Notes

H-Point Standard Addition Method for the Selective Simultaneous Determination of Nickel and Copper Using 1-(2-Pyridylazo)-2-naphthol in Tween 80 Micellar Media

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The H-point standard addition method (HPSAM) has been applied for the simultaneous determination of nickel and copper in trace levels, using 1-(2-pyridylazo)-2-naphthol (PAN) as a chromogenic reagent in aqueous Tween 80 micellar media. Under the optimum condition, the simultaneous determinations of nickel and copper by HPSAM were performed. The absorbances at one pair of wavelengths, 548 and 579 nm, were monitored with the addition of standard solutions of copper. The method is able to accurately determine copper-to-nickel ratios of 15:1 to 1:10 (Wt/Wt). The effects of diverse ions on the determination of nickel and copper to investigate the selectivity of the method were also studied. The recommended procedure was successfully applied to some water and alloy samples.

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Nickel and copper are metals that appear together, or alone, in many real samples. Monel (68% Ni, 32% Cu, traces of Mn and Fe) is used in an apparatus for handling corrosive materials, such as F_2; cupro-nickels (up to 80% Cu) are used for silver coinage and invar, which has a very small coefficient of expansion, are the other well-known Ni containing alloys. The stainless-steel industry is the largest user of nickel, both in the primary and recycled forms.[1] Urease as an enzyme contains nickel in its structure, and is considered to be essential to plants and some domestic animals. The essentially of nickel to humans has not been demonstrated. From health hazard and environmental viewpoints, some 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]

Several techniques, such as polarography,[3] high-performance liquid chromatography,[4] atomic-absorption spectrometry,[5] ICP-AES,[6] floatation–electrothermal atomic-absorption spectrometry,[7] chemometrics based methods,[8,9] spectrophotometric methods in micellar media[10] or after preconcentration using low-melting-point extractants,[11] have been applied for the simultaneous determination of Cu^{2+} and Ni^{2+} ions in different samples. Among the most widely used analytical methods are those based on UV-visible spectrophotometry, due to both the resulting experimental rapidity, simplicity and wide applications.

Bosch Reig and Campins-Falco developed a method, called the H-point standard addition method (HPSAM).[12] In this dual-wavelength spectrophotometry, two standard-addition curves at two selected wavelengths are constructed. The standard addition method has been presented to remove the matrix effects of samples with no elimination of constant spectral interferences of the components of the sample, but HPSAM transforms the incorrigible error to a constant systematic error. The error can then be estimated and corrected. The method has been applied to remove the blank bias error due to the use of an absorbent blank,[13] to liquid chromatography[14] and to the analysis of kinetic data,[12,15,16] with time as an additional variable. Further studies have shown high versatilities and applicabilities of the method.[17–19]

In this work, a selective H-point standard addition method has been developed for the simultaneous determination of copper and nickel. This determination was performed in a Tween 80 aqueous micellar solution using PAN as a chromogenic complexing agent at a low pH (1.89). The obtained selectivity was due to the low pH used, the buffer type and a mixture of masking agents that were added according to the recommended procedure.

Experimental

Reagents and chemicals

Polyoxyethylene(10)Octylphenyl Ether (Triton X-100), Polyoxyethylene(20)Sorbitan Monooleate (Tween 80) and sodium dodecylsulfate (SDS) were purchased from Merck. Stock solutions of these detergents as 6.4 – 10.7% (Wt/V) were prepared in 250 cm^3 volumetric flasks. A standard Ni^{2+} solution (2000 μg cm^{-3}) as chloride was prepared in a 250.0 cm^3 volumetric flask, which was then standardized[20] and used as a standard stock solution. A standard Cu^{2+} solution (1000 μg cm^{-3}) as sulfate was prepared in a 250 cm^3 volumetric flask, and was then standardized[21] and used as a stock solution. A 250 cm^3 solution of PAN (Merck) as 0.20% (Wt/V) in ethanol was prepared and used. Adjusting the pH values of the working solutions was carried out using universal buffers (acetic acid–phosphoric acid–boric acid mixture) for this study.

Apparatus

A Cecil CE 9020 UV-Vis scanning spectrophotometer was used to record the absorbance spectra of Cu^{2+}-PAN and Ni^{2+}-PAN complexes. A Cecil CE 1021 UV-Vis spectrophotometer equipped with a 10 mm quartz cell was used to measure the absorbances of the sample solutions.

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

pH	Nickel-PAN		Copper-PAN	
	λ_{max}/nm	Molar absorptivity/$dm^3\ cm^{-1}\ mol^{-1}$	λ_{max}/nm	Molar absorptivity/$dm^3\ cm^{-1}\ mol^{-1}$
1.81	569	4.59×10^4	555	2.08×10^4
1.89	569	4.62×10^4	555	2.13×10^4
1.98	569	4.67×10^4	555	2.14×10^4
2.09	567	4.87×10^4	556	2.74×10^4
2.21	566	4.99×10^4	558	3.44×10^4
2.56	566	4.97×10^4	558	3.76×10^4
3.29	566	5.03×10^4	558	3.99×10^4

Condition: 10 cm^3 solution containing 0.010% PAN, 3.2% Tween 80, universal buffer with different pHs and 10 μg Cu^{2+} or Ni^{2+}.

Procedure

A 3-cm^3 volume of a 10.7% Tween 80 solution, an appropriate amount of sample solution containing nickel and copper, a series of standard copper solutions in appropriate volume and 1 drop of 0.1 mmol cm^{-3} ammonia were added into a 10 cm^3 volumetric flask. Then, 0.5 cm^3 of 0.1 mmol cm^{-3} tartarate-fluoride solution and 1 cm^3 of ethanolic solution of 0.2% PAN were added. After 5 min, 0.5 cm^3 of a buffer solution with the pH equal to 1.89 was added and the volume was adjusted with double distilled water. The absorbances of the solutions were measured against its reagent blank at wavelengths of 548 and 579 nm for obtaining graphs. C_H and A_H were obtained from the intersection point of the two derived straight lines.

Results and Discussion

Optimization of variables

The effects of various parameters on the sensitivity and spectral characteristics of PAN complexes of nickel and copper were investigated by using a one at a time optimization method. One of the most important parameters is the pH. Experiments at various pHs showed that spectra of PAN and the Cu-PAN complex were dependent on the pH, but the Ni-PAN spectrum was approximately independent of the pH in the tested range. The spectral characteristics are given in Table 1. The shape of the absorption spectra, the maximum wavelengths and the apparent molar absorptivities changed when the pH was varied from 3.29 to 2.09 for copper and nickel. The shape and maximum wavelengths of the spectra of copper and nickel complexes were not changed at pH values lower than 2.09. Also, according to the results the molar absorptivities of the Cu-PAN and Ni-PAN complexes were decreased when the pH was lowered. The selectivity of the simultaneous determination is the most important parameter. Therefore, a determination at low pH is favored. According to the results, a pH of 1.89 was selected for the following studies.

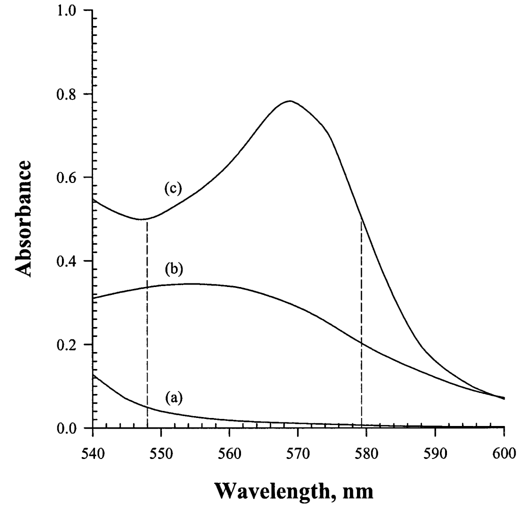

Fig. 1 Absorbance spectra of: a) 0.02% PAN against water, b) 1.0 μg cm^{-3} Cu-PAN complex, c) 1.0 μg cm^{-3} Ni-PAN complex, in 3.2% Tween 80 at pH 1.89.

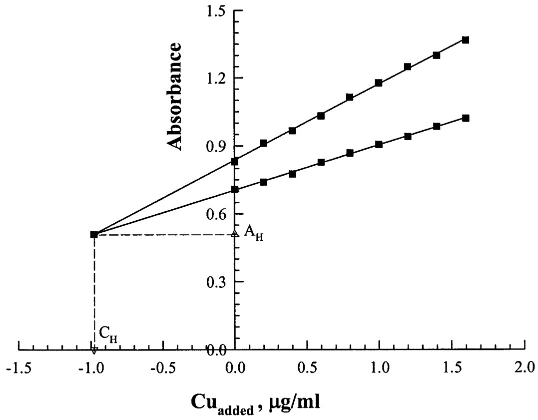

Fig. 2 H-point standard addition plot for the simultaneous determination of copper and nickel. Condition: 10.0 cm^3 solutions with pH equal to 1.89, 3.2% Tween 80, 0.02% PAN and 10 μg copper and 10 μg nickel when different standard copper solutions was added.

Various micellizing agents, such as Tween 80, Triton X-100 and SDS, were tested as solubilizing agents. After the spectra were recorded, the sensitivity and stability of the copper and nickel complexes formed were considered. In SDS solutions, low sensitivity for copper and nickel determination and low solubility for Ni-PAN complex were observed. Nonionic micelles are often preferred to anionic micelles for the determination of metal ions because the attractive forces between the negative head of the micelles and the positive charge of the metal ions cause a lower apparent formation constant between metal ions and ligands.[22] Although Tween 80 and Triton X-100 showed the same stability and sensitivity results, for further studies Tween 80 was selected as the working micellizing agent.

Optimization of the other parameters, such as the PAN and Tween 80 concentrations, was performed for copper at 555 nm and for nickel at 569 nm, spectrophotometrically. Based on the obtained results, PAN and Tween 80 concentrations of 0.02% and 3.2% were selected for further studies, respectively.

Sodium chloride and sodium nitrate as ionic buffers were tolerated in the range of 0.00 – 0.55 mmol cm^{-3}, but no considerable differences on the sensitivity were observed.

Absorption spectra

Figure 1 shows the absorbance spectra of the PAN complexes of copper and nickel in Tween 80 media. When copper is selected as the analyte, many pairs of wavelengths where they show the same absorbances for nickel complex are possible. In the selection of one pair of wavelengths for obtaining good accuracy, the absorbance differences at the two wavelengths for the copper complex must be considered to be as high as

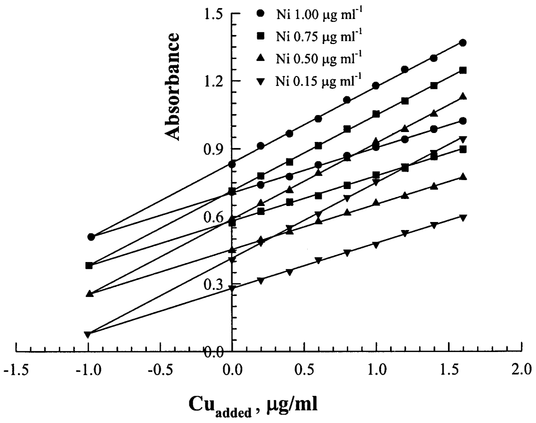

Fig. 3 H-point standard addition plot for the simultaneous determination of 10 μg copper and different amounts of nickel. Condition: 10.0 cm^3 solutions with pH equal to 1.89, 3.2% Tween 80, 0.02% PAN.

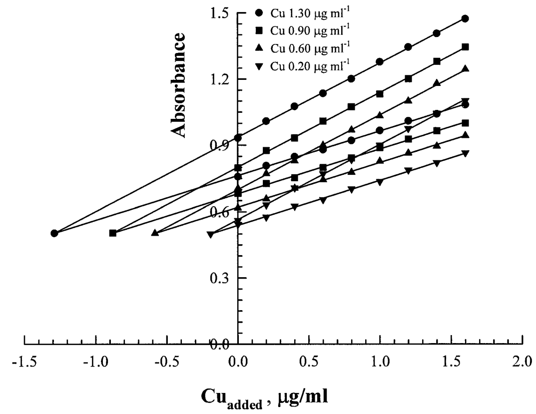

Fig. 4 H-point standard addition plot for the simultaneous determination of 10 μg nickel and different amounts of copper. Condition: 10.0 cm^3 solutions with pH equal to 1.89, 3.2% Tween 80, 0.02% PAN.

possible. Based on the absorbance spectra of the nickel and copper complexes, one of the best pairs of wavelengths are 548 and 579 nm. At these wavelengths, nearly the greatest sensitivity differences are attainable. In Fig. 2, the simultaneous determination of copper and nickel is presented by adding standard solutions of copper using the selected wavelengths.

Applicability of the HPSAM method

Several experiments for evaluating HPSAM on the simultaneous determination of copper and nickel in a series of samples containing a fixed amount of copper in the presence of various amounts of nickel (Fig. 3) or a fixed amount of nickel in the presence of various amounts of copper (Fig. 4) were carried out by the addition of copper standard solutions. The results show that the copper and nickel contents in the samples were determined accurately. Therefore, the applicability of the proposed procedure to determine copper and nickel has been clarified.

Analysis of copper-nickel binary mixtures

Known amounts of copper and nickel were determined to assess the proposed method. The accuracies and precisions are shown in Table 2. According to the obtained results, the applicability of the method for the simultaneous determination of copper and nickel in their binary mixtures is apparent.

Table 2 Determination of copper and nickel in different binary mixtures

A_H, C_H	Sample/μg cm^{-3}		Found/μg cm^{-3}	
	Copper	Nickel	Copper	Nickel
0.591, –0.22	0.20	1.20	0.22 ± 0.02	1.19 ± 0.03
0.258, –0.10	0.10	0.50	0.10 ± 0.01	0.52 ± 0.02
0.489, –1.03	1.00	1.00	1.03 ± 0.03	0.98 ± 0.03
0.505, –0.48	0.50	1.00	0.48 ± 0.03	1.01 ± 0.03
0.103, –0.19	0.20	0.20	0.19 ± 0.01	0.21 ± 0.02
0.105, –2.46	2.40	0.20	2.46 ± 0.04	0.21 ± 0.01
0.048, –1.17	1.20	0.10	1.17 ± 0.02	0.10 ± 0.01
0.484, –1.53	1.50	1.00	1.53 ± 0.03	0.97 ± 0.04
0.559, –0.42	0.40	1.10	0.42 ± 0.02	1.12 ± 0.04
0.241, –2.26	2.30	0.50	2.26 ± 0.04	0.48 ± 0.02

a. Mean ± S.D. (*n* = 5).

Interference study

The effects of the concentrations of foreign ions on the determination of 5.0 μg of copper and 5.0 μg of nickel in a mixture were studied. An ion was considered to be an interferent, when a concentration error was produced equal to, or more than, ± 3 × *S* (*S* is standard deviation of five replicate determination of 5.0 μg of copper or 5.0 μg of nickel in a mixture). Interferences of Co on the determination of Ni and Cu were removed by adding the following step to the recommended procedure: after the addition one drop of 0.1 mmol cm^{-3} ammonia, 1 cm^3 of 0.03 mmol cm^{-3} α-benzilmonoxime in ethanol and then the other mentioned reagents were added, consecutively. Under this circumstance, Co as yellow-colored Co^{3+}-α-benzilmonoximate[23] was not able to complex with PAN. To correct for the absorbances of Co^{3+}-α-benzilmonoximate, the absorbances of a blank in the absence of PAN and added standard solutions of Cu^{2+} must be subtracted from the absorbances of all the solutions. By using this blank correction procedure, interferences of up to 15-times that of cobalt were removed. According to these results, satisfactory selectivity was observed for the method. The obtained results are presented in Table 3.

Application

Some synthetic samples according to the composition of some industrial alloys as well as some alloys for presenting the applicability of the introduced procedure on the simultaneous determination of nickel and copper were examined (Table 4).

About 0.1 g of every alloy mentioned in Table 4 was digested in a 20 cm^3 solution of a mixture containing concentrated nitric and hydrochloric acid (15+5) by heating on a hot plate. After digestion, heating was continued untill near dryness of the solution. After the addition of 10 cm^3 water, the solution was neutralized with dilute sodium hydroxide and adjusted to 100.0 cm^3 in a volumetric flask. After appropriate dilution, an analysis of the solution was performed using the recommended procedure. According to the results, the proposed method can be applied to the analysis some of industrial Ni-Cu alloys in an accurate and precise manner.

For the analysis of water samples, 0.50 cm^3 of standard nickel and copper solutions were spiked into a 10 cm^3 flask together with 2 cm^3 of water samples; the nickel and copper contents were then analyzed by the proposed HPSAM procedure (Table 5).

A selective H-point standard addition method was established for the simultaneous determination of copper and nickel using

Table 3 Effect of foreign ions on the simultaneous determination of 5 μg nickel and 5 μg copper

Added ion	Tolerance limit ($Wt_{added\ ion}/Wt_{Cu}$)	Added ion	Tolerance limit ($Wt_{added\ ion}/Wt_{Ni}$)
NO_3^-, SO_4^{2-}, HPO_4^{2-}, Na^+, K^+, Ca^{2+}, Mg^{2+}, NO_2^-, F^-, ClO_3^-, IO_3^-, Cl^-, CH_3COO^-, SCN^-	>1000	NO_3^-, SO_4^{2-}, HPO_4^{2-}, Na^+, K^+, Ca^{2+}, Mg^{2+}, NO_2^-, F^-, ClO_3^-, IO_3^-, Cl^-, CH_3COO^-, SCN^-	>1000
Mn^{2+}, Al^{3+}, Cd^{2+}, MoO_4^{2-}, WO_4^{2-}, Zn^{2+}, Cr^{3+}, Sn^{2+}	150	Al^{3+}, Cr^{3+}, MoO_4^{2-}, Pb^{2+}, WO_4^{2-}, Sn^{2+}	500
CrO_4^{2-}, Pb^{2+}, Th^{4+}, Hg^{2+}	80	CrO_4^{2-}, UO_2^{2+}, Th^{4+}, Ag^+, Zn^{2+}, Cd^{2+}, Hg^{2+}, Mn^{2+}	200
UO_2^{2+}, Fe^{3+}, Ti^{3+}, Ag^+	40	Fe^{3+}, Bi^{3+}	50
Bi^{3+}, V^{3+}	20	Ti^{3+}, V^{3+}	20
Co^{2+} [b]	15	Co^{2+} [b]	15

a. Masked with iodide 0.005 M. b. Masked with α-benzilmonoxime then blank was corrected.

Table 4 Determination of copper and nickel in some synthetic and real alloys

Alloy	Found, % (n = 5)	
	Copper	Nickel
Monel 400[a] Ni(66%), Cu(31%), Fe(2.5%)	31.5 ± 0.5	65.6 ± 0.6
Alnico 350[ac] Al(7.8%), Ni(15%), Co(34%), Cu(3.5%), Ti(5%), Bal Fe	3.6 ± 0.1	15.2 ± 0.2
Neutroloy[b] Cu(55%), Ni(45%)	55.3 ± 0.7	44.7 ± 0.4
Permute[bc] Ni(21%), Co(30%), Cu(49%)	48.2 ± 0.6	20.5 ± 0.5
Lemaiguand[bc] Cu(39%), Ni(7%), Co(8%), Zn(7%), Sn(9%), Fe(30%)	39.7 ± 0.3	6.7 ± 0.3

a. Real alloy.
b. Synthetic alloy.
c. Masked with α-benzilmonoxime then blank was corrected.
± amounts are standard deviation.

Table 5 Determination of copper and nickel in different real water matrices

Sample	Concentration/μg cm^{-3}			
	Spiked		Found[a]	
	Copper	Nickel	Copper	Nickel
River water	0.30	0.60	0.32 ± 0.02	0.58 ± 0.02
River water	1.00	1.50	0.99 ± 0.02	1.47 ± 0.03
Tap water	0.70	0.70	0.73 ± 0.03	0.68 ± 0.03
Tap water	1.50	0.50	1.53 ± 0.03	0.49 ± 0.02

a. Mean ± S.D. (n = 4).

PAN in the Tween 80 micellar media. The proposed method was applied to assays of copper and nickel in their various binary mixtures, alloys and water matrices. The analytical results were satisfactory. The proposed method should be useful for the accurate, precise, rapid and simple determination of copper and nickel in their samples.

Acknowledgements

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