2-Hydroxy-3-Methoxy Benzaldehyde Thiosemicarbazone (HMBATSC) as a Spectrophotometric Reagent for the Simultaneous Determination of Indium (III) and Vanadium (IV) in Synthetic Mixtures

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Abstract

A simple and new simultaneous second order derivative spectrophotometric method was proposed for the analysis of two-component system containing Indium (III) and Vanadium (IV) without separation by using 2-hydroxy-3-methoxy benzaldehyde thiosemicarbazone (HMBATSC) as a new spectrophotometric reagent. The reagent reacts with Indium (III) and Vanadium(IV) forming intense green and blue colored solution at pH 6.0. Indium (III) and Vanadium (IV) present in the mixture were simultaneously determined without solving the simultaneous equations by measuring the second order derivative amplitudes at 420nm and 445nm respectively. The derivative amplitudes obey Beer's law in the range $0.131 – 37.22$ μg mL^{-1} of In(III) and $0.102 -4.068$ μg mL^{-1} of Vanadium (IV). A large number of foreign ions do not interfere in the present method. The present simultaneous method was used for the determination of micro amounts of Indium (III) and Vanadium (IV) in synthetic mixtures.

Introduction

The rapid developments in electronic and particularly in microcomputer technologies in the last ten years have led to a parallel growth of interest in the use of UV-visible derivative spectrophotometry as an analytical tool for;

1. The enhancement of the resolution of overlapping peaks, and
2. The elimination or reduction of background or matrix absorption.

The derivatization of spectra can lead to more accurate determination of the wavelengths of broad peaks, peak maxima which appear only as shoulders, as well as the isolation of small peaks from interfering large background absorption. In derivatizing spectral data, the process taking place is that of differentiating a curve, or more correctly, the mathematical representation of that curve, i.e., simply determining slope or gradient of the whole absorption envelop.

For quantitative analytical purposes, only the amplitudes versus concentrations are measured and here spectral distortion is an acceptable sacrifice as long as the impact of s/n (signal/noise) on the quantitative measurement precision is kept to a minimum. The quantitative analysis can be divided into two categories, i.e., single or multi-component analysis of overlapping absorption peaks.

The quantitative analysis of either one or several compounds depends on each compound obeying Beer's law in the zero order spectrum at a specified wavelength which is given as

$$A = \varepsilon.l.c$$

Where, $A = \log (I_o/I) =$ absorbance
(I_o and I are intensities of incident and transmitted radiation respectively)
$\varepsilon =$ the molar absorptivity
$c =$ the molar concentration
$l =$ the cell width

When 'ε' and 'l' are made constant, the analyte concentration is linearly related to the absorbance at the specified wavelength. Since, the derivative amplitude Dn is the derivatized component of absorbance by nth time, the derivative amplitude of nth derivative peak at a given wavelength is given by

$$D^n = \frac{d^n A}{d\lambda^n} = \frac{d^n \varepsilon.l.c}{d\lambda^n}$$

Similarly, the analyte concentration is linearly related to the amplitude of the nth derivative peak at the specified wavelength.

Due to its increased selectivity and sensitivity, compared to classical spectrophotometry, derivative spectrophotometry is widely applied in inorganic chemistry for the simultaneous determination of trace elements of similar chemical properties present in mixtures at different concentration levels. For this purpose, the first and second order derivatives are usually used, although in some cases higher order derivatives provide more reliable results. Most of the derivative spectrophotometric methods aimed at the simultaneous determination of inorganic solutes came to existence after 1990. The zero-crossing derivative spectral method is the most common and convenient procedure for the simultaneous determination of binary mixtures with their overlapping spectra (Figure 1). By a combination of zero-crossing derivative technique and derivative ratio spectra, we can resolve the ternary mixtures by solving simultaneous equations.
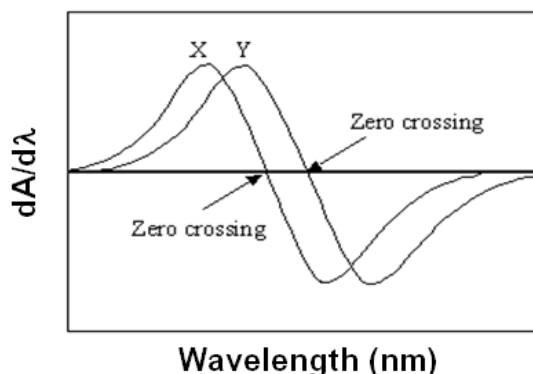
We are now reporting a simple simultaneous derivative spectrophotometric method for the analysis of binary mixture, In(III) and V(IV) without separation and without solving simultaneous equations. Indium and Vanadium are important alloying materials. They coexist in some fusible alloys, solids and in some lubricated films. Hence, their determination in these samples forms an important aspect of analytical chemistry. An attempt has been made in the present thesis to develop a simple and highly selective second order derivative spectrophotometric method for the simultaneous determination of indium and vanadium. Both In(III) and V(IV) react with 2-hydroxy-3-methoxy benzalde-hyde thiosemicarbazone forming an intense green and blue colored solutions at pH 6.0. Their second order derivative spectra showed highly resolved derivative amplitudes at suitable wavelengths with specific zero cross points which allows their simultaneous determination. The method has been applied for the simultaneous determination of indium and vanadium in binary synthetic mixtures.

Experimental

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

Chemicals and Solutions
Preparation of 2-Hydroxy-3-methoxy benzalde-hyde thiosemicarbazone (HMBATSC)
The reagent (HMBATSC) is prepared by the Sah and Daniels[1] procedure. 11.25g of 2-hydroxy-3-methoxy benzaldehyde (I) and 4,55g of thiosemicarbazide (II) are dissolved in sufficient volume of methanol and the mixture of 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 recrystallised twice from hot methanol. Pure light yellowish green crystals of 2-hydroxy-3-methoxy benzaldehyde thio-semicarbazone (HMBATSC) (III) (m.p.220-220°C) are obtained.
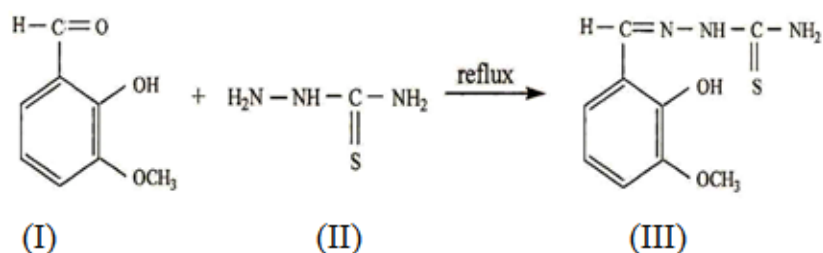
A 0.01M solution of HMBATSC in dimethyl formamide (DMF) was employed in the present studies.

Stock solution (0.01M) of Indium(III) solution was prepared by dissolving 0.5178g of $In_2(SO_4)_3$. H_2O (Himedia) in 2ml of 2M H_2SO_4 and diluting to 100ml with distilled water.

Stock solution (0.01M) of Vanadium(IV) solution was prepared by dissolving 0.253G\g of $VOSO_4.5H_2O$ (Moly.Chem) in 100ml of distilled water.

Buffer solutions were prepared by mixing 0.2M Sodium acetate and 0.2M acetic acid.

The working solutions were prepared daily by diluting the stock solution to an appropriate volume.

Procedure

Different aliquots of solutions containing 0.131-3.722 μg of In(III) or 0.102-4.068 μg of V(IV) were transferred into a series of 10ml standard flasks. 5ml of buffer solution (pH 6.0) and 3ml of HMBATSC ($1x10^{-2}$) were added to each of these flasks and diluted to the mark with distilled water. Second order derivative spectra were recorded for the two sets of solutions in the wavelength region 350-600nm against reagent blank. Calibration plots were prepared by plotting the derivative amplitudes measured at 420nm against the amount of indium and the amplitudes measured at 445nm against the amount of vanadium. In each of a set of different 10ml volumetric flasks, 5ml of buffer solutions (pH 6.0), and 1ml of HMBATSC ($1X10^{-2}M$) were taken and various values of chromium (VI) ($1X10^{-3}M$) solution were added. The resultant solutions were made up to the mark with distilled water. The absorbance was measured at 385nm against the reagent blank. The calibration plot was prepared by plotting the absorbance against the amount of chromium (VI).

Result & Discussions

The second order derivative spectra of In(III)-HMBATSC and V(IV)-HMBATSC species with different amounts of metal ions are shown in figure 2. It can be noticed in the figure that at 445nm where the In(III) complex is showing zero amplitude there is a proportional increase in the derivative amplitude of V(IV) complex species. Similarly at 420nm where vanadium species is showing zero amplitude, the indium species is exhibiting a proportional increase in derivative amplitude with the amount of In(III). Hence, the wavelengths 420 and 445nm were chosen for the determination

of indium and vanadium in a given mixture simultaneously by measuring the derivative amplitudes at 420nm and 445nm respectively.

The calibration plots drawn between the amount of indium and derivative amplitudes measured at 420nm and the amount of vanadium and the derivative amplitudes measured at 445nm are shown in figure 3 and 4 respectively. The plots indicate that Beer's law is obeyed in the range 0.131-3.722µg mL^{-1} of Indium and 0.102–4.068µg mL^{-1} of vanadium. The high values of correlation coefficients and closeness of intercepts to zero indicates the good linearity of the calibration plots and conformity to Beer's law.
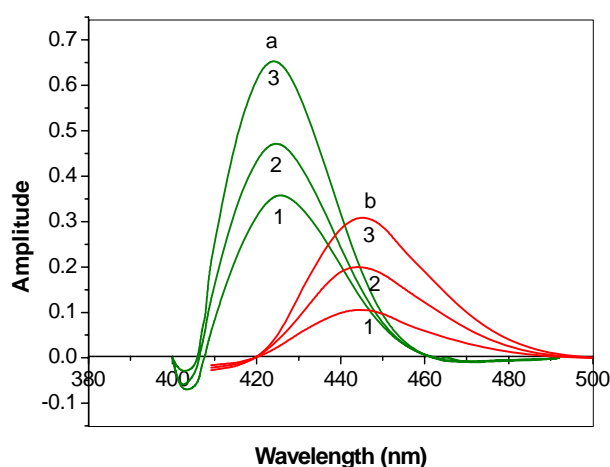

Figure 2: Second order derivative spectra of (a) In(III)- HMBATSC at different concentrations (b) V(IV) – HMBATSC. [In(III)] (µg mL^{-1}) : 1) 0.574; 2) 1.148; 3) 2.296 [V(IV)] (µg mL^{-1}) : 1) 0.760; 2) 1.145; 3) 2.231.
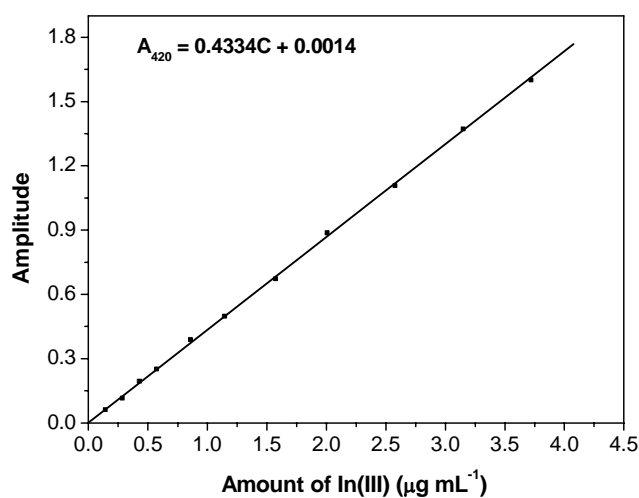

Figure 3: Calibration plot of [In(III)-HMBATSC] [HMBATSC] = 1.25×10^{-2}; pH= 6.0
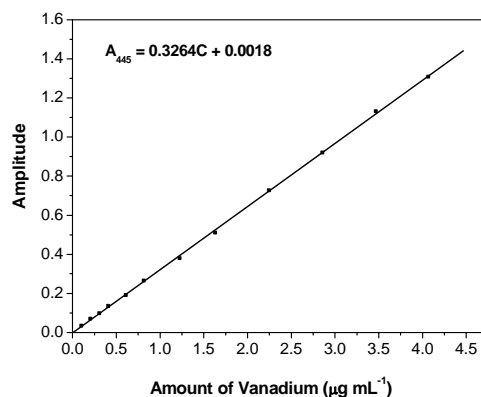
Figure 4: Calibration plot of [V(IV)-HMBATSC] [HMBATSC] = 1×10^{-2}; pH= 6.0.

The validity of the proposed simultaneous method was tested by determining indium and vanadium in various synthetic binary mixtures. The result obtained are shown in table 1. The recovery percentage and relative error values indicate the applicability of the proposed simultaneous derivative method for the determination of In(III) and V(IV) in binary mixture.

Application

The proposed simultaneous derivative spectro-photometric method was applied for the determination of In(III) and V(IV) in synthetic mixtures containing the other associated metal ions. The synthetic mixture were prepared as per the recommendations of Agrawal et al.,[2]. The indium and vanadium contents were determined by the proposed simultaneous methods and the results obtained are presented in table 2.

Table 1: Determination of Indium and Vanadium in various synthetic mixtures.

Amount Taken µg mL^{-1}		Amount found* µg mL^{-1}		Recovery (%)		Relative error (%)	
In(III)	V(IV)	In(III)	V(IV)	In(III)	V(IV)	In(III)	V(IV)
0.112	0.760	0.113	0.752	99.12	101.06	-0.90	+1.05
0.235	0.760	0.232	0.770	101.30	98.70	+1.30	-1.32
0.570	0.760	0.576	0.756	98.96	100.53	-1.10	+0.53
0.795	0.760	0.793	0.759	100.25	100.13	0.25	+0.13
1.145	0.760.	1.143	0.762	100.17	99.73	+0.80	-0.30
0.230	0.131	0.229	0.129	100.44	101.55	+0.43	+1.53
0.230	0.382	0.231	0.380	100.44	100.52	-0.43	+0.52
0.230	0.630	0.227	0.627	99.57	100.47	+1.30	+0.50
0.230	1.141	0.228	1.139	100.88	100.17	+0.90	+0.17
0.230	1.525	0.231	1.510	100.00	100.39	-0.43	+0.98

* Average of five determinations.

Table 2: Determination of In(III) and V(IV) in synthetic mixtures.

Composition	Amount taken µg mL^{-1}		Amount found* µg mL^{-1}		Relative error (%)	
	In(III)	V(IV)	In(III)	V(IV)	In(III)	V(IV)
Nb(V) 200; Zr(IV) 200; Ta(V) 100; Sn(IV) 200; In(III) 30 ; V(IV) 40	30	40	30.21	39.90	-0.7	+0.25

* Average of five determinations

The relative error values associated with the determinations indicate the suitably of the proposed derivative method for the analysis of natural complex materials containing indium and vanadium.

The analytical results of both In (III) and V(IV) determinations are compared and prescribed in Table 3.

Table 3: Comparison of analytical data of In(III) and V(IV).

Parameter	In(III)	V(IV)
Zero wave length (nm)	445	420
Analytical wave length (nm) measured	420	445
Beer's law range (µg mL^{-1})	0.131- 3.722	0.102- 4.068
Angular coefficient (m)	0.4334	0.3264
Y-intercept (b)	0.0014	0.0018
Correlation coefficient (r)	0.9997	0.9995
Standard deviation (s)	0.0034	0.0084

References

[1] Sah, P.T; Daniels, T.C. Rev. Trav.KIM; 1950, 69, 1945.

[2] Agrawal, Y.K. and Bhatt, V.J., Analyst, 1986, 111, 57.