular and stable toward heat, and can be safely heated in the reaction medium for 2 hours.

PROCEDURE FOR COPPER(II)

In practice, two slightly different procedures can be employed.

To about 25 ml. of standard copper(II) solution containing 10 to 25 mg. of the metal, 5 ml. each of 10% (w./v.) solution of sodium acetate or sodium potassium tartrate, $1N$ hydrochloric acid, and 95% ethyl alcohol was added. To this mixture, which may also contain varying amounts of foreign ions, an excess (20 to 25%) of 1% (w./v.) alcoholic solution of the reagent 3-hydroxy-1,3-diphenyltriazine was added with stirring, followed by 120 to 130 ml. of hot water. The pH was between 2.3 and 3.

Alternatively, the copper solution, which may or may not contain foreign ions, was diluted to 150 ml. and the same amount of sodium acetate or sodium potassium tartrate, $1N$ hydrochloric acid, and alcohol as described earlier was added to it. The reaction mixture was heated on the water bath for some time and then an excess (20 to 25%) of 1% (w./v.) solution of the reagent in alcohol was added with stirring.

In most of the estimations and separations, the earlier procedure, where the reagent was added before dilution, was preferred. In both cases, however, the copper complex separated as a light, chocolate-colored precipitate.

It was heated on a boiling water bath for 45 to 60 minutes with occasional stirring. The excess of the reagent present was hydrolyzed by this procedure. Unnecessary excess of the reagent, above what has been suggested in the procedure, should be avoided, as in that case a longer time will be necessary for its hydrolytic removal. During the course of heating, the complex became very granular and deepened in color and the medium became clear and was free from any colloidal suspension. The complex was filtered hot through a No. 2 or 3 weighed sintered crucible, washed once or twice with 0.5% (w./v.) hydrochloric acid solution, and then 5 to 6 times with hot water. The hydrolyzed reagent in the filtrate when tested on a spot plate with a drop of an alkali solution develops a blue to bluish-violet color due to the presence of p-aminophenol and phenol. The completeness of washing can, therefore, be easily tested by this method. The complex was dried to a constant weight at 120° to 125° C. for 30 to 45 minutes and weighed. The weight of the complex multiplied by 0.1303 gives the weight of copper.

The results are recorded in Table I.

In the case of separation of copper(II) from cerium(IV), zirconium(IV), iron(II), and iron(III), the same special precau-

Table I.   Determination of Copper(II) and Separation from Other Elements

Cu Taken, G.	Foreign Ion, G.	Cu Complex, G.	Cu Found, G.	Error, G.
0.02563	...	0.1966	0.02562	−0.00001
0.02563	...	0.1969	0.02565	+0.00002
0.01677	...	0.1282	0.01672	−0.00005
0.01677	...	0.1287	0.01677	0.00000
0.01281	...	0.0983	0.01281	0.00000
0.01281	0.05 Ni(II)	0.0979	0.01276	−0.00005
0.01281	0.05 Zn(II)	0.0979	0.01276	−0.00005
0.01281	0.05 Mn(II)	0.0982	0.01279	−0.00002
0.01281	0.05 Cd(II)	0.0985	0.01283	+0.00002
0.01281	0.05 Bi(III)	0.0979	0.01276	−0.00005
0.01281	0.05 Al(III)	0.0980	0.01277	−0.00004
0.01281	0.05 Cr(III)	0.0980	0.01277	−0.00004
0.01533	0.05 Hg(II)	0.1180	0.01536	+0.00003
0.01533	0.05 As(III)	0.1178	0.01534	+0.00001
0.01533	0.05 Pb(II)	0.1169	0.01525	−0.00008
0.01533	0.05 Sb(III)	0.1182	0.01538	+0.00005
0.01533	0.05 Zr(IV)	0.1179	0.01535	+0.00002
0.01533	0.05 UO2(II)	0.1180	0.01536	+0.00003
0.01533	0.05 Ce(IV)	0.1174	0.01530	−0.00003
0.01533	0.05 Th(IV)	0.1172	0.01528	−0.00005
0.01533	0.05 Be(II)	0.1179	0.01535	+0.00002
0.01533	0.05 PO4(III)	0.1177	0.01533	0.00000
0.01677	0.05 Co(II)	0.1286	0.01676	−0.00001
0.01677	0.05 Fe(II)	0.1289	0.01679	+0.00002
0.01677	0.05 Fe(III)	0.1283	0.01673	−0.00004
0.01677	0.05 NaNO3	0.1282	0.01672	−0.00005
0.01387	0.05 Ti(IV)	0.1062	0.01383	−0.00004
0.01387	0.05 Sn(IV)	0.1067	0.01390	+0.00003
0.01387	0.05 F′	0.1064	0.01386	−0.00001
0.01387	0.05 tungstate	0.1063	0.01385	−0.00002
0.01387	0.05 molybdate	0.1068	0.01391	+0.00004

Table II. Separation of Palladium(II) from Other Elements

Pd Taken, G.	Foreign Ion, G.	Pd Complex, G.	Pd Found, G.	Error, G.
0.02427	0.02 Iγ(III)	0.1210	0.02431	+0.00004
0.02427	0.02 Ru(III)	0.1211	0.02432	+0.00005
0.02427	0.02 Rh(IV)	0.1212	0.02434	+0.00007
0.02427	0.02 Th(IV)	0.1209	0.02429	+0.00002
0.02427	0.05 PO₄	0.1205	0.02422	−0.00001
0.02427	0.02 Fluoride	0.1208	0.02426	−0.00005
0.01554	0.02 Molybdate	0.0773	0.01553	−0.00001
0.01554	0.02 Ti(IV)	0.0770	0.01547	−0.00007
0.01554	0.02 Sn(IV)	0.0777	0.01561	+0.00007
0.01554	0.02 Tungstate	0.0775	0.01556	+0.00002
0.01054	0.02 Pb(II)	0.0523	0.01051	−0.00003

Table III. Determination of Titanium(IV) and Separation from Foreign Ions

TiO₂ Taken, G.	Foreign Ion, G.	TiO₂ Found, G.	Error, G.
0.01004	...	0.01005	+0.00001
0.01004	...	0.01010	+0.00003
0.01004	...	0.01010	+0.00006
0.01004	...	0.01006	+0.00002
0.01004	0.05 Zn(II)	0.01007	+0.00003
0.01004	0.05 Mn(II)	0.01008	+0.00004
0.01004	0.05 Cd(II)	0.01004	0.00000
0.01004	0.05 Co(II)	0.01001	−0.00003
0.01004	0.05 Ni(II)	0.01009	+0.00005
0.01004	0.05 Hg(II)	0.01006	+0.00002
0.01004	0.05 As(III)	0.01006	+0.00002
0.01004	0.05 UO₂(II)	0.01009	+0.00005
0.01004	0.05 U(IV)	0.01005	−0.00001
0.01004	0.05 Th(IV)	0.01004	0.00000
0.01004	0.05 Mg(II)	0.01002	−0.00002
0.01004	0.05 Be(II)	0.01005	+0.00001
0.01004	0.05 Cr(III)	0.01004	0.00000
0.01004	0.05 Al(III)	0.01006	+0.00002
0.01004	0.20 Al(III)	0.01003	−0.00001
0.01004	0.30 Al(III)	0.01007	+0.00003

tions are taken as in the case of palladium(II). The same purpose could be better achieved by using potassium or sodium fluoride for masking iron(II) and iron(III) and for preventing any possible hydrolysis of zirconium(IV). While copper(II) was being separated from lead(II), pH was adjusted by using acetic or nitric acid instead of hydrochloric acid, to avoid the precipitation of lead chloride. While copper(II) was separated from titanium (IV), tin(IV), and molybdate, a small amount (approximately 0.5 gram) of sodium or potassium fluoride was used as a masking agent to prevent the precipitation of titanium and molybdate complexes and hydrolysis of tin salts. Copper(II) obviously cannot be separated from palladium(II), as the two complexes have virtually identical properties; nor can it be quantitatively separated from vanadium(IV) and vanadate, because of partial coprecipitation. Silver, gold(III), and osmium(IV) interfere, as they are partially reduced to the metallic state by the reagent. Copper(II) cannot be estimated in the presence of cyanide, because of complete masking of the metal by cyanide.

SEPARATION OF PALLADIUM(II) FROM OTHER ELEMENTS

Procedure. The same procedure as for palladium was followed (11). Alternatively, as in the case of copper, the reaction mixture could be diluted to the ultimate volume after addition of the reagent. Some of the experiments recorded in the earlier communication were carried out by following this procedure; results, however, were independent of the procedure followed.

While palladium(II) was separated from titanium(IV), tin(IV), and molybdate, sodium or potassium fluoride was used as a masking reagent, as in the case of copper.

Palladium cannot be separated from elements that interfere in the case of copper. Looking into the very high specificity of the reagent and its low cost, it appears probable that this reagent may be used for the direct industrial isolation of palladium from its ores or other industrial mixtures.

ESTIMATION AND SEPARATION OF NICKEL(II)

Because the nickel specificity of 3-hydroxy-1,3-diphenyltriazine is not so high, it is mentioned only in brief outline. Nickel (II) can be estimated as a weighable precipitate at pH 4.4 to 7.0, preferably at 5 to 5.5, using sodium acetate solution as a buffering reagent. Sodium potassium tartrate gives slightly lower results. The excess of the reagent in this case has to be removed by washing with 20% hot alcohol. With this reagent nickel can be estimated as such or in the presence of zinc(II), manganese(II), cadmium(II), magnesium(II), arsenic(III), beryllium(III), phosphate, and fluoride.

PROCEDURE FOR TITANIUM(IV)

A number of titanium determinations were carried out according to the following procedure.

Ten milliliters of titanium(IV) solution containing 1.0040 grams of titanium dioxide per liter was taken in a 400-ml. beaker and 4 ml. of 1N hydrochloric acid and 5 ml. of 10% (w./v.) sodium acetate solution were added to bring its pH to about 2.3. A solution containing foreign ion may also be added at this stage. The requisite amount of a 1% (w./v.) solution of the reagent in hot methanol was added with stirring (0.5 gram of the reagent for every 10 mg. of titanium). The bright orange titanium complex was immediately precipitated. Then 200 ml. of hot water was added and the reaction mixture was kept on a boiling water bath, without any cover, for 1.5 to 2 hours with occasional stirring. This heating is necessary for complete removal of methanol, as the titanium complex is slightly soluble when the alcoholic concentration is more than 5%. The complex was then filtered hot, using ashless filter paper No. 40, washed with hot water to make it free from chloride and sulfate ions, and dried at 105° C. for 10 to 15 minutes. It was ignited to constant weight in a platinum crucible, with the usual precautions for igniting organic complexes. Use of hydrochloric acid and sodium acetate for stabilizing the pH was necessary. When pH is adjusted without these reagents by dilution only, the titanium complex formed is not very granular and has a tendency to pass through the filter paper.

The results of titanium determination are entered in Table III.

Titanium(IV) cannot be determined in the presence of zirconium(IV), zirconyl(II), thallium(II), cerium(IV), copper(II), palladium(II), iron(II), iron(III), molybdate, and vanadate, because of coprecipitation. Phosphate and tungstate precipitate the corresponding titanium salts and hence interfere in the determinations. Fluoride completely masks titanium. Titanium in the presence of tartrate give slightly lower results and hence it cannot be separated from antimony(III) and bismuth(III).

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