

***N*-Benzoyl-*N*-methylhydroxylamine as a Colorimetric Reagent for Determination of Titanium**

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N-Benzoyl-*N*-methylhydroxylamine forms an intense yellow, water-soluble complex with Ti^{4+} in the pH range 0.5 to 1.4 with a slight absorbance peak at 410 m μ . The colour development is instantaneous and is stable for over 18 hours. The reaction is not masked by tartrate and cyanide. The colour system obeys Beer's law in the concentration range 0.5 to 6.5 p.p.m. of titanium. The sensitivity of the colour reaction, as determined in Nessler's tubes, is 1 part of titanium in 10,000,000 parts of solution and on spot plate is 0.2 γ . The molecular extinction coefficient works out to 4.650×10^3 at 410 m μ . Most of the ions, which are commonly associated with titanium, do not interfere in the direct colorimetric determination of titanium by this reagent.

Functional grouping for titanium results in the formation of chelates containing two oxygen atoms in a five- or six-membered ring¹. Keto-oximes of the type



present such a possibility. Shome² found that *N*-benzoyl-*N*-phenylhydroxylamine formed a yellow precipitate with titanium. He employed this reaction for the gravimetric determination of titanium. *N*-Benzoyl-*N*-methylhydroxylamine possesses an identical functional grouping. Preliminary investigation showed that it developed an intense yellow colour with titanium. In the present investigation, this property has been successfully used in the direct colorimetric determination of Ti^{4+} with this reagent. The colour development is instantaneous and stable to light, air, and time. The reaction is not masked by cyanide and tartrate. Fluoride masks the reaction. Most of the commonly associated ions do not interfere.

EXPERIMENTAL

Reagent Solution.—To a well-cooled aqueous solution of methylhydroxylamine, prepared³ by reducing nitromethane (15 ml) with zinc dust in ammonium chloride medium, was added dropwise benzoyl chloride (32 g.) with stirring. Sodium bicarbonate (~ 25g.) was then added in small quantities at a time to keep the reaction mixture distinctly alkaline. The addition of benzoyl chloride was stopped when a test drop of the reaction mixture

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1. Okao and Sommer, *Anal. Chim. Acta*, 1956, 15, 345.

2. *Analyst*, 1950, 75, 27.

3. Beckmann, *Annalen*, 1909, 365, 204.

ture gave negative test with Tollen's reagent. Stirring was continued for another half an hour. It was filtered under suction and the filtrate was heated to dryness under reduced pressure. The compound was extracted from the residue with methanol. Small quantities of ether were added to the extract to throw out inorganic matter. It was filtered and the filtrate was concentrated over a water bath. Very light yellow-coloured needles separated on cooling; yield 8g. [Found: N, 8.15. Calc. for $C_8H_{10}O_2NNa$: N, 8.09%].

It is actually the sodium salt of *N*-benzoyl-*N*-methylhydroxylamine and has no sharp melting point. It is highly soluble in water (40.5 g./100 g. of water at 17°) and ethanol and sparingly soluble in ether, chloroform, and benzene. A 2% reagent solution (w/v) was prepared in distilled water.

Standard Titanium Solution.—Titanium dioxide (1 g.) was fused with potassium pyrosulphate (10 g.) for about 10 minutes. It was cooled and extracted with 200 ml of 6% H_2SO_4 (v/v) and diluted to 500 ml. Titanium content was estimated with 8-hydroxyquinoline⁴. It contained 1.326 g. of titanium per litre. It was suitably diluted to give a solution containing 25 p.p.m. of titanium.

Solution of Diverse Ions.—Reagent grade soluble salts were dissolved to give 0.1% (w/v) solutions of the respective ions.

A Bausch and Lomb 'Spectronic-20' was used for measuring the absorption using 1 cm cuvettes. pH measurements were made with a Beckman pH meter (model H-2). Visual colour comparisons were made with 50 ml Nessler's cylinders.

Spectral Characteristics of Titanium Complex.—A standard titanium solution (2 ml) containing 25 p. p. m. of titanium was taken in a 25 ml flask and a 10% sodium acetate solution (1 ml, w/v) and a suitable amount of 10% HCl solution were added so that the pH of the final solution was about 1.0. A 2% reagent solution (4 ml, w/v) was introduced into it and the volume was made to the mark. Absorbance was measured at different wave lengths using the reagent as blank.

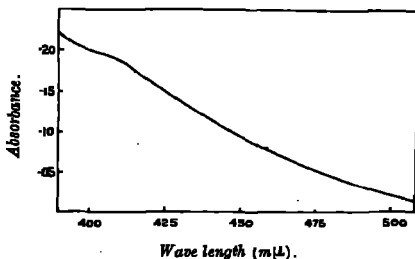


FIG. 1 Spectral characteristic of Ti complex (pH 1).

Fig. 1 shows the absorbance curve of titanium complex at pH 1.0. The colour of the complex is deep yellow and provides a slight peak at 410 mμ. Thus all the subsequent measurements were made at this wave length.

Effect of pH.—A series of solutions was prepared at different pH values, as given above, so that final pH of the solutions ranged between 0.4 and 3.0. Absorbance was measured at 410 m μ .

Fig. 2 shows the effect of change of pH on absorbance. Constant absorbance is shown in the pH range 0.5 to 1.4.

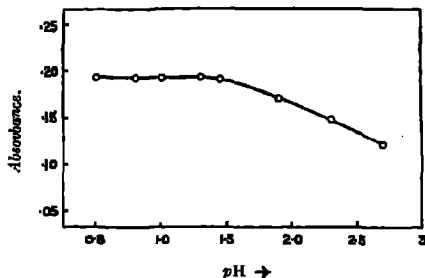


FIG. 2. Effect of pH.

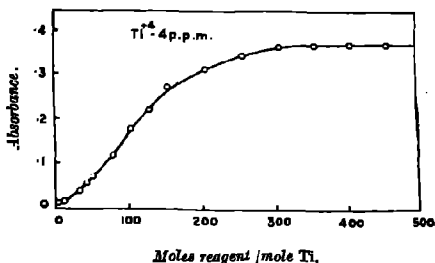


FIG. 3. Reagent conc. and mole ratio.

Effect of Time and Temperature.—The colour development was instantaneous and stable for more than 18 hours. The colour faded away at higher temperatures and reappeared on cooling. There was no difference, however, in the absorbance measured at 20° and 30°. Hence maintaining the temperature within 10° was considered desirable.

Reagent Concentration and Mole Ratio.—A series of solutions was prepared, as described earlier, in which mole ratio of titanium to reagent varied from 1 to 1 to 1 to 500 and the pH of the final solution was about 1.0. Absorbance was measured at 410 m μ .

Fig. 3 shows the effect of increase of concentration of reagent on absorbance. There is a very gradual and slow rise in absorbance, indicating that the complex is in a highly dissociated form in solution. Maximum absorbance was reached when the ratio of titanium to reagent was 1 to 340.

Beer's Law.—The titanium-reagent coloured complex obeyed Beer's law in the concentration range of 0.5 to 6.5 p.p.m. The molecular extinction coefficient worked out to 4.650×10^3 .

Sensitivity of the Reaction.—Sensitivity of the colour reaction was determined in the usual way and was found to be one part of titanium in 10,000,000 parts of the solution. Spot plate sensitivity was determined to be 0.2 γ in 0.15 ml of solution.

Recommended Procedure.—Titanium solution containing 15 to 150 γ of titanium was taken in a 25 ml flask. 10% sodium acetate solution (1 ml), a suitable quantity of HCl, and 10 ml of 2% reagent solution were introduced into it so that pH of the final solution was between 0.5 and 1.4. The volume was made to the mark and absorbance measured at 410 m μ , using the reagent as blank.

Tolerance of Diverse Ions.—The recommended procedure was followed to study the interference due to various diverse ions in the direct colorimetric determination of

Ti⁴⁺ with the reagent. Table I records the results. Hg²⁺, Sn²⁺, Pb²⁺, Cd²⁺, ~~Bi³⁺~~, ^{As³⁺}, UO₂²⁺, alkali metals, and alkaline earth metals do not show any colour reaction with the reagent and are not likely to interfere in this determination. Cu²⁺ produces no colour reaction in this pH range (0.5 to 1.4). Reaction of tungstate with the reagent is masked by using tartate. The interference due to Fe³⁺ was removed by reducing Fe³⁺ to Fe²⁺ by sodium dithionite. Ag⁺, Au³⁺, and V⁵⁺ interfere. Limiting concentrations have been found in the case of cobalt, manganese, chromium iron, and platinum.

TABLE I
Ti⁴⁺ = 2 p.p.m.

Ion.	Added as.	Conc. (p.p.m.).
Co ²⁺	Sulphate	30
Ni ²⁺	"	120
Cd ²⁺	"	120
Zn ²⁺	"	120
Mn ²⁺	"	40
Cu ²⁺	"	120
Al ³⁺	"	40
Cr ³⁺	"	8
Fe ²⁺	"	90
Pt ⁴⁺	Chloride	6
Tungstate	Sodium	120

Various organic compounds have been reported as colorimetric reagents for Ti. The following have been selected as most worthy of mention: pyrocatechol⁵, disodium 1,2-dihydroxybenzene-3,5-disulphonate⁶, ascorbic acid⁷, chromotropic acid⁸. *N*-Benzoyl-*N*-methylhydroxylamine is also a good reagent for this purpose. Fairly large amounts of diverse ions, which are usually associated with titanium, do not interfere.

The authors express their gratitude to Principal Bhim Sen for providing facilities in the College.

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Received September 8, 1962.

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