Extraction-Photometric Determination Of Cadmium(II) Using 1-(5-benzylthiazol-2-yl)azonaphthalen-2-ol

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Abstract – ***A new analytical reagent for photometric determination of cadmium(II) ions was proposed – 1-(5-benzylthiazol-2-yl)azonaphthalen-2-ol (BnTAN). The complexation reaction between cadmium(II) and BnTAN and was investigated using extraction-photometric method. A sensitive extraction-photometric technique of cadmium determination using 1-(5-benzylthiazol-2-yl)azonaphthalen-2-ol after extraction into toluene was developed. The lowest quantity of cadmium that can be determined is*** m_{min}***(Cd) = 0,30 μg. The hypothetical scheme of complexation reaction was predicted. The possibility of determination of other transition metals and the selectivity of the technique was studied too.***

Key words – extraction, spectrophotometry, cadmium, thiazolylazonaphthol dyes, UV/VIS absorption spectrum.

I. Introduction

Nowadays one of the most important tasks is the defense of our environment from various pollutants. Such pollutants as heavy metals are very dangerous for human's health and only radioactive isotopes are more harmful. According to standards the allowed concentrations of heavy metals such as cadmium in the natural and drinking waters and soils are very low. That's why it is high time to create some new methods of heavy metals detection with high sensibility.

Among various spectrophotometric reagents for the transition metals determination a significant place take thiazolylazonaphthol dyes. They have been widely used in many practical applications, such as textile dyeings, coloring polyamide fibers etc [1]. Especially 1-thiazol-2-ylazonaphthalen-2-ol (or TAN) derivatives have a great application in the analysis. These colored compounds usually interact with transition metals ions creating complexes that absorb light at a higher wavelengths. Basing on this bathochromic shift a new method of spectrophotometric analysis can be developed [2].

II. Experimental

Spectrophotometric studies were performed on a UV/VIS spectrophotometer 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 analytical researches were connected with an interesting organic reagent 1-(5-benzylthiazol-2-yl)azonaphthalen-2-ol (or BnTAN). This substance is a red azodye, insoluble in water and aqueous alcoholic solution, but soluble in pure ethanol, methanol, toluene, chloroform, carbon tetrachloride, dimethylsulfoxide and dimethylformamide. The alcoholic solution of BnTAN was prepared by a dissolution of an exact quantity of the previously purified sample in pure ethanol. 1-(5-benzylthiazol-2-yl)azonaphthalen-2-ol was purified by double recrystallization from acetone and ethanol followed by filtration and vacuum distillation.

Molecular absorption spectrum of the azodye has maximum at a wavelength of 490 nm. The Beer's Law is observed in a wide range of concentrations and the molar absorbtivity at 490 nm is high (approx. $3 \cdot 10^4$ $sm^{-1}M^{-1}$). The absorbtivity at the wavelengths $\lambda \geq 600$ nm is very small.

III. Results and Dicussion

An analytical effect was found connected with the change of colour of the reagent's solution after the reaction with Cd^{2+} ions in an alkali solution. A complex compound with the absorption maximum at λ_{max} = 595 nm was created. But further investigations in aqueous alcoholic solution were complicated because of the low solubility of the complex compound.

Literature data say that to prevent the creation of small colloidal particles in the solution extraction into organic solvents is usually recommended [3].

Drapkina *et al.* has shown that the similar reagent called brombenzthiazo (BrBTAN) interacts with cadmium(II) and zink(II) creating complexes that could be extracted into toluene and give high molar absorbtivity [4]. That's why further investigations were continued in toluene solutions.

After the extraction of reagent's solution in the absence and presence of cadmium(II) ions the following spectra were obtained (Fig. 1). Evidently the photometric reaction is enough contrasty because the shift of the absorption maximum is greater than 100 nm.

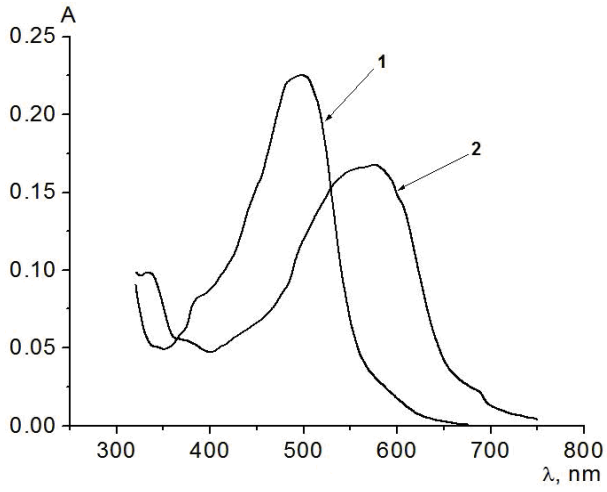


Fig. 1 Absorption spectra of the toluene solutions of 1-(5-benzylthiazol-2-yl)azonaphthalen-2-ol in the absence (1) and presence (2) of Cd(II) ions; (C(BnTAN) = $1,5 \cdot 10^{-5}$ M, C(Cd(II)) = $7,5 \cdot 10^{-5}$ M, C(NaOH) = $8,0 \cdot 10^{-2}$ M, l = 1,0 cm)

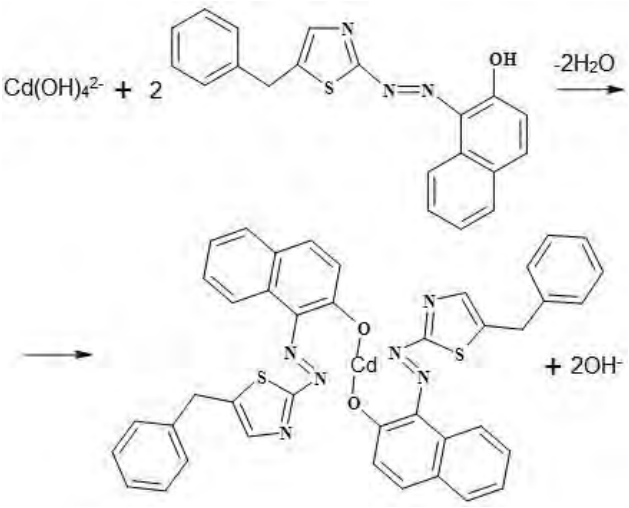
The mole-ratio method was applied to determine the stoichiometry between BnTAN and cadmium(II). The linear part of the A=f(C(Cd^{2+})) plot was used for the quantitative determination of the metal. According to the gathered data the optimal concentration ratio of the azodye and cadmium(II) is 1:2.

Some additional investigations were conducted to determine the composition of the complex. The result of the method of continuous variations or Job's method [5] is that the stoichiometry between BnTAN and Cd(II) is 1:2 too.

The optical density of the toluene solutions of cadmium-BnTAN complexes stais constant during 2 hours. After that it can be observed that the absorption at 590 nm becomes lower and the optical density at 490 nm is greater. This proves that the complex compound decomposes to the precursors.

Also the investigations were carried out to determine the optimal conditions of the cadmium extraction using 1-(5-benzylthiazol-2-yl)azonaphthalen-2-ol. There was set that the quantity of colored complex compound becomes greater when the Ph is raised and it is maximal at the alkali concentration of $8{,}0 \cdot 10^{-2}$ M.

After examining the main forms of Cd(II) existence in aqueous solutions [6] the assumptions can be made that in the complexation reaction only two forms can take part: tetramer $Cd_4(OH)_4^{4+}$ that dominates in wide comcentration limits in alkali solution or $Cd(OH)_4^{2-}$ form. That's why the hypothetical scheme of complexation reaction can be written in such way:



Basing on the gathered data of the research A sensitive extraction-photometric technique of cadmium determination using 1-(5-benzylthiazol-2-yl)azonaphthalen-2-ol after extraction into toluene was developed. It was tested on model solutions and its minimal detected weight of cadmium is 0.30 μg.

The most important task on this stage of the research is looking for the best conditions for Cd(II) determination in the presence of other transition metals because the selectivity of the developed technique in not good enough. Besides there is a possibility of an extraction-photometric determination of Zn(II), Cu(II) and Co(II) ions using the proposed azodye [7].

TABLE 1

METROLOGICAL CHARACTERISTICS OF THE EXTRACTION-PHOTOMETRIC DETERMINATION OF CD(II) IN TOLUENE SOLUTIONS USING 1-(5-BENZYLTHIAZOL-2-YL)AZONAPHTHALEN-2-OL

Limits of linear dependence $m_{Cd(II)}$, μg	0,15 – 2,25
Equation of the calibration curve A від $m_{Cd(II)}$, μg	A = (0,037±0,004) + (0,110±0,003) m
Correlation R	0,9976
The lowest limit of detection m_{min}, μg	0,30

Conclusion

Thiazolylazo dyes have been widely used in many analytical procedures and they have great potential for application in analytical chemistry. For this reason one of their representatives BnTAN was investigated.

Basing on the research a new technique of photometric determination of Cd(II) was developed because BnTAN creates a colored complex compound with some transition method. Though the method is very sensitive a lot of work must be done to improve its selectivity. Also there is a possibility to use BnTAN as an acid-base indicator [8].

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