

Spectrophotometric Determination of Binary Mixtures Containing Vanadium (v), Iron (iii), Cobalt (ii), and Copper (ii),

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Summary A spectrophotometric method for determination of iron (III), cobalt (II), copper (II) and vanadium (V) using 6-formyl-7-hydroxy-5-methoxy-2-methyl-8-(2-hydroxy-phenyl-azo) chromone has been studied, the method has been used for the determination of these ions in their binary mixtures. The optimum conditions for the color formation and the stoichiometry of the reaction leading to chelation have been studied. The values of molar absorptivity ϵ ($\text{Lmol}^{-1}\text{cm}^{-1}$), specific absorptivity a ($\text{Lg}^{-1}\text{cm}^{-1}$) and Sandell sensitivity S ($\mu\text{g cm}^{-2}$) are determined. The proposed method has been applied for colorimetric determination of iron (III), cobalt (II) and copper (II) in waste water samples. The mixtures have been analyzed using zero crossing measurements technique.

Introduction

Vanadium (V), Iron (III), cobalt (II), and copper (II) are metal ions which are possible to appear together in many real water samples. Several techniques have been reported and evaluated for the simultaneous determination of these metal ions in different media; some of these methods comprise X-ray spectrometry⁽¹⁻²⁾, atomic spectrometry⁽³⁾, mass spectro-metry⁽⁴⁾, inductively coupled plasma atomic emission spectrometry⁽⁵⁾, polarography⁽⁶⁾, chromatography⁽⁷⁾ and spectrophotometry⁽⁸⁻¹⁵⁾. The spectrophotometric methods are the most commonly used techniques and continue to enjoy wide popularity. The common availability of the instruments, the simplicity of procedures, speed, precision and accuracy of the technique; still make spectrophotometric methods attractive. Also spectrophotometric methods of analysis are more economic and simpler, compared to the other methods such as chromatography and electrophoresis. The main problem of spectrophotometric multicomponent analysis is overlap of the absorption spectra during the simultaneous determination of two or more active compounds in the mixtures without preliminary separation. Therefore, the simultaneous determination of multiple components by the use of normal UV-Vis spectrophotometric techniques is difficult. Derivative techniques in the ultraviolet-visible region are very useful when overlap or interference exists. They offer a powerful tool for quantitative analyses of binary mixtures. Numerous chromogenic reagents like cetylpyridinium chloride⁽¹⁶⁾, 1-(2-pyridylazo)-2-naphthol⁽¹⁷⁾, 1-(2-thiazolylazo)-2-naphthol⁽¹⁸⁾,

2-(benzothiazolylazo)-7-(4-methylphenylazo) chromotropic acid⁽¹⁹⁾, 3-(4-phenyl-2-pyridinyl)-1,2,4-triazine⁽²⁰⁾ and Ponceau S (2,7-naphthalene-disulfonic acid, 3-hydroxy-4-[[2-sulfo-4-(4-sulfophenyl)-azo] phenyl]azo] tetra sodium salt⁽²¹⁾ have been reported for the determination of the cited metal ions. The chromone azo dyes complexes with transition metal ions were prepared⁽²²⁾. Nevertheless their application as analytical reagents for the determination of the cited metal ions have not been studied before.

Experimental

Apparatus

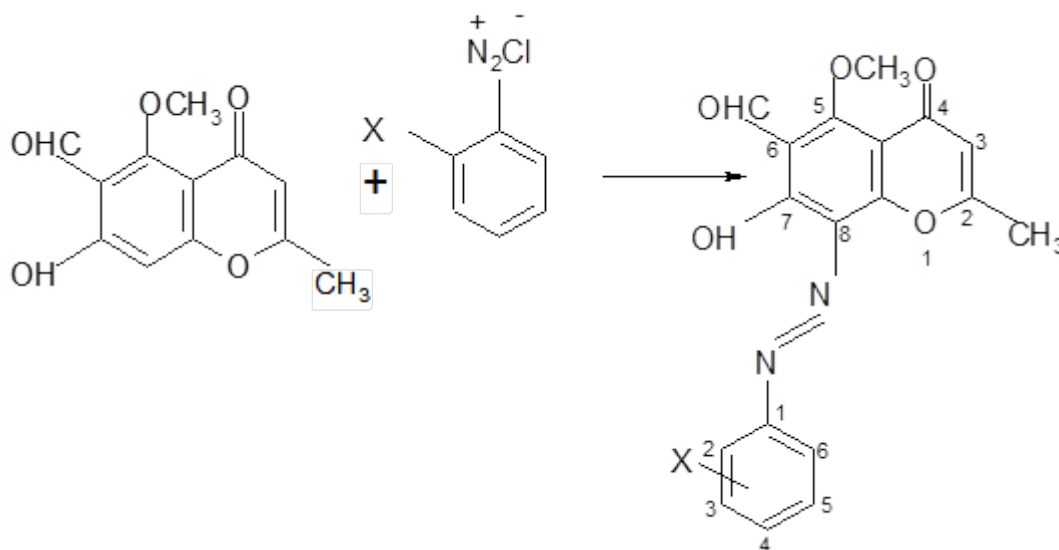
Ordinary and derivative spectra were recorded with UV/Vis –NIR 3101 PT Shimadzu spectrophotometer (optical path: 10 mm, scan speed 60 nm/min, wavelength interval 0.5 nm) equipped with a computer for storage and manipulation of spectrophotometric data. The absorption spectra of the reference and analyte solutions were determined using 1-cm quartz cells over the range 400 - 800 nm. pH measurements were made using Jenway pH-meter.

Reagents

All reagents used were of analytical grad. Bidistilled water was used for all the prepared solutions. Iron nitrate, cobalt perchlorate, copper acetate and vanadium ammonium sulfate standard stock solution were prepared and standardized⁽²³⁾. The organic solvents used included, acetone, dioxane, absolute ethanol, acetonitrile, dimethylsulfoxide (DMSO) and dimethylformamide (DMF). All these organic solvents were either purified with recommended methods⁽²⁴⁾ or obtained in spectroscopic grade solvents from BDH. A series of buffer solutions covering the range of pH values 2.0 to 12.0 were prepared as recommended by Thiel, Schulz and Coch⁽²⁵⁾.

Preparation of Chromone Azo Dye

Chromone azo dye was prepared by dissolving 0.01 mole of o-aminophenol in 10 mL of (1:1) HCl and a solution of about 0.75 g of sodium nitrite was added to the above solution at 0 °C with continuous stirring. The diazonium salt solution was added to 0.01 mole of chromone which prepared previously⁽²²⁾ (2.34 g in 100 mL of double distilled water) in presence of 4-5 grams of sodium hydroxide cooled to 5 °C. The formed colored product was kept over-night in a refrigerator. The product was acidified with dilute hydrochloric acid (1:1) to a pH 2-4, then filtered and washed with double distilled water several times, until the filtrate becomes free from chloride ions. The scheme of the chromone azo dye preparation is given below:



Scheme 1: Chromone azo dye preparation

X= o-OH

Results and discussion

To establish the optimal conditions for complexes formation, the different parameters such as effect of pH, selection of suitable wavelength, the sequence of addition, effect of solvents, effect of time, effect of temperature, effect of foreign ions and effect of surfactants or protective colloids are studied. Also, stoichiometry of the formed complexes was determined using spectrophotometric technique. The reaction between the metal ions and the chromone azo dye is utilized for the determination of the metal ions. The most suitable conditions for the formation of Cu(II)-I, Co(II)-I, Fe(III)-I and V(V)-I complexes were determined by mixing 1 mL of 10^{-3} M metal ion solution with 2 mL of 10^{-3} M ligand solution and completing with the desired buffer up to the mark of 10 mL measuring flask. The absorbances of these solutions were measured at the respective λ_{\max} of the complexes. A first derivative spectrophotometric method for simultaneous determination of binary mixtures containing a pair of: vanadium, iron, cobalt, and copper, ions using chromone azo dyes is presented. The proposed method is applied for spectrophotometric determination of these metal ions in waste water samples.

Determination of the ionization constant values of the dye

The ionization constants of the azo dye under investigation were determined by recording the absorption spectra of 2.0×10^{-4} M of the chromone azo dye in 50% (v/v) ethyl alcohol-water

mixture, and of varying pH values using Thiel buffers. Since the cited ligand contains two hydroxyl groups, the absorbance-pH curve illustrates two segmental shapes. The first one lies in the pH range 3-6 and the second one in the pH range 6.5-8, pH values higher than 8.0 are not recommended. This may be due to that the strong alkaline medium affect the stability of the studied dye.

Optimum conditions for complexes formation

The most suitable pH values for formation of the complexes were determined by scanning the absorption spectra of 1×10^{-4} M chelate solutions at different pH values using the same amount of the ligand and buffer as blank. The maximum absorbances of the formed complexes and suitable pH are summarized in table (1). To study the effect of sequence of addition,

Table (1): Molar absorptivity (ϵ), specific absorptivity (a), Sandell sensitivity (S).

Complex	Obeance of Beers law up to ($\mu\text{g/mL}$)	Ringbom rang ($\mu\text{g/mL}$)	Detection limit ($\mu\text{g/mL}$)	$\epsilon \times 10^3$	a	S	s	r	b
Cu – I	3.17	1.2-3.23	0.1-3.17	11.17	0.1758	0.00057	0.028	0.9994	0.0018
Co – I	2.94	1.07-2.95	0.06-2.9	6.34	0.1075	0.00093	0.036	0.9995	0.0052
Fe – I	3.06	1.35-2.57	0.06-3.1	6.09	0.1095	0.00091	0.032	0.9991	0.0009
V – I	2.60	1.02-2.08	0.15-2.6	4.67	0.0917	0.00109	0.037	0.9997	0.0027

a: specific absorptivity ($\text{mL g}^{-1} \text{cm}^{-1}$).

S: Sandell index ($\mu\text{g cm}^{-2}$).

s: standard deviation.

r: correlation coefficient.

b: intercept.

different sequences were tried; the sequence ligand-Metal-solvent-buffer is the best one for the formation of the complexes. All complexes are formed instantaneously, and they are stable for more than 24 hours, except Fe(III)-I is stable for 3 hours only. The effect of some organic solvents on the absorbance of the metal-ligand chelates was investigated; the studies reveal that 50% (v/v) ethyl alcohol-water mixture is the best solvent mixture. The effect of temperature on the color of the metal-ligand chelates was studied by measuring the absorbances of the complexes at different temperatures (from room temperature to 50°C). Raising the temperature from room temperature to 50°C had no effect on the color development of the complexes; however, raising the temperature more than 50°C leads to

decreasing of absorbance. To study foreign ions effect, the absorbance of solutions containing 1 mL of 10^{-3} mol/L V(V), Fe(III), Co(II), and Cu(II) together with 10 folds of variety of cations and anions followed by 2 mL 10^{-3} mol/L ligand solution and the buffer of the recommended pH up to the mark of 10 mL measuring flasks was measured. The data lead to the conclusion that up to 10 folds of Na^+ , K^+ , Hg^{2+} , Ca^{2+} , Al^{3+} , Ba^{2+} , Mn^{2+} , Pb^{2+} , Ni^{2+} , Br^- , F^- , I^- , Cl^- , nitrite, nitrate, sulfate, acetate, and phosphate don't interfere in the determination of Fe(III) and V(V), while Cu(II), Co(II), cyanide ions, and EDTA seriously interfere.

Molecular structure of the metal chelates

The stoichiometry of the chelates of metal ions with the investigated azo dye was determined by the aid of the molar ratio and continuous variation methods⁽²⁶⁾. The results revealed that dyes form with the above mentioned metal ions 1:1 as well as 1:2 (M:L). The stability constants of the metal chelates were determined by applying Harvey and Manning equation⁽²⁷⁾. It was found that that $\log \beta_1$ values varied from 4.18 to 4.99 and $\log \beta_2$ values varied from 8.37 to 9.06. So the formed complexes are fairly stable as indicated by the high values of the overall stability constants.

Method validation

The obeyance of V(V)-I, Fe(III)-I Co(II)-I, and Cu-I complexes to Beer's law were investigated in order to use such complexes for the spectrophotometric determination of these metal ions. Beer's law is satisfactorily obeyed up to 2.60, 3.06, 2.94, and 3.17 $\mu\text{g/mL}$ of the metal ions for V-I, Fe-I, Co-I, and Cu-I, complexes, respectively. Table (1) lists the molar absorptivity values (ϵ) expressed in $\text{L mol}^{-1}\text{cm}^{-1}$: such values indicate high sensitivity of the suggested methods. For accurate colorimetric analysis, Ringbom plots have been drawn by plotting log metal ion concentration in $\mu\text{g/mL}$ against percent transmittance and the linear portion of the S-shaped curve gives the accurate range of analysis. The reproducibility of the method was checked by analyzing a series of ten solutions of Fe(III) V(V), Co(II), and Cu(II), with concentrations of 1.95 2.03, 2.051, and 2.22, $\mu\text{g/mL}$, respectively. The relative standard deviation values were represented in Table (1).

Determination of Fe(III), Co(II), and Cu(II) in waste water

The applicability of method for the determination of cobalt, copper and iron in real water samples has been evaluated. Industrial waste water samples from different factories were collected. These samples were diluted to the level of the natural water and used as stock solutions for the determination of above mentioned metal ions using the reagent and applying the previously described procedures. The results of such analyses are listed in Table (2). It

was found that, the results obtained by the proposed methods are in good agreement with that obtained by the official ones. In conclusion, the proposed methods are simple, rapid, accurate selective and applicable for instantaneous determination of the studied metal ions in waste water samples. Statistical treatments of the data for the determination of copper, iron and cobalt ions in some water samples were studied. Each set of analytical results should be accompanied by an indication of the precision of the analysis. The t- test ⁽²⁸⁾ has been applied to investigate the agreement between mean values obtained from the determination of the studied metal ions in waste water samples. The F- test ⁽²⁸⁾ indicates if there is a difference between two methods based on their standard deviations. The standard deviation values for the determination of copper, iron and cobalt using the cited reagent were listed in Table (2). The performance of the proposed method was assessed by calculation of the t- and F-values compared with the reference methods which developed by Ruan⁽²⁹⁾. The calculated t- values and F- values at 95% confidence limits and four degrees of freedom are listed in Table (2). The obtained results reveal that, all the calculated t-values are less than the tabulated one (3.18), which indicates that there is no significance difference between the results of the two methods. Also, all the calculated F-values are less than the tabulated one (9.28). We can conclude that there is no significant difference in the precision of the two methods, and that the standard deviation results from random error only.

Table (2): Statistical treatment of the data obtained for determination of Fe(III), Co(II) and Cu(III) in waste water samples from steel factory and alloys factory .

Metal ion	Conc. By proposed method (µg/mL)	R.S.D %	t-test	F-test
Fe(III) from steel factory	18.8*	5.2	2.87	1.16
Fe(III) from alloys factory	4.1*	4.9	2.35	1.09
Cu(II) from steel factory	21.4*	2.3	1.91	1.65
Cu(II) from alloys factory	17.63*	2.9	1.06	1.8
Co(II) from steel factory	1.76*	5.1	2.23	2.7
Co(II) from alloys factory	1.85*	3.5	1.30	1.27

*The mean value of concentration in five waste water samples.

Analysis of binary mixtures of metal ions using first derivative spectrophotometry

This method is based on the measurements of the absolute value of the derivative spectrum of the mixture at a wavelength value where the intensity of one component of the mixture goes to zero (Figs. 1A, 2A). At this wavelength, the intensity is directly proportional to the other Binary mixtures containing Co(II) and Cu(II); Fe(III) and Co(II); Fe(III) and Cu(II); V(V) and Cu(II); or V(V) and Fe(III) were prepared. In each binary mixture the second component has constant concentration of 1×10^{-4} mol/L while the other one was regularly varied. The first derivative spectra were recorded using UV/Vis-NIR 3101 PT Shimadzu spectrophotometer. The concentration of each metal ion in the mixtures was determined by constructing a calibration graph between the concentration of the metal ion as abscissa and $dA/d\lambda$ as ordinate at the determined zero crossing point. A critical evaluation of the proposed methods is obtained by statistical analysis of the experimental results, given in Table (3). The high values of correlation coefficients indicate the good linearity of all calibration graphs and the validity of Beer's law to first – derivative measurements (Figs. 1B, 2B). The validity of the proposed methods was determined in several synthetic binary mixtures containing the metal ions under investigation. The results are shown in Table (4). Satisfactory results were obtained for the recovery of each metal ion in the mixtures indicating that the proposed methods are rapid, sensitive, selective and effective for the simultaneous determination of metal ions.

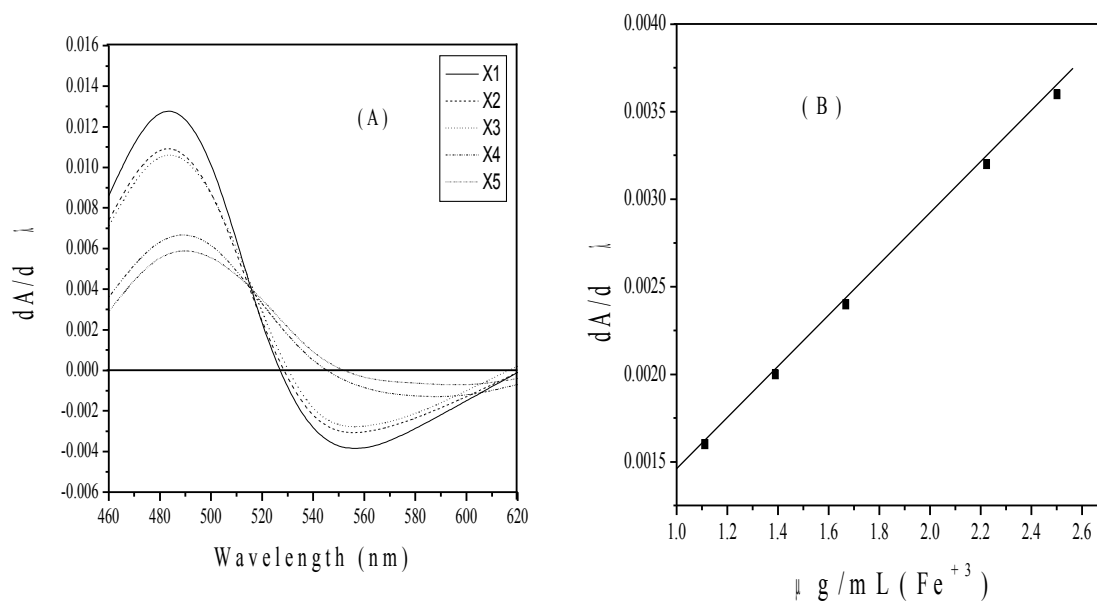


Fig. (1). First derivative absorption spectra of binary mixture containing constant concentration of Cu(II) and variable concentration of Fe(III) (A) and calibration curve of Fe(III) in presence of Cu(II) at 520 (B).

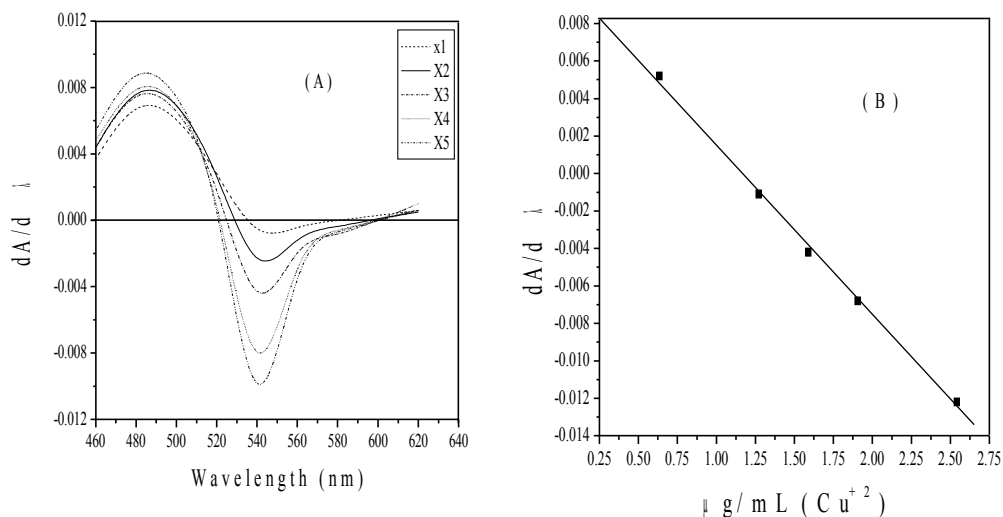


Fig (2). First derivative absorption spectra of binary mixture containing constant concentration of Fe(III) and variable concentration of Cu(II) (A) and calibration curve of Cu(II) in presence of Fe(III) at 550 nm (B).

Table (3): Zero crossing value (nm), slope (a), standard deviation (s), intercept (b), correlation coefficient (r) and range for simultaneous determination of metal ions .

Mixture	zero crossing value (nm)	Beers law up to $\mu\text{g/mL}$	A	s	b	r
Co + x Cu	530	2.23	5.39×10^{-5}	0.017	-0.0067	0.9998
Cu + x Co	520	2.37	0.00353	0.031	0.0009	0.9986
Co + x Fe	530	2.78	0.0030	0.025	0.0008	0.9999
Fe + x Co	530	2.65	0.0053	0.028	-0.0004	0.9993
Cu + x Fe	520	2.50	0.0076	0.029	0.0001	0.9999
Fe+ x Cu	550	2.53	-0.0602	0.019	0.01122	0.9990
Fe + x V	550	2.04	0.00755	0.032	0.0001	0.9991
V + x Fe	530	2.23	0.0029	0.024	0.0011	0.9997
Cu + x V	520	2.56	0.0011	0.034	0.0019	0.9999
V + x Cu	530	3.19	-0.2321	0.016	0.06374	0.9999

Table (4): First derivative spectrophotometric determination of binary mixtures containing Co(II), Cu(II), Fe(III) and V(V) using I reagent.

Mixtures	Metal ion	Taken conc. $\mu\text{g/mL}$	Found* conc. $\mu\text{g/mL}$	Recovery %	R.S.D. %

Cu + Co	Cu	1.27	1.21	94.8	1.9
	Co	2.63	2.51	95.2	2.9
Fe + Co	Fe	1.95	2.04	95.4	2.6
	Co	2.63	2.77	105.3	3.1
Fe + Cu	Fe	1.95	2.05	105.3	2.8
	Cu	2.52	2.67	106.3	1.7
Fe + V	Fe	1.11	1.19	100.7	2.5
	V	2.04	2.08	101.9	2.8
Cu + V	Cu	0.58	0.5813	101.6	1.6
	V	1.02	1.072	105.2	1.9

* Mean value of three determination (n=3).

R.S.D.: relative standard deviation.

Conclusion

One of the most important aspects of the present work is the simple and rapid determination of copper, cobalt and iron by chelation of the cited metal ions and chromone azo dye I in normal as well as in derivative modes. The sensitivity and selectivity of method was considerably improved by using derivative spectrophotometry. The method does not require tedious and expensive process of solvent extraction, hence avoiding the use of toxic and carcinogenic organic solvents. The method is not only sensitive but also economical (since it is cheaper than ICP- ASE and ASS and does not require any gas or maintenance) and less complicated. The method has been successfully applied for the determination of copper, cobalt and iron in real water samples.

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