

Short Communication

***α*-Methyl, 2 : 4-dihydroxy benzylidene, 2-aminoaniline (MDA) as an analytical reagent for the colorimetric determination of microamounts of chromium (VI)**

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Abstract

Chromium(VI) in acid medium showed deep red colour with *α*-methyl, 2 : 4-dihydroxy benzylidene-2-aminoaniline (MDA). The colour reaction obeyed Beer's law in the concentration range 0.26-6.8 $\mu\text{g/ml}$ at 490 nm with 1.0-5.2 $\mu\text{g/ml}$ being optimum concentration range. The stoichiometry of the colour reaction is 1 : 1. The molar absorptivity and Sandell's sensitivity are $6.9 \times 10^3 \text{ lit. mole}^{-1} \text{ cm}^{-1}$ and $0.0074 \mu\text{g/cm}^{-2}$ respectively.

Key words : *α*-Methyl, 2 : 4-dihydroxy benzylidene, 2-aminoaniline, chromium(VI), colorimetric method.

1. Introduction

During the investigation of the analytical applications of the reagent *α*-methyl, 2 : 4-dihydroxy benzylidene, 2-aminoaniline (MDA) synthesised in these laboratories, the authors found that the reagent showed a deep red colour with chromium(VI) in acid medium. It is therefore thought worthwhile to study the applicability of the reagent for a possible rapid colorimetric determination of chromium(VI) in acid medium. The results obtained in such studies are communicated herein.

2. Experimental

2.1. Preparation of the reagent

All the chemicals used were of analytical reagent grade. The reagent (MDA) was prepared by refluxing ethanolic solutions of *o*-phenylenediamine and 2 : 4-dihydroxyacetophenone for 8 hours. The solution was left overnight and the solid obtained was

recrystallised from alcohol (m.p. 193° C). ELICO CL-23 Spectrocolorimeter was used to measure the absorbance.

2.2. Procedure for the determination of chromium(VI)

To various aliquots of chromium(VI) solutions (0.20-7.0 $\mu\text{g/ml}$) taken in different 10 ml standard flasks, 3.0 ml of 1 M hydrochloric acid, 1 ml of 1×10^{-2} M reagent solution were added, and the contents of each flask were made up to the mark with distilled water. The absorbance was measured at 490 nm against reagent solution as blank. The absorbance data is used to construct the calibration curve (slope is 0.1342).

The procedure described is arrived at from the following observations :

- (i) The absorbance of the reaction mixture was maximum at 490 nm.
- (ii) The absorbance at 490 nm is the highest in hydrochloric acid and perchloric acid solutions. It, however, decreased in the presence of other acids, indicating that sulphate, nitrate, phosphate, and acetate interfere.
- (iii) The colour intensity of the reaction mixture was maximum at 0.3 M in a good working range of 0.2-0.6 M hydrochloric acid.
- (iv) An one fold excess of the reagent was found sufficient to obtain maximum colour intensity.

2.3. Results

Beer's law is obeyed in the range 0.26-6.80 $\mu\text{g/ml}$ of chromium(VI) and the optimum range for the accurate determination arrived from Ringbom's plot¹ is 1.0-5.2 $\mu\text{g/ml}$. Molar absorptivity and Sandell's sensitivity are respectively 6.9×10^3 lit. mole⁻¹ cm⁻¹, and 0.0074 $\mu\text{g. cm}^{-2}$. The stoichiometry of the colour reaction is established as 1:1 by Job's, Mole ratio and Slope ratio methods. There is no colour development on adding 'persulphate' to the reaction mixture in place of chromium(VI), indicating that the colour is probably not due to oxidation. The stability constant and limits of identification are 4.8×10^5 and 1:1,90,000 respectively.

2.4. Effect of diverse ions

In the determination of 2 $\mu\text{g/ml}$ of chromium (VI) the following ions did not interfere, the figures in the parentheses being the tolerance limits. Fluoride (1000 fold), thiocyanate (1000 fold), tartrate (500 fold), oxalate (150 fold), EDTA (100 fold), carbonate (50 fold), permanganate (2 fold), barium (1000 fold), calcium (1000 fold), nickel (200 fold), zinc (200 fold), cobalt (100 fold), uranium(VI) (100 fold), manganese (20 fold), and zirconium(IV) (20 fold).

Hundred fold each of iron(III), molybdenum (VI), 80 fold of tungsten, 10 fold of titanium (IV) did not interfere when masked with fluoride. Hundred fold of copper did not interfere when citrate was used as masking agent.

3. Conclusions

The present reagent ($\epsilon = 6.9 \times 10^3 \text{ lit. mol}^{-1} \text{ cm}^{-1}$) is more sensitive than resacetophenone oxime² ($\epsilon = 2.4 \times 10^3 \text{ lit. mol}^{-1} \text{ cm}^{-1}$) and gallacetophenone oxime³ ($\epsilon = 3.6 \times 10^3 \text{ lit. mol}^{-1} \text{ cm}^{-1}$). Chromium(III) is generally converted into chromium(VI) through persulphate oxidation, and since the latter does not interfere in the present method, it offers an additional advantage.

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