

NOTE

Spectrophotometric Determination of Magnesium(II) with 3-Hydroxy-3-*m*-Tolyl-1-*p*-Nitrophenyltriazene

USHA MAROO, PRADEEP MAROO, KAVITA SHARMA,
A.K. GOSWAMI and D.N. PUROHIT*
Department of Chemistry
Mohanlal Sikhadia University, Udaipur-313 001, India

3-Hydroxy-3-*m*-tolyl-1-*p*-nitrophenyltriazene has been used for the spectrophotometric determination of Mg(II). Magnesium forms a 1:2 (Mg:R) acetone soluble, cherry colour, complex with the reagent. The complex shows maximum absorbance at 530 nm. At working wavelength 560 nm, $\epsilon = 11,500 \text{ L mole}^{-1} \text{ cm}^{-1}$. For constant maximum colour development Mg : R was 1 : 6 and pH was between 10.4–10.8. Values of molar absorptivity, Sandell's sensitivity, stability constant ($\log \beta$) and free energy of formation were found to be $11,500 \text{ L mole}^{-1} \text{ cm}^{-1}$, 0.21 ng/cm^2 , 11.00 and $-15.101 \text{ kcal/mole}$ respectively. Beer's law is obeyed in the entire concentration range studied, *i.e.*, $1.0 \times 10^{-6} \text{ M}$ to $6.0 \times 10^{-6} \text{ M}$. It was possible to determine magnesium (0.12 ppm) in presence of two-fold molar excess of nineteen cations and anions.

Survey of six reviews¹⁻⁶ and literature which has appeared thereafter⁷⁻¹¹ on hydroxytriazenes reveals that so far no hydroxytriazenes have been used for spectrophotometric determination of magnesium. In this communications results of spectrophotometric determination of magnesium with 3-hydroxy-3-*m*-tolyl-1-*p*-nitrophenyltriazene have been reported. This is the first report regarding utility of hydroxytriazene in spectrophotometric determination of magnesium. Absorbance measurements were made on Systronic 108 spectrophotometer. Systronic pH meter 324 was used for pH measurements.

The reagent 3-hydroxy-3-*m*-tolyl-1-*p*-nitrophenyltriazene was prepared as per the reported method¹².

A $1.0 \times 10^{-2} \text{ M}$ stock solution of magnesium(II) was prepared by dissolving the required quantity of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (BDH, AR grade) in double distilled water. To prevent hydrolysis a few drops of concentrated H_2SO_4 were added to the solution. The solution was then standardised using $1.0 \times 10^{-2} \text{ M}$ EDTA solution at pH 9–10 using Eriochrome black-T¹³ as an indicator. The solutions of weaker strength were prepared by proper dilution of the stock solution with double distilled water.

The reagent solution of desired concentration was prepared by the dissolving the requisite quantity of 3-hydroxy-3-*m*-tolyl-1-*p*-nitrophenyltriazene in acetone.

Agar-agar (0.03 g) was added to 50 mL of water and heated till it dissolved. To it, 2 g of $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ was added. The solution was shaken till dissolution, filtered and cooled. To it, 0.6 g of NaOH was added and the solution was shaken again till dissolution. To it, 5 mL of a 3% solution of Rochelle salt ($\text{C}_4\text{H}_4\text{O}_6 \cdot \text{KNa}_4\text{H}_2\text{O}$) solution was added, diluted with water and made up to 100 mL. This solution was used to adjust the pH in alkaline medium.

Magnesium(II) formed cherry-coloured acetone-soluble complex under optimum conditions of magnesium to reagent (1:6) and in pH range 10.4–10.8. The cherry-coloured complex exhibited λ_{max} at 530 nm. However, working wavelength was chosen as 560 nm, such that the difference between the absorbance of the complex and reagent was maximum. All absorbance measurements were made against reagent blank.

Job's method¹⁴, Mole ratio method¹⁵ and Slope ratio method¹⁶ have been used to determine the composition of the magnesium complex. By all the three methods, the composition of the complex has been found to be 1:2 (Mg : R).

Beer's law was obeyed in the entire concentration range studied, *i.e.*, 1.0×10^{-6} M to 6.0×10^{-6} M. The molar absorptivity and Sandell's sensitivity values were determined and found as $115,00 \text{ L mole}^{-1} \text{ cm}^{-1}$ and 0.21 ng/cm^2 respectively. The standard deviation ' σ ' obtained from ten determinations was obtained as 0.0004 ppm by measuring the absorbance of ten solutions containing 0.12 ppm of Mg(II).

The mole ratio curves¹⁷ (Harvey and Manning's methods) were used to determine conditional stability constant. The value of $\log \beta$ was found as 10.51. Similarly Job's method curves¹⁸ were also used (Purohit's method) to determine the conditional stability constant. This method gives the value of $\log \beta$ as 11.00. Using the value of $\log \beta$ the value of free energy of formation of the complex at 27°C was calculated using the formula $\Delta G = -2.303 RT \log \beta$. By substituting the value of R (1.987), T (300) and $\log \beta = (11.00)$, the value of free energy of formation was obtained as $-15.101 \text{ kcal/mole}$.

The interference study revealed that 0.12 ppm of magnesium can be determined in presence of two fold molar excess of nineteen cations and anions namely: Na(I), K(I), NH_4^+ , Hg(II), Ba(II), Mn(II), Pb(II), Cr(III), Cl^- , Br^- , CH_3COO^- , CO_3^{2-} , SO_4^{2-} , I^- , NO_2^- , SO_3^{2-} , F^- , NO_3^- and oxalate.

However, Cd(II), Cu(II) and Zn(II) were found to interfere.

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(Received: 20 November 1998; Accepted: 1 June 1999)

AJC-1742