

SIMULTANEOUS DETERMINATION OF COBALT AND IRON USING FIRST-DERIVATIVE SPECTROPHOTOMETRIC AND H-POINT STANDARD ADDITION METHODS IN MICELLAR MEDIA

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Abstract. First-derivative spectrophotometric method based on zero-crossing over isodifferential technique and H-point standard addition method (HPSAM) are developed for simultaneous determination of cobalt (II) and iron (III) ions in micellar media. The 4-(2-pyridylazo) resorcinol (PAR) is used as chromogenic reagent for complexes formation of cobalt (II) and iron (III) ions. The measurements were carried out using cetyltrimethylammonium bromide as a surfactant, in buffered solution at pH 6 and temperature of 25° C. The linearity obtained in the range of 0.10-2.50 µg ml⁻¹ of Co²⁺ and 0.50-6.00 µg ml⁻¹ of Fe³⁺ in the presence of each other by using first-derivative spectrophotometric method. The results of applying H-point standard addition method show that Fe(III) and Co(II) ions can be determined simultaneously with concentration ratio of 30:1 and 1:8 of iron to cobalt. The proposed procedures have been applied successfully for the simultaneous determination of cobalt and iron in synthetic binary mixtures and real samples.

Keywords: Derivative spectrophotometry, H-point standard addition method, Cobalt, Iron, 4-(2-Pyridylazo) resorcinol, Cetyltrimethylammonium bromide.

Introduction

Iron and cobalt are metals which appear together almost in several samples, both natural and artificial. In most cases, the characterization of these samples includes the determination of their metal ion content. The need for iron and cobalt analysis in environmental and biochemical material has increased after reports on different roles of these metals in human health, diseases and industrials [1- 4].

Since simultaneous presence of iron and cobalt in many real samples, selective analytical techniques and methods have been put forward for simultaneous determination of both elements. Some simultaneous determination techniques and methods are derivative spectrophotometry, atomic absorption spectrometry, sequential flow injection technique, high-performance liquid chromatography, H-point standard addition and partial least squares methods [5-14].

Among the proposed methods for simultaneous determination of species, derivative spectrophotometry has been showed some advantages such as simplicity, speed, sensitivity and selectivity. This method is not affected by some sources of error that affect the precision and accuracy of spectrophotometric measurements. Moreover, it decreases and eliminates base-line shifts, which improves the accuracy of quantification. The use of the derivative also reduces the effects of scattered light produced by the thickness of the solution [15].

As the other words, a modified equilibrium standard-addition method called the "H-point standard addition method" (HPSAM) is developed for determination of unbiased analyte concentrations in the event that the presence of a direct interferent is known [16-18]. The method relies on the use of multipoint signal data (analytical signal data obtained at two accurately selected wavelengths) to transform otherwise uncorrectable to correctable errors and evaluate the analyte and interferent concentrations. The HPSAM has been applied with analytical spectroscopy to resolve mixtures of two components with extensively or fully overlapped spectra. One modification of the HPSAM uses absorbance increments as analytical signals as these only depend on the analyte concentration. By plotting the analytical signals versus added analytical concentration, two straight lines are obtained that have a common point H with coordinates (C_H , A_H); C_H is the unknown analyte concentration and the A_H is the analytical signal due to the interferent species [19, 20].

Micelles possess a high potential for multicomponent analysis, which can be used as special reaction media because they alter the rate, equilibrium position, products and stereochemistry of many reactions. However, micelles also change the effective microenvironment around dissolved solutes and their physicochemical properties, such as absorptivity, equilibrium constant and spectral profile [21].

In this work, first-derivative spectrophotometry method with zero-crossing technique and HPSAM was optimized for the simultaneous determination of Co^{2+} and

Fe³⁺ as 4-(2-pyridylazo) resorcinol (PAR) complexes in a cetyltrimethylammonium bromide micellar media at buffered pH 6.

Experimental

All of used chemicals were analytical reagent grade. Doubly distilled water was used throughout.

A standard Co²⁺ solution (1000 µg ml⁻¹) from hydrated cobalt(II) chloride salt is prepared with dissolving appropriate amounts in a volumetric flask. Standardization of the solution is performed by the standard procedure [22]. A stock iron solution containing 1000 µg ml⁻¹ Fe(III) is prepared by dissolving appropriate amounts of FeCl₃·6H₂O in 0.1 M sulfuric acid in a volumetric flask. The Fe(III) solution is standardized by using EDTA as a complexing agent and variamine blue as an indicator [23]. A 50-ml solution of 4-(2-pyridylazo) resorcinol monosodium salt monohydrate, C₁₁H₈N₃NaO₂·H₂O (PAR) with concentration of 5.0x10⁻⁴ M in water is prepared and used daily. Polyoxyethylene (20) sorbitan monooleate (Tween 80), sodium dodecylsulfate (SDS) and cetyltrimethylammonium bromide (CTAB) are purchased from Merck. Stock solution of these surfactants as 1-4% w/v is prepared in 100-ml volumetric flask. Adjusting the pH values of the working solution is carried out using acetic acid, sodium acetate, and sodium dihydrogen phosphate and sodium monohydrogen phosphate solutions. The foreign ions are prepared by using their suitable salts as analytical grade.

A carry 100 UV-Vis scanning spectrophotometer is used to record the absorbance spectra of Fe-PAR and Co-PAR complexes and measurement of absorbance of the solutions with a 1.0-cm path length quartz cell. The cell temperature is controlled by circulated water around the cell by thermostat. The slit width is set at 2-nm and a fast scan speed at 600 nm/min is used. The spectra are recorded between 400 and 700 nm at 1-nm intervals. The derivative wavelength difference is 5-nm and obtained with using Carry win UV software. A Metrohm 691 pH meter using a combined glass electrode is used for measurement of the pH.

In a 10-ml volumetric flask, 2 ml of a buffer solution with pH 6 (acetic acid-sodium acetate), 2 ml of PAR 5.0x10⁻⁴ M solution, 1 ml of CTAB 1.0% w/v and an appropriate of Co²⁺ and Fe³⁺ ions are added and diluted to the mark with double distilled water. Then, after 2-3 min, the spectra of the prepared solution are recorded and the first-derivative of the spectra is recorded over the 400-600 nm wavelength range. The amplitudes at zero-crossing points are measured at 492.8, 519.8 nm for Co and 500.3 nm for Fe in the first-derivative spectrum.

For the determination of Co²⁺ and Fe³⁺ ions using HPSAM, the synthetic solution containing Co(II) and Fe(III) ions at different concentration ratios were prepared with 2 ml of PAR 5.0x10⁻⁴ M solution and 1 ml of CTAB 1.0% w/v in 10-ml volumet-

ric flasks. The standard addition is made versus Fe^{3+} ion concentration and the absorbences of solutions are measured at wavelengths of 482 and 515 nm. The H-point graphs are prepared by using data of absorbance and added concentration of Fe^{3+} ion. The concentration of ferric ion is evaluated from C_H . To obtain concentration of Co(II) ion, A_H value and calibration curve of analytical signal versus Co^{2+} concentration is used. To construct of this calibration curve, the absorbance measurements at wavelengths of 482 and/or 515 nm were performed on samples with different concentrations of Co(II) , and A_H was evaluated for each sample.

Results and Discussion

4-(2-Pyridylazo) resorcinol as chromogenic complexation agent was known and can be form complex with some transition metal ions with mole ration of 1:2 metal to ligand. Normal absorption spectra of complex of Co^{2+} -PAR shows maximum absorption in wavelength (λ_{max}) of 510.0 nm, whereas, complex of Fe^{3+} -PAR shows two λ_{max} at wavelengths of 488.0 and 523.3 nm (Fig.1).

The effect of the various parameters on the spectral characteristics of PAR complexes of cobalt and iron are investigated by using one at a time optimization method. The effect of the pH on the change in the absorbance of Co^{2+} -PAR and Fe^{3+} -PAR complexes at λ_{max} wavelengths of them is investigated in the pH range of 3.0-7.0. The concentration of 2.0 and 3.0 $\mu\text{g ml}^{-1}$ of Co^{2+} and Fe^{3+} , respectively, are used in the presence of 7.5×10^{-5} M of PAR. The absorbance of both complexes is increased with increasing of the pH of the solution from 3.0 to 6.0. Whereas, the above of pH 6, with increasing of the pH, the absorbance of the complexes did not show any considerably change. Therefore, the buffered solution at pH 6 (acetic acid-sodium acetate) is selected as an optimum of pH and for further investigations. The effect of the concentration of reagent on the absorbance of the complexes is studied in the range of 1.0×10^{-5} to 2.5×10^{-4} M of PAR. The results are obtained for solution continuing of 2.0 and 3.0 $\mu\text{g ml}^{-1}$ of Co^{2+} and Fe^{3+} ions, respectively, at pH 6. By increasing of concentration of PAR from 1.0×10^{-5} to 1.0×10^{-4} M, the absorbance of both complexes is increased with a sharp slope. Then, in the above of 1.0×10^{-4} M of PAR, this increasing of absorbance is shown very slightly. As a result, the concentration of 1.0×10^{-4} M PAR is used optimum concentration for chromogenic agent in the solutions.

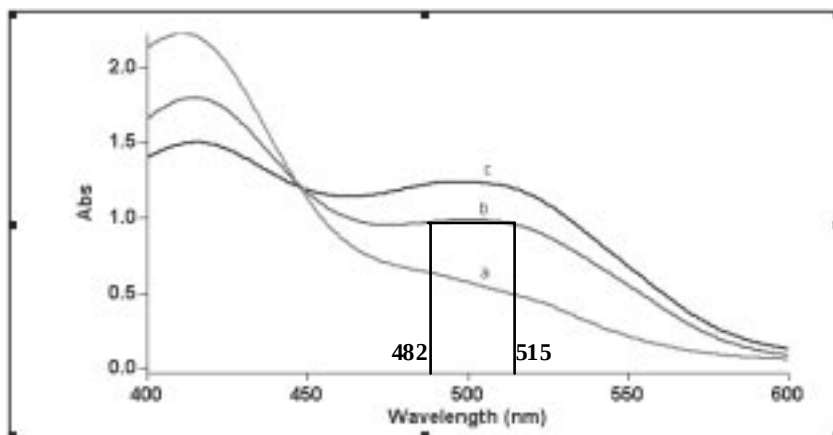


Fig. 1. Absorbance spectra of (a) Fe^{3+} -PAR (C_{Fe} ; $3.0 \mu\text{g ml}^{-1}$) , (b) Co^{2+} -PAR (C_{Co} ; $2.5 \mu\text{g ml}^{-1}$) and (c) Fe^{3+} -PAR and Co^{2+} -PAR (C^{Fe} ; $2.5 \mu\text{g ml}^{-1}$, C_{Co} ; $2.0 \mu\text{g ml}^{-1}$), conditions: C_{PAR} ; $1.0 \cdot 10^{-4} \text{ M}$, pH; 6 and t; 25°C

The absorbance of the complexes are stable from few minutes after preparation of the solution up to 24-h at 25°C . Also, with increasing of temperature of the solution from 25 to 45°C , the absorbance of them is found without any change. Thus, time and temperature did not show any influence on the absorbance of the solutions. Hence, the temperature of 25°C is used for recording spectra in all of experiments.

To obtain the high sensitivity in the spectrophotometric determination of Co(II) and Fe(III) ions, the effect of some surfactants on the spectral characteristics of the complexes in normal mode spectrophotometry was investigated. In the presence of CTAB as a surfactant with concentration of 0.10% w/v, the molar absorptivity coefficients of Co^{2+} -PAR and Fe^{3+} -PAR complexes are obtained 8.9×10^4 and $8.3 \times 10^4 \text{ cm}^{-1} \text{ M}^{-1}$ at the λ_{max} wavelengths of them, respectively. In the absence of any surfactant, the values ϵ of the complexes was calculated 6.7×10^4 and $6.1 \times 10^4 \text{ cm}^{-1} \text{ M}^{-1}$ for complexes of Co^{2+} and Fe^{3+} ions, respectively. Therefore, the sensitivity of the system and the sensitivity of the calibration curves are increased by increasing of ϵ in the micellar media with CTAB as a surfactant. Hence, CTAB is chosen for micelle formation in both the systems and its concentration was kept at 0.10% w/v. However, in the presence of CTAB as a surfactant, the stability of complexes was increased from $<2 \text{ h}$ to $>1 \text{ day}$.

First-derivative spectrophotometric method

As seen in Fig. 1, the normal absorption spectra of complexes of cobalt(II) and iron(III) have a clear overlapping. Therefore, to overcome this problem a suitable technique such as derivative spectrophotometry can be used to prepare analytical

calibration graphs for Co^{2+} and Fe^{3+} ions. Fig. 2 shows the first-derivative spectra of Co^{2+} and Fe^{3+} complexes. It is seen here an improvement in the resolution of the spectra. The result of this derivatization features that zero-crossing wavelengths in first-derivative spectra are seen at 500.3 nm for cobalt(II) complex and 492.8 and 519.8 nm for iron(III) complex. As a result, the amplitude of derivative spectra at the zero-crossing points at 500.3 nm is proportional to concentration of Fe^{3+} ions, vice versa, the signal amplitude at the wavelengths of 492.8 and 519.8 nm can be used to prepare of calibration curves for Co^{2+} ions. Therefore, simultaneous determination of Co^{2+} and Fe^{3+} ion concentrations in a solution can be carried out by measuring the amplitude of derivative spectra at zero-crossing points without any need separation of the cations. Selected measurements in these points exhibit the best response and least affect by the concentration of other ions in the optimized conditions of the other experimental variables.

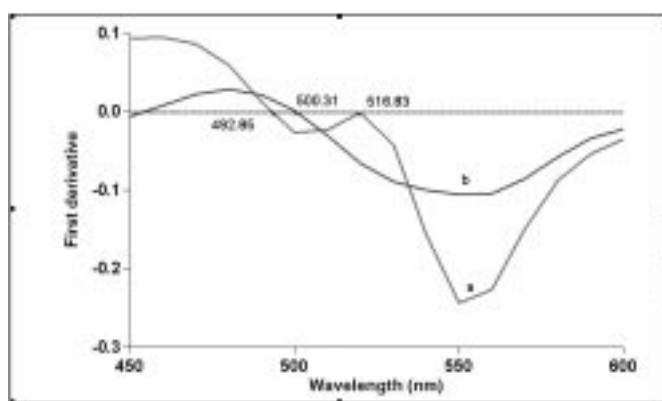


Fig. 2. First-derivative absorbance spectra of (a) Fe^{3+} -PAR, (b) Co^{2+} -PAR, conditions: C_{PAR} ; $1.0 \cdot 10^{-4}$ M, C_{Fe} ; $2.5 \mu\text{g ml}^{-1}$, C_{Co} ; $2.0 \mu\text{g ml}^{-1}$, pH; 6 and t; 25°C

Table 1. First-derivative spectrophotometric data for determination of cobalt (II) and iron (III) ions in CTAB media at pH 6

Method	λ (nm)	Calibration equation	Regression coefficient (r)	Analyte ion	Linear range ($\mu\text{g ml}^{-1}$)	Interfere Ion ($\mu\text{g ml}^{-1}$)
First-	492.8	$D = -0.0389 + 0.0054C$	0.9947	Co^{2+}	0.1-2.5	0.5-6.0 Fe^{3+}
First-	519.8	$D = -0.0115 + 0.0084C$	0.9976	Co^{2+}	0.1-2.5	0.5-6.0 Fe^{3+}
First-	500.3	$D = 0.1372 + 0.0017C$	0.9978	Fe^{3+}	0.5-6.0	0.1-2.5 Co^{2+}

As seen from Fig. 2, the isodifferential (or zero-crossing) points in first-derivate spectra are seen at wavelengths of 492.8 and 519.8 nm for Fe(III)-PAR complex and at 500.3 nm for complex of Co(II)-PAR. Therefore, the derivative amplitude at wavelengths of 492.8 and 519.8 nm are independent of Fe^{3+} ions concentration and are proportional to concentration of Co^{2+} ions in the solutions. Vice versa, the peak height at wavelength of 500.3 nm can be used to prepare calibration curve for Fe^{3+} ions, because the derivative amplitude is independent of concentration of Co^{2+} ions in the solutions at this point. For simultaneous determination of Co^{2+} and Fe^{3+} , the calibration curves for each ion in the presence of the other ion as an interfere ion are obtained and the results are showed in Table 1. The measurement of amplitudes of derivative spectra is carried out at zero-crossing points. The linear range for measuring Fe^{3+} ions concentration is obtained at the amplitude of $0.5\text{-}6.0\ \mu\text{g ml}^{-1}\ \text{Fe}^{3+}$ in the presence of $0.1\text{-}2.5\ \mu\text{g ml}^{-1}\ \text{Co}^{2+}$ as an interfere ion. The calibration graph for Co^{2+} ions is obtained in the range of $0.1\text{-}2.5\ \mu\text{g ml}^{-1}\ \text{Co}^{2+}$ ions in the presence of $0.5\text{-}6.0\ \mu\text{g ml}^{-1}\ \text{Fe}^{3+}$ ions. The results are shown a stability of isodifferential points over a large concentration range and a better sensitivity and reproducibility of the measurements.

The limits of detection are calculated by $\text{D.L} = S_b + K S_D$ equation, here S_b is the signal average of the blank solution for ten replicate analysis and S_D is the standard deviation of the results. At confidence interval of 95%, $K=3$ and finally, D.L is the signal corresponding to detection limit. By using this equation, theoretical detection limits of Co^{2+} and Fe^{3+} ions are obtained 0.05 and $0.37\ \mu\text{g ml}^{-1}$, respectively. The experimental amounts of detection limit are 0.1 and $0.5\ \mu\text{g ml}^{-1}$ for Co^{2+} and Fe^{3+} ions, respectively.

Table 2. Simultaneous determination of Co^{2+} and Fe^{3+} ions in binary mixtures by first-derivative spectrophotometric method with zero-crossing technique

Co^{2+} added ($\mu\text{g ml}^{-1}$)	Fe^{3+} added ($\mu\text{g ml}^{-1}$)	Co^{2+} found ($\mu\text{g ml}^{-1}$)	Fe^{3+} found ($\mu\text{g ml}^{-1}$)	%Recovery Co^{2+}	%Recovery Fe^{3+}
1.00	2.00	0.99 ± 0.03^a	1.97 ± 0.02	99.0	98.5
0.80	2.50	0.79 ± 0.02	2.44 ± 0.02	98.7	97.6
0.50	3.00	0.52 ± 0.03	2.95 ± 0.03	104.0	98.3
0.50	1.50	0.49 ± 0.02	1.53 ± 0.03	98.0	102.0
1.50	1.00	1.52 ± 0.02	0.99 ± 0.02	101.3	99.0
0.50	1.00	0.51 ± 0.03	1.05 ± 0.03	102.0	105.0
1.00	3.00	1.01 ± 0.04	2.98 ± 0.03	101.0	99.3
0.10	5.00	0.11 ± 0.03	5.05 ± 0.04	110.0	101.0
2.00	2.00	1.96 ± 0.03	1.95 ± 0.03	98.0	97.5
1.50	1.50	1.46 ± 0.02	1.49 ± 0.03	97.3	99.3

a: Standard deviation (n=5)

In order to investigate accuracy, precision and reproducibility of the proposed method for simultaneous determination of Co^{2+} and Fe^{3+} ions in a solution, several synthetic samples containing different amounts of cobalt (II) and iron (III) ions are analyzed by this method. The concentration of Co^{2+} ions is determined by the first-derivative amplitude at wavelength of 492.8 nm. The amounts of Fe^{3+} ions are also measured by the height of first-derivative spectra at wavelength of 500.3 nm and calibration equation for Beer's law for this point. Each sample analyzed five times. The standard deviation of the results and recovery percent for each concentration are collected in Table 2. The amounts of SD and the recovery percent between 97 and 105% are shown that the proposed method has a good accuracy and precision in the simultaneous determination of cobalt and iron ions.

H-point standard addition method

As indicated in Fig.1, the appropriate wavelengths pair for HPSAM is 482 and 515 nm. The analyte signals of Fe^{3+} ions are linear with concentration, whereas, the interferent signal of Co^{2+} ion remains constant by changing the analyte concentration at these wavelengths. The analytical signal is obtained from a mixture of the analyte and interferent is equal to the sum of the individual signals of the species. The higher value of slope increment and therefore, the smaller error of the analyte concentration are obtained by selection of 482 and 515 nm as wavelengths pair. To obtain good accuracy, the Fe^{3+} ion is considered as analyte, because, the spectrum of Fe-PAR complex is broad.

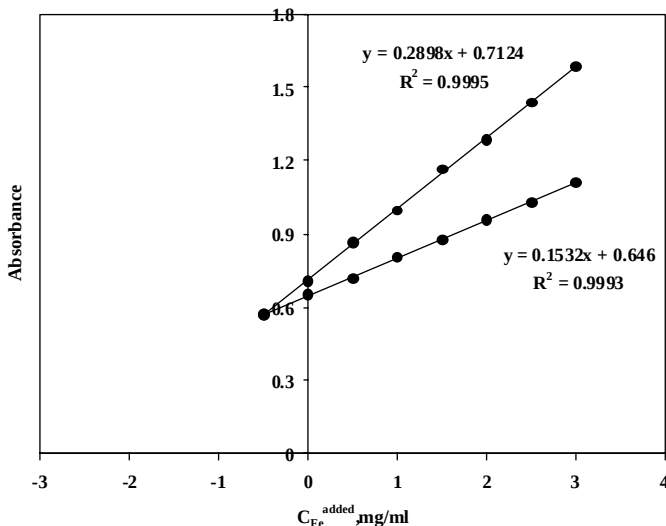


Fig. 3. Plot of HPSAM for simultaneous determination of Co^{2+} and Fe^{3+} ions with concentrations of 0.50 $\mu\text{g/ml}$ of Fe^{3+} ion and 1.50 $\mu\text{g/ml}$ Co^{2+} ion at pH; 6, C_{PAR} ; $1.0 \cdot 10^{-4}$ M, C_{CTAB} ; 0.10% w/v and t; 25°C

Several synthetic mixtures with different concentration ratios of Co^{2+} and Fe^{3+} ions are analyzed in order to obtain high accuracy and precision of HPSAM for simultaneous determination of cobalt and iron. The calibration curves at selected wavelengths are plotted by using data of absorbencies and standard concentrations of ferric ion that added to each mixture (Fig. 3). As seen from Fig. 3, the concentrations of Fe^{3+} ion (analyte) and Co^{2+} ion (interfere) in the each sample are determined by using C_H and A_H , respectively. The results are given in Table 3.

Table 3. Simultaneous determination of Co^{2+} and Fe^{3+} ions in binary mixtures by HPSAM

Co^{2+} added ($\mu\text{g ml}^{-1}$)	Fe^{3+} added ($\mu\text{g ml}^{-1}$)	Co^{2+} found ($\mu\text{g ml}^{-1}$)	Fe^{3+} found ($\mu\text{g ml}^{-1}$)	%Recovery Co^{2+}	%Recovery Fe^{3+}
0.10	0.30	0.11 ± 0.02^a	0.32 ± 0.03	110.0	107.0
0.70	0.50	0.72 ± 0.03	0.49 ± 0.02	102.8	98.0
1.50	1.00	1.53 ± 0.02	0.98 ± 0.03	102.0	98.0
2.00	1.50	2.03 ± 0.02	1.53 ± 0.04	101.5	102.0
0.10	0.50	0.10 ± 0.02	0.53 ± 0.02	100.0	106.0
2.50	1.50	2.49 ± 0.04	1.52 ± 0.03	99.6	101.3
1.00	3.00	1.02 ± 0.03	2.96 ± 0.02	102.0	98.7
2.50	1.00	2.53 ± 0.03	0.97 ± 0.03	101.2	97.0
0.50	2.00	0.53 ± 0.02	1.92 ± 0.02	106.0	96.0
2.50	3.00	2.46 ± 0.03	2.98 ± 0.03	98.4	99.3

a: Standard deviation (n=5)

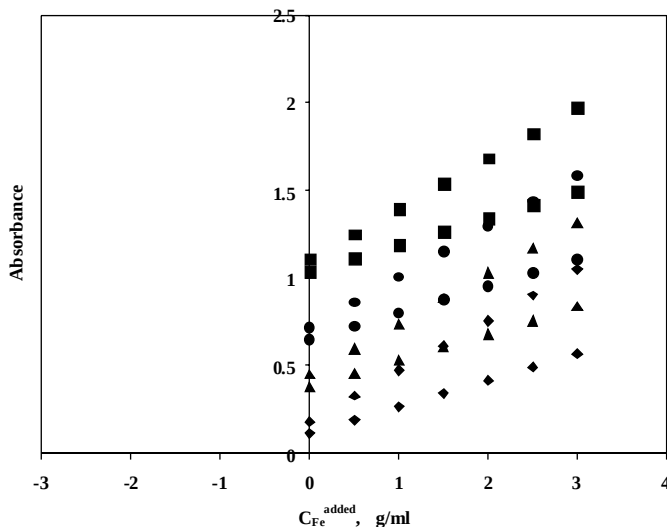


Fig. 4. Plot of HPSAM for simultaneous determination of Co^{2+} and Fe^{3+} ions in various mixtures with constant concentration of Fe^{3+} ion ($0.50 \mu\text{g/ml}$) and different concentration of Co^{2+} at pH; 6, $C_{\text{PAR}}; 1.0 \cdot 10^{-4} \text{ M}$, $C_{\text{CTAB}}; 0.10\% \text{ w/v}$ and t; 25° C

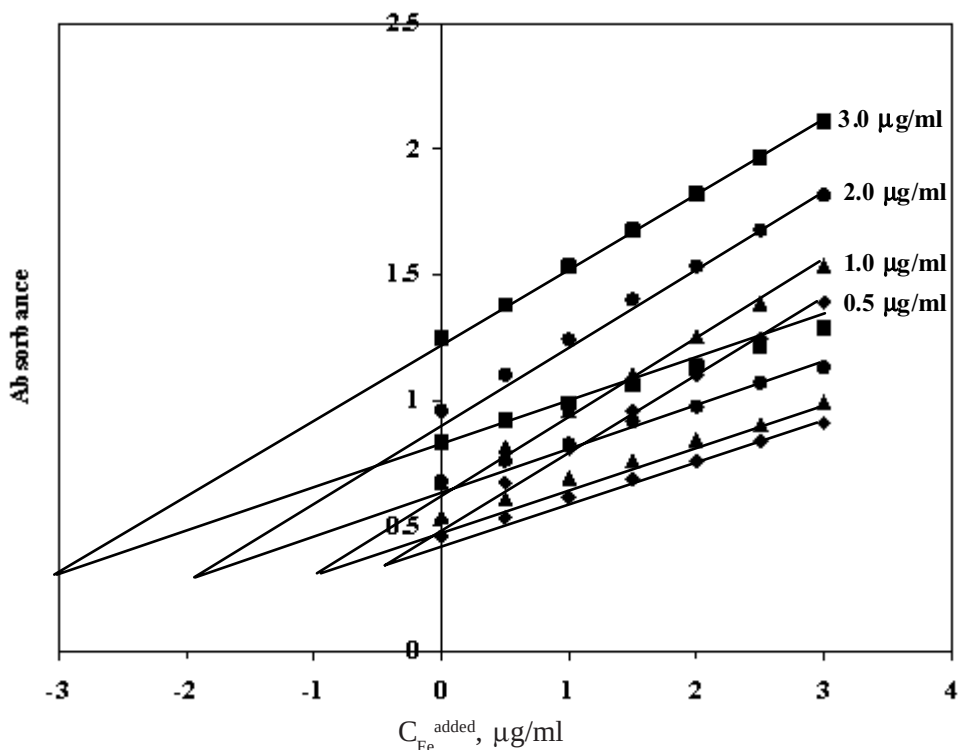


Fig. 5. Plot of HPSAM for simultaneous determination of Co^{2+} and Fe^{3+} ions in various mixtures with constant concentration of Co^{2+} ion ($1.00 \mu\text{g/ml}$) and different concentration of Fe^{3+} at pH; 6, $C_{\text{PAR}}: 1.0 \cdot 10^{-4} \text{ M}$, $C_{\text{CTAB}}: 0.10\% \text{ w/v}$ and $t; 25^\circ \text{C}$

The results of Table 3 show that iron and cobalt can be simultaneously determined accurately in the concentration ratio of Fe^{3+} to Co^{2+} from 30:1 to 1:8 by applying the proposed HPSAM. Figs. 4 and 5 show the H-point standard addition plots for several synthetic test solutions with constant concentration of Fe(III) and Co(II) ions, respectively. As can be seen from Fig. 4, the value of C_{H} (concentration of Fe^{3+}) is independent of the concentration of Co^{2+} ion. Fig. 5 also shows that the A_{H} value (absorbance, which is proportional to Co^{2+} ions concentration) is independent of ferric ion concentration.

Effect of foreign ions

The effect of presence of several cations and anions on the determination of Co^{2+} and Fe^{3+} ions ($2.00 \mu\text{g ml}^{-1}$) in micellar media have been investigated. The tolerance limit for each foreign ion is obtained when its presence at tested weight ratio produced a concentration relative errors lower than 3%. The results for both ions

(Table 4) have indicated that the most of the cations and anions did not show any significant spectral interference at weight ratio greater than 1000. The most interference is observed from presence of Zn^{2+} , Ni^{2+} and Cu^{2+} in the sample solution even in 1:1 weight ratio.

Table 4. Tolerance limits for the divers ions in the determination of Co^{2+} and Fe^{3+} ions (1 $\mu\text{g}/\text{ml}$ of each analyte)

Interfere ion	Tolerance limit ($\text{w}_{\text{Ion}}/\text{w}_{\text{M}}$)
Li^+ , Ag^+ , K^+ , NH_4^+ , Mg^{2+} , Sr^{2+} , Ba^{2+} , Ca^{2+} , Zr^{4+} , Th^{4+} , Ti(IV) , Mo(VI) , Cr(VI) , Mn(VII) , HCO_3^- , Br^- , Cl^- , F^- , NO_3^- , NO_2^- , HPO_4^{2-} , H_2PO_4^- , $\text{S}_2\text{O}_8^{2-}$, SO_4^{2-} , $\text{S}_2\text{O}_3^{2-}$, IO_3^- , ClO_3^-	1000
Mn^{2+} , Cr^{3+} , Sb^{3+} , Sn^{4+} , Ti(III) , V(IV) , V(V)	500
Cd^{2+} , Pb^{2+} , Hg^{2+} , Bi^{3+}	200
^a Al^{3+}	100
Zn^{2+} , Cu^{2+} , Ni^{2+} ,	1

M: Co(II) or Fe(III) , a: 0.1 M NaF was added as masking agent.

Table 5. Simultaneous determination of Co^{2+} and Fe^{3+} ions in real samples and standard deviation (n=3) using HPSAM and comparison with AAS (data in parenthesis)

Sample	Co^{2+} spiked	Fe^{3+} spiked	Co^{2+} found	Fe^{3+} found	%Rec. Co^{2+}	%Rec. Fe^{3+}
Metal alloys						
Remalloy: Co(12%), Fe (68%), Mo(17%), Mn(3%)			11.4 $\pm$ 1.2% (12.2 $\pm$ 1.5)	66.5 $\pm$ 1.4% (66.3 $\pm$ 1.3)	95.0	97.8
Sofcomag 25 alloy: Co(25%), Fe(75%)			23.8 $\pm$ 1.2% (26.0 $\pm$ 1.0)	73.7 $\pm$ 1.1% (75.9 $\pm$ 1.4)	95.2	98.3
Sofcomag 49 alloy: Co(49%), Fe(51%)			47.2 $\pm$ 1.6% (50.1 $\pm$ 1.5)	49.7 $\pm$ 1.4% (50.1 $\pm$ 1.3)	96.3	97.5
Alloy solution						
Tap water	0.50 $\mu\text{g}/\text{ml}$	2.00 $\mu\text{g}/\text{ml}$	0.52 $\pm$ 0.04 (0.55 $\pm$ 0.03)	2.11 $\pm$ 0.03 (2.07 $\pm$ 0.04)	104.0	105.5

Spiddasht spring water	1.50 $\mu\text{g/ml}$	2.50 $\mu\text{g/ml}$	1.46 $\pm$ 0.03 (1.53 $\pm$ 0.05)	2.55 $\pm$ 0.03 (2.48 $\pm$ 0.04)	97.3	102.0
	1.00 $\mu\text{g/ml}$	2.00 $\mu\text{g/ml}$	1.06 $\pm$ 0.05 (1.03 $\pm$ 0.03)	2.08 $\pm$ 0.03 (1.98 $\pm$ 0.04)	106.0	104.0
	2.00 $\mu\text{g/ml}$	3.50 $\mu\text{g/ml}$	2.06 $\pm$ 0.03 (1.98 $\pm$ 0.04)	3.43 $\pm$ 0.04 (3.55 $\pm$ 0.04)	103.0	98.0

Application of the methods

The proposed methods are successfully applied to the determination of cobalt and iron in metal alloys and spiked real water solutions (Table 5). The solution of metal alloys was prepared after dissolution of suitable amounts of them in nitric acid and after neutralization and dilution was used as real samples. The analysis of real samples is carried out by HPSAM and the results are compared with atomic absorption spectrophotometric method. The resulting values are in good agreement with the certified values.

Conclusion

First-derivative spectrophotometric method with zero-crossing over technique and H-point standard addition method (HPSAM) have been used for the simultaneous determination of cobalt (II) and iron (III) ions in CTAB micellar media. The first-derivative spectrophotometric procedure is shown over a wide dynamic range of 0.5-6.0 $\mu\text{g ml}^{-1}$ for Fe^{3+} and 0.1-2.5 $\mu\text{g ml}^{-1}$ for Co^{2+} in the presence of each other ion as an interfere ion in comparison to previous reports [24-26]. Detection limit for Fe^{3+} and Co^{2+} ions were obtained 0.37 and 0.05 $\mu\text{g ml}^{-1}$, respectively. The HPSAM can be used for simultaneously determination of iron and cobalt ions accurately in the concentration ratio of Fe^{3+} to Co^{2+} from 30:1 to 1:8. The proposed methods are applied successfully to assays of cobalt and iron in synthetic binary mixtures, metal alloy and alloy solution samples with high accuracy and precision.

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