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Research Article

Simultaneous Determination of Cobalt(II) and Nickel(II) by Fourth-Order Derivative Spectrophotometric Method Using 2-Hydroxy-3-Methoxy Benzaldehyde Thiosemicarbazone

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A simple and new simultaneous fourth derivative spectrophotometric method is proposed for the analysis of a two-component system containing cobalt(II) and nickel(II) without separation using 2-hydroxy-3-methoxy benzaldehyde thiosemicarbazone (HMBATSC) as a chromophoric reagent. The reagent reacts with cobalt(II) and nickel(II) at pH 6.0, forming soluble brown and yellow colored species, respectively. Cobalt(II) and nickel(II) present in the mixture are simultaneously determined without solving the simultaneous equations by measuring the fourth derivative amplitudes at 468.5 nm and 474.5 nm, respectively. The derivative amplitudes obey Beer's law at 468.5 nm and 474.5 nm for Co(II) and Ni(II) in the range 0.059–3.299 μg mL^{-1} and 0.058–3.285 μg mL^{-1}, respectively. A large number of foreign ions do not interfere in the present method. The present simultaneous method is used for the determination of micro amounts of cobalt in biological samples, nickel in plant samples, and in some alloy steels and soil sample.

1. INTRODUCTION

The direct spectrophotometric determination of metal ions in multicomponent systems is often complicated by interferences from the formulation matrix and spectral overlapping. Such interferences have been treated in many ways, such as solving two simultaneous equations [1] or using absorbance ratios at certain wavelengths [2–4]. However, during the application of these methods [1–4], the presence of spectral interferences or spectral overlap would certainly lead to erroneous results [5]. Other approaches aimed at solving this problem have been used; including pH-induced differential spectrophotometry [6], least squares [7], and orthogonal function [5, 7, 8] methods.

Derivative spectrophotometry is a useful means of resolving two overlapping spectra and eliminating matrix interferences in the assay of two-component mixtures using the zero-crossing technique [9–11]. In the absence of a zero-crossing point, two simultaneous equations can be solved to determine the components in such a mixture [12]. The latter method is based on criteria for selecting the optimum-working wavelength [2]. In addition, the component being determined should make a reasonable contribution to the total derivative reading of the mixture at the selected wavelength. Derivative spectrophotometric analysis of two-component mixtures is also carried out without the need to solve simultaneous equations. The compensation method [13] is also used for the purpose. It is a nonmathematical method for the detection and elimination of unwanted absorption during photometric analysis.

Cobalt alloys are used in some industrial products because of their sufficient hardness and resistivity against oxidation at high temperatures, for example, in the manufacturing of turbine blades and cutting tools. Cobalt-60 is used as an efficient radioactive tracer and an anticancer treatment agent in medicine. Some cobalt compounds, such as vitamin B_{12} (cyanocobalamine), are noted for their biological activities. Therefore, the determination of cobalt is valuable for the quality control of artificial and biological samples in a simple, selective, and sensitive manner. Nickel usually occurs in +2 oxidation state. It is one of the important alloying elements for steel and cast iron. The possibility that nickel may be an essential micro nutrient [14–16] for plants arose from urease, which is a nickel metallo-enzyme. Nickel is an important metal both industrially and biologically. It is one among the essential trace elements along with cobalt, copper, zinc, and manganese in the human diet [17]. Bertrand and Nakamure [18] observed in their experiments on synthetic nutrition that nickel and cobalt play a direct role in nutritional phenomenon. Nickel, which is bound to ribonucleic acid, has a special affinity for bone and skin and has been suggested to play an important role in pigmentation [19].

Thiosemicarbazones [20–26] are one of the important classes of reagents widely used for the spectrophotometric determination of metal ions. In the present paper, 2-hydroxy-3-methoxy benzaldehyde thiosemicarbazone (HMBATSC) is used as a spectrophotometric reagent for simultaneous determination of cobalt(II) and nickel(II).

In the present paper, 2-hydroxy-3-methoxy benzaldehyde thiosemicarbazone (HMBATSC) reacts with cobalt(II) and Ni(II) forming brown and yellow colored complexes at pH 6.0, respectively. The fourth-order derivative spectrum of Co(II) gives sufficient amplitude at 468.5 nm with zero amplitude at 474.5 nm at pH 6.0. On the other hand, Ni(II) complex with HMBATSC shows sufficient and measurable derivative amplitude at 474.5 nm and zero amplitude at 468.5 nm. This difference in amplitudes was utilized to develop a fourth-order derivative spectrophotometric method for the simultaneous determination of cobalt(II) and nickel(II) in a mixture without solving simultaneous equations by measuring the fourth-order derivative amplitude at 468.5 nm and 474.5 nm, respectively.

2. EXPERIMENTAL

The absorbance and pH measurements were made on a Shimadzu UV-visible spectrophotometer (model UV-160A) fitted with 1 cm Quartz cells and Phillips digital pH meter (model L1 613), respectively. Fourth-order derivative spectra were recorded with a scan speed of fast (nearly 2400 nm min^{-1}); slit width of 1 nm with nine degrees of freedom, in the required wavelength range (nm). The derivative amplitudes measured at required wavelengths were plotted against amount of cobalt(II) or nickel(II) to obtain the calibration plots.

3. REAGENTS

3.1. Preparation of 2-hydroxy-3-methoxy benzaldehyde thiosemicarbazone

The reagent (HMBATSC) was prepared by the reported procedure [27] and characterized by IR and NMR spectral data.

A 0.01 M solution of HMBATSC in dimethyl formamide (DMF) was used in the present studies.

3.2. Cobalt(II) solution

Stock solution of Co(II) (1×10^{-2} M) was prepared by dissolving appropriate amount of $Co(NO_3)_2\ 6H_2O$ in doubly distilled water containing a few drops of conc. HNO_3 in a 100 mL volumetric flask and standardized gravimetrically [28].

3.3. Nickel(II) solution

A 0.2808 g of $NiSO_4 \cdot 7H_2O$ was dissolved in doubly distilled water containing few drops of conc. H_2SO_4 in a 100 mL standard flask to get 1×10^{-2} M solution which is then standardized gravimetrically using dimethyl glyoxime [29].

The working solutions were prepared daily by diluting the stock solution to an appropriate volume. All other chemicals used were of analytical grade.

3.4. Buffer solutions

The buffer solutions were prepared by mixing 1 M hydrochloric acid, 1 M sodium acetate (pH 1.0–3.0), 0.2 M acetic acid, and 0.2 M sodium acetate (pH 3.5–7.0). The pH of these solutions was checked with a pH meter.

3.5. Preparation of alloy steel sample solutions [30]

A 0.1–0.5 g of steel sample was dissolved completely in minimum amount of aqua-regia by slow heating on sand bath and then heated to fumes of oxides of nitrogen. After cooling, 5–10 mL of 1 : 1 $H_2O : H_2SO_4$ mixture was added and evaporated to dryness. Sulphuric acid treatment was repeated three times to remove all the nitric acid. The residue was dissolved in 20 mL of distilled water, filtered, and the filtrate was made up to 100 mL in a calibrated volumetric flask with distilled water. The sample solution was appropriately diluted to obtain the concentrations in the required range.

3.6. Preparation of soil sample solution

Soil sample (S-18) was obtained from Geological Survey of India (GSI), Bangalore, India. 500 mg of the soil sample was treated with 1.0 mL of concentrated HCl. When the reaction was almost over, the mixture was heated on a hot plate and evaporated to dryness. The contents were dissolved in distilled water and filtered. The filtrate was collected in a 50 mL standard flask and made up to the mark with distilled water.

3.7. Biological samples (tea leaf and vehicle exhaust)

The tea leaf samples were supplied by Andra Pradesh Agricultural Research Institute (APARI), Hyderabad, India. The vehicle exhaust sample was collected from Environment Protection Training and Research Institute (EPTRI), Hyderabad, India. A 0.1 g of tea leaf sample was taken in a beaker and dissolved in conc. nitric acid (≈ 5 mL) with heating. The solution was cooled, diluted, and filtered. The filtrate was made up to 100 mL with water in a calibrated flask. Vehicle exhaust particles (1 g) were dissolved in a mixture of 18 mL of conc. nitric acid, 18 mL of conc. perchloric acid, and 2 mL of conc. hydrofluoric acid in a 100 mL teflon beaker, evaporated to a small volume, filtered through a filter paper, and made up to 100 mL with distilled water. An aliquot (10–50 mL) of the sample solution was taken individually and cobalt was determined from predetermined calibration plot. The results are presented in Table 5.

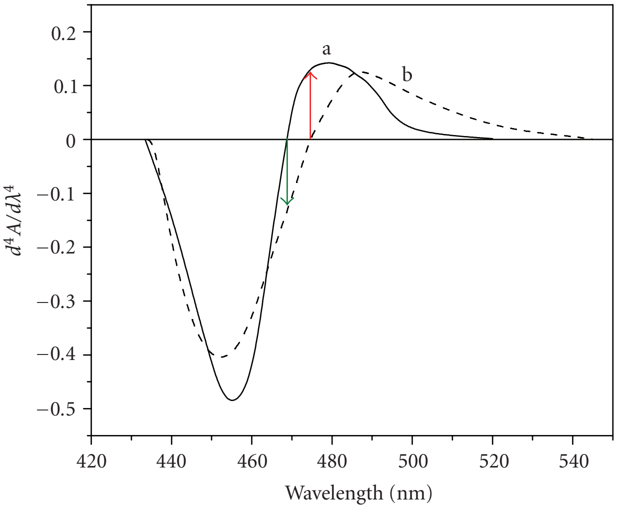

FIGURE 1: Fourth derivative spectra of (a) Co(II)-HMBATSC system versus reagent blank, (b) Ni(II)-HMBATSC system versus reagent blank; [Ni(II)] = [Co(II)] = 1.2×10^{-5} M; pH = 6.0.

3.8. Preparation of plant samples

Freshly collected samples were cleaned and dried for one hour in open air protecting from mineral contamination. The dried samples were finely powdered in a mortar. The powdered material was brought into solution by wet ashing method according to the procedures given in the literature [31]. The results are presented in Table 6.

4. RESULTS AND DISCUSSION

2-Hydroxy-3-methoxy benzaldehyde thiosemicarbazone (HMBATSC) reacts with cobalt(II) forming brown-colored complex and with vanadium(V) forming yellow-colored complex at pH 6.0. The fourth derivative spectra of [Co(II)-HMBATSC] and [Ni(II)-HMBATSC] at pH 6.0 were recorded in the wavelength region 420–550 nm and shown in Figure 1. From the figure, it can be seen that the third-order derivative spectrum of Co(II) complex shows zero amplitude at 474.5 nm and sufficient derivative amplitude at 468.5 nm, while Ni(II) complex has sufficient amplitude at 474.5 nm and zero amplitude at 468.5 nm, respectively. This will allow simultaneous determination of Co(II) and Ni(II) by fourth-order derivative spectrophotometric method by measuring the derivative amplitudes at 468.5 nm and 474.5 nm, respectively.

4.1. Verification of Beer's law validity

Individual calibration plots were constructed by plotting the fourth derivative amplitudes measured at 468.5 nm against the amount of Co(II) and plotting those measured at 474.5 nm against the amount of Ni(II) as shown in Figures 2 and 3, respectively. The plots reveal that Beer's law is obeyed in the range of 0.059–3.299 μg mL^{-1} of Co(II) and 0.058–3.285 μg mL^{-1} of Ni(II).

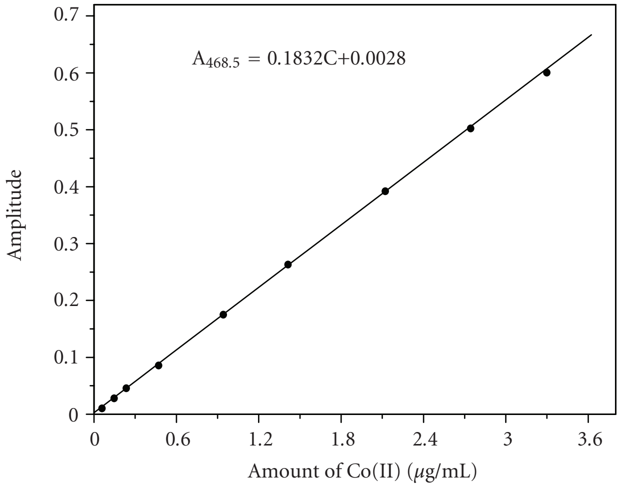

FIGURE 2: Calibration plot of Co(II)-HMBATSC, [HMBATSC] = 8×10^{-4} M; wavelength = 468.5 nm; pH = 6.0.

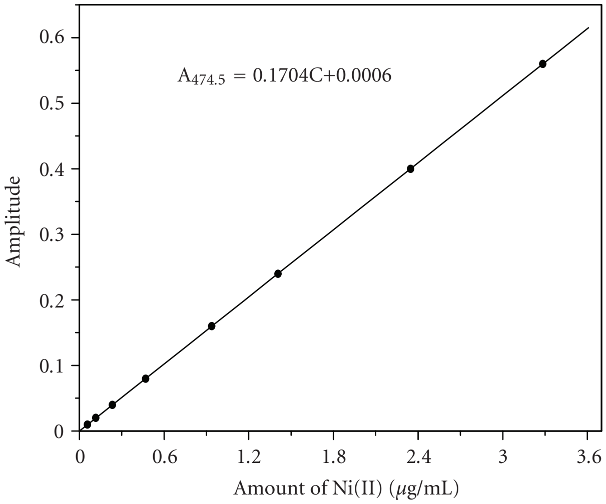

FIGURE 3: Calibration plot of Ni(II)-HMBATSC, [HMBATSC] = 8×10^{-4} M; wavelength = 474.5 nm; pH = 6.0.

4.2. Simultaneous determination of Co(II) and Ni(II)

Variable amounts of Co(II) and Ni(II) were treated with the required volume of the reagent at pH 6.0 in total volume of 10 mL and the fourth derivative spectra were recorded in the range of 420–550 nm. The derivative amplitudes were measured at 468.5 nm and 474.5 nm and the amounts of Co(II) and Ni(II) present in the mixture were computed from their respective calibration plots. The results are presented in Table 1.

Table 1: Simultaneous fourth-order derivative determination of Co(II) and Ni(II) in synthetic binary mixtures.

Amount taken (μg mL^{-1})		Amount found* (μg mL^{-1})		Relative error (%)	
Co(II)	Ni(II)	Co(II)	Ni(II)	Co(II)	Ni(II)
0.2357	0.2347	0.2362	0.2340	+0.21	−0.29
0.2357	0.4694	0.2352	0.4685	−0.21	−0.23
0.2357	0.7041	0.2354	0.7049	−0.12	+0.11
0.2357	0.9388	0.2361	0.9382	+0.16	−0.06
0.2357	1.1785	0.2365	1.1780	+0.33	−0.04
0.2357	0.2347	0.2362	0.2352	+0.21	+0.21
0.4714	0.2347	0.4708	0.2344	−0.10	−0.12
0.7071	0.2347	0.7081	0.2354	+0.14	+0.29
0.9428	0.2347	0.9420	0.2340	−0.08	−0.29
1.1735	0.2347	1.1742	0.2362	+0.05	+0.63

*Average of five determinations.

Table 2: Tolerance limits of diverse ions.

Diverse ion	Tolerance limit (μg mL^{-1})		Diverse ion	Tolerance limit (μg mL^{-1})	
	In the presence of 1.173 μg mL^{-1} of Ni(II)	In the presence of 1.18 μg mL^{-1} of Co(II)		In the presence of 1.173 μg mL^{-1} of Ni(II)	In the presence of 1.18 μg mL^{-1} of Co(II)
Ascorbic acid	3000	3200	Pb(II)	2200	2000
Tartrate	2800	2700	W(VI)	1900	1800
Citrate	2600	2500	U(VI)	1800	1750
EDTA	2400	2400	Zr(IV)	1500	1400
Thiourea	2000	2100	Cd(II)	1300	1200
Formate	1900	2000	Li(I)	1200	1100
Urea	1700	1800	Th(IV)	1000	950
Bromate	1650	1700	Na(I)	950	900
Oxalate	1600	1650	Te(IV)	800	800
Bromide	1500	1400	K(I)	750	800
Phosphate	1450	1400	Cu(II)	700	750
Nitrate	1400	1350	Al(III)	650	600
Chloride	1200	1300	Zn(II)	550	450
Sulphate	1100	1150	Pt(IV)	400	400
Acetate	1050	1000	Fe(II)	350	400
Thiosulphate	1000	900	Pd(II)	300	350
Iodide	850	800	V(V)	250	300
Fluoride	800	700	Ru(III)	250	250
—	—	—	Ti(IV)	220	200
—	—	—	Cr(III)	200	180
—	—	—	Ce(IV)	180	150
—	—	—	Mo(VI)	150	140
—	—	—	Mn(II)	130	125

4.3. *Effect of foreign ions*

The effect of various foreign ions on the determination of Co(II) and Ni(II) was studied to find out the tolerance levels of these foreign ions in the present method. The results are presented in Table 2.

5. APPLICATIONS

The present simultaneous method was used for the determination of cobalt and nickel in alloy steels and soil samples.

A known aliquot of the sample was treated with 5 mL of buffer solution (pH 6.0), 0.5 mL of HMBATSC (1×10^{-2} M)

Table 3: Simultaneous determination of Co(II) and Ni(II) in alloy steel samples.

Sample	Certified value (%)		Amount found by present method* (%)		Relative error (%)	
	Co(II)	Ni(II)	Co(II)	Ni(II)	Co(II)	Ni(II)
Eligiloy M-1712[(a)]	40.00	15.00	39.94	15.10	−0.15	+0.67
BCS 406/1[(b)]	0.016	0.14	0.017	0.128	+0.63	−1.54
Alloy steel[(c)]	23.72	11.22	23.68	11.30	−0.16	+0.71

*Average of five determinations;

(a) 20% Cr, 40% Co, 15% Ni, 0.15% C, 15% Fe, 2% Mn, 7% Mo, 0.05% Be.

(b) 0.066% Mn, 1.06% Cr, 0.05% Mo, 0.14% Ni, 0.016% Co, 0.091% Cu, 0.19% V^{z}.

(c) 51.15% Fe, 11.22% Ni, 5.09% Cu, 23.72% Co, 6.98% Al, 0.79% Ti, 0.235% Mn, 0.57% Si.

Table 4: Analysis of soil sample.

Sample and composition (ppm)	Certified (GSI) value (ppm)		Amount found by present method* (ppm)		Relative error (%)	
	Co(II)	Ni(II)	Co(II)	Ni(II)	Co(II)	Ni(II)
S-18 20.20 Pb(II) 20.30 Zn(II) 88.85 Cu(II)	40.35	50.50	39.98	50.84	−0.92	+0.67

*Average of five determinations.

Table 5: Analysis of cobalt in biological samples.

Sample	Amount of cobalt (mg/g)	
	Certified value	Present method*
Tea leaves	0.12 ± 0.008	0.117 ± 0.04
Vehicle exhaust	3.3 ± 0.3	3.25 ± 0.05

*Average of five determinations.

Table 6: Determination of nickel in plant leaves.

Sample	AAS method [32]	Present method*
Pisum sativum (Hulls)	2.060 ± 0.003	2.065 ± 0.004
Mangifera indica leaves	2.150 ± 0.004	2.152 ± 0.002
Eucalyptus leaves	1.038 ± 0.002	1.033 ± 0.005
Azadirachta indica leaves	1.481 ± 0.005	1.485 ± 0.003

*Average of five determinations.

and made up to the volume in a 10 mL volumetric flask with distilled water. The fourth derivative curves were recorded and the derivative amplitudes were measured at 468.5 nm and 474.5 nm. The amounts of Co(II) and Ni(II) were computed from the measured amplitudes with the help of predetermined calibration plots. The results obtained are given in Tables 3 and 4.

6. CONCLUSIONS

The present method is simple, sensitive, and highly selective for the simultaneous determination of Co(II) and Ni(II) in admixtures without separation and without solving simultaneous equations.

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