Stability Constants of Cobalt(II) and Copper(II) Complexes with 3-[(o-Carboxy-p-nitrobenzene)azo]chromotropic Acid and Selective Determination of Copper(II) by Competition Coordination

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A method for selective determination of copper(II) based on the reactions of copper(II) or cobalt(II) with 3-[(o-carboxy-p-nitrobenzene)azo]chromotropic acid (CNBAC) at pH = 11.4 was developed. Results have shown that two complexes, Co(CNBAC)_2 and Cu(CNBAC), were formed, whose cumulative stability constants were $5.22 \times 10^9$ and $7.61 \times 10^5$ dm$^3$ mol$^{-1}$, respectively, and their molar absorption coefficients were $1.19 \times 10^4$ and $2.12 \times 10^4$ dm$^3$ mol$^{-1}$ cm$^{-1}$ at 610 nm. The competition coordination of Cu$^{II}$ and Co$^{II}$ with CNBAC was applied for selective determination of Cu$^{II}$ by the spectral correction technique. In the absence of any masking reagent, the recommended method was selective and was applied for quantitative determination of copper(II) in river and waste water samples.

Key words: competition coordination for selective determination; spectral correction technique; determination of copper(II); stability constants; 3-[(o-carboxy-p-nitrobenzene)azo]chromotropic acid

INTRODUCTION

Copper often exists in wastewater, ore, metal material, and so on. Chromogenic reagents, 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol,$^1$ dithizone, di(2-pyridylmethane)-2-(5-nitropyridyl) hydrazone,$^2$ mono- and bidentate pyridylazo compounds,$^3$ 2-nitroso-1-naphtholsulfonic acid$^4$ and others$^6$–$^8$ were applied to the determination of copper(II) by spectrophotometry. Synthesis of the novel ligand, 3-[(o-carboxy-p-nitrobenzene)azo]chromotropic acid (CNBAC), was performed and its structural formula is given below.

CNBAC forms complexes with many metal ions such as Ni$^{II}$, Cd$^{II}$, Zn$^{II}$, Pb$^{II}$ and alkaline earths(II). Therefore, its selectivity is poor in the detection application. Selective detection of a metal was not possible unless several masking reagents were used simultaneously. Recently, the competition coordination for selective determination (CCSD) was developed$^9$ using a metal to substitute for another metal from the complex. Thus, the first metal must have a much stronger complexation with the ligand than other metals. We found that copper(II) has the strongest complexation with CNBAC of most metals at pH = 11.4. Therefore, Cu$^{II}$ may substitute for many metals from their CNBAC complexes. In the present work, Co$^{II}$ was selected because of its sensitive reaction with CNBAC. The CCSD process of Cu$^{II}$ is described simply as follows: enough Co$^{II}$ is added into a CNBAC solution to bind complete CNBAC and then a
trace amount of CuII is added into the mixture to substitute for the CoIII from only the Co-CNBAC complex to form the Cu-CNBAC complex. The substitution reaction between CuIII and Co-CNBAC complex at pH = 11.4 was investigated in detail by a spectral correction technique10 instead of standard spectrophotometry. The method is selective without the use of masking reagents because of the excessive amount of CoIII. The spectral correction technique enabled easier determination of the complex ligand to metal ratio, stability constant and molar absorption coefficient than classical methods, e.g., the mole ratio,11 continuous variations,12 and equilibrium shift methods.13 Determination of the trace amount of CuIII in water samples was performed.

EXPERIMENTAL

Apparatus and Reagents

The absorption spectra were recorded with a TU1901 spectrophotometer (PGeneral, Beijing) and the independent absorbance of solution was measured with a Model 722 (Shanghai 2nd Instruments), both with 1.0-cm cells. A conductivity meter Model DDS-11A (Tianjin Second Analytical Instruments) was used to measure the conductivity together with a Model DJS-1 conductivity immersion electrode (electrode constant 0.98) (Shanghai Tienkuang Devices) in the production of deionized water of 0.5–1 \( \times 10^{-9} \) cm\(^{-1}\). The solution pH was measured on a pHS-2C acidity meter (Leici Hai 2nd Instruments), both with 1.0-cm cells. A conductivity meter (Shanghai Tienkuang Devices) was used to measure the conductivity together with a Model DJS-1 conductivity immersion electrode (electrode constant 0.98) (Shanghai Tienkuang Devices) in the production of deionized water of 0.5–1 \( \times 10^{-9} \) cm\(^{-1}\). The solution pH was measured at pH = 11.4, and then diluting it to 100 cm\(^3\) with deionized water.

Standard CoIII (1.000 g dm\(^{-3}\)) and CuIII (1.000 g dm\(^{-3}\)) solutions were prepared by dissolving 1.000 g of high-purity metals in hydrochloric and nitric acids and then diluted to 1000 cm\(^3\) with deionized water. Standard solutions of CoIII and CuIII, both 10.0 mg dm\(^{-3}\), must be prepared daily. CNBAC (1.20 mmol dm\(^{-3}\)) solution was prepared by dissolving 0.3200 g of 3\{carboxy-p-nitrobenzene\}azo]chromotropic acid (\( \sigma \) (CNBAC) > 98 %) in 500 cm\(^3\) of deionized water. It should be stored in a dark bottle and at \( T < 5 \) °C. The Co-CNBAC complex solution was prepared by mixing 10 cm\(^3\) of the hydrated cobalt chloride (A. R., Shanghai Reagents) solution (1.5 %) prepared in deionized water with 50.0 cm\(^3\) of 1.20 mmol dm\(^{-3}\) CNBAC and 10 cm\(^3\) of buffer solution, pH = 11.4, and then diluting it to 100 cm\(^3\) with deionized water.

The novel chromogenic reagent contained 0.600 mmol dm\(^{-3}\) Co(CNBAC) complex (1:1) because CoIII concentration is more than 10 times that of CNBAC where the free CNBAC approaches zero. The buffer solution, pH = 11.4, was prepared with disodium hydrogen phosphate (A. R., Shanghai Chemicals) and NaOH.

Methods

Determination of Stability Constants of CoIII and CuIII Complexes with CNBAC. – Into a 25 cm\(^3\) calibrated flask, 10.0 \( \mu \)g of CoIII or CuIII, 2.5 cm\(^3\) of buffer solution and 1.00 cm\(^3\) of 1.20 mmol dm\(^{-3}\) CNBAC were added. The mixture was diluted to 25 cm\(^3\) with deionized water and thoroughly mixed. Thus, the final mass concentration, \( \gamma \), of CoIII (or CuIII) in the sample was 0.4 \( \mu \)g cm\(^{-3}\) and the molar concentration of CNBAC was 0.048 \( \mu \)mol cm\(^{-3}\). After 10 min, the absorbances were measured at 525 and 610 nm against the blank treated in the same way without CoIII or CuIII. Finally, the real absorbance (\( A_c \)) of the complexes was calculated by the relation:

\[
A_c = \frac{\Delta A - \beta \Delta A'}{1 - \alpha \beta} \quad \text{where}
\]

\[
\alpha = \frac{\varepsilon^\lambda (ML_n)}{\varepsilon^{\lambda_1} (ML_n)} \quad \alpha = \frac{\varepsilon^\lambda (L)}{\varepsilon^{\lambda_1} (L)}
\]

Here, symbols \( \Delta A \) and \( \Delta A' \) are the absorbances of the M-L (metal-ligand) solution against the L solution without M, measured at the peak wavelengths (\( \lambda_1 \)) and the valley wavelength (\( \lambda_2 \)). The correction coefficients \( \alpha \) and \( \beta \) are constants. The symbols \( \varepsilon^\lambda (ML_n) \), \( \varepsilon^{\lambda_1} (ML_n) \), \( \varepsilon^\lambda (L) \) and \( \varepsilon^{\lambda_1} (L) \) are the molar absorption coefficients of the complex (ML) solution without free L and the L solution without M against water reference, measured at \( \lambda_1 \) and \( \lambda_2 \).

The fraction of the effective CNBAC, \( r (CNBAC)_{eff} \) and the mole ratio of CNBAC to CoIII or CuIII, \( r (CNBAC, CoIII) \) and \( r (CNBAC, CuIII) \), were calculated according to Eq. (2).

\[
x = A_c - \Delta A \frac{A_o}{A_a} \quad \text{and} \quad r = \frac{c(L)}{c(M)}
\]

The symbols \( c(M) \) and \( c(L) \) denote the initial concentration of CoIII or CuIII and CNBAC, respectively. \( A_o \) is the absorbance of CNBAC solution against water at 610 nm (cf. Figure 1).

Determination of CuIII in Water. – A known volume of a sample containing less than 25.0 \( \mu \)g of CuIII was put into a 25 cm\(^3\) volumetric flask. 2.5 cm\(^3\) of pH = 11.4 buffer solution and 3.0 cm\(^3\) of the Co-CNBAC complex (0.600 mmol dm\(^{-3}\)) were added, diluted to 25 cm\(^3\) with deionized water and mixed well. After 20 min, the absorbances were measured at 525 and 610 nm against a reagent blank without CuIII.

RESULTS AND DISCUSSION

Absorption Spectra and Analysis

Figure 1 shows the absorption spectra of the CNBAC, Co-CNBAC, Cu-CNBAC and Cu-Co-CNBAC solutions at pH = 11.4. From curve 1, it is seen that the absorption maximum of CNBAC is located at 550 nm. Similarly, curve 2 and 3 show that the maximum of the Co-CNBAC complex is located at 550 nm and that of the Cu-CNBAC complex at 610 nm. Spectra 4 and 5 show that both the Co-CNBAC and Cu-CNBAC solutions have the maximum at 610 nm and the valley at 550 nm. Hence, such two wavelengths were selected in studying the complexing of
CoII and CuII with CNBAC. The correction constants were calculated to be \( L_{610/525} = 0.145 \) from curve 1, \( L_{525/610} = 2.46 \) from curve 2, and \( L_{525/610} = 0.371 \) from curve 3. The following relations were used to calculate the real absorbance of the Co-CNBAC and Cu-CNBAC complexes at 610 nm:

\[
A_{c(Co-CNBAC)} = 1.56(L - 0.145)A' \quad \text{and} \quad A_{c(Cu-CNBAC)} = 1.06(L - 0.145)A'.
\]

Curve 6 in Figure 1 shows that the maximum of the Cu-Co-CNBAC solution is located at 610 nm and the valley at 525 nm. The two wavelengths were used in studying the quantitative determination of CuII. \( L_{610/525} = 1/\alpha L_{525/610} = 0.407 \) from curve 2, and \( \alpha L_{525/610} = 0.371 \) from curve 3. The following expression was used to calculate the real absorbance of the Cu-CNBAC complex formed in the substitution reaction: \( A_e = 1.18(\Delta A - 0.407\Delta A') \).

Effect of pH on the Formation of CoII and CuII Complexes with CNBAC

The effect of pH on the formation of CoII and CuII complexes with CNBAC is shown in Figure 2. We observed that the ligand to metal ratio (r) in the Cu-CNBAC complex remained almost constant when pH > 10.4. In this work, a pH = 11.4 buffer solution was used. We observed that other metals can also form a similar violet complex at pH = 11.4, e.g., NiII, PbII, ZnII, CdII, CuII and MgII. However, all of these will not react with CNBAC because no free CNBAC exists in the presence of plenty of CoII.

Determination of Stability Constants of CoII and CuII Complexes with CNBAC

By varying the addition of 1.20 mmol dm\(^{-3}\) CNBAC, the absorbances of the Cu-CNBAC and Co-CNBAC solutions were measured. The variation of r is shown in Figure 3. From curve 1, it follows that r approaches a maximum at 2 in the Co-CNBAC system when more than 1.8 mol CNBAC (i.e. more than 1.5 cm\(^3\) of 1.20 mmol dm\(^{-3}\) CNBAC) was added into 25 cm\(^3\) of sample solution containing 0.400 gc m\(^{-3}\) of CoII. Similarly, curve 2 shows that r approaches a maximum at 1 in the Cu-CNBAC system when more than 1.20 mol CNBAC (>1.0 cm\(^3\) of 1.20 mol dm\(^{-3}\) CNBAC) was added into 25 cm\(^3\) of sample solution containing 0.400 gc m\(^{-3}\) of CuII. The variation of r is shown in Figure 3. From curve 1, it follows that r approaches a maximum at 2 in the Co-CNBAC system when more than 1.8 mol CNBAC (i.e. more than 1.5 cm\(^3\) of 1.20 mmol dm\(^{-3}\) CNBAC) was added into 25 cm\(^3\) of sample solution containing 0.400 gc m\(^{-3}\) of CoII. Similarly, curve 2 shows that r approaches a maximum at 1 in the Cu-CNBAC system when more than 1.20 mol CNBAC (>1.0 cm\(^3\) of 1.20 mol dm\(^{-3}\) CNBAC) was added into 25 cm\(^3\) of sample solution containing 0.400 gc m\(^{-3}\) of CuII. The variation of r is shown in Figure 3. From curve 1, it follows that r approaches a maximum at 2 in the Co-CNBAC system when more than 1.8 mol CNBAC (i.e. more than 1.5 cm\(^3\) of 1.20 mmol dm\(^{-3}\) CNBAC) was added into 25 cm\(^3\) of sample solution containing 0.400 gc m\(^{-3}\) of CoII. Similarly, curve 2 shows that r approaches a maximum at 1 in the Cu-CNBAC system when more than 1.20 mol CNBAC (>1.0 cm\(^3\) of 1.20 mol dm\(^{-3}\) CNBAC) was added into 25 cm\(^3\) of sample solution containing 0.400 gc m\(^{-3}\) of CuII.

Figure 1. Absorption spectra of CNBAC and its CoII and CuII complex solutions at pH=11.4: 1) CNBAC (0.048 \( \mu \)mol cm\(^{-3}\)) solution; 2) Co (0.400 \( \mu \)mol cm\(^{-3}\)) – CNBAC (0.096 \( \mu \)mol cm\(^{-3}\)) complex solution (no longer containing free CNBAC), and 3) Cu (0.120 \( \mu \)mol cm\(^{-3}\)) – CNBAC (0.024 \( \mu \)mol cm\(^{-3}\)) complex solution (no longer containing free CNBAC); 4) Co (0.400 \( \mu \)mol cm\(^{-3}\)) – CNBAC (0.048 \( \mu \)mol cm\(^{-3}\)) solution; 5) Cu (0.400 \( \mu \)mol cm\(^{-3}\)) – CNBAC (0.048 \( \mu \)mol cm\(^{-3}\)) solution; 6) Cu (0.800 \( \mu \)mol cm\(^{-3}\)) – Co(CNBAC) (0.048 \( \mu \)mol cm\(^{-3}\)) solution. 1, 2 and 3 against water reference and the other against the reagent blank without CoII and/or CuII.

Figure 2. Effect of pH on the ratio (r) of CNBAC to CoII and CNBAC to CuII: 1) solution containing 0.048 \( \mu \)mol cm\(^{-3}\) CNBAC and 0.400 \( \mu \)g cm\(^{-3}\) CuII, and 2) solution containing 0.048 \( \mu \)mol cm\(^{-3}\) CNBAC and 0.400 \( \mu \)g cm\(^{-3}\) CoII.

Figure 3. Effect of addition of the CNBAC solution on the ratio, r(CNBAC, CoII) and r(CNBAC, CuII): 1) solution containing 0.400 \( \mu \)g cm\(^{-3}\) CoII, and 2) solution containing 0.400 \( \mu \)g cm\(^{-3}\) CuII.
mmol dm\(^{-3}\) (CNBAC) was added. Thus, the complexes Co(CNBAC)\(_2\) and Cu(CNBAC) were formed.

The stepwise stability constant (\(K_n\)) and stepwise molar absorption coefficient (\(\varepsilon\)) of M-L complex can be calculated by means of expressions\(^{15}\):

\[
K_n = \frac{r + 1 - n}{(n - r)(c(L) - c(M))}
\]

\[
\varepsilon^{\lambda_2}(ML_n) = \frac{A_c}{2c(M)(r + 1 - n)} - \frac{n - r}{r + 1 - n} \varepsilon^{\lambda_2}(ML_{n-1})
\]

Symbol \(n\) denotes the step number of the complex and \(l\) is the absorbing path length of the absorption cell. \(r\) is between \(n - 1\) and \(n\). In order to determine the molar absorption coefficients and stability constants of the Co-CNBAC and Cu-CNBAC complexes, three solutions were prepared: the first containing 0.400 \(\mu g\) cm\(^{-3}\) Co\(^{II}\) and 0.080 \(\mu mol\) cm\(^{-3}\) CNBAC, the second containing 0.400 \(\mu g\) cm\(^{-3}\) Co\(^{II}\) and 0.040 \(\mu mol\) cm\(^{-3}\) CNBAC, and the third containing 0.400 \(\mu g\) cm\(^{-3}\) Cu\(^{II}\) and 0.080 \(\mu mol\) cm\(^{-3}\) CNBAC. Four replicated determinations of each were made. The stepwise molar absorption coefficients and stability constants of both the Co-CNBAC and Cu-CNBAC complexes are given in Table I. The cumulative stability constants of Co(CNBAC)\(_2\) and Cu(CNBAC) are 5.22 \(\times 10^5\) and 7.61 \(\times 10^5\) dm\(^3\) mol\(^{-1}\) respectively, at an ionic strength of 0.025 mol dm\(^{-3}\) at 25 °C. Table I shows that the 1\(^{st}\)-step stability constant of Co(CNBAC)\(_2\) was much less than that of Cu(CNBAC). Therefore, trace amounts of Cu\(^{II}\) only from the Co(CNBAC) complex to form the Cu(CNBAC) complex. This substitution reaction was applied to the determination of trace amounts of Cu\(^{II}\) with high selectivity.

**Effect of Addition of Co-CNBAC Complex on the Formation of Cu-CNBAC Complex**

By varying the addition of 0.600 mmol dm\(^{-3}\) Co(CNBAC), the absorbances of the Cu-Co(CNBAC) solutions were measured at 610 and 525 nm and their curves are shown in Figure 4. Curve 3 approaches a maximum when more than 2.0 cm\(^3\) of 0.600 mmol dm\(^{-3}\) Co(CNBAC) (>1.2 \(\mu mol\) Co(CNBAC)) was added. So, 3.0 cm\(^3\) of 0.600 mmol dm\(^{-3}\) Co(CNBAC) was used in the quantitative determination of Cu\(^{II}\). We observed that \(x\) was only 15 % when 3.0 cm\(^3\) of 0.600 mmol dm\(^{-3}\) Co(CNBAC) was added. Thus, 85 % of the Co(CNBAC) complex added was not substituted by Cu\(^{II}\). It is indubitable that such excessive amount of Co(CNBAC) severely affected the measurement of the real absorbance of the Cu-CNBAC complex. Therefore, standard spectrophotometry is inapplicable to the CCSD of a metal. In contrast, the spectral correction technique can provide an accurate trace detection.

**Time of Formation of Cu-CNBAC Complex**

Figure 5 shows that the substitution of Cu\(^{II}\) from Co(CNBAC) with Cu\(^{II}\) at 25 °C reached equilibrium in 20 min. Initial solution contained 0.400 \(\mu g\) cm\(^{-3}\) Cu\(^{II}\) and 0.072 \(\mu mol\) cm\(^{-3}\) Co(CNBAC). We observed that the substitution of Cu\(^{II}\) from Co(CNBAC) complex with Cu\(^{II}\) was slower than the direct reaction of Cu with CNBAC.

<table>
<thead>
<tr>
<th>(n) ((a))</th>
<th>(K_n) (\times 10^4)</th>
<th>(\varepsilon) (\times 10^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1^{st})</td>
<td>9.24</td>
<td>6.04</td>
</tr>
<tr>
<td>(2^{nd})</td>
<td>5.65</td>
<td>1.19</td>
</tr>
<tr>
<td>Cu(CNBAC)</td>
<td>(1^{st})</td>
<td>7.61</td>
</tr>
</tbody>
</table>

\((a)\) Step number. \((b)\) At 610 nm.
CCSD of Copper(II)

Calibration Graph, Precision and Detection Limit. – A series of standard solutions containing less than 1.20 \( \times 10^{-9} \) g cm\(^{-3} \) Cu\(^{II} \) were prepared and the absorbance of each solution was measured. The results are shown in Figure 6. We can observe that the calculation data (line 2) is much more linear between 0 and 1.00 \( \times 10^{-9} \) g cm\(^{-3} \) Cu\(^{II} \) than the measurement data (line 1), and the slope of line 2 is more than that of line 1. Therefore, the spectral correction technique regularly renders a better accuracy and a higher sensitivity than those obtained in standard spectrophotometry. The regression equation of line 2 is:

\[
A = 0.199x + 0.009.
\]

Ten replicate determinations of two standard solutions containing 0.080 and 0.400 \( \times 10^{-9} \) g cm\(^{-3} \) Cu\(^{II} \) were carried out. The relative standard deviations (RSDs) were 3.4 and 2.2 %, respectively. However, the RSDs were over 12 % in standard spectrophotometry. The conventional formula

\[
L_{\text{min}} = kS_b/S \quad (k = 3, S = \text{the line slope and } S_b = \text{SD})
\]

of 20 replicated determinations of reagent blanks was used to calculate the detection limit of Cu\(^{II} \) to be 0.04 \( \mu \)g cm\(^{-3} \).

Effect of Foreign Ions on Cu\(^{II} \) Determination. – Because of the presence of excess Co\(^{III} \), no masking reagent was added. We have observed that none of the following ions affected direct determination of 0.400 \( \times 10^{-9} \) g cm\(^{-3} \) Cu\(^{II} \) (error < 10 %): 80 \( \mu \)g cm\(^{-3} \) Cl\(^{-} \), SO\(_4^{2-} \), SO\(_3^{2-} \), CH\(_3\)COO\(^{-} \), NH\(_4^{+} \), Ca\(^{2+} \), Mg\(^{2+} \); 20 \( \mu \)g cm\(^{-3} \) Al\(^{3+} \), V\(^{5+} \), Mo\(^{6+} \), Cr\(^{3+} \); 10 \( \mu \)g cm\(^{-3} \) Pb\(^{2+} \), Cd\(^{2+} \), Mn\(^{2+} \), Fe\(^{2+} \) and 4 \( \mu \)g cm\(^{-3} \) Ni\(^{2+} \), Hg\(^{2+} \), Fe\(^{3+} \).

Analysis of Copper(II) in River and Waste Water. – To test the method, Cu\(^{II} \) was determined in two samples: river water and wastewater. Six replicated determinations of each sample were carried out and two replicated standard additions of each sample were made to check the accuracy of the recommended method. The final results are given in Table II. It is seen that the recovery of Cu\(^{II} \) is between 91.0 and 106 % and the RSD is less than 5.58 %. Therefore, the recommended method is accurate and selective.

### Table II. Determination of Cu\(^{II} \) in two different water samples with Co(CNBAC\(_2\)) as the chromogenic reagent

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \gamma ) (Cu(^{II} )) / ( \mu )g cm(^{-3} )</th>
<th>RSD</th>
<th>Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Added</td>
<td>Found</td>
<td></td>
</tr>
<tr>
<td>Wastewater</td>
<td>0.105 (±0.006)(^{(a)})</td>
<td>5.58</td>
<td>106–91.0</td>
</tr>
<tr>
<td></td>
<td>0.100</td>
<td>0.211–0.196</td>
<td>–</td>
</tr>
<tr>
<td>River water</td>
<td>0.618 (±0.009)(^{(a)})</td>
<td>1.53</td>
<td>104–93.2</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>1.66–1.55</td>
<td>–</td>
</tr>
</tbody>
</table>

\(^{(a)}\) Average of six determinations, standard deviation in parentheses.

CONCLUSIONS

The spectral correction technique is, in fact, one of the dual-wavelength spectrophotometric methods, but different from the others\(^{16–19}\) in operation. Not only does it give an accurate determination of a trace metal (M), but also the calculation of stability constants of a complex becomes simple. Because the current chromogenic reagent (L) itself often has a very high molar absorption coefficient, its light absorption occupies a large and assignable fraction. Solely the free L maintains a strict dynamic equilibrium of the reaction between M and L. The
spectral correction technique may provide the absorbance fraction of each of the colour mixtures, so that the formation constants of the complex are determined easily. The competition coordination reaction is often applied in analytical complexometry, e.g., complexometric titration. The spectral correction technique makes the competition coordination more suitable for high selectivity spectrophotometry. We believe that the combination of the CCSD and the spectral correction technique will play an important role in a selective spectrophotometric approach.

REFERENCES

SAŽETAK

Konstante stabilnosti kompleksa kobalta(II) i bakra(II) s 3-[(o-karboksip-nitrobenzen)azonikromotropnom kiselinom i selektivno određivanje bakra(II) kompeticijskom koordinacijom

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Reakcije između bakra(II) i kobalta(II) s 3-[(o-karboksip-nitrobenzen)azonikromotropnom kiselinom (CNBAC) bile su primetljive pri pH = 11,4. Rezultati su pokazali nastajanje dvaju kompleksa, Co(CNBAC)₂ i Cu(CNBAC), čije su kumulativne konstante stabilnosti iznosile 5,22 × 10⁹ dm³ mol⁻¹ odnosno 7,61 × 10⁵ dm³ mol⁻¹, a njihovi molarni apsorpcijski koeficijenti 1,19 × 10⁴, odnosno 2,12 × 10⁴ dm³ mol⁻¹ cm⁻¹ kod 610 nm. Kompetijska koordinacija bakra(II) i kobalta(II) s CNBAC primijenjena je za selektivno određivanje bakra(II) spektrotnom koreksijskom tehnikom. U odsutnosti maskirajućih reagensa, ta je metoda selektivna i iskorištena je za kvantitativno određivanje bakra(II) u uzorcima riječne i otpadnih voda.