

Direct and simultaneous spectrophotometric determination of Ni (II) and Co (II) using diethanoldithiocarbamate as complexing agent.

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Abstract: A direct spectrophotometric method for simultaneous determination of Co(II) and Ni(II), with diethanoldithiocarbamate (DEDC) as complexing agent, is proposed using the maximum absorption at 360 and 638 nm (Co(II)/DEDC) and 390 nm (Ni/DEDC). Adjusting the best metal/ligand ratio, supporting eletrolite, pH, and time of analysis, linear analytical curves from $1.0 \cdot 10^{-6}$ - $4.0 \cdot 10^{-4}$ for Co(II) in the presence of Ni $1.0 \cdot 10^{-6}$ - $1.0 \cdot 10^{-4}$ mol L⁻¹ were observed. No further treatment or calculation processes have been necessary. Recoveries in different mixing ratios were of 99%. Interference of Fe(III), Cu(II), Zn(II) and Cd(II), and anions as NO₃⁻, Cl⁻, ClO₄⁻, citrate and phosphate has been evaluated. The method was applied to natural waters spiked with the cations.

Keywords: Simultaneous determination, Cobalt, Nickel, Dithiocarbamate, Spectrophotometry.

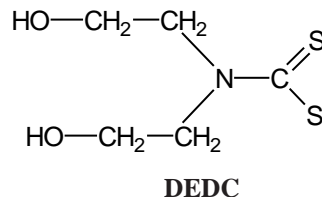
Introduction

Several methods have been proposed for the simultaneous determination of Co(II) and Ni(II). Electroanalytical techniques, optical, chromatographic and flow injection methods are widely described with this purpose [1-8].

The spectrophotometric methods are the most usually used and mathematical handling of the data is frequently required [9-13].

The present work is based on the differences in the color of solutions containing Co(II) or Ni(II) and dithiocarbamates (DTC). The best advantage of this procedure is that the results can be obtained by direct measurements and any further mathematical treatment is necessary. The choice of bis-2-hydroxyethylthiocarbamate (DEDC), was made on the basis of the higher solubility of

its complexes in relation to other DTC's, due to the presence of two -OH groups in its the structure:



The DTC, which are the products of reactions between an amine and carbon disulfide, has been applied in the medicine, as coadjuvants in AIDS, cancer, tuberculosis treatment and heavy metals removal from leaving organisms [14]; in the agriculture, as anti-fungicidal and anti-bacterial agents [15]; in industry as rubber vulcanizations agents, lubricants, anti-oxidizing agents

and catalysts [16]; in chemistry as synthesis intermediates, determination of metallic species and thermoanalytical studies [17, 18].

Experimental

Apparatus

Spectrophotometric experiments were made with an HP-8451A diode array spectrophotometer and 10 mm quartz cells. The pH was measured with a Corning IA-250 pHmeter and a Metrohm EA 121 glass electrode.

Atomic absorption was measured on a Hitachi Z-8100 atomic absorption spectrophotometer, using air-acetylene flame.

Reagents and Solutions

All the chemicals and solvents used were of analytical grade, PA, and used without any further purification.

The pH was adjusted with McIlvaine buffer solutions, and the ionic strength controlled to 0.5 mol L⁻¹ with KCl [19].

The metal ions stock solutions were prepared from NiCl₂·6H₂O and CoCl₂·6H₂O salts (Merck), and standardized by flame atomic absorption.

DEDC was synthesized by the reaction of ethanolamine and carbon disulfide in presence of ammonium hydroxide into an ice bath, and recrystallized from ethanol/water mixtures, as described elsewhere [20].

Procedures

Maximum Wavelength Absorption and ϵ Determination for the Complexes

Spectra were obtained from solutions containing the ligand and each metal both 1.0 10⁻⁴ mol L⁻¹ and using the ligand, one metal or mixtures, in different proportions. The attribution of the peaks of the complexes was performed on the basis of the increase in its absorbance when the metallic

concentration was increased using a metallic solution with the same concentration as blank.

The molar absorptivity coefficients were determined with each metal concentration ranging from 1.0 10⁻⁵-5 10⁻⁴ and the ligand 1.0 10⁻⁴-5.0 10⁻³ mol L⁻¹.

C_L/C_M Ratio optimization

In these experiments the concentration of the metal was fixed in 1.0.10⁻⁴ mol L⁻¹, and the ligand was varied in the range 1.0 10⁻⁵-8.0 10⁻³ mol L⁻¹, with each cation separately in phosphate buffer (pH=7). The absorbances were measured at the maximum wavelengths determined as above using the phosphate buffer as reference.

Mixtures of 3.0 10⁻⁵ mol L⁻¹ of each metal and the ligand varying from 3.0 10⁻⁵ - 3.0 10⁻² mol L⁻¹ in phosphate buffer were used to determine the best C_L/C_M ratio.

Ionic Strength Controller Salt Effect

The controller salt influence was investigated using KCl, NaCl, KNO₃, NaNO₃, NaClO₄, and McIlvaine buffer system at fixed ionic strength of 0.50 mol L⁻¹. The ratio C_L/C_M was fixed according to a previous study and the absorbance measured at the λ_{max} of each complex.

Using McIlvaine buffers the pH influence on the system was also investigated for 5.5, 6.5, 7.5 and 8.3. This pH range was used to prevent the ligand decomposition [21], and metallic hydrolysis.

Influence of Time and Temperature

Fixing the parameters already studied, the complex stability was evaluated by measuring the absorbance as a function of the time (0-130 min), for each complex individually. The influence of the temperature on the absorbance was also investigated from 15-41°C, using a thermostatic bath ($\pm 1^\circ\text{C}$).

Evaluation of the effect of interferents

The influence of the presence of cations generating colored (Fe(III) and Cu(II)) and colorless complexes (Zn(II) and Cd(II)) with DEDC was investigated in the $1.0 \cdot 10^{-6}$ - $1.0 \cdot 10^{-4}$ range and fixing the Ni and Co concentrations at $5.0 \cdot 10^{-5}$ and the DEDC at $5.0 \cdot 10^{-3}$ mol L⁻¹.

Evaluation of the Method in Synthetic Samples

The method was evaluated by measuring the metals intentionally added to mineral (drinking) water samples.

In this study the concentration of one cation was fixed while varying the concentration of the second one, at a fixed ligand concentration. In the first series of experiments Ni(II) was fixed at $1.0 \cdot 10^{-4}$, $5.0 \cdot 10^{-5}$ and $1.0 \cdot 10^{-5}$, with Co(II) varying

from 10^{-3} - 10^{-5} mol L⁻¹. In a second series Co(II) was fixed at $1.0 \cdot 10^{-4}$, $5.0 \cdot 10^{-5}$ and $1.0 \cdot 10^{-5}$, and Ni(II) varied in the 10^{-3} - 10^{-5} mol L⁻¹ range. In both cases the ligand concentration was maintained 100 times higher than the fixed metal, using all the parameters defined in the previous experiments.

Results and Discussion

The Co(II)/DEDC solutions showed green color with maximum absorption at 360 and 638 nm, while Ni(II)/DEDC are yellowish-green with λ_{\max} at 390 nm in agreement with Yoshida *et al* [22]. The spectra are presented in Figure 1. The strong band at 330 nm was assigned to the ligand [23].

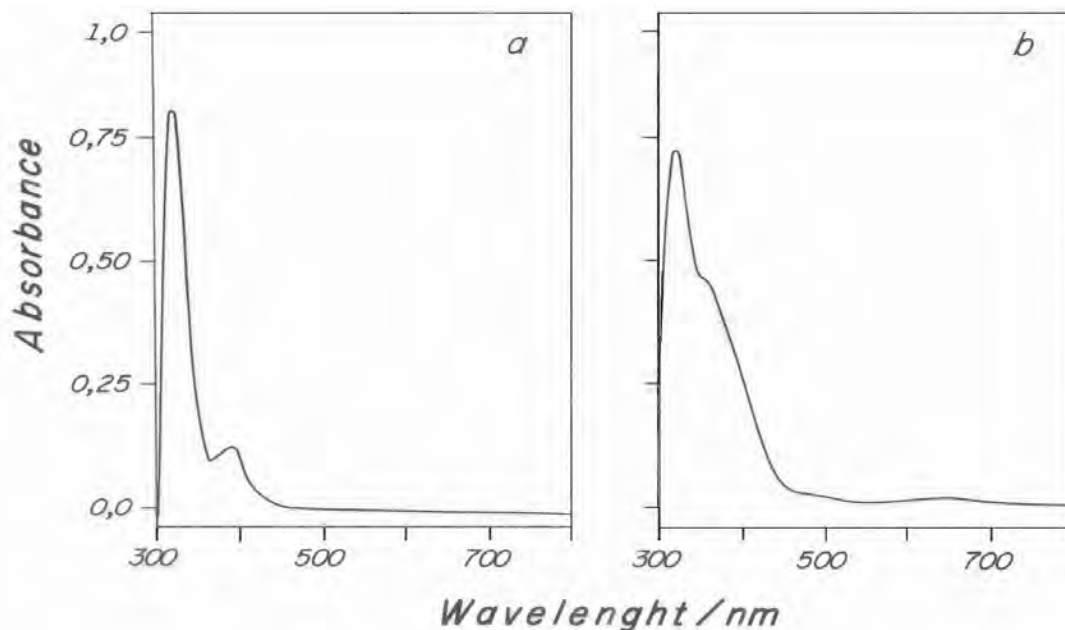


Figure 1. The absorption spectra of complexes. a) Ni/DEDC λ_{\max} - 390nm. b) Co/DEDC λ_{\max} - 360 and 638 nm.

The peaks were attributed to the complexes on the basis of their presence in the spectra obtained using either metallic solutions or ligand as blank.

The molar absorptivity coefficients, ϵ , were determined by plotting absorbance vs. the complex concentration ($C_M \approx C_{\text{cpx}}$; in ligand excess). The values obtained are presented in Table 1, at the maximum absorption wavelengths.

Table 1. Molar Absorptivity of the complexes

| Complex | $\lambda_{\text{m\acute{a}x}}$ (nm) | $\epsilon(\text{cm}^{-1}\text{mol}^{-1}\text{L}) \cdot 10^3$ |
|------------------------|-------------------------------------|--|
| Co ²⁺ /DEDC | 360 | 45.4 |
| | 638 | 1.71 |
| Ni ²⁺ /DEDC | 390 | 4.57 |

Since the $\epsilon_{638} < \epsilon_{360}$, more concentrated Co(II) solutions can be determined at 638 nm, while less concentrated ones can be determined at 360 nm, extending the detection range for this cation.

The limiting ligand/metal concentration ratio is different for solutions containing the individual cations or mixtures of them. For solutions containing only Co(II) or Ni(II), the ratio is about $C_L/C_M = 10$. For the mixtures of the two cations the limiting ratio $C_L/C_{\text{Ni+Co}} = 100$.

It must be addressed that the limiting value should not be attributed to precipitation. If precipitation had occurred the absorbance value should decrease while increasing the ligand concentration. Therefore the limiting value was most probably due to the presence of enough ligand to reach the maximum coordinating capacity of the system at such conditions. When they are mixed the differences in the affinity of the cations for the ligand make necessary much more ligand to reach saturation. Examples of curves of absorbance vs. the C_L/C_M ratio are presented in the Figure 2.

According to the results presented in Table 2 different ionic strength controlling salts and the pH ranging from 5.5 to 8.3, had no significant change in the measured absorbance. In addition the temperature range of 5-40°C and a measuring time of 0-130 min (results not presented) showed no influence in the measurements. According to these results, McIlvaine Buffer pH=7.0, $\mu = 0.50 \text{ mol L}^{-1}/\text{KCl}$ and temperature of 25.0°C, were adopted to perform the determinations.

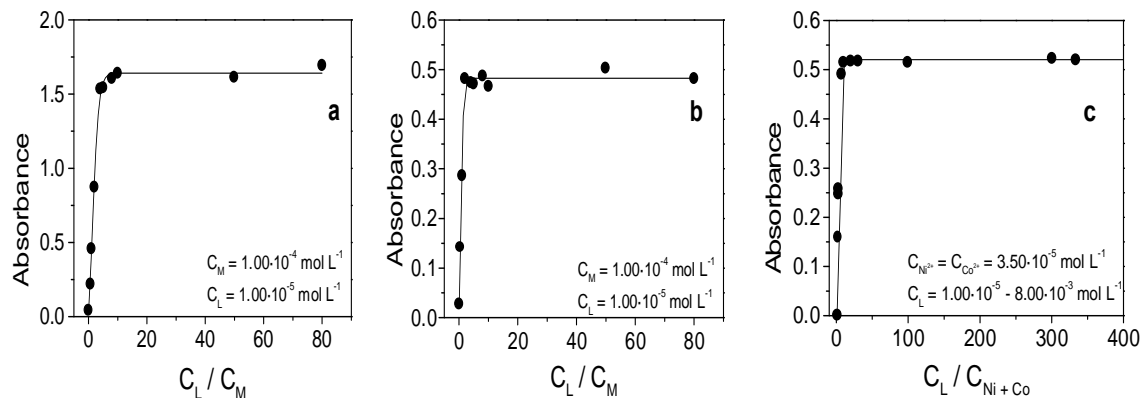
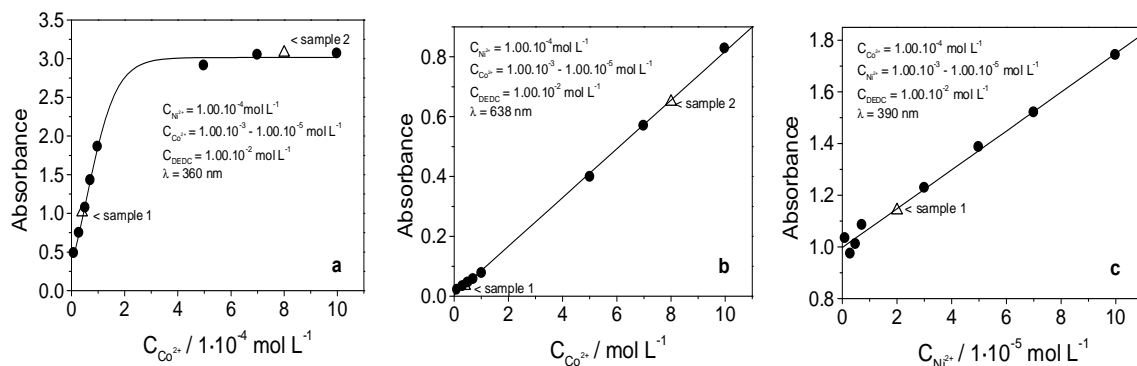


Figure 2. Determination of the limiting ligand concentration.

Table 2. Controlling Ionic Strength Salts and pH influence

| | | Absorbance | | |
|--|--------------------|------------------------|---------|------------------------|
| | | Co ²⁺ /DEDC | | Ni ²⁺ /DEDC |
| | | 360nm | 638nm | 390nm |
| Salt (0.50 mol L ⁻¹) | KCl | 1.558 | 0.06316 | 0.4760 |
| | NaCl | 1.558 | 0.06090 | 0.4977 |
| | KNO ₃ | 1.634 | 0.06284 | 0.4953 |
| | NaNO ₃ | 1.601 | 0.06000 | 0.4936 |
| | NaClO ₄ | 1.600 | 0.06221 | 0.4630 |
| | phosphate/citrate | 1.624 | 0.05994 | 0.5134 |
| pH | 5.49 | 1.609 | 0.06413 | 0.5166 |
| | 5.58 | 1.610 | 0.08569 | 0.5025 |
| | 6.58 | 1.653 | 0.07044 | 0.5155 |
| | 7.45 | 1.770 | 0.06499 | 0.4853 |
| | 8.32 | 1.655 | 0.06744 | 0.5318 |

The precision of the method was checked using synthetic samples and analytical curves. Examples for Ni and Co determinations are presented in Figure 3. In the Tables 3 and 4 the results for the determination of cations, fixing one and varying the concentration of the other, in different concentration ranges and mixing ratios are presented. The mean recovery was 99.0% for both cations.

**Figure 3.** Example of analytical curves for Co²⁺ and Ni²⁺ determination and the absorbance of samples 1 and 2.**Table 3.** Results of Method Application in Synthetic Samples, with Different Ni²⁺ Concentrations.

| C _{Ni²⁺} , mol L ⁻¹ | C _{DEDC} , mol L ⁻¹ | C _{Co²⁺} , mol L ⁻¹ calc. | λ, nm | C _{Co²⁺} , mol L ⁻¹ found | Corr. Coef. | Recovery % ^{a)} |
|--|---|---|-------|---|-------------|--------------------------|
| 1.0 10 ⁻⁴ | 1.0 10 ⁻² | 1.49 10 ⁻⁵ | 360 | 1.60 10 ⁻⁵ | 0.9998 | 107 |
| | | | 638 | 1.37 10 ⁻⁵ | 0.9998 | 92.0 |
| 5.0 10 ⁻⁵ | 5.0 10 ⁻³ | 2.61 10 ⁻⁴ | 360 | - | - | - |
| | | | 638 | 3.05 10 ⁻⁴ | 0.9995 | 116 |
| 1.0 10 ⁻⁵ | 1.0 10 ⁻³ | 7.46 10 ⁻⁶ | 360 | 6.91 10 ⁻⁶ | 0.9995 | 92.0 |
| | | | 638 | 6.53 10 ⁻⁶ | 0.9994 | 87.6 |

a) mean of two determinations

The effect of the presence of Fe(III), Cu(II), Zn(II) and Cd(II), are summarized in Table 5. All these cations influenced in the Ni(II) determination except Fe³⁺ when the interfering cation concentration was ten times smaller. Satisfactory results were obtained for the Co(II) determination in all the cases using $\lambda=360$ nm. Precipitation occurred in the presence of Fe(III) and Cu(II) at 10^{-4} mol L⁻¹. It has been observed that alkali metals and anions as NO₃⁻, Cl⁻, ClO₄⁻, citrate and phosphate had no significant influence in the determination.

Table 4. Results of Method Application in Synthetic Samples, with Different Co²⁺ Concentrations.

| C _{Co²⁺} , mol L ⁻¹ | C _{DEDC} , mol L ⁻¹ | C _{Ni²⁺} , mol L ⁻¹ | | λ , nm | C _{Ni²⁺} , mol L ⁻¹ | Corr. Coef. | Recovery % ^{a)} |
|--|---|--|-------|-----------------------|--|-------------|--------------------------|
| | | calc. | found | | | | |
| 1.0 10 ⁻⁵ | 1.0 10 ⁻³ | 5.00 10 ⁻⁵ | 390 | 5.08 10 ⁻⁵ | 0.9928 | 101 | |
| 1.0 10 ⁻⁴ | 1.0 10 ⁻² | 2.00 10 ⁻⁵ | 390 | 2.20 10 ⁻⁵ | 0.9985 | 110 | |
| 1.0 10 ⁻⁴ | 1.0 10 ⁻² | 9.00 10 ⁻⁵ | 390 | 7.93 10 ⁻⁵ | 0.9985 | 88.1 | |
| % mean recovery | | | | | | 99.70 | |

^{a)} mean of two determinations

Table 5. Studies of Some Interfering Cations for Ni²⁺ and Co²⁺.

| Interferant (complex colour) | Conc. Mol L ⁻¹ | Ni/DEDC | | Co/DEDC | |
|----------------------------------|------------------------------|-----------------------------|-------|---|------|
| | | Found / mol L ⁻¹ | rec % | Fo ^{und} / mol L ⁻¹ | rec% |
| Zn ²⁺ (colourless) | 1.0 10 ⁻⁴ | 3.9 10 ⁻⁵ | 130 | 5.31 10 ⁻⁵ | 85.0 |
| | 1.0 10 ⁻⁵ | 4.4 10 ⁻⁵ | 150 | 4.25 10 ⁻⁵ | 106 |
| | 1.0 10 ⁻⁶ | 4.5 10 ⁻⁵ | 147 | 5.31 10 ⁻⁵ | 106 |
| Cd ²⁺ (colourless) | 1.0 10 ⁻⁴ | 4.5 10 ⁻⁵ | 150 | 4.56 10 ⁻⁵ | 91.0 |
| | 1.0 10 ⁻⁵ | 4.4 10 ⁻⁵ | 147 | 5.61 10 ⁻⁵ | 112 |
| | 1.0 10 ⁻⁶ | 4.1 10 ⁻⁵ | 137 | 4.56 10 ⁻⁵ | 91.0 |
| Fe ²⁺ (brown) | 1.0 10 ⁻⁴ | precipitation | | precipitation | |
| | 1.0 10 ⁻⁵ | 6.0 10 ⁻⁵ | 200 | 5.07 10 ⁻⁵ | 101 |
| | 1.0 10 ⁻⁶ | 3.0 10 ⁻⁵ | 100 | 5.07 10 ⁻⁵ | 101 |
| Cu ²⁺ (blue) | 1.0 10 ⁻⁴ | precipitation | | precipitation | |
| | 1.0 10 ⁻⁵ | 5.5 10 ⁻⁵ | 183 | 5.08 10 ⁻⁵ | 102 |
| | 1.0 10 ⁻⁶ | 4.2 10 ⁻⁵ | 140 | 5.08 10 ⁻⁵ | 102 |

Conclusions

The proposed spectrophotometric method is simple, rapid and inexpensive. It provides gain in sensitivity without need of additional step as extraction or heating. The method does not involve stringent reaction conditions and gives precise and accurate results. Its usefulness to Co(II) and Ni(II), in presence of diethanoldithiocarbamate complexing agent, suggests its use as an attractive

alternative to many other previously reported methods for analysis related in literature.

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Determinação espectrofotométrica simultânea direta de Ni(II) e Co(II) usando dietanolditiocarbamato como agente complexante.

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Resumo: Um método espectrofotométrico simultâneo para a determinação de Co(II) e Ni(II), na presença do ligante dietanolditiocarbamato (DEDC), é proposto usando-se os comprimentos de onda dos máximos de absorção em 360 e 638 nm (Co(II)/DEDC) e 390 nm (Ni/DEDC). Após otimizar a melhor razão metal/ligante, eletrólito suporte, pH e tempo de análise, curva analíticas lineares foram obtidas nos intervalos de concentração $1,0 \cdot 10^{-6}$ - $4,0 \cdot 10^{-4}$ para Co(II) na presença de Ni $1,0 \cdot 10^{-6}$ - $1,0 \cdot 10^{-4}$ mol L⁻¹. Nenhum tratamento de amostra ou processo de cálculo foi necessário. Coeficientes de recuperação da ordem de 99% foram obtidos e a interferência de Fe(III), Cu(II), Zn(II) e Cd(II), além de alguns ânions foi avaliada. O método foi aplicado, com sucesso, em amostras de água mineral nas quais os cátions foram intencionalmente adicionados.

Palavras chave: Determinação simultânea, cobalto, níquel, ditiocarbamato, Espectrofotometria.

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