

Simultaneous Spectrophotometric Determination of Vanadium(V) and Iron(III) in Micellar Medium by H-Point Standard Addition Method

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ABSTRACT: *H-Point Standard Addition Method (HPSAM) was applied for the simultaneous determination of V(V) and Fe(III). The method is based on the complex formation of V(V) and Fe(III) with chromazurol S (CAS) in acidic media and in the presence of cetyltrimethylammonium bromide (CTAB) as a micellizing agent. Acidic media and the presence of a micellar system improve selectivity and sensitivity. Fe (III) and V (V) could be determined simultaneously in the range of 0.1-2 and 0.2-2 µg/mL, respectively, and with the ratio 1:20 to 10:1 Fe(III)/V(V) in the mixed samples. The proposed method was successfully applied to the simultaneous determination of Fe(III) and V(V) in tap, river, saliva and plasma samples.*

KEY WORDS: *Vanadium (V), Iron (III), H-point standard addition, Spectroscopy.*

INTRODUCTION

The industrial use of vanadium is widespread in the industry, catalyst industry, ceramic and electronic equipments. This element in trace amounts is an essential element for cell growth at µg / L levels, but can be toxic at higher concentrations. The toxicity of vanadium is dependent on its oxidation state [1], vanadium (V) being more toxic than vanadium (IV). Owing to its toxic and essential nature (e.g. to marine algae and green plants) in biological systems there has been considerable interest in the determination of vanadium in environmental samples [2].

Iron is an integral part of many proteins and enzymes and is an essential component of proteins involved in oxygen transport, regulation of cell growth and

differentiation. Iron deficiency limits oxygen delivery to cells, leading to fatigue, poor work performance, decreased immunity and death. A Recommended Dietary Allowance (RDA) of 8 and 18 mg / day of Fe has been recommended for the average 19-50 year old males and females, respectively [3]. Hence, the determination of trace amount of vanadium and iron is important in metallurgy and environmental analytical chemistry, and there is a growing need for procedures with high sensitivity and selectivity because they have important roles in biological, industrial and medical science. In addition these two elements were always together in the nature; therefore, it is important to measure them in the presence of each other [4].

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Various spectrophotometric methods for the individual or simultaneous determination of vanadium (V) and Fe(III) have been reported. These methods are as follows: Atomic spectrometry techniques – mainly Flame Atomic Absorption Spectrometry (FAAS) [5], Graphite Furnace Atomic Absorption Spectrometry (GFAAS) [6], Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) [7], Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and X-Ray Fluorescence (XRF) Spectrometry [8], spectrophotometry using chemometrics methods [9].

Although some of these methods provide high sensitivity and specificity, they also have drawback such as high costs for equipment and assays, time-consumption and complicated operation as well as being unsuitable for applications where mobility of the analytical equipment is of advantage. Among the most widely used analytical methods are those based on the UV-Vis spectrophotometry techniques, due to both the resulting experimental rapidity and simplicity and the wide application [10]. Spectrophotometric methods play a prominent role, but the selectivities of most spectrophotometric procedures are not satisfactory, owing to the close related properties, and separation procedures that must be introduced in most cases [11]. For achieving quantitative information from such systems without previous chemical separation several chemometric methods have been developed.

H-point standard addition method, which is a modification of the standard addition method, is a simple two variable chemometric technique. The greatest advantage of HPSAM is that it can remove the presence of an interference and reagent blank [12, 13]. This method has been applied in different analytical techniques, including spectrophotometry [14–17], spectrofluorimetry [18], kinetic spectrophotometry [19–20] and chromatographic techniques [21]. In order to apply HPSAM to resolve mixtures, the interferent(s) species should be known. Two methods namely Generalized H-Point Standard Addition Method (GHPSAM) [22–24] and H-Point Curve Isolation Method (HPCIM) [25] were proposed to solve this problem.

In the present work a very simple, sensitive, selective and low cost procedure for simultaneous determination of Fe(III) and V(V) using HPSAM is described. This method is based on the complex formation of Fe(III) and

V(V) with CAS under acidic conditions in micellar medium.

EXPERIMENTAL SECTION

Apparatus

For recording the UV-Vis spectra, Varian Bio300 UV-Vis spectrophotometer with a 1.0 cm quartz cell was used. A 780 pH-meter (Metrohm), equipped with a combined glass electrode, was used for pH measurement. The computations were made with a Pentium IV computer.

Reagents

All reagents were of analytical reagent grade and used without further purification. Doubly distilled water was used throughout the study. A stock solution (1000 $\mu\text{g} / \text{mL}$) of iron(III) and vanadium(V) were prepared by dissolving $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Merck) and V_2O_5 (Merck), respectively. A stock solution of chromazurol S (0.005 M) was prepared by dissolving an appropriate amount of chromazurol S (Merck) in water. A stock solution of cationic surfactant (0.02 M) was prepared from cetyltrimethylammonium bromide (Merck). All of the solutions were prepared fresh daily. A buffer of (pH=3.0) was prepared by using boric acid, phosphoric acid, acetic acid and appropriate concentration of sodium hydroxide.

Procedure

Several samples containing different concentration ratio of Fe(III) and V(V) were prepared and standard addition of Fe(III) were made. The way each mixture was prepared is as follows: appropriate amount of sample solution containing iron and vanadium, 0.5 ml of 0.005 M of CAS, 1.0 mL of buffer solution pH =3.0 and 1.0 mL of 0.02 M of CTAB were added into 10 mL volumetric flasks and made up to mark with doubly distilled water. After 4 min, about 3mL of the above solutions was transferred to a spectrophotometric cell and the absorbances were measured at 585 and 487 nm and the H-point graphs were obtained. The concentration of iron (C_H) was evaluated from the point of intersection of the two straight lines plotted for each H-point graph. The concentration ranges of Fe(III) and V(V) for construction of HPSAM calibration graph were 0.1-2 and 0.2-2 $\mu\text{g}/\text{mL}$, respectively.

RESULTS AND DISCUSSION

Preliminary study of system

CAS forms colored chelates with many metal ions [26]. Interest in CAS is related to its chelating ability towards metal ions and to the analytical applications based on the micelle enhanced absorption of its metal chelates. The absorption spectra of CAS-Fe(III) and CAS-V(V) complexes are shown in Fig. 1.

Optimization

To take full advantages of the procedure, the reagent concentration and reaction conditions must be optimized. It was found that the complex formation kinetics of V(V) and Fe(III) with CAS in micellar medium is quite fast and measured absorbance for two complexes depend on the concentration of surfactant. In the field of metal ion complex, at a concentration above the Critical Micelle Concentration (CMC) micelles form a ternary complex with advantageous properties, such as hyperchromic and bathochromic displacements that can modify the sensitivity of the method by affecting the interferences and matrix effects. Micellar system are convenient to use because they are optically transparent, readily available and stable [27]. For this purpose many surfactants (CTAB, SDS, Triton X-100 and Triton X-114) have been tested. Among the several surfactants the best results obtained with CTAB. After selection of this surfactant as micellar medium the concentration of it has also been optimized. Best results obtained with 2×10^{-3} M.

The influence of pH values on the spectrum of each complex at a constant concentration was investigated separately. By increasing pH from 2.5 to 6.0, the spectrum of vanadium complex showed that the maximum absorbance occurred at pH=3.5. The spectrum of the iron complex showed a decrease in maximum absorbance at pH >3 so, for achieving higher sensitivity and stability, pH=3.0 was selected as optimum for simultaneous determination of V(V) and Fe(III).

Absorbance of CAS-metal ion-CTAB has been found to increase with increase in concentration of ligand. An excess concentration of ligand has been chosen to ensure quantitative subsequent formation of complexes in the whole the calibration region for two metal ions. The maximal and stable absorbance was gained with 2.5×10^{-4} M CAS.

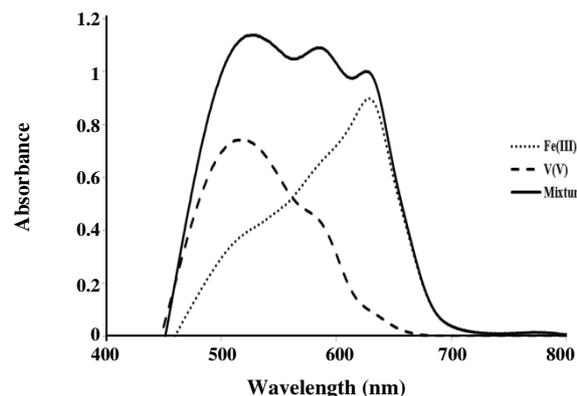


Fig. 1: Absorption spectra of (1) V-CAS-CTAB (2) Fe-CAS-CTAB and (3) their mixture complexes. Condition: 2.5×10^{-4} M CAS, pH=3.0, 2×10^{-3} M CTAB, $1 \mu\text{g} / \text{mL}$ Fe(III) and V(V).

H-Point Standard Addition Method (HPSAM)

HPSAM can be used for an unknown sample containing an analyte X and an interferent Y. The determination of concentration of X by HPSAM under these conditions requires the selection of two wavelengths. To select the appropriate wavelengths, the following principles were applied. At the selected wavelengths, (1) the analyte signals must be linear with concentrations (2) the interferent signal must remain constant with changing the analyte concentration, and (3) the analytical signal obtained from a mixture containing the analyte and the interferent should be equal to the sum of the individual signals of the two species. In addition, the difference in the slopes of the two straight lines measured at two selected wavelengths (λ_1 and λ_2) must be as large as possible, in order to get good accuracy and sensitivity [25]. In the proposed system, Fe(III) and V(V) ions can be considered as the analyte and interferent, respectively. In this case, it is possible to select several pairs of wavelengths with the same absorbance for the vanadium complex. By considering this criteria that the higher the value for slope increment, the smaller the error for the analyte concentration, the best wavelengths pair of 585 and 487 nm were chosen. After appropriate selection of the two wavelengths, known amounts of analyte are successively added to the mixture (analyte and interference) and the resulting absorbances are measured at the two selected wavelengths which can be expressed by:

$$A_{\lambda_1} = b_0 + b + M_{\lambda_1} C_1 \quad (1)$$

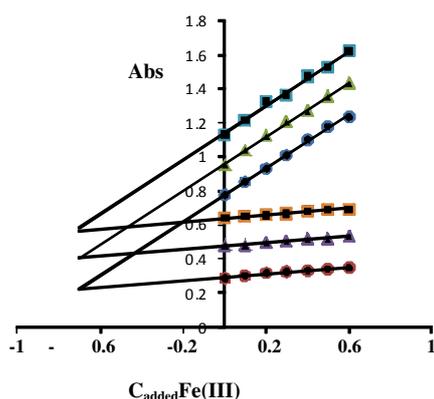


Fig. 2: Plots for HPSAM for fixed V(V) concentration (0.8 µg/mL) and different concentrations of Fe(III): ● 0.5 µg/mL, ▲ 0.8 µg/mL, ■ 1.2 µg/mL.

$$A_{\lambda_2} = A_o + A' + M_{\lambda_2} C_I \quad (2)$$

where A_{λ_1} and A_{λ_2} are the analytical signals measured at λ_1 and λ_2 , respectively; b_o and A_o ($b_o \neq A_o$) the original analytical signal of X at λ_1 and λ_2 , respectively; b and A' the analytical signals of Y at λ_1 and λ_2 , respectively; M_{λ_1} and M_{λ_2} the slopes of the standard addition calibration lines at λ_1 and λ_2 , respectively and C_I is the added X concentration. The two straight (calibration) lines intersect at the so-called H-point ($-C_H, A_H$). Since at H-point, A_{λ_1} is equal to A_{λ_2} and also C_I is equal to $-C_H$, then

$$C_H = \frac{(A_o - b_o) + (A - b)}{M_{\lambda_1} - M_{\lambda_2}} \quad (3)$$

Now, the following conclusion can be made from Eq. (3):

(i) If the interference (Y) is known and the analytical signals corresponding to Y, b (at λ_1) and A (at λ_2) do not change with the additions of analyte, then

$$A_H = b \quad (4)$$

and similarly,

$$A_H = A' \quad (5)$$

At H-point, C_H is independent of the concentration of interferent and A_H is also independent of the analyte concentration. Figs. 2 and 3 show the effect of change in concentration of analyte and interference on the position of H-point. To evaluate the interference concentration from the ordinate value of the H-point (A_H) a calibration graph or the absorbance value of interference standard is needed.

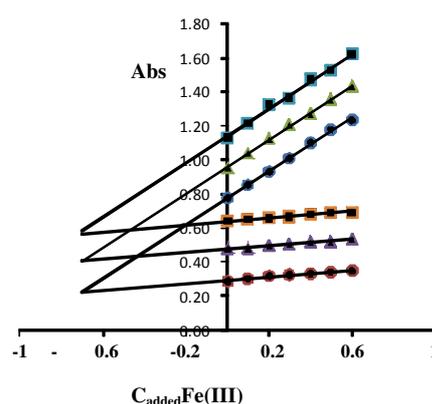


Fig. 3: Plots for HPSAM for a fixed Fe(III) concentration (0.7 µg/mL) and different concentrations of V(V): ● 0.5 µg/mL, ▲ 1 µg/mL, ■ 1.5 µg/mL.

(ii) If the interference, Y, is the unknown, to calculate the analyte concentration, X, in the presence of the unknown interference, the Generalized H-Point Standard Addition Method (GHPSAM) must be applied where it is not necessary to know spectral characteristic of the species accompanying the analyte.

Reproducibility

Under optimum conditions simultaneous determination of Fe(III) and V(V) were made by using HPSAM. To check the reproducibility of the method five replicate experiments for the analyze of Fe(III) and V(V) mixtures were done (Table 1). A good Relative Standard Deviation (RSD) (%) was obtained for Fe(III) and V(V), 2.68 and 3.11%, respectively.

Accuracy

Several synthetic samples with a different concentration ratio of Fe(III) and V(V) were analyzed by using the suggested method. As can be seen from Table 2, the accuracy of the results is satisfactory in all cases, when the concentration ratio of Fe(III) and V(V) vary from 1:20 to 10:1.

Limit of detection

Limit of detection was calculated as $LOD = 3S_{CH}$, where S_{CH} is the standard deviation of several ($n=5$) replicated measurements of zero concentration of analyte with the HPSAM. The corresponding values obtained for Fe(III) and V(V) were 0.022 and 0.040 µg/ml, respectively.

Table 1: Results of five replicate experiments for the analysis of Fe(III) and V(V) in mixture by HPSAM.

A-C equation	R	Taken	($\mu\text{g} / \text{mL}$)	Found	($\mu\text{g} / \text{mL}$)
		Fe(III)	V(V)	Fe(III)	V(V)
$A_{585}=0.7949C+0.8031$	0.997	0.6	0.8	0.62	0.81
$A_{487}=0.0997C+0.3722$	0.9821				
$A_{585}=0.797C+0.8021$	0.9985	0.6	0.8	0.6	0.84
$A_{487}=0.0868C+0.3735$	0.9855				
$A_{585}=0.7884C+0.8058$	0.9993	0.6	0.8	0.62	0.83
$A_{487}=0.09 C +0.3735$	0.9944				
$A_{585}=0.8277C+0.7959$	0.9964	0.6	0.8	0.59	0.78
$A_{487}=0.0975C+0.3622$	0.9798				
$A_{585}=0.7796C+0.8003$	0.9922	0.6	0.8	0.63	0.84
$A_{487}=0.0900C+0.3632$	0.9896				
Mean				0.61	0.82
Standard deviation				0.0164	0.0255
RSD (%)				2.68	3.11

Table 2: Results of several experiments for the analysis of Fe (III)-V (V) mixture in different concentration ratios by HPSAM.

A-C equation	R	Taken	($\mu\text{g} / \text{mL}$)	Found	($\mu\text{g} / \text{mL}$)
		Fe (III)	V (V)	Fe (III)	V (V)
$A_{585}=0.7906C+0.8063$	0.9896	0.1	2	0.1	2.09
$A_{487}=0.0915C+0.7357$	0.9788				
$A_{585}=0.7884 C+ 0.8478$	0.9946	0.4	1.5	0.42	1.48
$A_{487}=0.0902 C+ 0.5535$	0.9925				
$A_{585}=0.7505 C+ 1.0262$	0.9877	0.9	1	0.85	1.07
$A_{487}=0.0993 C+ 0.4689$	0.9792				
$A_{585}=0.7502 C+ 1.549$	0.9955	2	0.2	1.89	0.21
$A_{487}=0.1094 C+ 0.3394$	0.9848				
$A_{587}=0.7895 C+ 0.4697$	0.9989	0.25	0.65	0.26	0.68
$A_{487}=0.0881 C+ 0.2851$	0.983				

Selectivity

The effect of different ions at different concentration on the absorbance of a solution mixture containing $1\mu\text{g} / \text{mL}$ of each metal ion was studied. An ion was considered as interferent, when it caused a variation in the absorbance of the sample greater than $\pm 5\%$. This variation of absorbance was evaluated at two wavelengths, corresponding to the maximum absorption of Fe(III) and V(V)

complexes, to establish the different effects of the interfering ions on Fe(III) and V(V). The results (Table 3) indicate that most of the cations and anions did not interfere.

Application of the method

To evaluate the applicability of proposed method to real samples, biological and environmental complex

Table 3: Influence of foreign ions on the determination of 1.0 µg / mL of Fe(III) and V(V) solution.

Ions	Tolerance ratio
Na ⁺ , K ⁺ , Cl ⁻ , ClO ₃ ⁻ , Br ⁻ , SO ₄ ²⁻ , NO ₃ ⁻ , NH ₄ ⁺ , I ⁻	800
CH ₃ COO ⁻ , SCN ⁻ , CN ⁻ , SO ₃ ²⁻ , HPO ₄ ²⁻ , S ₂ O ₃ ²⁻	400
F ⁻ , PO ₄ ³⁻ , CO ₃ ²⁻	150
Ca ²⁺ , Mg ²⁺ , Al ³⁺ , Zn ²⁺ , Co ²⁺ , Mo ²⁺ , Cr ²⁺ , Pb ²⁺ , Ni ²⁺ , Mn ²⁺ , Sb ²⁺ , Ba ²⁺	60
Oxalate, Citrate, Tartrate, EDTA	20
Ag ⁺ , Sn ²⁺	5 (50) ^a
Bi ³⁺ , Ti ⁴⁺	5

a) After addition of 0.5 mL NaF 0.2 % and 2mL KI 0.1 % for masking of Sn(II) and Ag(I) respectively.

Table 4: Simultaneous determination of Fe(III) and V (V) in real samples using HPSAM.

Samples	A-C equation	R	Spiked (µg / mL)		Found (µg / mL)	
			Fe (III)	V (V)	Fe (III)	V (V)
Plasma	A ₅₈₅ =0.7978C+0.5676	0.9962	0.35	0.7	0.36(103%) ^a	0.73(104%)
	A ₄₈₇ =0.0906C+0.3107	0.9938				
Saliva	A ₅₈₅ =0.7509C+1.0695	0.9976	1	1	0.95(95%)	0.97(97%)
	A ₄₈₇ =0.1016C+0.4721	0.9899				
Tap water	A ₅₈₅ =0.7974C+1.1102	0.9987	0.5	2	0.51(102%)	1.98(99%)
	A ₄₈₇ =0.0952C+0.7497	0.9764				
River water	A ₅₈₅ =0.787C+1.1457	0.9890	0.7	1.5	0.73(104%)	1.58(105%)
	A ₄₈₇ =0.0937C+0.627	0.9910				

a) Values of recovery are given in parenthesis.

Table 5: Comparison of the proposed method with some recent studied procedures.

Methods	pH	Dynamic Range Fe(III), µg / mL	Dynamic Range V(V), µg / mL	References
Extraction-spectrophotometry	2	0.6-7.2	0.6 -8	28
Kinetic spectrophotometry	1.7	0.15-15	0.003-0.7	29
Flow injection	5	0.055-1.1	0.055-1.1	30
Kinetic spectrophotometry	2	6 -12	0.3 -2	31
HPSAM	5	0.2 -15	0.2 -8	11
HPSAM	6.5	0.2 -23	0.5 -8	9
Chemometrics	4	0.02-1	0.055-1	32
HPSAM	3	0.04-2	0.05-2.5	This work

matrix samples were spiked with Fe(III) and V(V) and proposed method was applied for determination of these species. The results are shown in Table 4. The recoveries are close to 100%, indicating that there is no serious interference in such samples and therefore, the proposed method is suitable for simultaneous determination Fe(III) and V(V) in plasma, saliva and water samples.

CONCLUSIONS

An accurate and simple method was proposed for simultaneous determination of Fe(III) and V(V) in real

samples. The suggested method shows application of HPSAM with CAS in micellar medium. The micellar medium of CTAB was used for making a suitable chemical system for analysis. The method also offers good selectivity, accuracy and precision that can be applied for different Fe(III) and V(V) concentration ratio. No extraction step is required because the amount of the colored complex is directly measured. A comparison of the proposed system with some recent studied procedures is given in Table 5. Some of these methods have not suitable pH for Fe(III) or lower limit in dynamic range.

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