pH Controlled Condition for Selective Simultaneous Determination of Nickel and Cobalt in Alloys by First Derivative Spectrophotometry

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Abstract

1-(2-Pyridylazo)-2-naphthol (PAN) has been used for the simultaneous determination of nickel and cobalt at trace levels. PAN complexes of nickel and cobalt in the pH 1.89 form red and green colored complexes, respectively which are soluble in aqueous Tween 80 micellar media. Under optimum conditions, calibration graphs for simultaneous determination by first derivative spectrophotometry were obtained. Zero crossing first derivative spectrophotometry at 641 and 580 nm was used for the simultaneous determination. The method is able to determine cobalt to nickel ratio 15:1 to 1:6 (Wt/Wt), accurately. Accuracy and reproducibility of the determination method on the known various amounts of cobalt and nickel in their binary mixtures were tested. Effects of diverse ions on the determination of cobalt and nickel to investigate selectivity of the method were also studied. The recommended procedure was applied to various nickel-cobalt alloys.

Key words: Nickel, Cobalt, Simultaneous determination, Derivative spectrophotometry.

Introduction

Nickel and cobalt are metals of prime environmental concern. These toxic metals are significant for environmental surveillance, food control, occupational medicine, toxicology and hygiene. Cobalt alloys are used in some industrial products because of their sufficient hardness and resistance against oxidation at high temperatures, for example in manufacturing of turbine blades and cutting tools. Cobalt-60 is used as an efficient

radioactive tracer and an anti-cancer treatment agent in medicine. Some cobalt compounds such as vitamin B_{12} (cyanocobalamin) are important for biological activities [1]. Therefore, determination of cobalt is valuable for quality control of artificial and biological samples in a simple, selective and sensitive manner. Nickel is the metal component of the enzyme urease and as such is considered to be essential to plants and some domestic animals. Essentially of nickel to man has not been demonstrated. More attention has been focused on the toxicology of nickel in low concentrations, such as the fact that nickel can cause allergic reactions and that certain nickel compounds may be carcinogenic [2]. The determination of cobalt and nickel in various samples which it is found at low levels requires the use of sensitive and selective procedures.

Several techniques such as flame AAS after preconcentration by chelating agents or modified resins [3,6] or electrothermal AAS [7,8] high performance liquid chromatography [9,12], voltammetry [13,17], continuous flow or stopped flow techniques [18,19], chemometrics based methods [20,24], spectrophotometric methods in micellar media [25], x-ray spectrometry [26] and atomic fluorescence spectrometry[27] have been applied for the simultaneous determination of these ions in different samples. Among the most widely used analytical methods are those based on the UV-visible spectrophotometry techniques, due to both the resulting experimental rapidity and simplicity.

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 [28].

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

Experimental

Reagents and chemicals

Water used in this work was doubly distilled water and all of the reagents used were of analytical grade reagents. A solution of 1-(2-pyridylazo)-2-naphthol (Merck) as 0.20%

(Wt/V) in ethanol was prepared and used. Standard nickel(II) solution (2000 μg ml^{-1}) as stock solution was prepared in a 250.0 ml volumetric flask and then was standardized [29]. Standard solution of cobalt(II) as 1000 μg ml^{-1} was prepared by dissolving appropriate amounts of hydrated cobalt(II) chloride in doubly distilled water and adjusting the volume to 250.0 ml in volumetric flask by doubly distilled water. Standardization of the solution was performed by the standard procedure cited [29]. Tween 80, Ttriton X-100 and sodium dodecylsulfate (SDS) were purchased from Merck and their solutions as 6.4% (Wt/V) were prepared into 250 ml volumetric flasks. Universal buffers (acetic acid-phosphoric acid-boric acid mixture) were used at different pHs for this study.

Apparatus

Absorbance measurements, zero and first derivative spectra were obtained by a Cecil CE 9020 UV-Vis scanning spectrophotometer equipped with one pair of 10-mm light path quartz matched cells. Measurements of pH were made using a Metrohm 691 pH-meter equipped with a glass-saturated calomel combined electrode.

Procedure

To a 10.0-ml volumetric flask were added 5 ml of Tween 80 in 6.4% concentration, one drop of 0.1 M ammonia solution, the required volume of neutralized sample solution containing cobalt and nickel, 0.5 ml of 0.1 M tartarate-fluoride solution and 1.0 ml of ethanolic solution of 0.20% PAN. After 5 min standing for completing of complexation reaction, 0.5 ml of universal buffer with pH equal to 1.89 and 0.5 ml of 0.1 M o-phenanthroline were added and the volume was adjusted to the mark with double distilled water. First order derivative spectra of the sample solution were recorded against its reagent blank in the wavelength range of 540-680 nm with $\Delta\lambda$=2 nm using a scan speed of 200 nm/min. The first derivative analytical signals were at zero crossing wavelengths of 580 and 641 nm, respectively for nickel and cobalt determination. Nickel and cobalt concentrations can be determined using the same manner prepared calibration graphs.

Results and Discussion

The effects of various parameters on the simultaneous determination of nickel and cobalt were investigated. One at a time optimization procedure for obtaining of optimum condition was evaluated.

One of the most important parameters is pH. Experiments in various pHs show that spectra of PAN and Co-PAN complexes were dependent to pH but Ni-PAN spectrum was independent, approximately. Some spectra and their characteristics have been given in Fig. 1 and Table 1. The shape of absorption spectra, maximum wavelengths and molar absorptivities change considerably when pH varies from 3.29 to 2.09 for cobalt. The shape and maximum wavelength of the spectra of cobalt complex do not change at pHs lower than 2.09. For Ni-PAN, sensitivity decreases when pH is lowered but the shape of Ni-PAN spectra do not change considerably when pH is lowered. In the viewpoints of selectivity and spectral resolution low pH is better but in the viewpoint of sensitivity high pHs are favored. However, selectivity is the most important parameter in the simultaneous determination. According to these results, pH 1.89 was selected for the next studies.

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

pH	Cobalt-PAN		Nickel-PAN	
	λ_{max} (nm)	Molar absorptivity L cm^{-1} mol^{-1}	λ_{max} (nm)	Molar absorptivity L cm^{-1} mol^{-1}
1.81	581	2.83×10^4	569	4.59×10^4
1.89	581	2.96×10^4	569	4.62×10^4
1.98	581	2.80×10^4	569	4.67×10^4
2.09	581	2.69×10^4	567	4.87×10^4
2.21	580	2.36×10^4	566	4.99×10^4
3.29	545	2.63×10^4	566	5.03×10^4

Condition: 10 ml solution containing 0.010% PAN, 3.2% Tween 80, universal buffer with different pHs and 10 μg Co(II) or Ni(II).

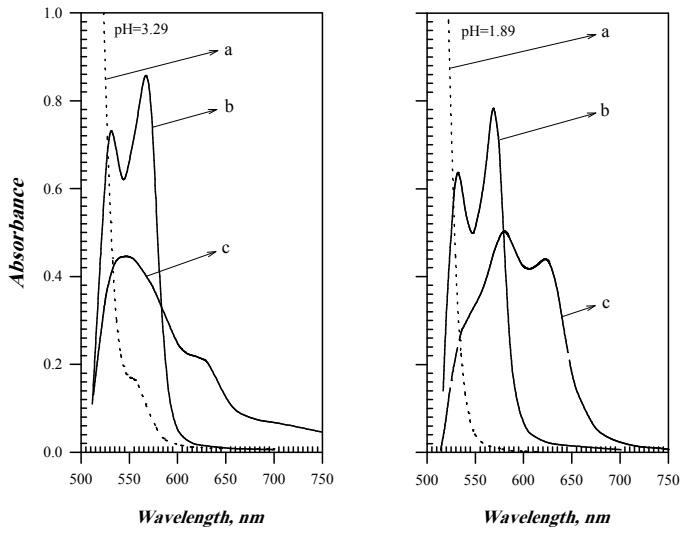

Fig. 1: Absorbance spectra at pH equal to 1.89 and 3.29. a) 0.01% PAN against water, b) 1.0 µg ml^{-1} Ni-PAN complex, c) 1.0 µg ml^{-1} Co-PAN complex, in 3.2% Tween 80.

Various micellizing agents such as Tween 80, Ttriton X-100 and SDS were tested as solubilizing agents. The spectra were recorded then sensitivity and stability of the cobalt and nickel complexes formed were considered. In SDS solutions less sensitivity for cobalt and nickel determination and low solubility for Ni-PAN complexe were observed. Better sensitivity was observed in Tween 80 against Triton X-100 for cobalt determination. For further studies Tween 80 was selected as micellizing agent.

Optimization of PAN concentration at pH 1.89 was performed for cobalt at 580 nm and for nickel at 569 nm, spectrophotometrically. PAN concentration was verried at fixed concentration of Tween 80 as 3.2% (Wt/V). According to the obtained results, sensitivity was maximum and constant in the PAN concentration range of 0.002-0.02% (Fig. 2). PAN precipitates in the concentrations higher than 0.02%. PAN as 0.02% was selected for further studies.

The effect of Tween 80 concentration on the sensitivity was also studied. Tween 80 concentrations in the range of 1.9-3.2% did not cause greater sensitivity. In Tween 80 concentrations less than 1.9%, PAN and its nickel complex formed precipitated. Tween 80 concentration of 3.2% was accepted for further studies.

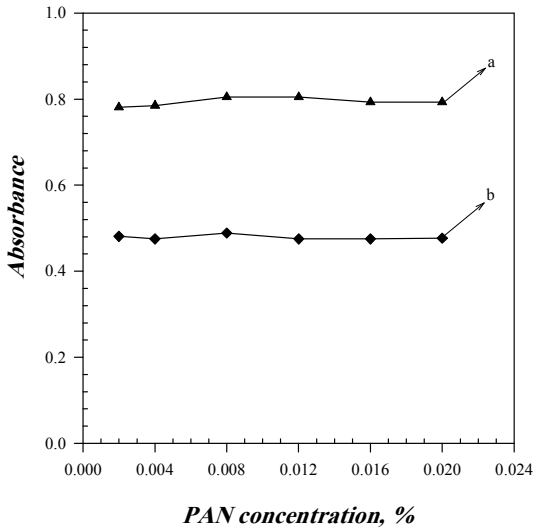

Fig. 2: Effect of PAN concentration on the sensitivity.
Condition: 10 ml solution at pH 1.89 containing 3.2% Tween 80 and a) 1.0 µg ml^{-1} nickel or b)1.0 µg ml^{-1} cobalt.

The effect of ionic strength on the sensitivity of the nickel and cobalt determination was investigated. Different concentrations of sodium chloride and sodium nitrate as ionic buffers were tolerated from 0.00 to 0.40 M but any sensible differences on the sensitivities were not observed.

First derivative spectra

Optimum condition (3.2% Tween 80, 0.02% PAN and pH 1.89) were applied to obtain first derivative spectra. The spectra have been shown in Fig. 3. Suitable zero crossing wavelengths that can be applied for sensitive determination of nickel and cobalt are 580 and 641 nm, respectively.

In the zero crossing derivative methods, it is necessary that zero crossing wavelengths do not change by varying concentration of the related species. Zero crossing method can not be used for determination of species which their spectra are shifted with concentration. First derivative spectra of the solutions containing fixed amounts of cobalt in the presence of different amounts of nickel also vice versa have been given in Fig. 4 as overlays.

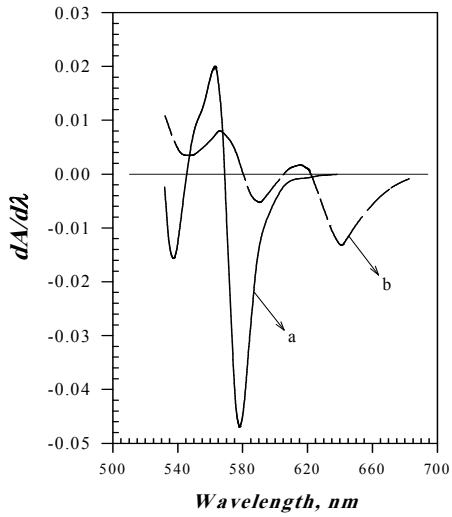

Fig. 3: First derivative spectra of nickel and cobalt complexes of PAN. a) Ni-PAN, b) Co-PAN. Condition: 10 ml solution at pH 1.89 containing 3.2% Tween 80, 0.02% PAN and 1.0 μg ml^{-1} cobalt or nickel .

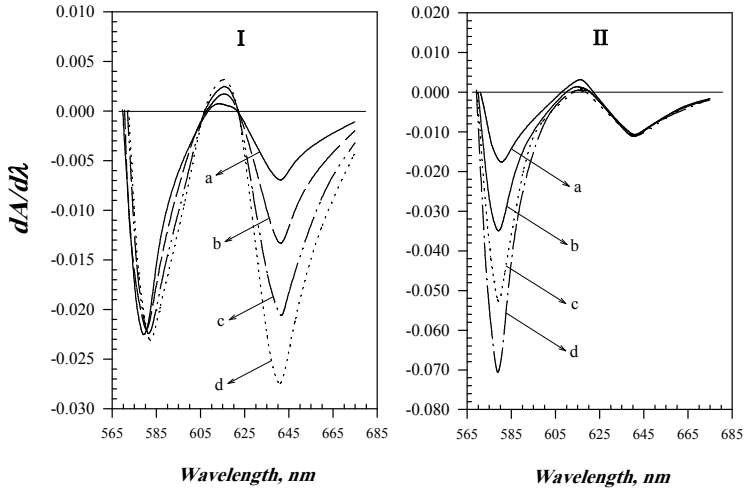

Fig. 4: First derivative spectra of the solutions containing:

I) fixed 0.5 μg ml^{-1} nickel and cobalt concentration of a) 0.5 μg ml^{-1}, b) 1.0 μg ml^{-1}, c) 1.5 μg ml^{-1} and d) 2.0 μg ml^{-1}.

II) fixed 0.8 μg ml^{-1} cobalt and nickel concentration of a) 0.4 μg ml^{-1}, b) 0.8 μg ml^{-1}, c) 1.2 μg ml^{-1} and d) 1.6 μg ml^{-1}.

Condition: 10 ml solution at pH 1.89 containing 3.2% Tween 80 and 0.02% PAN.

Calibration, accuracy and precision

Two first derivative spectrophotometric calibration graphs were constructed at zero crossing wavelengths for the simultaneous determination of nickel and cobalt. These obtained linear curves are in Table 2.

Precision and accuracy of the analytical first derivative method was also evaluated for ten different samples. The results have been presented in Table 3.

Table 2. Calibration parameters for the simultaneous determination of nickel and cobalt.

Calibration equation	Wavelength (nm)	Linear range ($\mu g\ ml^{-1}$)	Regression^2
$\Delta Abs/\Delta\lambda = -2.10\times10^{-5} + 1.38\times10^{-2}\ C_{Co}$	41	0.02-3.00	0.9998
$\Delta Abs/\Delta\lambda = 1.13\times10^{-4} + 4.29\times10^{-2}\ C_{Ni}$	580	0.01-2.00	0.9998

Effects of foreign ions

The effects of foreign ions on the determination of a mixture containing 5 μg Ni and 5 μg Co were examined. The results obtained are shown in Table 4. According to these results, approximately all of the metal ions did not interfere that may be due to low pH used and mixture of masking agents that were added according to the proposed procedure. Copper interferences were removed by o-phenanthroline as masking agent. The foreign ion study showed Co-PAN complex is not formed when o-phenanthroline is added before PAN. When o-phenanthroline is added after addition of PAN, the Co-PAN complex formed is not decomposed. This may be due to oxidation of Co(II) to Co(III) and then formation of Co(III)-PAN inert complex. By addition of o-phenanthroline after formation of metal-PAN complexes, interferences of copper are removed without decomposition of Co-PAN complex. The other ions such as HPO_4^{2-}, ClO_3^-, IO_3^-, Ba^{2+}, Mg^{2+}, Ca^{2+}, F^-, Cl^-, Br^-, I^- and CH_3COO^- in the concentration of 1000 $\mu g\ ml^{-1}$ had not any interference effects.

Table 3. Simultaneous determination of cobalt and nickel in some their binary mixtures.

Sample	Cobalt (μg ml^{-1})		Nickel (μg ml^{-1})	
Taken		Found	Taken	Found
1	0.100	0.102±0.003	0.020	0.019±0.001
2	0.100	0.104±0.005	0.600	0.592±0.004
3	0.500	0.504±0.005	0.500	0.495±0.003
4	0.200	0.195±0.006	1.00	1.02±0.02
5	0.300	0.310±0.009	1.50	1.47±0.01
6	2.00	2.03±0.02	0.150	0.148±0.003
7	1.00	0.99±0.02	0.400	0.406±0.009
8	3.00	2.98±0.03	0.200	0.203±0.004
9	1.00	1.02±0.01	1.00	0.98±0.01
10	2.00	2.02±0.03	1.00	1.02±0.002

± amounts are standard deviation of eight replicate analysis.

Table 4. Effect of foreign ions on the determination of 5 µg cobalt and 5 µg nickel.

Ion added	Amount(µg)	Error percent for cobalt at 641 nm	Error percent for nickel at 580 nm
SCN^{-a}	500	+0.4	-0.3
Mn^{2+a}	500	+0.6	+3.5
Al^{3+a}	500	+0.4	+0.6
WO_4^{2-a}	500	+0.6	+0.7
Cr^{3+a}	500	+0.3	+0.4
Sn^{2+a}	500	-0.7	-0.4
MoO_4^{2-a}	500	+0.7	+0.5
Zn^{2+a}	500	+0.4	+0.4
Cd^{2+a}	500	+0.1	+0.4
Pb^{2+a}	500	+0.4	+1.1
CrO_4^{2-a}	500	+0.5	+3.1
Ag^{+a}	500	-0.4	+0.5
Hg^{2+ab}	500	+0.2	+0.7
Fe^{3+a}	500	+0.3	+1.0
UO_2^{2+a}	500	+0.7	+3.5
Bi^{3+}	250	+2.6	+5.6
Ti^{3+}	100	+1.9	+3.1
V^{3+}	100	+4.3	+3.6
Cu^{2+}	250	-2.8	-4.1
Co^{2+}	100		+4.9
Ni^{2+}	40	+3.6	

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

Table 5: Determination of cobalt and nickel in some synthetic and real alloys.

Sample	Cobalt found, %(n=5)	Nickel found, %(n=5)
[a]Borcher alloy 1: Cr(30%), Co(35%) Ni(35%).	35.2±0.4	35.4±0.3
[a]Borcher alloy 4: Cr(30%), Co(34%) Ni(34%), Ag(2%).	34.4±0.3	33.7±0.4
[a]Inconel 700: Ni(45%), Co(30%) Cr(15%), Mo(3%) Ti(2.2%), Al(3.2%) bal Fe.	30.2±0.3	45.4±0.6
[a]Alnico 350: Al(7.8%), Ni(15%) Co(34%), Cu(3.5%) Ti(5%), Bal Fe.	33.9±0.3	15.3±0.1
[b]Waspaloy: Ni(57.5%), Co(13.5%) Cr(19.5%), Mo(4.2%) Fe(1%), Al(1.2%) Ti(3%).	13.4±0.2	56.9±0.5
[b]Fenicoloy: Ni(29%), Co(17%) Fe(53.8%), Mn(0.2%).	16.9±0.2	29.3±0.3
[b]Permute: Ni(21%), Co(30%) Cu(49%).	29.4±0.3	20.7±0.2
[b]Lemaiguand: Cu(39%), Ni(7%) Co(8%), Zn(7%) Sn(9%), Fe(30%).	8.12±0.10	6.90±0.05

a. Real alloy. b. Synthetic alloy. ± amounts are standard deviation.

Application

Some synthetic samples according to the composition of some industrial alloys as well as some alloys for presentation of applicability of the introduced procedure on the simultaneous determination of nickel and cobalt were examined (Table 5).

About 0.1 g of every alloy mentioned in Table 5 was digested in 20 ml solution of a mixture containing concentrated nitric and hydrochloric acid (15+5) by heating on a hot plate. After digestion, heating was continued till near dryness of the solution. After addition of 10 ml water, the solution was neutralized with dilute sodium hydroxide and was adjusted to 100.0 ml in a volumetric flask. After appropriate dilution analysis of the solution was performed by using the recommended procedure.

According to the results, the proposed method can be applied to some industrial alloys of nickel and cobalt in an accurate and precise manner.

Conclusions

A sensitive and selective first derivative spectrophotometric method was established for simultaneous determination of cobalt and nickel using PAN in the Ttween 80 micellar media. The proposed method was applied to assays of cobalt and nickel in their various binary mixtures and alloys. The analytical results were satisfactory. The proposed method should be useful for accurate, precise, rapid and simple determination of cobalt and nickel in their alloy samples.

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