Kinetic Fluorimetric Determination of Vanadium(IV) by Catalytic Oxidation of Chromotropic Acid by Hydrogen Peroxide

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Summary: A kinetic spectrofluorimetric method has been described for the determination of vanadium(IV) based on catalytic oxidation of chromotropic acid by hydrogen peroxide. The reaction was followed by measuring emission at 460 nm and excitation at 360 nm. The method could be used for the determination of vanadium within 2-10 μg/mL. The relative percent error for test solutions was in range of 0-0.1%. The effect of diverse ions on the determination of vanadium is also reported.

Introduction

The presence of vanadium in trace quantity in potable water has been reported to have a beneficial effect on the health of individuals [1]. A number of methods have been reported on the preconcentration [1] and determination of vanadium using voltametric methods [2], spectrophotometric methods [1], atomic absorption [3], inductively coupled plasma atomic emission spectroscopy [4], and gas [5] and liquid chromatography [6]. Vanadium has been determined by its catalytic effect on the oxidation of pyrogallol red by potassium bromide in which a fixed time method is used and the reaction is followed spectrophotometrically [7]. Another kinetic spectrophotometric method for the determination of vanadium has also been reported based on catalytic oxidation of 3,5-diaminobenzoic acid dihydrochloride by potassium bromate [8].

Chromotropic acid (disodium salt of 4,5-dihydroxynaphthalene 2,7-disulphonic acid) has been used for kinetic determination of copper (II) and iron(II) [9] using spectrophotometer.

Recently chromotropic acid has been reported as a metallofluorescence reagent for the determination of beryllium(II) and aluminum (III) [10]. Aluminum has been determined in environmental and biological samples [11]. The present work describes a simple kinetic fluorimetric method for vanadium determination using chromotropic acid.

Results and Discussion

In order to select suitable wavelength for fluorescence system, excitation and emission spectra of the chromotropic acid with hydrogen peroxide was recorded (Fig. 1). The excitation and emission wavelengths were selected at 360 nm and 460 nm, respectively.

In preliminary study a decrease in fluorescence intensity of chromotropic acid was observed by addition of vanadium (IV) in the presence of hydrogen peroxide. The decrease in fluorescence was measured after fixed time (15 min). Thus the effect of variable were determined to optimize the conditions for the possible determination of vanadium quantitatively.

Effect of chromotropic acid

The effect of chromotropic acid concentration on the emission intensity was examined at final concentration in the range of $1x10^{-6}$ to $8x10^{-6}$M. The fluorescence intensity increased with the concentration of chromotropic acid as expected, but concentration of $4x10^{-4}$M was selected to enable to arrange instrumental setting with reasonable sensitivity.

Effect of hydrogen peroxide

The effect of concentration of hydrogen peroxide on the fluorescence intensity was examined with $2x10^{-3}$ to $10x10^{-3}$M H_2O_2 and it was

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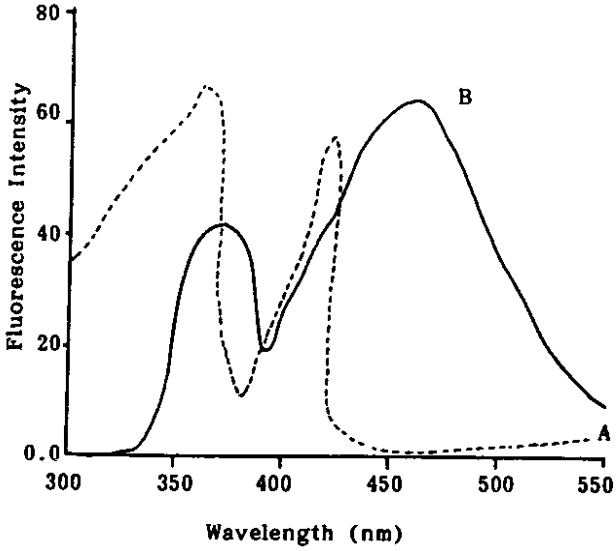

Fig. 1: Change in fluorescence intensity versus A) Excitation wavelength B) Emission wavelength.

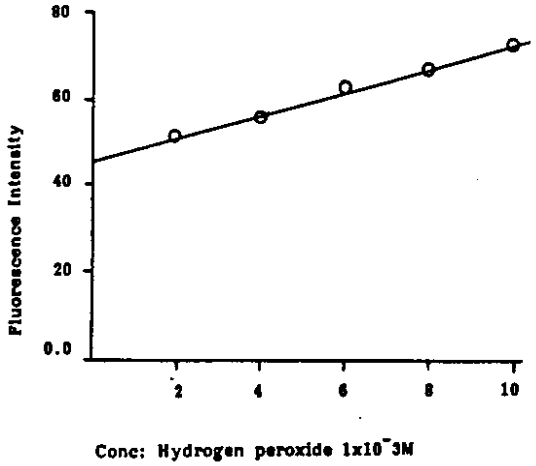

Fig.2: Change in fluorescence intensity with concentration of hydrogen peroxide.

observed that fluorescence intensity increased with increase of hydrogen peroxide concentration (Fig. 2) but a final concentration of $8x10^{-3}M$ was selected to enable to measure the fluorescence after an interval of 15 min.

Effect of temperature

The influence of the temperature of the reaction media in the range 30-50°C was studied and it was observed that fluorescence intensity increases with temperature, but for the simplicy of the operational conditions temperature 30°C was fixed for the study.

Effect of pH

Effect of pH in the range of 2-11 was investigated to obtain a better fluoresence intensity of the chromotropic acid hydrogen peroxide system and to obtain a maximum decrease in fluorescence intensity due to the addition of vanadium owing to the catalysed reaction. It was observed that a maximum fluorescence intensity with an optimum slope for the catalysed reaction was observed in - alkaline media. The disodium hydrogen phosphate buffer pH 10.6 proved optimal and was used.

From this optimized condition a linear calibration curve was obtained by plotting the decrease in fluorescence intensity with a concentration range of 2-10 µg/ml of vanadium. The validity of the calibration curve was checked by the analyses of a test vanadium solution and the relative % error was found within 0-0.1%.

Finally, the effect of diverse ions for the determination of vanadium(IV) (2 µg/ml) was determined. It was observed that calcium(II), magnesium(II), chloride and sulphate did not interfere. Copper(II), lead(II), iron(II), cobalt(II), nickel(II) and nitrate could be tolerated up to ten

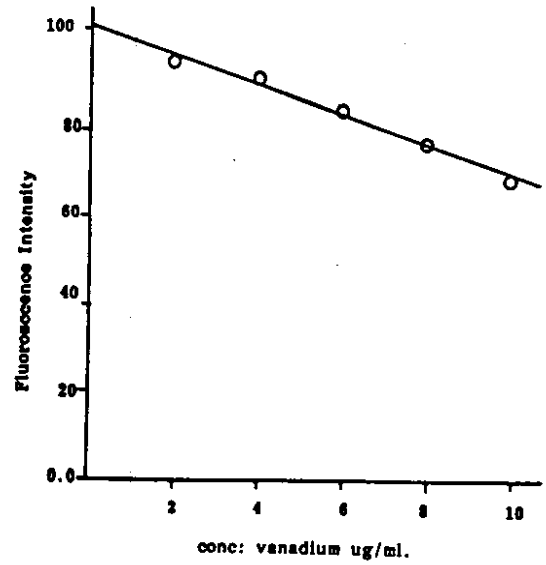

Fig.3: Vanadium calibration curve.

times the concentration of Vanadium. Chromium(VI) and manganese (II) interfered even at a concentration similar to vanadium.

Experimental

Hitachi F-1200 spectrofluorometer was used.

Solutions

Chromotropic acid disodium salt (Merck) $1x10^{-3}$) M was prepared by dissolving (0.04 g) in water (100 mL). Hydrogen peroxide ($1x10^{-1}$) M was prepared by diluting (1 mL, 30% H_2O_2) to 100 mL with water. Buffer solutions in pH range 2-11 were prepared from one or more of the following reagents, hydrochloric acid (0.1 M), sodium chloride (1M), acetic acid (1M), sodium acetate (1M), ammonium acetate (1M), sodium bicarbonate (1M), sodium carbonate (saturated solution), disodium hydrogen phosphate (0.05M), sodium hydroxide (0.1M). Disodium hydrogen phosphate and sodium hydroxide buffer (pH 10.6) was adjusted the concentration of potassium chloride (0.1 M) to obtain constant ionic strength. Stock solution (1000 ppm) were prepared from following: $VOSO_4$, $CuSO_4.5H_2O$; $NiSO_4.6H_2O$, $(CH_3COO)_2.Pb.3H_2O$; $CdCl_2.H_2O$, $NaNO_3$, $(CH_3COO)_2Co.4H_2$;$MnCl_2$ and $K_2Cr_2O_7$.

Analytical procedure

Chromotropic acid (1.0 ml of $1x10^{-4}$M) and vanadium(IV) (0.5-2.5 mL) containing (50-250 µg) were transferred to 25 volumetric flask. To separate flask was added hydrogen peroxide (2 mL of $1x10^{-1}$M) and disodium hydrogen phosphate sodium hydroxide buffer solution pH 10.6 (1 mL). Both were mixed together and final volume made to 25 mL. The fluorescence intensity was measured at (Ex 360 nm and Em 460 nm) after 15 min. from mixing of the reagent. A blank was prepared following the same procedure except addition of vanadium was omitted.

Conclusion

A kinetic spectrofluorimetric method for the determination of vanadium (IV) is proposed based on the decrease in fluorescence intensity (at Em 460 nm, Ex 360 nm) with vanadium concentration (2-10 µg/ml) of chromotropic acid ($4x10^{-6}$M) and hydrogen peroxide ($8x10^{-3}$M) system at pH 10.6. The fluorescence was measured after constant time of 15 min. A number of common ions were examined and only chromium(VI) and manganese(II) interfered.

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