First- and Second-Derivative Spectrophotometry for Simultaneous Determination of Copper and Cobalt by 1-(2-Pyridylazo)-2-naphthol in Tween 80 Micellar Solutions

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1-(2-Pyridylazo)-2-naphthol (PAN) has been used for the simultaneous determination of copper and cobalt at trace levels. PAN at pH 1.89 forms red and green complexes with copper and cobalt, respectively, which are soluble in aqueous Tween 80 micellar media and are stable for at least 3 days. Under optimum conditions, calibration graphs were obtained for individual determination of copper and cobalt by zero- and first-derivative spectrophotometry and for simultaneous determination by first- and second-derivative spectrophotometry. Zero-crossing first-derivative spectrophotometry at 555 and 581 nm for cobalt and copper was used for the simultaneous determination, respectively. The second derivative method at 577 and 565 nm was also used for cobalt and copper simultaneous determination, respectively. The method enabled the determination of copper to cobalt ratios of 1:10 to 12:1 (Wt/Wt) accurately. The accuracy and reproducibility of the determination method on known various amounts of copper and cobalt in their binary mixtures were tested. Effects of diverse ions on the determination of copper and cobalt to investigate the selectivity of the method were also studied. The recommended procedures were applied to various alloys, different water matrices and vitamin B_{12} and B-complex ampoules.

Key Words: Copper, Cobalt, PAN, Simultaneous, Derivative spectrophotometry.

Introduction

Copper and cobalt are metals that appear together in many real samples. Several techniques such as X-ray fluorescence[1], atomic fluorescence spectrometry[2], polarography [3,4], high performance liquid chromatography[5−7], atomic absorption spectrometry[8,9], chemometrics-based methods[10−13], spectrophotometric methods in micellar media[14], flow system with electrochemical detection[15], time resolved chemiluminescence[16], and deriva-

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tive spectrophotometry[17]have been applied for simultaneous determination of these ions in different samples. Among the most widely used analytical methods are those based on UV-visible spectrophotometry techniques, due to both experimental rapidity and simplicity and the wide application.

For a single-peak spectrum, the first derivative is a plot of the gradient $dA/d\lambda$ of the absorption envelope versus wavelength. Derivative spectra can be produced by processing the spectrophotometer output. The use of derivative spectra can increase the detection sensitivity of minor spectra features and reduce the error caused by the overlap of the analyte spectral band by interfering bands of other species in the sample. It is possible to measure the absolute value of the derivative of the sum curve at an abscissa value (wavelength) corresponding to a zero-crossing of one of the components in the mixture. This is termed a zero-crossing measure and can be applied to the first and second derivatives. The zero-crossing derivative spectroscopic mode allows the resolution of binary mixtures of analytes by recording their derivative spectra at wavelengths at which one of the components exhibits no signal. Zero-crossing measurements for each component of the mixture are therefore the sole function of the concentration of the others[18].

Multidentate azo ligands have been used in various analytical procedures. Reagents such as 4-(2-pyridylazo)-resorcinol[19−23], 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol[24], 1-(2-pyridylazo)-2-naphthol[25−29], 1-(2-thiazolylazo)-2-naphthol[30], 2-(4-methyl-2-quinolylazo)-5-diethyl-aminophenol[31], and 2-(2-quinolylazo)-5-diethyl-aminophenol[32] have been reported to be sensitive and relatively selective for the determination of nickel, silver, cobalt, copper, cadmium, manganese, zinc and iron. The reagents were designed for use in solvent extraction. Spectrophotometric analysis in micellar solutions against solvent extraction based methods has found widespread uses in recent years because of the solubilizing and stabilizing properties of micellar solutions[33].

This paper reports a simple, sensitive and selective method by zero-, first- and second-derivative spectrophotometry in micellar solutions for the individual and simultaneous determination of copper and cobalt. The method is based on the formation of complexes of Cu(II) and Co(III) ions with 1-(2-pyridylazo)-2-naphthol (PAN) in the Tween 80 micellar media.

Experimental

Reagents and chemicals

The water used in this work was doubly distilled and all of the reagents used were analytical grade. A solution of 0.20% of 1-(2-pyridylazo)-2-naphthol (Merck) in ethanol was prepared and used. Cu(II) solution (1000 μg mL^{-1}) was prepared and then standardized[34]. A standard solution of Co(II) as 1000 μg mL^{-1} was prepared and was standardized by the standard procedure[35]. Diluted copper and cobalt solutions were prepared daily by diluting the appropriate volume of these stock solutions with deionized water. Tween-80 was purchased from Merck and its solution was prepared as 6.4% (Wt/V). Universal buffers (acetic acid-phosphoric acid-boric acid mixture) at different pHs were used.

Apparatus

A Cecil CE 9020 UV-Vis scanning spectrophotometer equipped with 10-mm quartz cells was used to record the zero-, first- and second-order derivative spectra. A Cecil CE 1021 UV-Vis spectrophotometer was utilized

to measure the absorbances of the solutions. A Metrohm model 691 pH-meter was used for adjusting pHs of the solutions and preparing working buffers.

## Procedure for individual and simultaneous determination of copper and cobalt

One milliliter of buffer solution of pH 1.89, 5.0 mL of 6.4% Tween 80 solution, 1.0 mL of sample solution containing cobalt or copper, 1.0 mL of 0.03 M tartarate-fluoride solution and 1.0 mL of ethanolic solution of 0.10% PAN were added to a 10.0 mL volumetric flask and then its volume was adjusted with doubly distilled water. The sample solution was transferred into a spectrophotometer cell and its absorbance was measured at 555 nm for copper or 581 nm for cobalt against a blank solution for individual determination of copper or cobalt. The spectrum of the sample solution was also recorded against its blank for individual first-order derivative spectrophotometric determination of copper or cobalt in the wavelength range 500-700 nm with $\Delta\lambda = 2$ nm using a scan speed of 600 nm/min. The analytical signals were at 578 nm for copper and at 642 nm for cobalt where the maximum sensitivities for first-derivative spectrophotometry were obtained. Copper or cobalt concentrations can be determined using their previously prepared zero- and first-derivative spectrophotometric calibration graphs.

For simultaneous determination the first- and second-derivative spectra of the sample solution after color development was recorded against its blank in the wavelength range 500-700 nm with $\Delta\lambda = 2$ nm using a scan speed of 600 nm/min. Zero crossing was used for the simultaneous determination of copper and cobalt. The first-derivative analytical signals were at 581 nm for copper and at 555 nm for cobalt. Furthermore, second-order derivative signals were at 577 nm for cobalt and at 565 nm or 592 nm for copper. Copper and cobalt concentrations can be determined using their previously prepared first- and second-order derivative calibration graphs.

Results and Discussion

The effects of various parameters on the simultaneous determination of copper and cobalt were investigated. One of the most important parameters is pH. Experiments in various pHs show that the spectra of PAN, Cu-PAN and Co-PAN complexes are dependent on the pH of the solution. These spectra and their characteristics are given in Figure 1 and Table 1. The shape of the absorption spectra, maximum wavelengths and molar absorptivities change considerably when pH is varied from 3.29 to 2.09 for copper and from 3.29 to 2.21 for cobalt. The shape and maximum wavelengths of the spectra of copper and cobalt complexes do not change at pHs lower than 2.21 and 1.98, respectively. In addition, according to the results, the molar absorptivitiy of the Cu-PAN complex decreases when pH decreases. In terms of selectivity and spectral separation, a low pH is better but in terms of sensitivity, high pHs are favored. However, selectivity is the most important parameter in the simultaneous determination methods. According to the results pH 1.89 was selected for subsequent studies.

Optimization of the other parameters such as PAN and Tween 80 concentrations was performed spectrophotometrically for copper at 555 nm and for cobalt at 581 nm. PAN concentration was varied at a fixed concentration of Tween 80 as 3.2% (Wt/V). Based on the obtained results, sensitivities are maximum and constant in the PAN concentration range 0.004-0.012%. A lower concentration of PAN causes low sensitivity and in higher concentrations PAN precipitates.
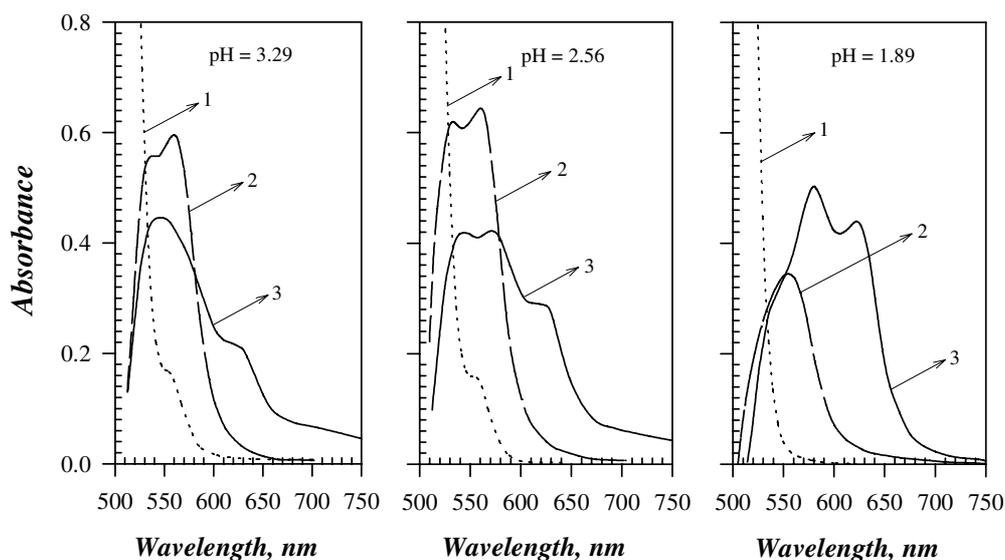
Figure 1. Absorbance spectra at different pHs. 1) 0.01% PAN against water, 2) 1.0 μg mL^{-1} Cu-PAN complex, 3) 1.0 μg mL^{-1} Co-PAN complex, in 3.2% Tween 80.

Table 1. Effect of pH on the spectral characteristics of copper and cobalt complexes of PAN.

	cobalt-PAN		copper-PAN	
pH	Maximum wavelength (nm)	Molar absorptivity L cm^{-1} mol^{-1}	Maximum wavelength (nm)	Molar absorptivity L cm^{-1} mol^{-1}
0.1 M HClO$_4$	581	2.78×10^4	555	1.81×10^4
1.81	581	2.79×10^4	555	2.08×10^4
1.89	581	2.83×10^4	555	2.12×10^4
1.98	581	2.80×10^4	555	2.14×10^4
2.09	581	2.69×10^4	556	2.74×10^4
2.21	580	2.36×10^4	558	3.44×10^4
2.56	572	2.49×10^4	558	3.99×10^4
3.29	545	2.63×10^4	558	3.76×10^4

Conditions: 10 mL of aqueous solution containing 0.010% of PAN, 3.2% of Tween 80, universal buffer with different pHs and 10 μg of Cu(II) or Co(II).

The effect of Tween 80 concentration on sensitivity was also studied. Tween 80 concentrations greater than 3.2% did not cause greater sensitivity or solubilizing power. Thus a PAN concentration of 0.01% and a Tween 80 concentration of 3.2% were selected for further studies.

The stability of the complexes formed was checked at the optimum condition. The results showed that the samples were stable and precipitation was not observed.

The effect of ionic strength on the sensitivity of the copper and cobalt determination was investigated. Different concentrations of sodium chloride and sodium nitrate as ionic buffers were tolerated in the range 0.00 to 0.50 M but considerable differences in the sensitivities were not observed.
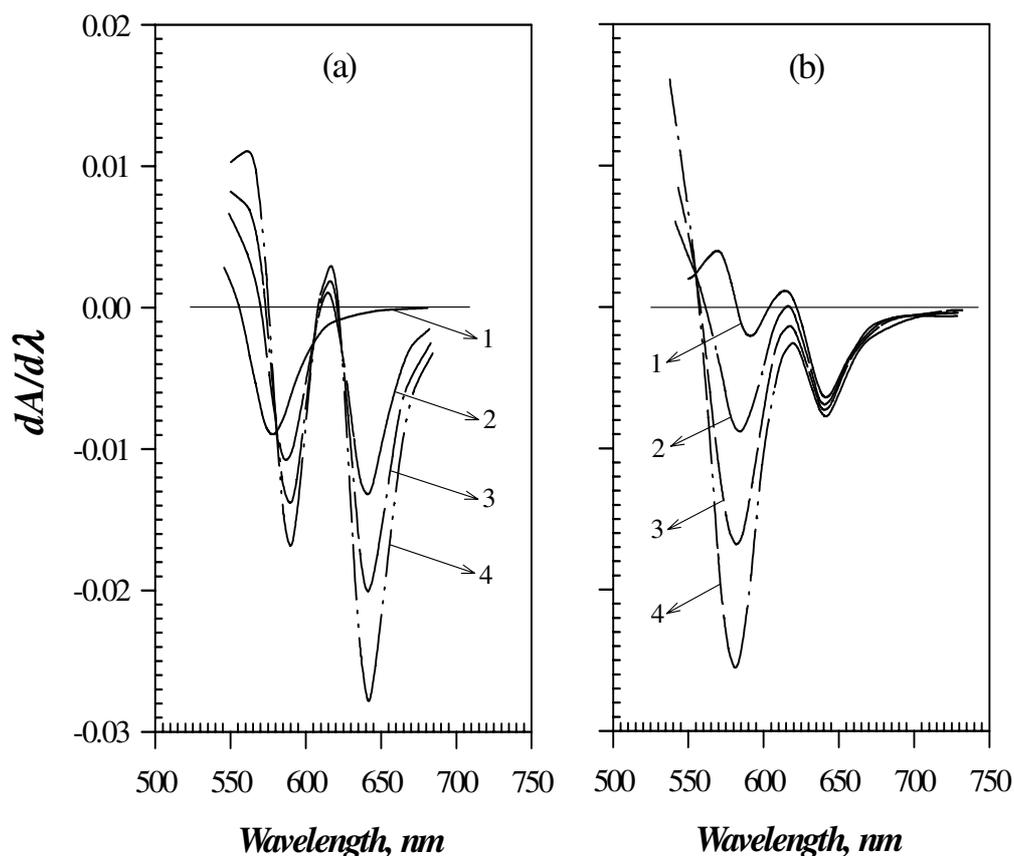
Derivative spectra

The first- and second-derivative spectra of the Cu-PAN and Co-PAN complexes in the Tween 80 micellar media are shown in Figure 2. Zero-crossing wavelengths in the first-derivative spectra of Cu-PAN and Co-PAN that can be used for their sensitive simultaneous determination are 581 and 555 nm, respectively. For second-order derivative simultaneous determination of copper and cobalt, 565 (or 592) and 577 nm can also be applied.
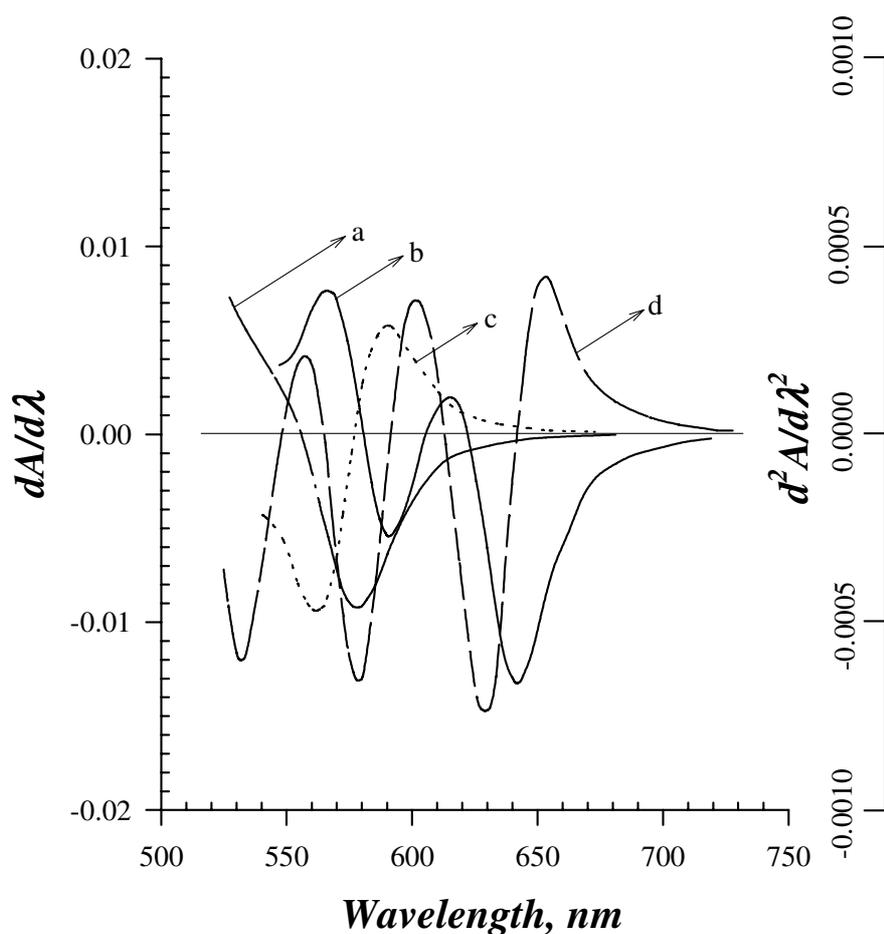
Figure 2. Derivative spectra of copper and cobalt complexes of PAN. a) first derivative of Cu-PAN, b) first derivative of Co-PAN, c) second derivative of Cu-PAN, d) second derivative of Co-PAN. Conditions: 10 mL solution at pH 1.89 containing 3.2% Tween 80, 0.01% PAN and 1.0 μg mL^{-1} cobalt or 1.0 μg mL^{-1} copper.

In the zero-crossing derivative method it is necessary that zero-crossing wavelengths do not change with varying concentrations of the related species. To evaluate the condition, changes in the pre-mentioned zero-crossing wavelengths for cobalt and copper were tested in the presence of different concentrations of another species. According to the results given in Figures 3 and 4, no shift in the zero-crossing wavelengths was observed.

Figure 3. First derivative spectra of the solutions containing: a) fixed 1.0 μg mL^{-1} copper and 1: 0.0 μg mL^{-1}, 2: 1.0 μg mL^{-1}, 3: 1.5 μg mL^{-1} and 4: 2.0 μg mL^{-1}cobalt. b) fixed 0.5 μg mL^{-1} cobalt and 1: 0.0 μg mL^{-1}, 2: 1.0 μg mL^{-1}, 3: 2.0 μg mL^{-1} and 4: 3.0 μg mL^{-1}copper. Conditions: 10 mL solution at pH 1.89 containing 3.2% Tween 80 and 0.01% PAN.

Effects of foreign ions

When Cu or Co is determined with PAN, the other ions in real samples might interfere. The effects of foreign species on the first-derivative spectrophotometric determination of 5 μg Cu or 5 μg Co were investigated individually under the selected conditions. Effects of diverse ions on the determination of copper and cobalt are shown in Table 4. Solutions containing 5 μg copper or 5 μg cobalt and various amounts of foreign ions, given in Table 4, were prepared and the proposed first-order derivative procedure for their determination was followed. The only relatively serious interfering species was nickel. To prevent interferences by nickel, the addition of masking agents such as EDTA, citrate and 1, 10-phenanthroline was tested but was not successful. The other ions such as HPO$_4^{2-}$, ClO$_3^-$, IO$_3^-$, Ba^{2+}, Mg^{2+}, Ca^{2+}, F$^-$, Cl$^-$, Br$^-$, I$^-$, CH$_3$COO$^-$ and NO$_2^-$ in the concentration of 1000 μg mL^{-1} did not show interference effects.
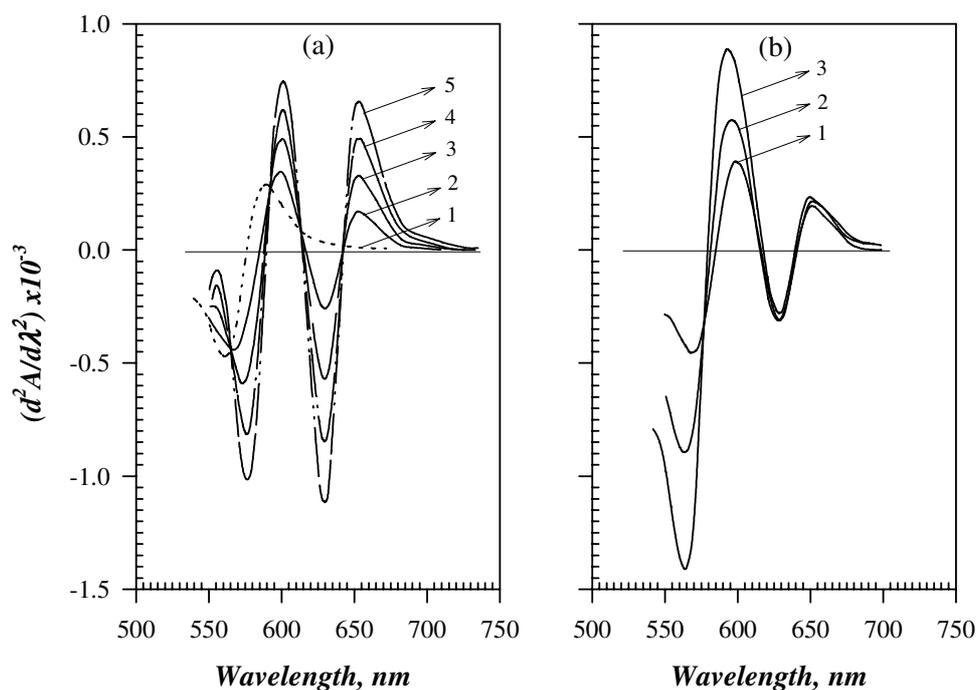
Figure 4. Second derivative spectra of the solutions containing: a) fixed 1.0 μg mL^{-1} copper and 1: 0.0 μg mL^{-1}, 2: 0.5 μg mL^{-1}, 3: 1.0 μg mL^{-1}, 4: 1.5 μg mL^{-1} and 5: 2.0 μg mL^{-1} cobalt. b) fixed 0.5 μg mL^{-1} cobalt and 1: 1.0 μg mL^{-1}, 2: 2.0 μg mL^{-1} and 3: 3.0 μg mL^{-1} copper. Conditions: 10 mL solution at pH 1.89 containing 3.2% Tween 80 and 0.01% PAN.

Calibration, accuracy and precision

Two spectrophotometric and 2 first-order derivative spectrophotometric calibration graphs were constructed for the individual determination of copper and cobalt. First- and second-order calibration graphs were also obtained for the simultaneous determination of copper and cobalt. The obtained calibration parameters are presented in Table 2. The precision and accuracy of the zero-, first- and second-order derivative spectrophotometric methods were also evaluated for the analysis of 8 samples. The results are presented in Table 3. Ten absorbance blank measurements at 555 and 581 nm show limits of detection of about 7 and 4 ng mL^{-1} for copper and cobalt, respectively ($3 \times S_b$).

Recoveries and precisions of Cu(II) and Co(II) in their binary mixtures

Known different solutions containing copper and cobalt were analyzed by the procedure to evaluate its validity. The recoveries and precisions of the first- and second-derivative simultaneous determination procedures are given in Table 5. According to the results, the applicability of the method for the simultaneous determination of copper and cobalt in their binary mixtures is clarified.

Table 2. Calibration data for the determination of copper and cobalt.

Calibration equation	Wavelength	Linear range	Regression
	(nm)	(μg mL^{-1})	
Individually determination			
Spectrophotometry:			
Abs. = -1.44 $\times$ 10^{-2} + 4.90 $\times$ 10^{-1} C$_{Co}$	581	0.1-4.0	0.9998
Abs. = -3.4 $\times$ 10^{-4} + 3.37 $\times$ 10^{-1} C$_{Cu}$	555	0.05-4.0	0.9998
First-derivative spectrophotometry:			
Δ Abs/$\Delta\lambda$ = -7.4 $\times$ 10^{-5} + 1.29$\times$10^{-2} C$_{Co}$	642	0.025-4.0	0.9998
Δ Abs/$\Delta\lambda$ = 2.37 $\times$ 10^{-4} + 8.92$\times$10^{-3} C$_{Cu}$	578	0.05-5.0	0.9995
Simultaneous determination			
First-derivative spectrophotometry:			
Δ Abs/$\Delta\lambda$ = -3.18 $\times$ 10^{-5} + 4.73$\times$10^{-3} C$_{Co}$	555	0.025-2.5	0.9996
Δ Abs/$\Delta\lambda$ = -4.4 $\times$ 10^{-5} + 8.68$\times$10^{-3} C$_{Cu}$	581	0.05-4.5	0.9998
Second-derivative spectrophotometry:			
Δ^2 Abs/$\Delta\lambda^2$ = 5.3 $\times$ 10^{-6} + 6.12 $\times$ 10^{-4} C$_{Co}$	577	0.05-3.5	0.9997
Δ^2 Abs/$\Delta\lambda^2$ = -1.1 $\times$ 10^{-7} + 4.57 $\times$ 10^{-4} C$_{Cu}$	565	0.05-4.0	0.9998
Δ^2 Abs/$\Delta\lambda^2$ = 1.02 $\times$ 10^{-5} + 2.70 $\times$ 10^{-4} C$_{Cu}$	592	0.1-4.0	0.9993

Table 3. Accuracy and precision of the recommended procedures.

Co Taken (μg mL^{-1})	Co Found (μg mL^{-1}) RSD% (n = 8)			Cu Taken (μg mL^{-1})	Cu Found(μg mL^{-1}) RSD% (n = 8)			
	Abs. 581 nm	ΔAbs/$\Delta\lambda$ 642 nm	Δ^2Abs/$\Delta\lambda^2$ 577 nm		Abs. 555 nm	ΔAbs/$\Delta\lambda$ 578 nm	Δ^2Abs/$\Delta\lambda^2$ 565 nm	592 nm
0.025		0.024		0.050	0.048	0.050	0.054	
	(6.0)				(4.6)	(4.9)	(5.1)	
0.050	0.053	0.048	0.100	0.102	0.104	0.096	0.096	
		(2.6)	(5.3)		(2.5)	(3.1)	(3.7)	(4.5)
0.100	0.094	1.02	0.98	2.00	1.95	1.95	2.04	2.07
	(4.9)	(1.9)	(2.3)		(0.6)	(1.1)	(0.8)	(0.6)
2.00	1.99	1.97	2.02	4.00	4.01	3.96	3.94	3.97
	(1.1)	(0.7)	(1.0)		(0.9)	(1.1)	(0.9)	(0.7)
3.50	3.54	3.46	3.55	5.00	4.93			
	(0.8)	(1.0)	(0.9)			(0.8)		
4.00	3.94	3.96	3.95					
	(0.9)	(1.1)	(1.2)					

Table 4. Effect of foreign ions on the individually first derivative determination of 5 μg of copper and 5 μg of cobalt.

Ion added	Amount (μg)	Error percent for cobalt at 555 nm	for Error percent for copper at 581 nm
SCN^{-a}	500	+0.7	-0.8
Mn^{2+a}	500	+1.1	+5.5
Al^{3+a}	500	+0.2	+0.5
WO_4^{2-a}	500	+0.8	+0.6
Cr^{3+a}	500	+0.2	+0.4
Sn^{2+a}	500	-0.6	-0.8
MoO_4^{2-a}	500	+1.1	+0.5
Zn^{2+a}	500	-1.1	+0.6
Cd^{2+a}	500	-0.3	+0.5
Pb^{2+a}	500	+0.4	+4.4
CrO_4^{2-a}	500	+0.2	+0.9
Ag^{+a}	500	-0.7	-0.8
Hg^{2+ab}	500	+0.8	+1.0
Fe^{3+}	250	-4.9	+4.1
UO_2^{2+}	250	+3.5	+7.5
Bi^{3+}	100	+3.1	+5.3
V^{3+}	50	+1.2	+4.4
Co^{2+}	40		+3.7
Cu^{2+}	40	+3.3	
Ni^{2+}	5	+1.8	+5.7

[a]Maximum concentration tested.
[b]Masked with iodide 0.003 M.

Application

Synthetic samples according to the composition of some industrial alloys, some water samples, and B_{12} and B-complex ampoules to test applicability of the introduced procedures for the determination of copper and cobalt were examined.

The alloys selected have many industrial applications as powders, foils and wires. To select the alloys for analysis these aspects were considered. For analysis of the alloys in Table 6 the copper or cobalt contents of the analyzed solutions were 1.0 μg mL^{-1}and the cobalt content of the synthetic solution of Lemaiguand was 0.40 μg mL^{-1}. The other ions in solutions were adjusted according to their percentages.

Table 5. First- and second-derivative simultaneous determination of copper and cobalt in some of their binary mixtures.

Sample	Cobalt (μg mL^{-1}) RSD% (n = 4)			Copper (μg mL^{-1}) RSD% (n = 4)		
	Taken	Found		Taken	Found	
		Δ Abs/$\Delta\lambda$	Δ^2Abs/$\Delta\lambda^2$		ΔAbs/$\Delta\lambda$	Δ^2Abs/$\Delta\lambda^2$
1	0.200	0.195	0.205	0.200	0.192	0.195
		2.0	1.7		2.5	2.1
2	3.00	2.91	2.93	0.30	0.309	0.305
		1.1	1.3		3.4	3.9
3	3.00	2.94	2.94	1.00	1.03	1.04
		1.4	1.6		1.9	1.5
4	0.500	0.511	0.503	0.500	0.514	0.508
		1.0	1.0		1.2	1.3
5	0.200	0.210	0.208	2.00	1.94	1.98
		3.7	3.3		1.4	1.4
6	0.200	0.193	0.195	2.40	2.44	2.49
		3.8	4.1		1.4	1.6
7	2.00	1.97	1.96	0.200	0.207	0.201
		1.3	1.1		4.1	3.6
8	1.00	1.04	1.06	3.00	2.92	2.96
		2.3	2.4		1.8	1.5
9	1.50	1.51	1.53	1.50	1.54	1.51
		2.4	2.7		1.7	1.6

Drinking water resources must contain levels of copper and cobalt below their critical values. Evaluation of the method for the analysis of high amounts of the 2 metals in drinking water and lake water matrices should be performed. For analysis of the water samples, 0.50 mL of standard copper and cobalt solutions was spiked into a 10.0 mL flask together with 2.0 mL of the tap and natural water samples. Then the copper and cobalt contents were analyzed by simultaneous first- and second-derivative spectrophotometric procedures (Table 7).

B$_{12}$ vitamin contains Co(III) and a corrin ring that has a key role in some biological activities of blood. B$_{12}$ has been prepared as ampoules lonely or with the other B series vitamins (B-complex). Quality control of these drugs can be performed by determining their cobalt contents. The contents of 2.0 mL B-complex ampoules alone or 4 $\times$ 1.0 mL B$_{12}$ ampoules were decomposed in a 50 mL round-bottom flask by heating with 10 mL of a mixture containing concentrated nitric and sulfuric acids (10+1) on a hot plate until near dryness[36]. Dropwise addition of concentrated nitric acid is needed for obtaining a colorless or yellow residue. The residue was neutralized with dilute sodium hydroxide solution, and then was diluted to an appropriate volume (50 mL). The cobalt contents were analyzed using 2.0 or 4.0 mL of the solutions by the recommended first-derivative procedure. The standard method using nitroso-R salt was also used[35] as a reference method. The results are given in Table 8.

Table 6. Determination of copper and cobalt in some synthetic alloys.

Sample	Cobalt found, % (n = 4)		Copper found, % (n = 5)	
	Zero derivative	First derivative	Zero derivative	First derivative
Gold Label:	2.93 ± 0.06	2.97 ± 0.07		
Cr (4%), W (18%)				
Co (3%), V (1.5%)				
bal Fe.				
Remalloy:	12.1 ± 0.3	12.1 ± 0.3		
Mo (17%), Co (12%)				
Mn (3%), bal Fe.				
Manganin:			82.9 ± 0.9	83.4 ± 1.2
Mn (12%), Ni (4%)				
Cu (84%)				
Aluminum 2024:			4.52 ± 0.08	4.48 ± 0.10
Al (93.5%), Cu (4.4%)				
Mn (0.6%), Mg (1.5)				
Brass 422:			88.2 ± 1.7	88.5 ± 1.3
Cu (87.5%), Zn (11.5%)				
Sn(1%)				
Lemaiguand:	7.92 ± 0.13^{a}	8.05 ± 0.11^{a}	38.7 ± 0.5^{b}	39.1 ± 0.6^{b}
Cu (39%), Ni (7%)				
Co (8%), Zn (7%)				
Sn (9%), Fe (30%)				

$\pm$ amounts are standard deviation.

a: Simultaneous determination by first-derivative procedure.

b: Simultaneous determination by second-derivative procedure.

Table 7. Determination of copper and cobalt in different real water matrices.

Sample	Spiked, $\mu g\ mL^{-1}$		Found, $\mu g\ mL^{-1}$			
	Copper	Cobalt	Copper		Cobalt	
			$\Delta\ Abs/\Delta\lambda$	$\Delta^2 Abs/\Delta\lambda^2$	$\Delta Abs/\Delta\lambda$	$\Delta^2 Abs/\Delta\lambda^2$
Shoorabil water	0.50	0.50	0.52 ± 0.02	0.50 ± 0.01	0.51 ± 0.01	0.53 ± 0.01
Tap water	0.50	0.50	0.51 ± 0.01	0.52 ± 0.02	0.49 ± 0.02	0.50 ± 0.02
Tap water	1.00	1.00	1.03 ± 0.01	1.01 ± 0.03	0.99 ± 0.02	1.02 ± 0.03

$\pm$ amounts are standard deviation.

Table 8. Determination of cobalt in vitamin ampoules.

Sample	Cobalt found[#](μg) RSD% (n = 4)	Cobalt found[$]($\mu$g) RSD% (n = 5)
1	371.4	361.2
	1.5	1.5
2	366.4	372.4
	1.6	1.8
3	47.1	46.5
	2.1	1.6
4	46.6	46.3
	1.9	1.5
5	46.1	45.9
	2.1	1.9

1: B. complex (Lorestan); vitamin B_{12} (8 mg), vitamin B_6 (4 mg),

vitamin B_2 (4 mg), vitamin B_1 (10 mg).

2: B. complex (Ferdos); vitamin B_{12} (8 mg), vitamin B_6 (4 mg),

vitamin B_2 (4 mg), vitamin B_1 (10 mg).

3: vitamin B_{12}(Osveh); 1000 μg.

4: vitamin B_{12}(Ferdos); 1000 μg.

5: vitamin B_{12}(Darupakhsh); 1000 μg.

: Analyzed by the recommended first derivative procedure.

$: Analyzed by nitroso-R method.

Conclusion

A sensitive and selective method was established for individual and simultaneous determination of cobalt and copper using zero-, first- and second-order derivative spectrophotometry with PAN in Tween 80 micellar media. The proposed procedures were applied to assays of copper and cobalt in their binary, synthetic alloys, vitamin and water samples. In Table 9 some methods are introduced for the determination of cobalt or/and copper using PAN as chelating agent. Simplicity, low cost, low organic solvent consumption, long linearity range and capability of simultaneous determination are the advantages of the proposed method against some of the introduced methods. The proposed method should also be useful for accurate, precise and rapid determination of cobalt and copper in various samples.

Table 9. Comparison of some copper and cobalt determination methods using PAN.

Metal determined	Method	Reference
Cobalt	extraction with chloroform; copper interferes; λ_{max}=640 nm with working range of 0.1-2.4 μg mL^{-1}	37
Cobalt	cloud point extraction using mixed micelles; working range and recovery percent were 0.025-0.200 μg mL^{-1} and 98-102%, respectively	38
Cobalt	extraction with chloroform; RSD was in the range of 1-3%; λ_{max}=630 nm with working range of 0.2-3.0 μg mL^{-1}	39
Cobalt	sorption by surfactant coated alumina then atomic absorption spectrometry; RSD was in the range of 1.4-4.0%; preconcentration factor was 100	40
Cobalt	in mixed micellar solution; λ_{max}=625 nm with molar absorptivity of 1.9×10^4 L mol^{-1} cm^{-1} and working range of 0.40-3.20 μg mL^{-1}; RSD was about 1.0%	25
Copper	in Triton X-100 micellar solution; λ_{max}=520 nm with molar absorptivity of 1.14×10^5 L mol^{-1} cm^{-1} and working range of 0.00-0.60 μg mL^{-1}; RSD was about 1.4-4.0%	41
Copper	extraction with Co-PAN-CCl$_4$; λ_{max}=565 nm with molar absorptivity of 2.27×10^4 L mol^{-1} cm^{-1} and working range of 0.3-12.0 μg mL^{-1}	42
Copper	in Triton X-100 micellar solution; λ_{max}=555 nm with molar absorptivity of 5.21×10^4 L mol^{-1} cm^{-1} and working range of 0.08-4.00 μg mL^{-1}	43
Copper	electrothermal atomic absorption spectrometry; RSD was less than 10% recovery was in the range of 90-100%; detection limit was 1.9 pg	44
Copper	automatic liquid-liquid extraction-spectrophotometry; working range and RSD were 0.025-0.50 μg mL^{-1} and 6%, respectively	45
Copper	a neural network-differential pulse stripping method; working range was in the range of 0.005-0.550 μg mL^{-1}	46
Copper and Lead	optical sensor; optimum pH was 5.0; detection limit for copper and lead was 3.2×10^{-7} and 1.0×10^{-8} M, respectively	47
Cobalt, Copper and Nickel	precipitation then atomic absorption spectrometry; recovery was in the range of 98.4-101.2%	48
Cobalt, Copper and Nickel	a chemometrics method after solid phase separation; preconcentration factor was 100	49
Cobalt and Copper	in Tween 80 micellar solution; working ranges by first-derivative spectrophotometry for cobalt and copper were 0.025-2.500 and 0.050-4.500 μg mL^{-1}, respectively; simultaneous determination of cobalt to copper ratio was in the range 10:1 to 1:12	This work

Acknowledgments

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