

## Simultaneous Determination of Cobalt and Nickel in Wastewater with 2-Hydroxyl-5-benzeneazoformoamithiozone by Spectral Correction Technique

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A new chromogenic reagent, 2-hydroxyl-5-benzeneazoformoamithiozone (HBASA) was synthesized and it can complex Co(II) and Ni(II) at pH 6.0 with high sensitivity and good selectivity. The complexations were characterized by a spectral correction technique. Complexes Co(HBASA)<sub>2</sub> and Ni(HBASA) were formed and their stepwise stability constants ( $K_n$ ) and stepwise molar absorptivities ( $\epsilon_n$ ) were worked out. The spectral correction matrix method was applied to the simultaneous determination of Co and Ni. At the range from 0 to 12.0  $\mu\text{g}/25\text{-mL}$  Co and Ni, the correction absorbances ( $A_\beta$ ) of the mixed complexes' solutions have good linearity. The limit of detection is 0.01 mg/l Co and 0.03 mg/l Ni and the relative standard deviation (RSD) is 2.5% for Co and 5.6% for Ni. This method was applied to the analysis of wastewater. The recovery of Co was between 94.5 and 109% and that of Ni between 99.0 and 111%.

**Keywords:** Spectral correction technique; Spectrophotometry; Metal complex; Determination of Co and Ni; 2-Hydroxyl-5-benzeneazoformoamithiozone.

### INTRODUCTION

Nickel is the metal component of the enzyme urease and as such is considered to be essential to plants and some domestic animals. Cobalt is known to be essential at trace levels to man, animals, and plants for metabolic processes. Even though cobalt is not considered to be as toxic as most of the heavy metals, it is an equally harmful element. Toxicological effects of large amounts of cobalt include vasodilation, flushing, and cardiomyopathy in humans and animals. The high consumption of nickel and cobalt-containing products in industry inevitably leads to environmental pollution at all stages of production, recycling, and disposal. Both Ni and Co are found in natural water at low concentrations. Most of them in natural water come from discharge of industrial wastewater, e.g., ore dressing, metallurgic, and electroplating plants. It is very important and necessary to develop reliable, fast, and sensitive methods for the determination of heavy metals in environmental samples. Several techniques have been proposed and evaluated for the simultaneous quantification of metal ions, such as ICP-AES,<sup>1</sup> adsorptive stripping

voltammetry,<sup>2</sup> chromatography,<sup>3</sup> and ETAAS.<sup>4</sup> Spectrophotometry is an ancient but conventional approach in trace analysis. Since the last century, it has been applied and studied extensively. In order to analyze heavy metals at trace level in water samples, many chromophores with high sensitivity and selectivity have been synthesized, and a new approach and chemometrics have been developed. Like many other heavy metals, Co and Ni can be spectrophotometrically detected upon reacting with many organic compounds, for example with nitroso-R-salt,<sup>5</sup> alpha-benzilmonoxime,<sup>6</sup> isonitroso-5-methyl-2-hexanone,<sup>7</sup> carboxyphenylhydrazoethylacetate,<sup>8</sup> dimethylglyoxime,<sup>9</sup> and calixarene.<sup>10</sup> However, the simultaneous determination of metal ions by the use of the UV-visible spectrometry techniques and conventional metalochromic indicators in aqueous solution is difficult without any separation processes because of overlapped absorption spectra. Recently, some new techniques, such as derivative spectrophotometry,<sup>11</sup> cloud point extraction,<sup>12</sup> H-point standard addition method,<sup>13</sup> and partial least squares<sup>14,15</sup> have been confirmed to be useful in extracting qualitative and quantitative information from overlapping bands of different

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components of a sample. Besides, the spectral correction matrix method<sup>16</sup> which derives from the spectral correction technique<sup>17,18</sup> can not only perform the simultaneous determination of several components but also it can be applied to characterization of the complexes. In the present work, the synthesis of a new chromogenic ligand, 2-hydroxyl-5-benzeneazo-formoamithiozone (HBASA) was carried out and its structure is given in Fig. 1. It complexes both Co(II) and Ni(II) with good selectivity. Because of the mixing of three color compounds including Ni-HBASA and Co-HBASA complexes and the excess HBASA, it is impossible to measure the light-absorption value of each color compound by ordinary spectrophotometry. The spectral correction technique was applied instead of single wavelength method to the characterization of Co(II) and Ni(II) complexes with HBASA. Moreover, the correction matrix method was utilized for the simultaneous determination of Co and Ni in wastewater with satisfactory results. The limits of detection of Co and Ni are 0.01 and 0.03 mg/l.

## PRINCIPLES

The following expression is developed for the determination of the real absorbance ( $A_c$ ) of metal (**M**) complex ( $\text{ML}_N$ ) formed with a chromogenic ligand (**L**).

$$A_c = \frac{A_\beta}{1 - \alpha\beta} \quad (1)$$

where

$$A_\beta = A_\lambda - \beta A_{\lambda_0} \quad (2)$$

The symbols  $A_\lambda$  and  $A_{\lambda_0}$  are the absorbances of the **M-L** reac-

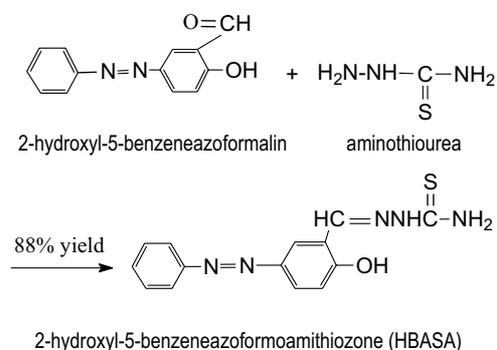


Fig. 1. Synthesis reaction of HBASA.

tion solution at wavelengths  $\lambda$  and  $\lambda_0$  against the reagent blank, respectively. The correction constants  $\beta$  and  $\alpha$  are calculated by the relations:

$$\alpha = \frac{\varepsilon_{ML}^{\lambda_0}}{\varepsilon_{ML}^{\lambda}} \quad (3)$$

and

$$\beta = \frac{\varepsilon_L^{\lambda}}{\varepsilon_L^{\lambda_0}} \quad (4)$$

The symbols  $\varepsilon_{ML}^{\lambda_0}$ ,  $\varepsilon_{ML}^{\lambda}$ ,  $\varepsilon_L^{\lambda_0}$  and  $\varepsilon_L^{\lambda}$  are the molar absorptivities of **ML** and **L** at  $\lambda_0$  and  $\lambda$ , respectively. Although  $\varepsilon_{ML}^{\lambda_0}$  and  $\varepsilon_{ML}^{\lambda}$  cannot be measured directly, their ratio can be determined by measuring a **ML** complex solution in which the molarity of **M** must be much more than that of **L**. This is attributed to the fact that **M** reacts with the entire **L**. In such a solution, only one color compound, **ML** complex, exists so the absorbance ratio of such a solution at  $\lambda_0$  and  $\lambda$  is on behalf of the ratio  $\varepsilon_{ML}^{\lambda_0}/\varepsilon_{ML}^{\lambda}$ . The ratio ( $\gamma$ ) of **L** coordinated in the **ML** complex to **M** is calculated by means of:

$$\gamma = \eta \times \frac{C_L}{C_M} \quad (5)$$

where

$$\eta = \frac{A_c - \Delta A_\lambda}{A_\lambda^0} \quad (6)$$

The symbol  $\eta$  is the fraction of **L** to coordinate **M**.  $C_M$  and  $C_L$  are the initial molarities of **M** and **L**.  $\Delta A_\lambda$  is the absorbance of the **M-L** solution measured at  $\lambda$  against the reagent blank and  $A_\lambda^0$  is that of the reagent blank at  $\lambda_0$ .  $\gamma$  will increase with increase of **L** molarity and then approaches to a maximum  $N$ .  $N$  is just the maximal coordination number of **L** on **M**. In addition, the following expressions were established for determination of the stepwise stability constant ( $K_n$ ) and the cumulative constant ( $K$ ):

$$K_n = \frac{\gamma + 1 - n}{(n - \gamma)(C_L - \gamma C_M)} \quad (7)$$

and

$$K = \prod_{n=1}^N K_n \quad (8)$$

For this purpose, such an **M-L** solution must be prepared to form the complex ratio ( $\gamma$ ) between  $n-1$  and  $n$ . Besides, the stepwise molar absorptivity ( $\varepsilon_n^{\lambda}$ , not apparent  $\varepsilon_a^{\lambda}$ ,  $n = 1, 2, \dots, N$ ) of complex **ML** is calculated by the relation:

$$\varepsilon_n^\lambda = \frac{A_c}{\delta C_M (\gamma + 1 - n)} - \frac{n - \gamma}{\gamma + 1 - n} \varepsilon_n^\lambda \quad (9)$$

$\delta$  is the cell thickness (cm) and the others have the same meanings as the equations above.

In order to perform the simultaneous determination of multi-components, the spectral correction matrix method was developed. It was once coupled with partial least squares to further improve the application.<sup>19</sup> The main equation is given below.

$$\begin{pmatrix} a_{11} & a_{12} & \dots & a_{1m} \\ a_{21} & a_{22} & \dots & a_{2m} \\ \dots & \dots & \dots & \dots \\ a_{m1} & a_{m2} & \dots & a_{mm} \end{pmatrix} \begin{pmatrix} X_1 \\ X_2 \\ \dots \\ X_m \end{pmatrix} = \begin{pmatrix} A_{\lambda_1} - \beta_1 A_{\lambda_0} \\ A_{\lambda_2} - \beta_2 A_{\lambda_0} \\ \dots \\ A_{\lambda_m} - \beta_m A_{\lambda_0} \end{pmatrix} \quad (10)$$

The symbol  $a_{ij} = A_{\beta ij}/X_j$  is the linear slope of  $j$ -th metal at  $i$ -th wavelength  $\lambda_i$ , which was regressed from the standard series ( $X_j$ -microgram of  $j$ -th metal).

## EXPERIMENTAL

### Apparatus and Reagents

A Model UV-VIS 265 spectrophotometer (Shimadzu, Japan) was used to record the scan spectra of HBASA and its metal complex solutions. A Model UV-120 (Shimadzu, Japan) with 10-mm cell was used to measure the absorbance of a single solution. A Model pHs-2C acidometer (Shanghai Leici Instruments, China) was used to adjust the acidity of the solutions.

Standard Co(II) (100.0 mg/l) solution was prepared by dissolving 0.263 g of cobalt sulfate absolute (Beijing Chemicals, China) in 1000 mL of deionized water. In the same way, standard and Ni(II) (100.0 mg/l) solution was prepared by dissolving 0.6728 g of ammonium nickel sulfate (Beijing Chemicals, China) in 1000 mL of deionized water. Standard Co(II) and Ni(II) (both at 10.0 mg/l) work solutions were prepared by diluting the solutions above. HBASA (0.100 mmol/l) solution was prepared by dissolving 17.1 mg of 2-hydroxyl-5-benzeneazoformoamithiozone (HBASA) in 500 mL of ethyl alcohol absolute (AR, Shanghai Zhenxing Chemicals, China). It should be stored in a dark bottle at 5 °C. A series of phosphate buffer solutions, pH from 5.0 to 7.0 in 0.5 of interval were prepared to adjust the acidity of the reaction solutions. In addition, ethyl alcohol absolute was used to raise the

solubility of HBASA and its metal complex.

### Recommended Procedures

#### Synthesis of HBASA

At first, an intermediate named 2-hydroxyl-5-benzene-azoformalin was synthesized.<sup>20</sup> The mixture of 2-hydroxyl-5-benzeneazoformalin and aminothiourea at 1:1 of the molar ratio was dissolved in 70% ethyl alcohol. The solution was put into a reactor and boiled with reflux for 1 h. The hot mixing liquid was filtered and then the residue remaining on the filter paper was washed with ethyl alcohol absolute. Eventually, some light yellow foliated crystals, 2-hydroxyl-5-benzeneazoformoamithiozone (HBASA) were obtained. The synthesis reaction is given in Fig. 1. The molecular structure of HBASA was confirmed by element analyzer, FIR and NMR. Before further use, it must be dried at 100 °C.

#### Characterization of the Co-HBASA and Ni-HBASA complexes

10.0  $\mu$ g of Co(II) was put into a 25-mL volumetric flask. 2.5 mL of pH 6.0 buffer solution, 10 mL of ethyl alcohol absolute, and a known volume of 0.100 mmol/l HBASA was added. The solution was diluted to scale line with deionized water and mixed well. After 5 min, the absorbances of the solutions were measured at 310 ( $\lambda_0$ ) and 240 ( $\lambda_1$ ) against water reference, respectively. In the meantime, a reagent blank without Co and Ni was prepared and measured with the same method as above. Thereafter  $\beta$ ,  $\alpha$ ,  $\eta$ , and  $\gamma$  were calculated by Equations (3)-(6). With the same method, the Ni-HBASA solutions were prepared and measured but with 20.0  $\mu$ g of Ni(II) instead of 10.0  $\mu$ g of Co(II).

#### Determination of Co and Ni

Because most Co and Ni in wastewater usually exist in adsorption state, e.g. on a suspending solid, a sample must be pretreated by nitrating. 10 mL of concentrated hydrochloric acid and 10 mL of concentrated nitric acid were added in 50 mL of a sample. It was boiled on an electrical furnace till the residual liquid is about 10 mL. After cooling, it was neutralized with NaOH solution. Thereafter, it was filtered and the filtrate was diluted to 50 mL with deionized water. A known volume of such a clarifying solution containing less than 12.0  $\mu$ g of Ni(II) and 12.0  $\mu$ g of Co(II) was put in a 25-mL volumetric flask. 2.5 mL of pH 6.0 buffer solution, 10 mL of ethyl alcohol absolute, and 5.0 mL of 0.100 mmol/l HBASA were added. The solution was diluted to volume with deionized water and mixed well. After 5 min, the absorbances of the solution were measured against water at 310 ( $\lambda_0$ ), 360 ( $\lambda_1$ ) and 420 nm ( $\lambda_2$ ), respectively. Thus,  $A_\beta$  of the mixed complex at

360 and 420 nm was calculated by Equation (2). Eventually, Co and Ni contents in samples were calculated from the calibration regression equation.

## RESULTS AND DISCUSSION

### Absorption spectra and calculation of $\beta$ and $\alpha$

Fig. 2 shows the absorption spectra of HBASA, Ni-HBASA, and Co-HBASA solutions at pH 6. From curve 1, the maximal light-absorption of HBASA is located at 310 nm. The peaks of the Ni-HBASA and Co-HBASA complexes are located in the visible light region. This is attributed to the fact that the metal complexation results in the spectral red shift. From curves 4 and 5, the peak and valley absorptions of Co-HBASA and Ni-HBASA solutions were both at 240 and 310 nm. Therefore, two such wavelengths were used in the characterization of the complexations. In addition, in the visible light region, the complexes have different absorptions. It demonstrates that Co and Ni will form different complexes with HBASA. Thus, three such wavelengths: 310, 360 and

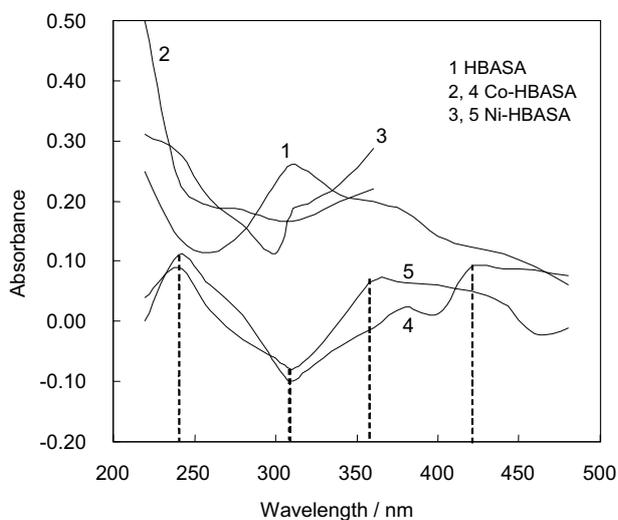


Fig. 2. Absorption spectra of HBASA, Co-HBASA and Ni-HBASA solutions at pH 6.0: 1- HBASA (0.004  $\mu\text{mol/mL}$ ), 2- Co (100  $\mu\text{g}$ )-HBASA (0.004  $\mu\text{mol/mL}$ ) complex solution where Co molarity is much more than HBASA, 3- Ni (100  $\mu\text{g}$ )-HBASA (0.004  $\mu\text{mol/mL}$ ) complex solution where Ni molarity is much more than HBASA, 4- Co (10  $\mu\text{g}$ )-HBASA (0.004  $\mu\text{mol/mL}$ ) solution, 5- Ni (20  $\mu\text{g}$ )-HBASA (0.004  $\mu\text{mol/mL}$ ) solution. All 1, 2 and 3 against water and the others against reagent blank.

420 nm were chosen in simultaneous determination of Co and Ni. From curves 1, 2, and 3, the correction constants were worked out:  $\beta_{240/310}^{\text{HBASA}} = 0.401$ ,  $\alpha_{310/240}^{\text{Co-HBASA}} = 0.715$  and  $\alpha_{310/240}^{\text{Ni-HBASA}} = 0.650$ . They were used to perform the calculation of  $\eta$ ,  $\gamma$ ,  $K_n$ , and  $\varepsilon_n$ .

### Effect of pH

By varying pH of the solutions, the effect on  $A_c$  of the various independent metal complex solutions at 240 nm is shown in Fig. 3. The light absorptions of the complexes reach maximum at pH between 6.0 and 6.5. In acidic medium, the protonation of  $-\text{NH}_2$  and  $-\text{NH}-$  of HBASA will be unfavorable to the complexation with Co and Ni. In basic medium, the deprotonation of  $-\text{OH}$  of HBASA and decomposition of azo organic compound will occur. Surely pH 6.0 was the most adaptable so it was used in this work.

### Effect of HBASA and characterization of the complexes

Fig. 4 gives the effect of the addition of HBASA solution on  $A_c$  of the Co and Ni complexes. With increase of HBASA molarity, more and more ligand will participate in the coordination with Co(II) and Ni(II). As a result,  $A_c$  of the complex increases and then approaches to maximum when HBASA is more than 0.010 mmol/l. Enough HBASA is added so that both Co(II) and Ni(II) can complex completely. Thus, the complexes with the highest coordination number of HBASA can be formed. From curves 1 and 2, 5.0 mL of 0.100 mmol/l HBASA is enough in the simultaneous determination

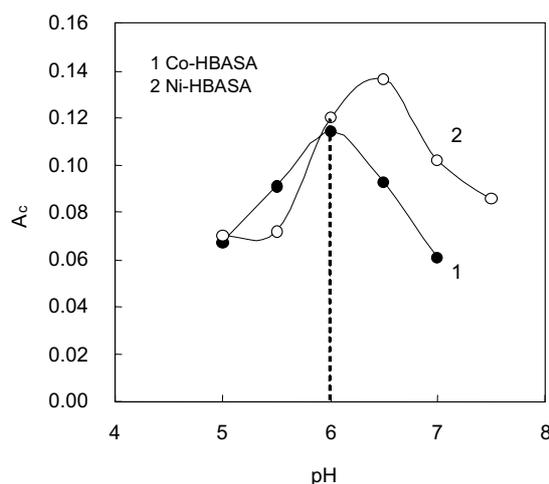


Fig. 3. Effect of pH on  $A_c$  of the complexes at 240 nm: 1- Co (10  $\mu\text{g}$ )-HBASA (0.004  $\mu\text{mol/mL}$ ) solution and 2- Ni (20  $\mu\text{g}$ )-HBASA (0.004  $\mu\text{mol/mL}$ ) solution.

of Co and Ni.

The effective fraction ( $\eta$ ) of HBASA to complex Co and Ni and the complex ratio ( $\gamma$ ) of HBASA to Co and Ni were calculated and their changes are shown in Fig. 5. From curves 3 and 4,  $\gamma$  increase with increase of HBASA molarity and then approach to maximum at about 2 and 1. Therefore, both complexes  $\text{Co}(\text{HBASA})_2$  and  $\text{Ni}(\text{HBASA})$  were formed. From curves 1 and 2,  $\eta$  is only approximately 50% at the work molarity (0.020 mmol/l) of HBASA. Unquestionably,

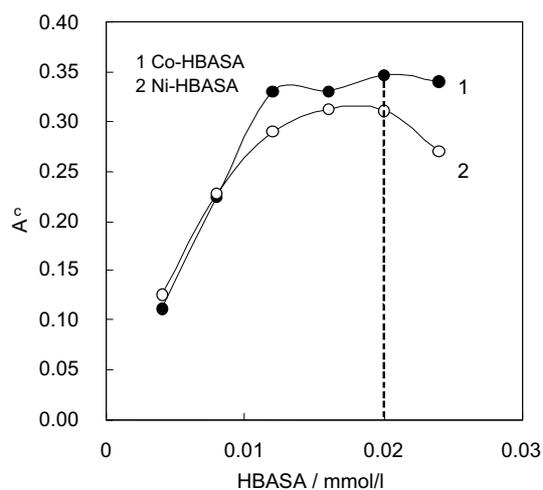


Fig. 4. Effect of HBASA molarity on  $A_c$  of the complexes at 240 nm: 1- Co (10  $\mu\text{g}$ )-HBASA (0.004  $\mu\text{mol/mL}$ ) solution and 2- Ni (20  $\mu\text{g}$ )-HBASA (0.004  $\mu\text{mol/mL}$ ) solution.

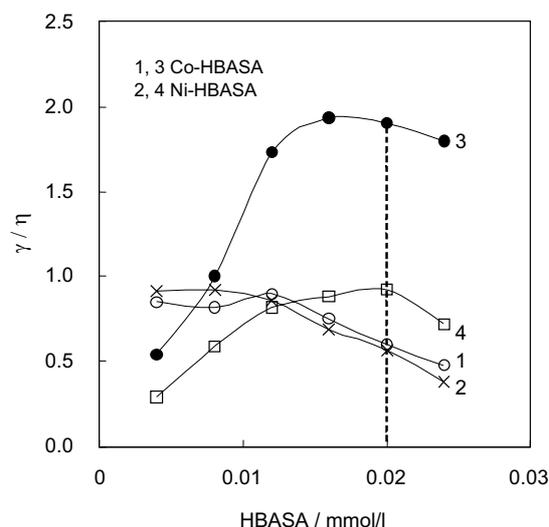


Fig. 5. Effect of HBASA molarity on  $\eta$  (1 and 2) and  $\gamma$  (3 and 4): 1 and 3- Co (10  $\mu\text{g}$ )-HBASA solution, 2 and 4- Ni (20  $\mu\text{g}$ )-HBASA solution.

half of HBASA has not reacted with Co and Ni. Thus, the excess HBASA will inevitably affect the direct measurement of absorbance of the complexes. The ordinary single-wavelength spectrophotometry is incapable of such a complexation. On the contrary, the spectral correction technique was applied instead of the traditional method because it can eliminate the effect of excess chromogenic reactant.

By preparing and measuring the three solutions, respectively containing 10.0  $\mu\text{g}$  of Co and 0.100  $\mu\text{mol}$  of HBASA, 10.0  $\mu\text{g}$  of Co and 0.280  $\mu\text{mol}$  of HBASA, and 20.0  $\mu\text{g}$  of Ni and 0.200  $\mu\text{mol}$  of HBASA,  $A_c$  and  $\gamma$  were calculated by Equations (1) and (5). Thereafter, both  $K_n$  and  $\epsilon_n$  of each complex were further obtained by Equations (7) and (9), and they are listed in Table 1. From  $K_n$  of  $\text{Co}(\text{HBASA})_2$ ,  $K_2 < K_1$  and  $\epsilon_2 > \epsilon_1$ . Apparently, this phenomenon accords with the common nature of a complex. From all values of  $\epsilon_n$ , the Co-HBASA and Ni-HBASA complex reactions are very sensitive.

In addition, the presence of ethyl alcohol is found to stabilize the complexations. Otherwise, the light absorption of HBASA and its metal complexes became unstable owing to floc formation. At room temperature, the Co and Ni complexations with HBASA are rapid in the presence of ethyl alcohol at pH 6.0.  $A_c$  of the complexes reached maximum and remained almost constant after 5 min.

### Calibration graph

Two series of standard Co (0-12.0  $\mu\text{g}$ ) and Ni (0-12.0  $\mu\text{g}$ ) solutions were prepared, and the absorbance of each was

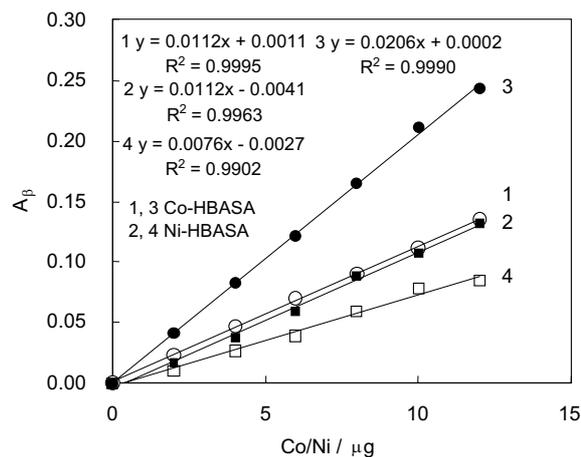


Fig. 6. Plots  $A_\beta$  vs  $X_{\text{Co}}$  and  $A_\beta$  vs  $X_{\text{Ni}}$  for the determination of Co(II) (both 1 and 3) and Ni(II) (both 2 and 4) at pH 6.0: 1 and 2 – at 360 nm, 3 and 4 – at 420 nm. The solutions contained 0.020 mmol/l HBASA.

Table 1. Characterization of the complexes

Complex	$K_n$	$K$	$\epsilon_{240nm}, l \cdot mol^{-1} \cdot cm^{-1}$
Co(HBASA)	$K_1 = 1.92 \times 10^5$	$2.19 \times 10^{10}$	$2.17 \times 10^4$
Co(HBASA) <sub>2</sub>	$K_2 = 1.14 \times 10^5$		$3.67 \times 10^4$
Ni(HBASA)	$K_1 = 1.13 \times 10^5$	$1.13 \times 10^5$	$2.60 \times 10^4$

measured.  $A_\beta$  of each solution were calculated and the standard curves are shown in Fig. 6. The measurement points exhibit the good linearity between 0 and 12.0  $\mu g$  of Co and Ni. The regression equations were followed:  $A_{\beta 1}^{Co} = 0.0112X_{Co}$  at 360 nm,  $A_{\beta 2}^{Co} = 0.0206X_{Co}$  at 420 nm,  $A_{\beta 1}^{Ni} = 0.0112X_{Ni}$  at 360 nm, and  $A_{\beta 2}^{Ni} = 0.0076X_{Ni}$  at 420 nm. Therefore,  $a_{11} = 0.0112$ ,  $a_{21} = 0.0206$ ,  $a_{12} = 0.0112$  and  $a_{22} = 0.0076$ . The following matrix was established for calculation of Co and Ni contents:

$$\begin{pmatrix} 0.0112 & 0.0112 \\ 0.0206 & 0.0076 \end{pmatrix} \begin{pmatrix} X_{Co} \\ X_{Ni} \end{pmatrix} = \begin{pmatrix} A_{360nm} - 0.769A_{310nm} \\ A_{420nm} - 0.473A_{310nm} \end{pmatrix} \quad (11)$$

#### Precision and limit of detection

Ten replicated determinations of a standard mixed solution simultaneously containing 2.50  $\mu g$  of Co(II) and 2.50  $\mu g$  of Ni(II) were carried out. The results are shown in Table 2. The relative standard deviations (RSDs) are 2.5 and 5.6%, respectively. As given in Table 2, the average of RSDs by the single wavelength spectrophotometry is 5.3%. Thus, the precision obtained by the spectral correction technique is better than the traditional method.

From 0.010 of  $A_c$ , the limit of detection (LOD) of Co

and Ni was calculated. Results show that  $LOD_{Co} = 0.01$  mg/l and  $LOD_{Ni} = 0.03$  mg/l.

#### Effect of foreign ions

No masking reagent was added and the recommended procedure was carried out. None of the following ions will affect the independent determination of 10  $\mu g$  of Co (< 10% error): 1 mg of  $Cl^-$ ,  $PO_4^{3-}$ ,  $SO_4^{2-}$ ,  $NO_3^-$ ,  $NH_4^+$ , Ca(II), Mg(II), V(V), Zn(II), Sb(III), Mo(VI), Mn(II), Fe(II), Al(III); 30  $\mu g$  of Ag(I) and 20  $\mu g$  of Cu(II). Serious influence of 2.0  $\mu g$  of Ni(II) on  $A_\beta$  of the Co-HBASA complex was found. In the same way, only 1.0  $\mu g$  of Co(II) was found to affect the independent determination of 10  $\mu g$  of Ni. Consequently, the simultaneous determination of Co and Ni is essential, and most of the other ions co-existing in wastewater will interfere with the direct determination.

#### Analysis of samples

As a test of the recommended method, two wastewater samples from ore dressing and metallurgical plants were analyzed. After measuring the absorbance of the colored solutions, Co and Ni contents were calculated by Equation (11). Results are listed in Table 3. The recoveries of Co and Ni are between 94.5 and 108%, 99.0 and 111%, respectively.

Table 2. Determination of standard Co and Ni solutions

Added: Co + Ni, $\mu g$	Absorbances measured					Found: Co + Ni, $\mu g$	RSD %: Co + Ni
	$\Delta A_1$	$\Delta A_2$	$\Delta A'$	$A_{\beta 1}$	$A_{\beta 2}$		
2.50 + 2.50	0.011	0.041	-0.051	0.050	0.065	2.43 + 2.30	2.5 + 5.6 (5.3%)*
	0.013	0.043	-0.049	0.051	0.067	2.53 + 2.30	
	0.010	0.047	-0.047	0.055	0.069	2.47 + 2.70	
	0.015	0.046	-0.051	0.054	0.070	2.60 + 2.40	
	0.010	0.042	-0.050	0.051	0.066	2.45 + 2.37	
	0.010	0.039	-0.057	0.053	0.066	2.39 + 2.58	
	0.013	0.046	-0.052	0.053	0.071	2.47 + 2.50	
	0.014	0.043	-0.052	0.054	0.068	2.48 + 2.61	
	0.011	0.041	-0.055	0.053	0.067	2.40 + 2.60	
	0.014	0.044	-0.051	0.053	0.068	2.51 + 2.53	

\* obtained from  $\Delta A_1$

Table 3. Determination of Co and Ni in wastewater

Sample from	Added: Co + Ni mg/l	Found: Co + Ni mg/l	Recovery, %: Co + Ni
Ore dressing Wastewater	0 + 0	0.225 + 0.186	
		0.215 + 0.188	
		0.220 + 0.182	
		0.214 + 0.188	
		0.230 + 0.181	
		0.220 + 0.180	
		Average: 0.221 + 0.184	
0.200 + 0.200	0.410 + 0.392	94.5 + 104*	
	0.429 + 0.400	104 + 108	
	0.432 + 0.401	105 + 108	
Metallurgical Wastewater	0 + 0	0.355 + 0.250	
		0.336 + 0.252	
		0.344 + 0.245	
		0.334 + 0.273	
		0.314 + 0.240	
		0.333 + 0.250	
		Average: 0.336 + 0.252	
0.200 + 0.200	0.555 + 0.460	109 + 104	
	0.558 + 0.450	111 + 99.0	
	0.540 + 0.455	102 + 101	

\* e.g. 94.5% =  $[(0.410 - 0.221)/0.200] \times 100\%$

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