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Research Article

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Simultaneous derivative spectrophotometric determination of Chromium (VI) and Vanadium (IV)

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ABSTRACT

A simultaneous second order derivative spectrophotometric method was developed for the determination of chromium (VI) and vanadium (IV) using 2-hydroxy-3-methoxy benzaldehyde thiosemicarbazone (HMBATSC) as a chromophoric reagent. The reagent reacts with chromium (VI) and vanadium (IV) at pH 6.0. Cr (VI) and V (IV) present in the mixture were simultaneously determined without solving the simultaneous equations by measuring the second order derivative amplitudes at 410 nm and 440 nm respectively. The derivative amplitudes obey Beer's law in the range 0.143-3.44 μgml^{-1} of Cr (VI) and 0.102-4.068 μgml^{-1} of V (IV). Large number of foreign ions does not interfere in the present method. The present simultaneous method was used for the determination of micro amounts of chromium (VI) and vanadium (IV) in synthetic mixtures.

Keywords: Cr (VI) and V (IV), Direct Spectrophotometry, 2-hydroxy-3-methoxy benzaldehyde thiosemicarbazone (HMBATSC)

INTRODUCTION

Chromium exists in natural water in two stable oxidation states, Cr (III) and Cr (VI). Among these two predominant forms, Cr (III) is considered to be essential to mammals for the maintenance of glucose, lipid and protein metabolism; where as Cr (VI) is a toxic and carcinogenic form [1-3]. On the other hand, the introduction of chromium salts into soils has been some positive effects due to activation of some biochemical processes [4]. Cr (VI) compounds toxicity derives from its ability to diffuse through cell membrane and oxidize biological molecules [5]. Because of the above reasons the determination of chromium in environmental and biological samples is of great interest.

Vanadium is one of the most important micro-elements in environmental chemistry because of its toxic nature; therefore, the determination of vanadium in environmental samples, especially in fuel oil, foodstuffs, and coal fly ash, is of great importance. Vanadium compounds are toxic to human beings and animals. Vanadium poisoning is an industrial hazard [6]. Vanadium has also been reported as the index element in urban environmental pollution, especially air pollution [7].

Chromium-vanadium steel refers to steel alloys incorporating carbon, manganese, phosphorus, sulfur, silicon, chromium, and vanadium. Some forms can be used as high-speed steel. Chromium and vanadium both make the steel more hardenable. Chromium also helps resist abrasion, oxidation, and corrosion. Chromium and carbon can both improve elasticity.

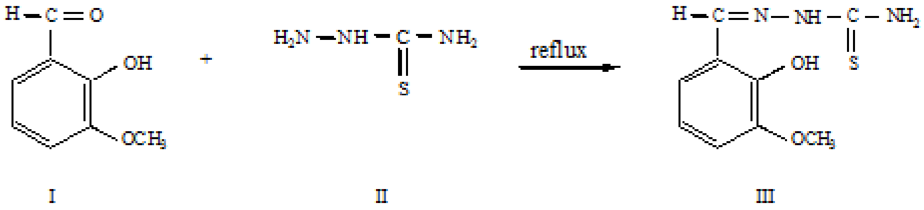
Literature search suggests several techniques such as X-ray fluorescence, atomic absorption spectrometric, atomic fluorescence spectrometric, electrochemical, chromatographic, etc. have been published for the individual determinations of chromium and vanadium in different samples. However, very rare methods are available for the simultaneous determination of Cr (VI) and V (IV). UV-Vis spectrophotometric analytical procedures are most widely used for the simultaneous determination of metals. The obvious reasons being experimental simplicity, rapidity, and the wide applicability of these procedures. However, in many cases traditional spectrophotometric techniques are not suitable for simultaneous determination, because the absorption spectra overlap and are not suitable for simultaneous quantitative analysis. In particular derivative spectrophotometry has been extremely useful analytical technique for the simultaneous determination of binary mixtures. In this work, it was aimed to develop a simple and sensitive determination of chromium (VI) and vanadium (IV) by second order derivative spectrophotometery [8-15].

The present work describes 2-hydroxy-3-methoxybenzaldehyde thiosemicarbazone (HMBATSC) as a chromophoric reagent for a simple, sensitive and selective determination of in chromium (VI) and vanadium (IV) by second order derivative spectrophotometry. The reagent HMBATSC has been used to develop determination of metal ions individually and also simultaneously. The simplicity and low operating costs of spectrophotometric methods made spectrophotometry as an attractive alternative technique for the determination of metal ions in different matrices.

EXPERIMENTAL SECTION

A shimadzu UV-visible spectrophotometer (model UV-160A) fitted with 1cm quartz cells and slit width of 2mm was used to measure absorbance of all analytical species. All spectral measurements were performed using the blank solution as a reference measurement of pH was carried on a Phillips digital pH meter(model LI 613).

The reagent (HMBATSC) is prepared by sah and daniels procedure. 11.25gms of 2-hydroxy-3-methoxy benzaldehyde (I) and 4.55gms of thiosemicarbazide (II) are dissolved in sufficient volume of methanol and the mixture refluxed for 60minutes. The contents are allowed to cool and the product separated by filtration. A crude sample (yield 80%) is obtained ($C_9H_{11}O_2SN_3$). The resultant product is recrystallized twice from hot methanol. Pure light yellowish green crystals of 2-hydroxy-3-methoxy benzaldehyde thiosemicarbazone (III) with melting point 220-225^{0}C are obtained.



A 0.01 M solution of HMBATSC in dimethylformamide (DMF) was employed in the present studies. Stock solution (0.01M) of Chromium (VI) was prepared by dissolving 0.914gms of potassium chromate in 100ml of distilled water and standardized . Required amount of vanadyl sulfate was dissolved in distilled water and made up to the mark in a 100ml volumetric flask to get 0.1M stock solution. Working solutions were prepared by diluting appropriate volume of this stock solution with distilled water.

Procedure

Various known aliquots of solutions containing of 0.143-3.44 µgml^{-1} of Cr (VI) and 0.102-4.068 µgml^{-1} of V (IV). were taken in various 10ml volumetric flasks each containing 5ml of buffer solution of the selected pH. The contents of each flask were made up to the mark with distilled water and the derivative spectra of these solutions were recorded against reagent blank in the wavelength 380-520nm with scan speed fast and with suitable degrees of freedom. Derivative amplitudes were measured at 410nm of Cr (VI) and 440nm of V (IV) against the concentrations of metal ions. The slope and intercept of the plots and Beer's law range were evaluated.

RESULTS AND DISCUSSION

The second order derivative spectra of Cr (VI)-HMBATSC and V (IV)-HMBATSC with different amounts of metal ions are shown in Fig 1. It can be noticed in the figure that [Cr (VI)-HMBATSC] show considerably large derivative amplitude at 410nm and zero amplitude at 440nm and [V(IV)-HMBATSC] complex gives sufficient amplitude at 440nm and zero amplitude at 410nm. Hence Cr (VI) and V (IV) were simultaneously measured by second derivative amplitudes at 410nm and 440nm respectively.

The calibration plots drawn between the amount of chromium with the derivative amplitudes at 410nm and the amount of vanadium with the derivative amplitudes measured at 440nm .The plots indicate that Beer's law is obeyed in the range 0.143-3.44 µgml^{-1} of Cr (VI) and 0.102-4.068 µgml^{-1} of V (IV). The high values of correlation coefficients and closeness of intercepts to zero indicate the good linearity of the calibration plots and conformity to Beer's law. The amounts of chromium and vanadium present in the mixtures were computed from the measured amplitudes with the help of predetermined calibration graph and the results are given in table 1. The analytical characteristics of Cr (VI) and V (IV) are given in table 2.

Table 1: Simultaneous second order derivative spectrophotometric determination of Cr (VI) and V (IV)

Amount taken* (µgml^{-1})		Amount found* (µgml^{-1})		Relative error (%)	
Cr (VI)	V(IV)	Cr (VI)	V(IV)	Cr (VI)	V(IV)
0.574	0.279	0.572	0.276	-0.38	+0.43
0.574	0.558	0.578	0.564	+0.37	-0.37
0.574	0.837	0.578	0.832	+0.21	+0.27
0.574	0.279	0.573	0.278	-0.38	-0.37
1.148	0.279	1.148	0.275	+0.47	+0.76
2.296	0.279	2.292	0.285	+0.05	-0.70

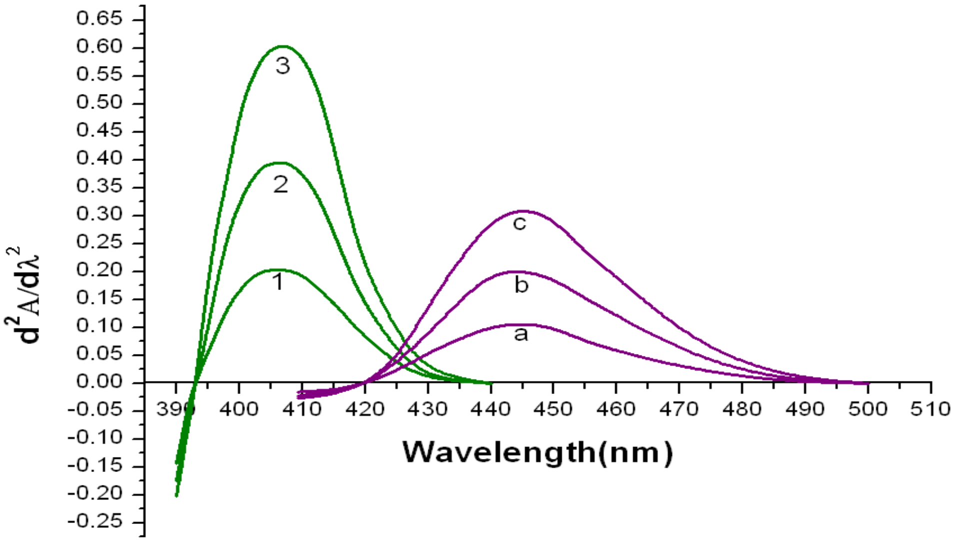


Figure 1: Second Derivative Spectra of Cr (VI) – HMBATSC (Green lines) and V (IV) – HMBATSC (violet lines) at Different Concentrations

a) [Cr (VI) (µg ml^{-1}) : 1) 0.65 2) 1.30 3) 1.95

b) [V (IV) (µg ml^{-1}) : 1) 0.760 2) 1.145 3) 2.231

Applications

The proposed method has been applied for the determination of chromium (VI) and vanadium(IV) in synthetic water samples. The results are in perfect agreement with those obtained by direct atomic-absorption spectrometry (AAS).

Simultaneous Determination of chromium (VI) and Vanadium (IV) in synthetic water Samples

Various synthetic water samples were prepared and the amount of chromium (VI) and Vanadium (IV) present in the sample solutions were determined by applying the general procedure. The results are compared with those obtained with AAS. The results are reported in Table 3.

Table 3: Simultaneous determination of Cr (VI) and V (IV) in synthetic samples

S.No	Metal ions taken		Metal ions found		Present method		Recovery	
	Cr(VI)	V(IV)	Cr(VI)	V(IV)	Cr(VI)	V(IV)	Cr(VI)	V(IV)
Sample 1	3.0	2.00	2.97	1.98	2.94	1.86	95.3	96.3
Sample 2	4.0	2.50	3.98	2.47	3.92	2.41	96.5	97.5
Sample 3	5.0	3.00	4.96	2.98	2.85	2.87	97.8	98.2

Table 2: Analytical characteristics of Cr (VI) and V(IV)

Parameter	Cr(VI)	V(IV)
Zero cross wavelength(nm)	440	410
Analytical wavelength measured	410	440
Beer's law range (µg ml^{-1})	0.143-3.44	0.102-4.068
Angular coefficient	0.3025	0.3402
Y-intercept	0.0011	0.0065
Correlation coefficient (r)	0.9996	0.9998
Standard deviation (s)	0.0124	0.0054

CONCLUSION

The present method is simple, sensitive, and highly selective for the simultaneous determination of Cr (VI) and V (IV) in admixtures without separation and without solving simultaneous equations. The developed method was applied for determination of Cr (VI) and V (IV) in synthetic water samples

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