Direct and simultaneous spectrophotometric determination of Fe (III) and Ni (II) using salicylaldehyde acetoacetic acid hydrazone – Applications

V Srilalitha[1], A Raghavendra Guru Prasad[2*], K Raman Kumar[3], V Seshagiri[4], LK Ravindranath[4]

1) C.M.R. Institute of Technology, Hyderabad, A.P., India,

2) ICFAI Foundation for Higher Education, Hyderabad, A.P., India,

3) Malla Reddy College of Engineering, Hyderabad, A.P., India,

4) Sri Krishnadevaraya University, Anantapur, A.P., India.

(*) guruprasadar@yahoo.co.in

Resumen

Un método espectrométrico rápido, simple y sensible ha sido desarrollado para la determinación de Fe(III) y Ni(II) usando la hidrazona del ácido saliciladehido acetoacético (SAAH) como reactivo cromofórico. Las curvas de calibración lineal fueron obtenidas en cada caso. El método propuesto es aplicado para la determinación simultánea de Fe(III) y Ni(II) empleando su espectros de primer orden. El método está basado en la medición de cruzamiento cero de las amplitudes de la primera derivada. Las amplitudes de la primera derivada a 525 nm y 395 nm obedecen la ley de Beer en el rango de concentración 0,054-0,270 μg/mL y 0,112-0,561 μg/mL para Fe(III) y Ni(II), respectivamente. Un gran número de iones no interfieren en el presente método. El método es usado para la determinación de cantidades micro de Fe(III) y Ni(II) en mezclas de acero y en mezclas sintéticas.

Palabras clave: Espectrofotometría; Fe(III); Ni(II); Determinación simultánea; Medición a cruzamiento cero; Applicaciones

Abstract

A rapid, simple and sensitive spectrophotometric method has been developed for determination of Fe (III) and Ni (II) using salicylaldehyde acetoacetic acid hydrazone (SAAH) as a chromophoric reagent. The linear calibration ranges were obtained in each case. The proposed method is applied for the simultaneous determination of Fe (III) and Ni (II) utilizing their first order spectra. The method is based on the zero crossing measurement of first derivative amplitudes. The first derivative amplitudes at 525 nm and 395 nm obey Beer's law in the concentration range 0.054-0.270 μg/mL and 0.112-0.561 μg/mL for Fe (III) and Ni (II) respectively. A large number of foreign ions do not interfere in the present method. The method is used for the determination of micro amounts of Fe (III) and Ni (II) in alloy steels and in synthetic mixtures.

Keywords: Spectrophotometry; Fe (III); Ni (II); Simultaneous determination; Zero crossing measurement; Applications.

Introduction

Iron (III) and nickel (II) are the most important transition metals occurring in real samples. Both these metals are thoroughly studied because of their frequent natural occurrence and industrial significance. Both these metals found to be vital and toxic to biological systems. Hence the determination these metals are very important. Several techniques such as X-ray fluorescence[1], atomic absorption spectrometric[2,3], atomic fluorescence spectrometric[4], electrochemical[5], chromatographic[6,7], etc. have been reported for the simultaneous determination of these metals. However, only few methods are available for the simultaneous determination of Fe (III) and Ni (II). UV-Vis spectrophotometric analytical procedures[8,9] 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 analyses. In particular derivative spectrophotometry has been an extremely useful analytical technique for the simultaneous determination of binary mixtures. In this article the authors present simple and sensitive zero order spectrophotometric method for the micro determination of Fe (III) and Ni (II)

when they are present independently. The first order spectra of their mixture were utilized for the simultaneous determination of the said metals by employing zero crossing measurement method[10].

Experimental

Apparatus

The absorbance measurements were carried out on Shimadzu UV-visible spectrophotometer (Model UV-160A). pH measurements were made using ELICO pH meter Model L1-10, ELICO Private Limited, Hyderabad, India.

Reagents and solutions

All chemicals and solvents used were of analytical reagent grade procured from Merck, India. Double distilled water was used for the preparation of solutions. Working solutions were prepared by appropriate dilutions of the standard solution.

The standard solutions of Fe (III) and Ni (II) were prepared by dissolving appropriate amounts of ferric chloride and nickel (II) sulphate, respectively, in 100 ml standard flasks.

The buffer solutions were prepared by mixing 1M hydrochloric acid and 1M sodium acetate (pH 1.0-3.0) and 0.2M acetic acid and 0.2M sodium acetate (pH 3.5-7.0).

Synthesis of SAAH[11]

Equimolar solutions of acetoacetic acid hydrazide and salicylaldehyde prepared in aqueous methanol were refluxed for two hours. The contents were allowed to cool to the room temperature and the product was separated by filtration. A crude product obtained was filtered, washed with water, dried and recrystallised from hot aqueous methanol to get pure light yellowish crystals of salicylaldehyde acetoacetic acid hydrazone (SAAH). 0.01M solution of SAAH in dimethyl formamide was employed for the studies. Acetoacetic acid hydrazide was synthesized by thoroughly shaking a mixture of equimolar quantities of hydrazine hydrochloride and acetoacetic acid. The reaction was carried out in ice cold conditions. The crude compound obtained was recrystallised from ethanol to get pale yellow crystals. (Melting point: 107°C)
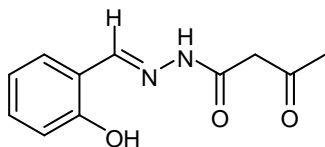
Figure 1: Structural formula of salicylaldehyde acetoacetic acid hydrazone

General experimental procedure

Aliquots of standard metal solution of required concentration were taken in different 10 ml standard flasks. 5 ml of buffer solution of required pH, 1 ml of SAAH solution of required concentration, 1 ml of dimethylformamide were added to each of these flasks and diluted to 10 ml with double distilled water. The absorbance values of the solutions were recorded at 395 nm and 405 nm for Fe(III)-SAAH complex solution and Ni(II)-SAAH complex solution respectively against reagent solution as blank. The calibration graph was prepared by plotting the absorbance values against concentration of the respective metal.

General procedure for the simultaneous determination

Different aliquots of each of the standard metal solutions of required concentration were taken in different 10 ml standard flasks. 5 ml of buffer solution of required pH, 1 ml of SAAH solution of required concentration, 1 ml of dimethylformamide were added to each of these flasks and diluted to 10 ml with double distilled water. The first derivative amplitudes were recorded at 525 nm for Fe (III) and 395 nm for Ni (II) against the reagent solution as blank. The calibration plot was constructed by plotting the first derivative amplitudes against respective concentra-tions of metal ions.

Determination of metal ions in synthetic mixtures

Synthetic mixtures of metal ions were analyzed by the proposed general procedure.

Preparation of alloy sample

1 g of the alloy sample was dissolved in a mixture of 2 ml of concentrated hydrochloric acid and 10 ml of concentrated nitric acid. The solution was evaporated to a small volume. 5 ml of 1:1 sulfuric acid was added and the solution was evaporated to dryness. The residue left over was extracted with 15 ml of water and the solution was diluted to 100 ml with double distilled water. This serves as the stock solution. The stock solution was appropriately diluted to prepare working solutions.

Results and discussion

The selected reagent 'SAAH' gives brownish yellow and yellow colored soluble complexes with Fe (III) and Ni (II) respectively in the appropriate pH media. Further the Figure 2 revealed that spectral features of the metal ion and the reagent were completely different from those of the complex solution. The absorption spectrum of the Fe(III)-SAAH and Ni(II)-SAAH systems showed maximum absorbance at 395 nm and 405 nm respectively. Hence further investigation was carried out at 395 nm and 405 nm for Fe (III) and Ni (II) respectively.
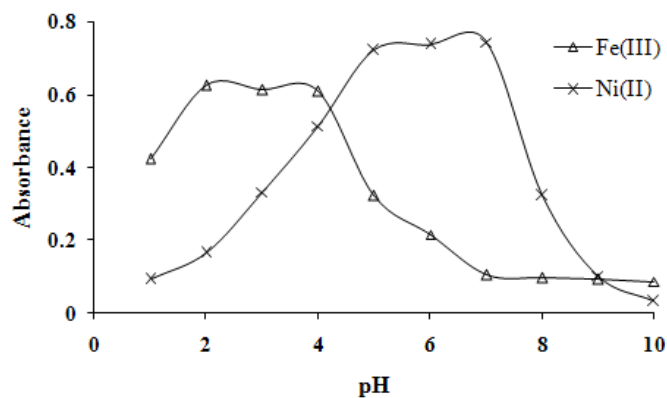
The color reaction was found to be instantaneous and the absorbance of the complex solution was found to remain constant for five hours at room temperature indicating the high stability of colored species.

(A)   (B)
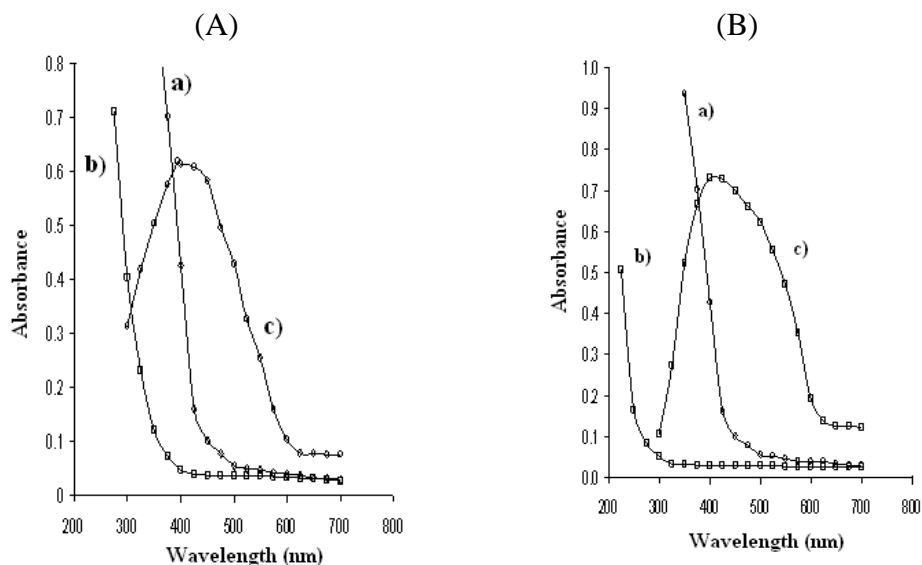
Figure 2: A) Absorption spectra of a) SAAH against buffer blank, [SAAH] = 2×10^{-5} M, pH = 3, b) Fe (III) against buffer blank, [Fe (III)] = 2×10^{-6} M, pH = 3, c) Fe (III)-SAAH complex against reagent blank, [Fe (III)] = 2×10^{-6}M, [SAAH] = 2×10^{-5} M, pH = 3. B) Absorption spectra of a) SAAH against buffer blank, [SAAH] = 2×10^{-5} M, pH = 6, b) Ni (II) against buffer blank, [Ni (II)] = 2×10^{-6} M, pH = 6, c) Ni (II)-SAAH complex against reagent blank, [Ni (II)] = 2×10^{-6}M, [SAAH] = 2×10^{-5} M, pH = 6.

Optimization of experimental variables

Effect of pH. A preliminary study of the reaction between respective metal and SAAH solution was carried out in various pH media and presented in the Figure 3 for Fe(III)-SAAH and Ni(II)-SAAH systems. The figures revealed that for Fe(III)-SAAH system, the color intensities were fairly high in the pH range 2 to 4 at 395.0 nm. Whereas for Ni(II)-SAAH system, high absorbance was noticed in the pH range 5 to 7 at 405.0 nm. Hence an optimum pH of 3 and 6 is selected for the further studies of Fe(III)-SAAH and Ni(II)-SAAH systems respectively.

of 2 fold and 10 fold were required for Fe(III)-SAAH and Ni(II)-SAAH complexation reactions respectively. Further it was noted that the presence of excess of the reagent does not alter the intensity of the color reaction.

Analytical determination of metal ion

The absorbance value of the series of solutions containing different concentrations of the metal ion was determined. The calibration graph drawn between the metal ion concentration and the absorbance is shown in the Figure 4.

Figure 3: Effect of pH on absorbance.

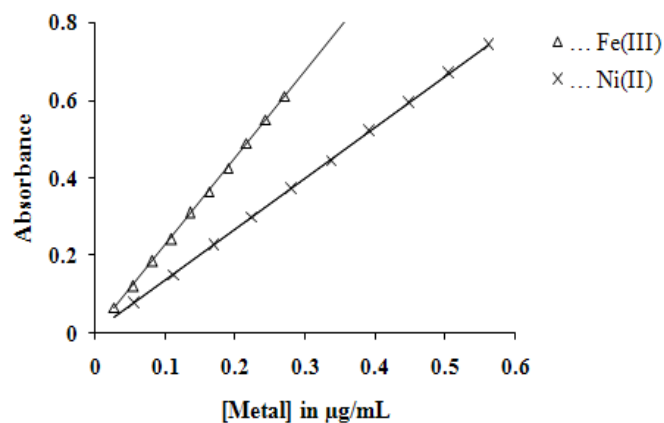[Fe (III)] = 2×10^{-6} M; [SAAH] = 2×10^{-5} M;

[Ni (II)]=2×10^{-6} M; [SAAH] = 2×10^{-5} M.

Effect of reagent (SAAH) concentration. The studies relating to the effect of various concentrations of the reagent on the color reaction revealed that a reagent excess

Figure 4: Analytical determination of metal; [SAAH] = 2×10^{-5} M; pH = 3; λ_{max} = 395 nm for Fe (III) and [SAAH] = 2×10^{-5} M; pH = 6; λ_{max} = 405 nm for Ni (II).

The plots revealed that Fe (III) and Ni (II) can be determined in the concentration ranges 0.0270–0.2704 μg/mL and 0.0561–0.5614 μg/mL, respectively.

Stoichiometry and stability constant of the complex

The stoichiometry of the complexes determined by mole ratio method[12] was found to be 1:1 (Metal:Ligand) for both Fe(III)-SAAH and Ni(II)-SAAH complexes. The stoichiometry was further confirmed by Job's method of continuous variation.[13] The stability constant of the complex calculated by Job's Method was found to be 2.966×10^7 for Fe(III)-SAAH complex and 1.047×10^9 for Ni(II)-SAAH complex.

Effect of diverse ions

The influence of various cations and anions on the proposed method was investigated and the results are presented in Table 1. The tolerance limit was considered to be the amount that caused a $\pm 1\%$ deviation in the absorbance value. As revealed by the table, the common ions, such as Cu (II), Hg (II), Mn (II), Pb (II), Zn (II), F^-, Cl^-, Br^-, CH_3COO^-, NO_2^-, NO_3^-, SO_4^{2-}, and HPO_4^{2-} did not interfere with the determination.

The analytical parameters corresponding to the determination is given in Table 2.

Table 1: Tolerance limit of diverse ions, [Fe (III)] = 0.0168 µg/mL in case of tolerance studies of Fe(III) and [Ni (II)] = 0.0587 µg/mL in case of tolerance studies of Ni (II)

Anion	Tolerance limit (µg/mL)		Cation	Tolerance limit (µg/mL)	
	Fe(III) determination	Ni(II) determination		Fe(III) determination	Ni(II) determination
Citrate	1890.0	1890.00	Bi(III)	167.18	167.18
Tartrate	1184.0	1776.00	W(VI)	18.39	36.77
Iodide	1269.0	1776.60	Mo(VI)	9.59	9.59
Hypo	1489.1	992.72	Mn(II)	5.49	21.98
Oxalate	1232.0	1056.00	Ag(I)	32.36	43.15
Bromide	479.46	319.64	Al(III)	40.47	53.96
Thiourea	304.48	456.72	Cu(II)	12.71	25.42
Nitrate	620.00	620.00	Pb(II)	41.44	41.44
Urea	360.00	360.00	Hg(II)	40.04	40.12
Acetate	472.00	472.00	Zn(II)	45.76	26.15
Chloride	70.90	212.70			
Phosphate	379.58	189.94			
Fluoride	114.00	114.00			

Table 2: Analytical parameters of the proposed method

Parameter	Fe (III)	Ni (II)
Beer's law range	0.0270–0.2704 µg/mL	0.0561–0.5614 µg/mL
Method detection limit	1.0658×10^{-2} µg/mL	1.2264×10^{-2} µg/mL
Limit of quantification	2.1317×10^{-2} µg/mL	2.4528×10^{-2} µg/mL
Molar absorptivity	61.2×10^3 L mol^{-1} cm^{-1}	302.5×10^3 L mol^{-1} cm^{-1}
Stability constant	2.966×10^7	1.047×10^9.
Sandell's Sensitivity	0.9126×10^{-3} µg cm^{-2}	0.1941×10^{-3} µg cm^{-2}
Regression equation	Y = 2.2465X + 0.0022	Y = 1.3134X + 0.0032
Correlation coefficient	0.9998	0.9999

Simultaneous determination of Fe (III) and Ni (II)

As revealed by the Figure 3, an optimum pH of 4.5 was chosen to perform the simultaneous determination of Fe (III) and Ni (II).

The zero order spectrum of a mixture of Fe (III), Ni (II) and SAAH against the reagent blank is shown in the Figure 5. The spectral profile indicated that the resolution of the metal complexes was not possible using the zero order spectra. Therefore first order spectrophotometry was utilized for the quantitative determination of Fe (III) and Ni (II) in their binary mixtures.
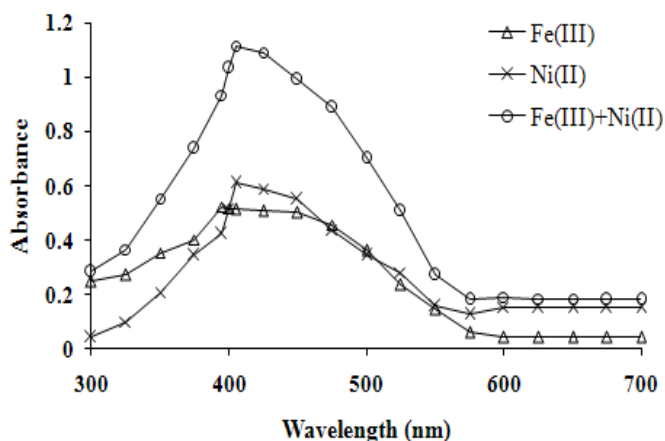

Figure 5: Zero order spectra of a) Fe (III)-SAAH complex against reagent blank, [Fe (III)]=2×10^{-6}M, [SAAH]=2×10^{-5} M, pH = 4.5; b) Ni (II)-SAAH complex against reagent blank, [Ni (II)]=2×10^{-6}M, [SAAH] = 2×10^{-5} M, pH = 4.5; c) Mixture of Fe(III), Ni(II) and SAAH against reagent blank, [Fe (III)] = 2×10^{-6}M, [Ni (II)] = 2×10^{-6}M, [SAAH] = 4×10^{-5} M, pH = 4.5.

The zero crossing measurement technique[14] was used to analyze the mixture containing Fe (III) and Ni (II). The analytical determination Fe (III) was performed by measuring the first derivative amplitudes at 525 nm (Zero crossing wavelength of Ni (II)) and that of Ni (II) was performed at 395 nm (Zero crossing wavelength of Fe (III)). The first order spectra shown in the Figure 6 revealed that the amplitudes measured at 525 nm were independent of concentration of Ni (II), similarly those measured at 395 nm were independent of concentration of Fe (III).

The calibration plots constructed between the first derivative amplitude and the concentration of respective metal ions shown in the Figure 7 revealed that the linear calibration ranges pertaining to the simultaneous determination were 0.054-0.270 μg/mL and 0.112-0.561 μg/mL for Fe (III) and Ni (II) respectively. The analytical parameters corresponding to the simultaneous determination are shown in Table 3.
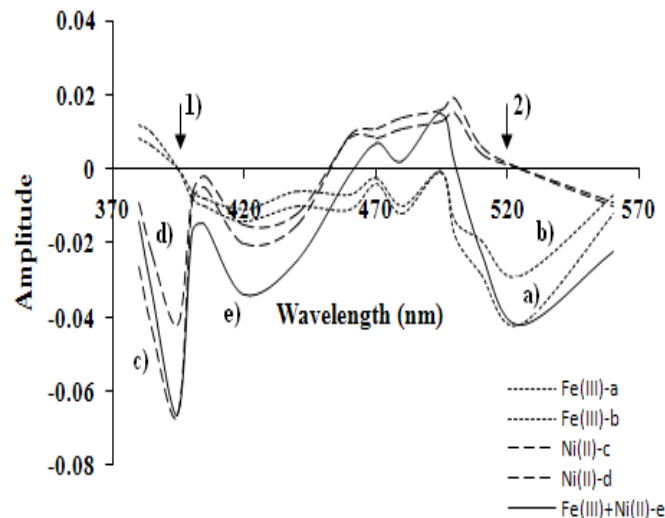
Figure 6: First order spectra of a) and b) Fe (III)-SAAH complex against reagent blank at [Fe (III)] = 0.2700 and 0.1890 μg/mL respectively. [SAAH] = 2×10^{-5} M, pH = 4.5; c) and d) Ni (II)-SAAH complex against reagent blank at [Ni(II)] = 0.561 and 0.3370 μg/mL respectively. [SAAH] = 2×10^{-5} M, pH = 4.5; e) Mixture of Ni(II) (0.5610 μg/mL), Fe(III) (0.2700 μg/mL) and SAAH (4×10^{-5} M) against reagent blank; pH = 4.5; 1) Zero crossing at 395 nm–analytical wavelength for Ni (II) and 2) Zero crossing at 525 nm– analytical wavelength for Fe (III).
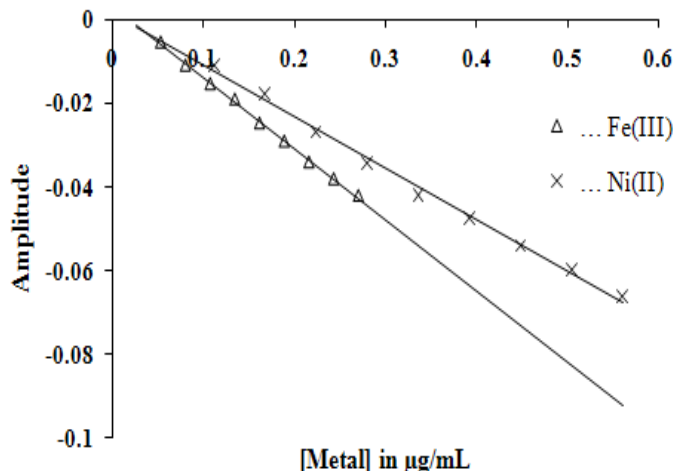
Figure 7: Simultaneous determination of Fe (III) and Ni (II); [SAAH] = 4×10^{-5} M; pH = 4.5.

Applications

The applicability of the proposed methods was demonstrated for the synthetic mixtures of the studied metals and the alloys containing these two metals. The data are presented in Tables 4 and 5.

Table 3: Analytical parameters of the proposed simultaneous determination.

Parameter	Fe (III)	Ni (II)
Beer's law range	0.054-0.270 µg/mL	0.056-0.561 µg/mL
Method detection limit	0.9716×10^{-2} µg/mL	1.5751×10^{-2} µg/mL
Limit of quantification	1.9432×10^{-2} µg/mL	3.1502×10^{-2} µg/mL
Regression equation	$Y = -0.169X + 0.003$	$Y = -0.124X + 0.002$
Correlation coefficient	0.9980	0.9960

Table 4: a) Determination of Fe (III) and Ni (II) in synthetic mixtures.

Fe (III) in µg/mL		Ni(II) in µg/mL		Recovery (%)		RSD (%)	
Added	Found*	Added	Found*	Fe (III)	Ni(II)	Fe (III)	Ni(II)
0.15	0.147±0.0025	0.25	0.253±0.0029	98	101.2	2.4136	1.6183
0.25	0.246±0.0029	0.35	0.346±0.0031	98.4	98.85	1.6638	1.2330

b) Simultaneous determination of Fe (III) and Ni (II) in synthetic mixtures

Added in µg/mL		Found* in µg/mL		Recovery (%)		RSD (%)	
Fe (III)	Ni (II)	Fe (III)	Ni (II)	Fe (III)	Ni (II)	Fe (III)	Ni (II)
0.15	0.25	0.145±0.0023	0.246±0.0038	96.67	98.4	2.2397	2.1317
0.25	0.35	0.254±0.0029	0.357±0.0054	101.6	102	1.5848	2.1169

*t value at 95% confidence level is 2.26.

Table 5: a) Determination of iron (III) in alloy samples

Alloy sample	Composition	Iron (III) (%)		Error (%)
		Certified	Found	
Gun metal	Zn = 1.37%; Sn = 9.22%; Cu = 87.95%; Pb = 1.13%; Fe = 0.01%; P = 0.07%; Ni = 0.24%.	0.01	0.0097	0.03
Brass	Zn= 24.11%; Sn = 1.85%; Cu = 70.80%; Pb = 2.52%; Fe = 0.31%; P = 0.06%; Mn = 0.12%; Ni = 0.17%.	0.310	0.305	0.016
BAS 180/2	Cu= 68.12%; Ni = 30.35%; Fe = 0.68%; Mn = 0.75%; C = 0.04%; S = 0.006%; Co = 0.005%; Pb = 0.003%.	0.680	0.665	0.022
BAS 307	Ni = 41.9%; Fe = 36.00%; Cr = 12.46%; Mo = 5.83%; Ti = 2.95%; Si = 0.28%; Al = 0.24%; Co = 0.21%; Mn = 0.08%; Cu = 0.032%; C = 0.03%.	36.00	35.12	0.024

b) Determination of nickel (II) in alloy samples

Alloy sample	Composition	Nickel(II) (%)		Error (%)
		Certified	Found	
BCS 364	Cu = 80.00%; Sn = 9.35%; Pb = 9.25%; Ni = 0.28%; Sb = 0.18%; Zn = 0.13%; As = 0.065%; P = 0.056%; Al= 0.002%; Si = 0.003%	0.28	0.26	0.071
Gun metal	Zn = 1.37%; Sn = 9.22%; Cu = 87.95%; Pb= 1.13%; Fe = 0.01%; P = 0.07%; Ni = 0.24%	0.24	0.23	0.042
Monel 400	Ni = 63.01 %; C= 0.15%; S = 0.0024%; Mn = 0.07%; Si = 0.50%; Fe = 2.50%; Cu = 31.00%;	63.01	62.60	0.007

c)   Simultaneous determination of Fe (III) and Ni (II) in alloy samples

Alloy simple	Composition	Certified (%)		Found (%)		Error (%)	
		Fe (III)	Ni (II)	Fe (III)	Ni (II)	Fe (III)	Ni (II)
Brass	Zn= 24.11%; Sn = 1.85%; Cu = 70.80%; Pb = 2.52%; Fe = 0.31%; P = 0.06%; Mn = 0.12%; Ni = 0.17%.	0.310	0.170	0.316	0.176	0.02	0.035
BAS 180/2	Cu= 68.12%; Ni = 30.35%; Fe = 0.68%; Mn = 0.75%; C = 0.04%; S = 0.006%; Co =0.005%; Pb = 0.003%.	0.680	30.05	0.688	31.02	0.012	0.032

Conclusion

A simple, rapid and sensitive method was reported for the spectrophotometric determination of Fe (III) and Ni (II). The simultaneous determination of Fe (III) and Ni (II) can be performed by first order spectrophotometry using the zero crossing wavelength method. The proposed method has been successfully applied for the determination of Fe (III) and Ni (II) in synthetic mixtures and alloys when they are present alone and together.

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