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EXTRACTION-PHOTOMETRIC DETERMINATION OF COBALT USING 1-(5-BENZYL-2-THIAZOLYL)-AZO-2-NAPHTHOL

A. Tupys, O. Tymoshuk

Ivan Franko National University of Lviv,
Kyryla and Mefodiya str., 6, 79005 Lviv, Ukraine
e-mail: otymoshuk@ukr.net

The complexation reaction of cobalt with 1-(5-benzyl-2-thiazolyl)-azo-2-naphthol was investigated using extraction-photometric method. A new extraction-photometric technique of cobalt determination using 1-(5-benzyl-2-thiazolyl)-azo-2-naphthol after extraction into toluene was developed (m_{min}(Co) = 2,0 μg). A way to eliminate the influence of Ni(II) ions was found. The developed technique was approved on a real object.

Key words: extraction-photometric method, cobalt, nickel, naphthol derivatives.

Nowadays the interest to the analytical chemistry of cobalt is rather great. It is caused by the various application of cobalt and its compounds. It is used as an alloying component of special alloys with high hardness and heat resistance. A lot of cobalt compounds have a high catalytic activity and serve as a catalysts for the synthesis of various chemical compounds. Radioactive isotopes of cobalt are widely used in medicine. A large number of cobalt complex organic compounds affect on the metabolism of plants and animals. Algae can concentrate cobalt from water. The content of cobalt in plants and animals is ranging from 10^{-5} to 10^{-3} wt. %. Cobalt affects on the activity of enzymes. B_{12} vitamin is a cobalt containing compound. Cobalt and its compounds are used as catalysts in various chemical processes. In addition, cobalt is an integral part of semiconductors and nanomaterials, and change of its content leads to significant changes of products' operational characteristics [1].

This all leads to the need to develop new methods for qualitative detection and quantitative determination of cobalt as the main component and as the impurities in the technical and biological materials of various composition. Particular attention researchers pay to the development of methods for the determination of trace amounts of cobalt. For this purpose spectrophotometric, kinetic and electrochemical methods of analysis are used. Many studies are devoted to the synthesis of new organic reagents for the development of new methods of cobalt determination, which would be characterized as highly selective and sensitive.

Spectrophotometric studies were performed on a spectrophotometer UV/VIS ULAB with a thickness of the absorbing layer 1 cm and a photocolorimeter CPC-3 in cuvettes with a thickness of the absorbing layer 1–5 cm. Acidity of the solution was controlled by pH-meter (150M) with argentum chloride electrode and a glass indicative electrode using diluted solutions of NaOH and HCl.

All research work was carried out using reagents with "chemically pure" and "particularly clean" qualifications. Alcoholic solution of azodye, 1-(5-benzyl-2-thiazolyl)-azo-2-naphthol, was prepared by dissolving an accurate sample of previously purified reagent. The exact weight of metallic cobalt powder with mass ~ 0.05–0.1 g was dissolved in 1M nitric acid solution.

1-(5-Benzyl-2-thiazolyl)-azo-2-naphthol – a representative of the naphthol derivatives group (Fig. 1).

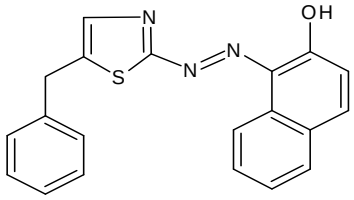

Fig. 1. Structural formula of 1-(5-benzyl-2-thiazolyl)-azo-2-naphthol

Electronic absorption spectra of 1-(5-benzyl-2-thiazolyl)-azo-2-naphthol in the absence and in the presence of cobalt (II) ions in toluene extracts were obtained. The spectrum of the complex compound is characterized by a shift of the absorption maximum towards longer wavelengths, which is about 60 nm (Fig. 2).

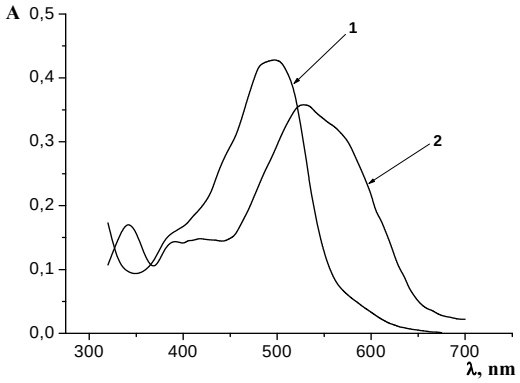

Fig. 2. Electronic absorption spectra of 1-(5-benzyl-2-thiazolyl)-azo-2-naphthol in the absence (1) and in the presence (2) of Co^{2+} ions;
C (Reag) = 2,9· 10^{-5} M, C(Co^{2+}) = 9,0·10^{-5} M, C(NaOH) = 8,0·10^{-2} M, l = 1,0 cm

Because of the existence of different forms of cobalt in the solution [2] the outcome of complex compound with a variable concentration of hydrogen ions was investigated (Fig. 3).

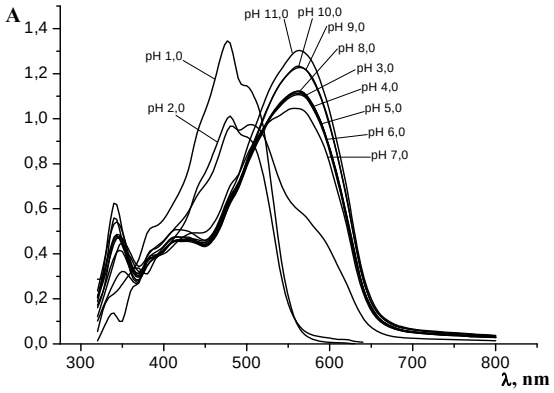

Fig. 3. Absorption spectra of toluene solutions of 1-(5-benzyl-2-thiazolyl)-azo-2-naphthol in the presence of Co^{2+} ions at pH = 1-12; C(Reag) = $5.9 \cdot 10^{-5}$ M, C(Co^{2+}) = $3.3 \cdot 10^{-4}$ M, l = 1.0 cm

The obvious conclusion from the corresponding spectra – effective extraction occurs at pH> 3. Within the pH range of 11.5–13.5 view of the spectrum is similar to the absorption at pH 11. That's why further studies were performed at pH 12–13.

There have been conducted a number of measurements and evaluated the dependence of optical density of toluene extracts from the ratio of components reagent: cobalt in water-alcohol solution. The stoichiometric ratio of the components from the alkaline solution was found using the mole-ratio method (Fig. 4) and the method of continuous variations (Fig. 5), and according to studies it is C(Co^{2+}):C (Reag) = 1:2, which is consistent with literature data [3,4].

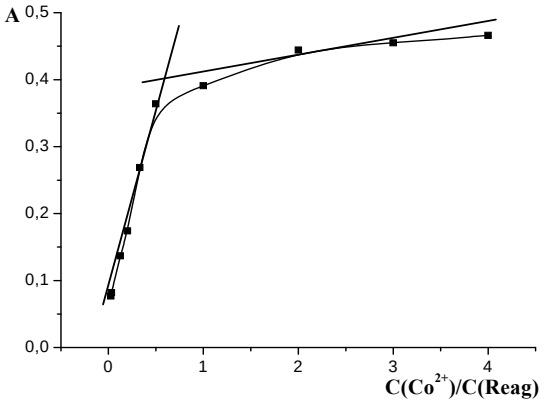

Fig. 4. Dependence of toluene extract optical density from the ratio of components in the system Co^{2+} – 1-(5-benzyl-2-thiazolyl)-azo-2-naphthol;
C(Reag) = $5.8 \cdot 10^{-5}$ M, pH = 12, l = 1,0 cm, λ = 565 nm

Basing on the dependence between the output of complex compounds and the concentration of metal ions the method of extraction-photometric determination of cobalt with 1-(5-benzyl-2-thiazolyl)-azo-2-naphthol at pH = 11 was designed. Metrological characteristics are:

Limits of linear dependence $m_{Co(II)}$, μg – 1.8–42.7;
Equation of gradual schedule $A = f(m(Co^{2+}))$, μg –
A =(0.062±0.004) + (0.0159±0.0004)m;
The correlation coefficient R – 0.9987;
The lowest limit of detection m_l, μg – 4.0.

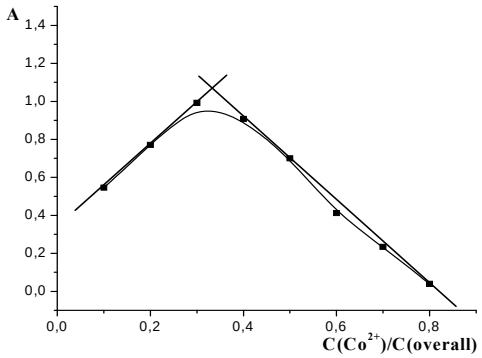

Fig. 5. Setting the ratio of the interaction in the system
Co(II) – 1-(5-benzyl-2-thiazolyl)-azo-2-naphthol by the method of continuous variations;
C(total) = $9.0 \cdot 10^{-5}$ M, pH = 12, l = 1,0 cm, λ = 565 nm

The next stage of the research was the study of the selectivity problem of this extraction photometric determination method. With nickel ions organic reagent forms a similar compound with Co^{2+}, but the reversibility of complexation reaction is probably much more significant, and as evidence there is the presence of the dye absorption zone even when Ni^{2+} ions are in significant excess (Fig. 6).

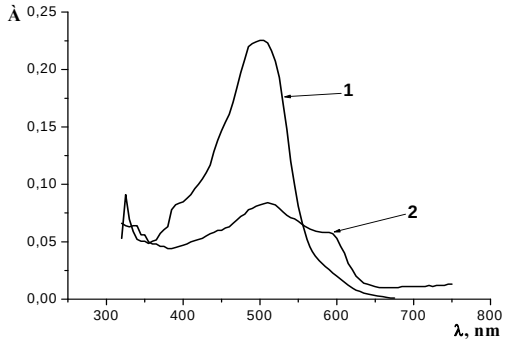

Fig. 6. The absorption spectrum of 1-(5-benzyl-2-thiazolyl)-azo-2-naphthol in toluene solution
in the absence (1) and in the presence (2) of Ni^{2+} ions;
C(Reag) = $1.5 \cdot 10^{-5}$ M, C(Ni^{2+}) = $7.5 \cdot 10^{-5}$ M, C(NaOH) = $8.0 \cdot 10^{-2}$ M, l = 1.0 cm

In the case of Ni^{2+} ions, an attempt of its preliminary separation as dymethylglyoksimate was made after extraction into chloroform from aqueous solutions at pH 5.5 [5-7]. Under these conditions cobalt ions are not extracted. In order to eliminate unwanted competing processes, acidic solution were neutralized with sodium carbonate instead of ammonia. Performed studies (Fig. 7) showed that triple extraction with 10 ml of chloroform is sufficient for quantitative separation of nickel if its content does not exceed 0.22 mg.

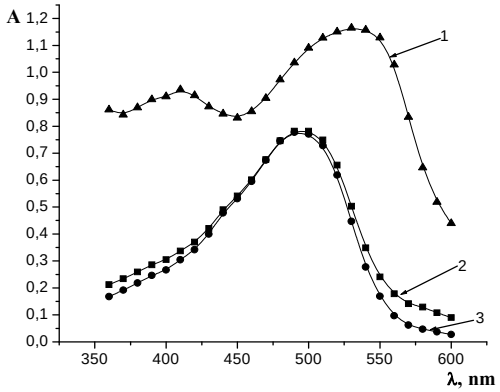

Fig. 7. The absorption spectrum of 1-(5-benzyl-2-thiazolyl)-azo-2-naphthol in toluene solution at the presence of Ni^{2+} ions in the initial solution after preliminary separation of nickel by triple extraction of its dymethylglyoksimate into chloroform, C(Reag) = $4{,}5\cdot10^{-5}$ M , m(Ni) = 2.2 mg (1); 0.44 mg (2); 0.22 mg (3); C(NaOH) = $8.0\cdot10^{-2}$ M, l = 1.0 cm.

At the glass factory “Decor” (village Pisochna, Nikolaev district, Lviv region) which produces high quality tableware and decorative items from colorless lime-sodium glass, the quantitative analysis of the blend on the cobalt content using 1-(5-benzyl-2-thiazolyl)-azo-2-naphthol was carried out. Potassium thiocyanate solution was used for qualitative analysis, and to quantify the Co content method of comparison was carried out.

The results of the investigation showed that the content of Co_2O_3 which is added to increase the transparency of the glass is about 15,0 μg per 1 g of the blend, which agree well with data of glass production technology on this plant.

So the interaction of 1-(5-benzyl-2-thiazolyl)-azo-2-naphthol with Co^{2+} ions in the environment of toluene was investigated [8]. The stoichiometric ratio of the components in the extraction-photometric determination from alkaline solution was established using photometric methods and it is C(Co^{2+}):C(Reag) = 1:2. An extraction-photometric method of cobalt determination using 1-(5-benzyl-2-thiazolyl)-azo-2-naphthol after extraction into toluene was developed (m_l(Co) = 2,0 μg). An obstructive influence of Ni(II) ions can be succesfully eliminated by its preliminary extraction into chloroform as dymethylglyoksimate at pH 5.5 [9, 10]. The developed method was tested on a real object – the blend from which the glass is brewed.

1. *P'atnyc'kiy I. V.* Analytical chemistry of cobalt. Moscow : Nauka, 1965.
2. *Pavlov V.N., Bondar V.V.* Polarographic behavior of divalent cobalt, nickel and iron // The success of chemistry. 1973. Vol. 42. N 6. P. 987–1008.
3. *Itabashi E.* Influence of sulfide formation on the reduction of nickel in thiosulfate solutions at mercury electrodes // J. Electroanal. Chem. 1980. Vol. 106. P. 115–126.
4. *Ulahovich N.A., Postanova I.B., Budnikov G.K.* Extraction and anodic voltammetry of iron (II), cobalt (II), manganese (II) mixed-complexes with amines and dithiophosphate // J. of analytical chemistry. 1985. Vol. 40, N 8. P. 1502–1507.
5. *Krapivkina T.A., Brainina H.Z.* Preconcentration and determination of cobalt trace in salts of nickel by film polarography // Zavodskaya Laboratoria. 1970. Vol. 36. N 3. P. 263–265.
6. *Mamdouh S. , Khalil A., Hindavy M.* Spectroscopic studies on some azo compounds and their cobalt, copper and nickel complexes // Spectrochimica Acta. 2004. Vol. A60. P. 2807–2817.
7. *Taher M.A., Balani S., Puri V.K.* Atomic-absorbance determination of nickel traces after preconcentration on naphthalene immobilized 1-(2-pyridylazo)-2-naphthol or its complex on microcrystalline naphthalene // J. of analytical chemistry. 2000. Vol. 55, N10. P. 1080–1085.
8. *Basargin N.N., Rozovskiy Yu.G.* New organic reagents in the analysis of noble metals. Moscow : Metallurgy, 1982.
9. *Ganer M. Hassanein A., Seraji H.* Synthesis and characterization of Co(II), Ni(II) and Cu(II) complexes involving hydroxyl antipyrine azodyes // J. of Molecular Structure. 2008. Vol. 875. P. 322–328.
10. *Lemos V., Santos L., Bezerra M.* Determination of cobalt and manganese in food seasonings by flame atomic absorption spectrometry after preconcentration // J. of food composition and analysis. 2010. Vol. 23. P. 277–281.

ЕКСТРАКЦІЙНО-ФОТОМЕТРИЧНЕ ВИЗНАЧЕННЯ КОБАЛЬТУ З ВИКОРИСТАННЯМ 1-(5-БЕНЗИЛ-2-ТІАЗОЛІЛ)-АЗО-2-НАФТОЛУ

А. Тупис, О. Тимошук

Львівський національний університет імені Івана Франка,
вул. Кирила і Мефодія, 6, 79005 Львів, Україна
e-mail: otymoshuk@ukr.net

Екстракційно-фотометричним методом досліджено комплексоутворення кобальту з 1-(5-бензил-2-тіазоліл)-азо-2-нафтолом у різних середовищах. Розроблено екстракційно-фотометричний метод визначення кобальту з використанням 1-(5-бензил-2-тіазоліл)-азо-2-нафтолу екстракцією у толуен ($m_н$(Co) = 2,0 мкг). Знайдено спосіб усунення впливу Ni(II), що заважає аналізу. Розроблену методику апробовано на реальному об'єкті.

Ключові слова: екстракційно-фотометричний метод, кобальт, нікель, нафтолові похідні.

ЭКСТРАКЦИОННО-ФОТОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ КОБАЛЬТА С ИСПОЛЬЗОВАНИЕМ 1–(5-БЕНЗИЛ-2-ТИАЗОЛИЛ)-АЗО-2-НАФТОЛА

А. Тупыс, О. Тимошук

Львовский национальный университет имени Ивана Франко,
ул. Кирилла и Мефодия, 6, 79005 Львов, Украина
e-mail: otymoshuk@ukr.net

Экстракционно-фотометрическим методом исследовано комплексообразование кобальта с 1-(5-бензил-2-тиазолил)-азо-2-нафтолом в разных средах. Разработано экстракционно-фотометрический метод определения кобальта с использованием 1-(5-бензил-2-тиазолил)-азо-2-нафтола екстракцией в толуол ($m_н$(Co) = 2,0 мкг). Найден способ устранения мешающего влияния Ni(II). Разработанную методику апробовано на реальном обьекте.

Ключевые слова: экстракционно-фотометрический метод, кобальт, никель, нафтоловые производные.

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