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Simultaneous Kinetic Spectrophotometric Determination of V(IV) and V(V) by H-point Standard Addition Method

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The H-point standard addition method was applied to kinetic data for simultaneous determination of V(IV) and V(V) or selective determination of V(IV) in presence of V(V). The method is based on the difference in the rate of complex formation between V(IV) and V(V) with methyl thymol blue. The linear dynamic ranges for the two analytes of V(IV) and V(V) are 0.18-3.15 and 0.25-4.00 μg mL^{-1}, respectively. The proposed method was successfully applied for the determination of vanadium in two different oxidation states in several synthetic mixtures and also in blood serum and water samples.

Key Words: Vanadium, Speciation analysis, H-Point standard addition method, Methyl thymol blue, Kinetic spectrophotometric.

INTRODUCTION

Metal speciation is important in a variety of environmental, biological, geological and medical applications. Vanadium is an important element in environmental and biological studies. Vanadium's role in physiological systems includes normalization of sugar levels, participation in various enzyme systems as an inhibitor and a co-factor and catalysis of the oxidation of various amines. The studies also showed that the vanadium(IV) and vanadium(V) are essential for cell growth at mg dm^{-3} levels, but can be toxic at higher concentrations. The toxicity of vanadium is dependent on its oxidation state, as vanadium(V) being more toxic than vanadium(IV)[1]. It is thus clear that the presentation of simple, selective, precise and inexpensive methods for the simultaneous determination of V(IV) and V(V) is very important.

The most widely used techniques for the separation and preconcentration of vanadium include liquid-liquid extraction[2], coprecipitation[3] and ion exchange and sorption[4-6]. Vanadium speciation usually requires powerful detection techniques such as atomic absorption spectrometry (AAS)[7,8], inductively coupled plasma mass spectrometry (ICP-MS)[9-12], inductively coupled plasma optical emission spectrometry (ICP-OES) with separation and preconcentration by hollow-fibre liquid phase microextraction[13], or UV-visible spectrophotometry with post-column derivatization[14] or separation by stacking capillary electrophoresis[15]. These methods are all useful and offer high sensitivity for vanadium species in real samples. However, they need expensive instruments such as ICP-OES and ICP-MS and time consuming

separation or derivatization step. Despite of success of mentioned methods, there is still more interest in the application of spectrophotometric methods in determination of metals ions, due to both rapidity and simplicity of the technique. However simul-taneous determination of multielements by the use of traditional spectrophotometry is difficult because generally, the absorption spectra overlap and superimposed curves are not suitable for quantitative evaluation. Quantitative spectrophotometry has been greatly improved by the use of multivariate statistical methods. Kinetic spectrophoto-metric determination of vanadium (IV) in the presence of V(V) have been made by H-point standard addition method (HPSAM) and using xylenol orange as chromo-genic reagent[1].

The H-point standard addition method is a modification of the standard addition method that transforms the incorrigible error resulting from the presence of a direct interference in the determination of an analyte into a constant systematic error. This error can then be evaluated and eliminated. This method also permits both proportional and constant errors produced by the matrix of the sample to be corr-ected directly. The basis of the method was estabilished previously[16,17]. Absorbance increments as analytical signals were used when only the analyte concentration was required[18].

Two variants of H-point standard addition method can be used for the treatment of kinetic data[19]. One is applied when the reaction of one component is faster than that of the other or the latter dose not take place at all. This variant of the method is based on the assumption that only analyte X evolves with time and the other species Y or interferents do not affect the analytical signal with time. In this case the variables to be fixed are two times t_1 and t_2 at which the species Y, which does not evolve with time or over the range between these times, should have the same absorbance[20]. The other variant of the method is used when the rate constants of the two components are time-dependent. In this case, the two species in a mixture, X and Y, both evolve with time.

In this study, the first variant of kinetic based H-point standard addition method is suggested as a simple, precise and accurate method for simultaneous determination of vanadium(IV) and vanadium(V), based on the their different complex formation rate with methyl thymol blue as chromogenic reagent.

EXPERIMENTAL

UV-Visible absorbance digitized spectra were recorded on a UV-vis GBC 916 spectrophotometer. Measurements of pH were made with a PMT 1003 pH-meter using a combined glass electrode. The computations were made on a Pentium 133 MHz computer.

All solutions were prepared with double distilled water. Chemicals used were of analytical grade and were purchased from E. Merck. Stock vanadium(V) and (IV) solutions (1000 μg mL^{-1}), were prepared from ammonium metavanadate and vanadyl sulfate monohydrate, respectively and standardized[21,22]. Methyl thymol blue (MTB) solution (M) was prepared from its sodium salt daily.

Procedure: 2 mL of buffer solution with pH = 3 and 1 mL of MTB (1×10^{-3} M) were added to a 10 mL volumetric flask and made up to the mark with water. Then 2 mL of the above solution was transferred to a spectrophotometer cell and appropriate volumes of V(IV) and V(V) (in µL) were added to the cell and the variation of absorbance *versus* time was recorded immediately. The absorbance was measured at 580 nm with 1 s intervals for each sample after preparation of a sample solution against of blank sample. The blank sample was prepared by dilution of 2 mL of buffer solution with pH = 3 and 1 mL of MTB 1×10^{-3} M to 10 mL with water. Simultaneous determination of V(IV) and V(V) with HPSAM was performed by measuring absorbances at just 15 and 120 s after initiation of reaction for each sample solution. The concentration ranges of V(IV) and V(V) for construction of HPSAM calibration graph were 0.18-3.15 and 0.25-4.00 µg mL^{-1}, respectively.

RESULTS AND DISCUSSION

Vanadium(IV) and vanadium(V) form colored complexes with MTB (Fig. 1). The rate of complex formation between MTB and V(IV) is slower than V(V) complex formation under acidic conditions. Fig. 2 shows the change in visible absorption spectra of the V(IV)-MTB system as a function of time.

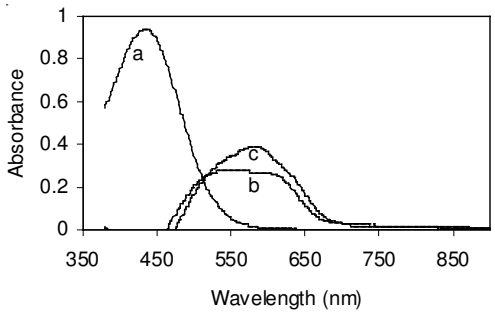

Fig. 1. Absorption spectra of (a) pH = 3.0, 1×10^{-4} M methyl thymol blue (MTB); (b) a plus 2.00 µg mL^{-1} vanadium(V); (c) a plus 2.80 µg mL^{-1} vanadium(IV)

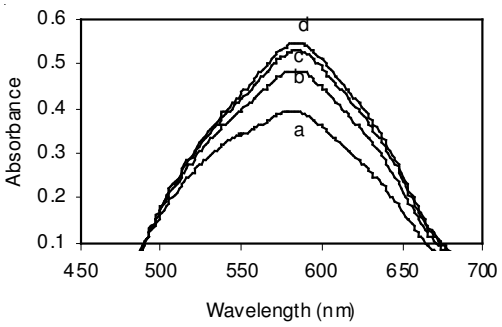

Fig. 2. Variation of visible spectra of methyl thymol blue (MTB) (1×10^{-4} M) solution in presence of 2.8 µg mL^{-1} vanadium(IV), as a function of time. Time interval 30 s

Effect of variables: In order to find the optimum conditions or to obtain maximum absorbance changes for V(IV)-MTB complex and maximum absorbance for V(V)-MTB complex, the effects of variables were studied.

The study on the influence of pH on rate of V(IV)-MTB complex formation showed that the maximum change in the fixed time period (105 s) occurred at *ca.* pH = 3.0. The rate of complex formation above pH 3 was so fast that the complex formation reaction was almost complete before 15 s and thus the change in absorbance between 15 and 120 s was very small (Fig. 3). The absorbance for V(V)-MTB complex was also suitable at pH = 3.0. Therefore, 580 nm and pH = 3.0 were selected for monitoring the kinetics of the system. However, under the same condition, the complexation of V(V) was fast.

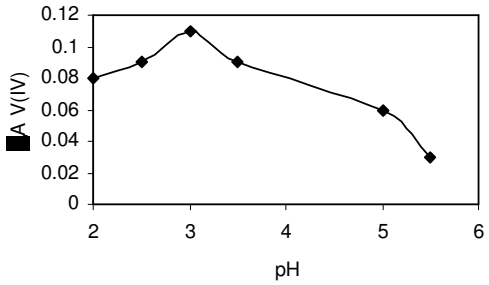

Fig. 3. Effect of pH on the change in absorbance of the V(IV)-MTB system in a fixed time 105 s

The influence of MTB concentration on the changes of absorbance of V(IV)-MTB complex and on the absorbance of V(V)-MTB complex absorbance in the range of 1.0×10^{-5}- 1.5×10^{-4} M was studied. The results show that by increasing MTB concentration up to 7×10^{-5} M, the absorbance changes for V(IV) complex and absorbance for V(V) complex increases and after that, it is constant. The amount of molarity was selected for MTB concentration, because it ensures maximum sensitivity and sufficient excess reagent.

Temperature effect was also investigated in the range of 5-45 ºC. The results showed that with increasing of temperature to 15 ºC the absorbance changes for V(IV) complex increased and then were constant to 30 ºC and finally, decreased after 30-45 ºC. The absorbance of V(V) complex did not affect by temperature changes in this range. Therefore 25 ºC was selected for simplicity.

The influence of ionic strength on the changes of absorbance of V(IV)-MTB complex and on the absorbance of V(V)-MTB complex was also studied. The signals were constant in the studied range.

Application of H-point standard addition method (HPSAM): In order to test applicability of HPSAM to the simultaneous determination of V(IV) and V(V) the kinetic curves for each of them and for the mixture of them were drawn (Fig. 4). As shown when V(IV) is selected as the analyte, it is possible to select several pairs of times where there are the same absorbance values for V(V). The pair of time,

which gave the highest accuracy, was selected for further work. The criteria for choosing the optimum time pair were as follows. The best pair of time should give the greatest slope increment[23] and also the change in absorbance related to V(V) concentration is negligible. For this reason the time pair 15-120 s was employed for obtaining the highest accuracy. Fig. 5 give a sample of H-point standard addition calibration curve constructed at two selected times.

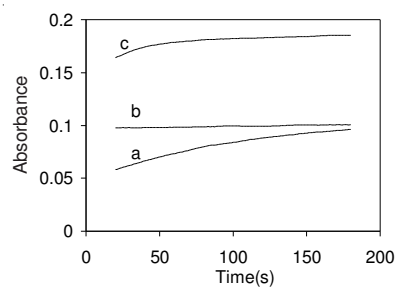

Fig. 4. Kinetic curve for (a) 0.70 mg mL^{-1} V(IV); (b) 0.70 mg mL^{-1} V(V) (c) mixture of 0.70 mg mL^{-1} V(IV) and 0.70 mg mL^{-1} V(V).

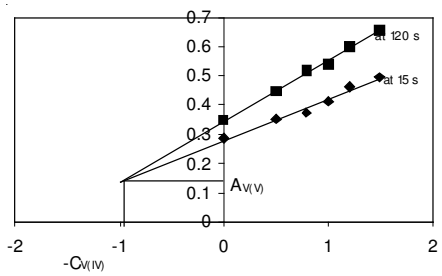

Fig. 5. Plot of HPSAM for simultaneous determination of V(IV) (1.00 μg mL^{-1}) and V(V) (1.00 μg mL^{-1})

According to the theory of HPSAM at H-point[19], C_H (concentration of V(IV) at H-point) is independent of the concentration of V(V) and so, A_H (absorbance of V(V) at H-point) is also independent of the concentration of V(IV). Figs. 6 and 7 clearly show the effect of change in concentration of V(IV) and V(V) on the position of H-point. So, again as shown in Fig. 7, the value of A_H is independent of the amounts of V(IV) in the sample. This analytical signal enables calculation of the concentration of V(V) from a calibration curve (The calibration equation for V(V) was obtained as $A = 0.1748C_{V(V)} - 0.0273$).

An absorbance increment as an analytical signal can be employed in another version of HPSAM to allow the V(IV) concentration to be calculated with no systematic, constant or proportional error. The plot of $\Delta A_{t_1-t_2}$ against the added analyte concen-tration will have a constant point ($-C_H$, O)[19]. Thus, for the determination of V(IV) in presence of V(V), the absorbance increment as an analytical signal was used. The application of the HPSAM in the $\Delta A_{t_1-t_2}$ - C_{added} variant yields the concentration

of V(IV) directly from the intercept on the X-axis. However, in order to ensure the absence of constant and proportional errors from the calculated concentration, all the possible $\Delta A_{t_1-t_2}$ - C_{added} lines for V(IV) complex should intersect at the same point, namely, that corresponding to the unknown concentration, C_H, as this would indicate that the time evaluation of the matrix would be a horizontal line. Table-1 shows the results from employing this version of HPSAM on the synthetic mixtures of V(IV) and V(V). The results obtained by this procedure were in good agreement with those given above.

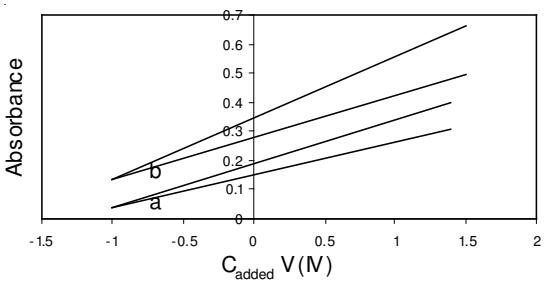

Fig. 6. Plots of HPSAM for fixed V(IV) (1.00 μg mL^{-1}) concentration and different concentrations of V(V): (a) 0.50 μg mL^{-1} and (b) 1.00 μg mL^{-1} V(V)

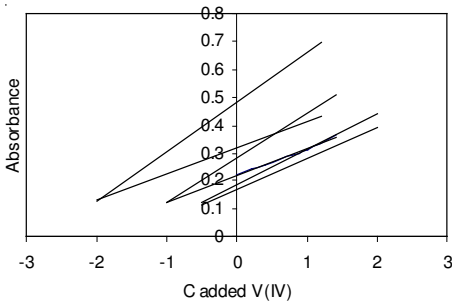

Fig. 7. Plots of HPSAM for fixed V(V) concentration (1.00 μg mL^{-1}) and different concentrations of V(IV): (a) 0.50 μg mL^{-1} (b) 1.00 μg mL^{-1} and (c) 2.00 μg mL^{-1} of V(IV)

TABLE-1
APPLICATION OF SIGNAL INCREMENT VERSION
OF HPSAM IN A SYNTHETIC MIXTURE

	Time interval (s)			
	15-120	30-180	20-60	15-100
Found V(IV) concentration (μg mL^{-1})	1.96	2.07	1.89	1.92

Actual concentration of V(IV) and V(V) were 2.00 and 1.00 μg mL^{-1}.

Accuracy, precision and selectivity of the method: Under the optimum conditions, simultaneous determination of different binary mixtures of V(IV) and V(V) were made using HPSAM. Table-2 shows, the accuracy of the results is satisfactory.

To check the reproducibility of the method, five replicate experiments were made and the relative standard deviation (RSD) was obtained as 2.7 and 3.2 % for 1.00 μg mL^{-1} V(IV) and V(V), respectively.

TABLE-2
RESULTS OF FIVE EXPERIMENTS FOR THE ANALYSIS OF V(IV) AND V(V)

Present in the sample (μg mL^{-1})		Found (μg mL^{-1})	
V(IV)	V(V)	V(IV)	V(V)
0.50	0.50	0.53	0.52
0.50	1.00	0.45	0.94
1.00	1.00	0.97	0.97
2.00	1.00	2.05	0.96
1.00	0.50	0.98	0.51

The effects of some of cations and anions on the determination of 1 μg mL^{-1} of V(IV) and V(V) were studied with the optimized conditions described above. The tolerance limit is defined as the of foreign-ion concentration causing an error smaller than 5 % for the simultaneous determining these species. The results indicate that 100 μg mL^{-1} of Na^+, K^+, NH_4^+, Ag^+, Ba^{2+}, Ca^{2+}, Mg^{2+}, Ni^{2+}, Sn^{2+}, Hg^{2+}, Al^{3+}, Cd^{2+}, Cl^-, CN^-, CO_3^{2-}, IO_3^- and NO_3^- and 10 μg mL^{-1} of Co^{2+} and 5 μg mL^{-1} Zn^{2+}, Cu^{2+}, Pb^{2+} and As^{3+} and 2 μg mL^{-1} Fe^{3+} did not interfere under working conditions.

Application: Several synthetic samples with different concentrations of other species were analyzed by HPSAM. As can be seen from Table-3, the accuracy of the results is satisfactory in all cases. In addition, for the validation of the method, environmental and biological complex matrix samples were spiked with V(IV) and V(V) and the proposed method applied for determination of the analyte. The results are shown in Table-3 and the results are satisfactory.

TABLE-3
SIMULTANEOUS DETERMINATION OF V(IV) AND V(V) IN DIFFERENT SAMPLES

Sample	Spiked (μg mL^{-1})		Found[a] (μg mL^{-1})	
	V(IV)	V(V)	V(IV)	V(V)
Synthetic[b]	1.00	1.00	0.95 ± 0.04	0.93 ± 0.03
Synthetic[c]	1.00	0.50	0.99 ± 0.05	0.52 ± 0.04
Synthetic[d]	1.50	0.75	1.51 ± 0.06	0.83 ± 0.02
Tap water	1.00	0.50	0.97 ± 0.02	0.45 ± 0.03
Mineral water	0.80	0.25	0.77 ± 0.02	0.26 ± 0.01
Blood serum	1.00	1.00	1.10 ± 0.10	1.00 ± 0.09

[a]: Mean ± SD (n = 3). The composition of synthetic samples was: [b]: Cd(II) 40, Cu(II) 5, Pb(II) 5, Ca(II): 5, Zn(II): 2, Na(I) 100 μg mL^{-1}; [c]: K(I) 50, Ni(II) 10, Ag(I) 10, Cu(II) 5, Pb(II) 5, Mg(II) 5 μg mL^{-1}; [d]: K(I) 50, Cd(II) 50, Mg(II) 5, Hg(II) 5, Cu(II) 5, Fe(III) 1 μg mL^{-1}.

Conclusion

In this study, H-point standard addition method method was applied for the simultaneous determination of V(IV) and V(V) based on the difference in the rate

of complex formation between V(IV) and V(V) with methyl thymol blue. This method was fast, inexpensive and reproducible. The proposed method was used for the determination of vanadium in two different oxidation states in several synthetic mixtures and also in blood serum and water samples.

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