

Spectrophotometric determination of Zinc(II) in solutions samples using 1-azobenzene-3-(3-hydroxyl-2-pyridyl)-triazene in the Surkhandarya region

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Abstract. In this paper has been studied a new sensitive and selective chromogenic reagent, 1-azobenzene-3-(3-hydroxyl-2-pyridyl)-triazene (ABHPT), was synthesized. It has been found that reacts with zinc (II) in a borax buffer solution (pH 10.0) to form 2: 1 red complexes with the maximum absorption at 530 nm. The apparent molar absorptivity of the complex is 2.6×10^5 L/(mol cm). A new method for the spectrophotometric determination of trace Zinc(II) was developed. Beer's law is obeyed for 0–15 μg of zinc (II) in 25 mL of solution. The limit of quantification, limit of detection, and relative standard deviation are 0.74 ng/mL, 0.25 ng/mL, and 1.0%, respectively.

Keywords: zinc (II), absorption, 1-azobenzene-3-(3-hydroxyl-2-pyridyl)-triazene, Surkhandarya region.

Introduction

Being a type of trace element both in organisms and human bodies, zinc (II) has important biological functions [1]. Excess zinc (II) may lead to many serious diseases such as lung cancer [2]. Thus, the determination of zinc (II) in biological samples is becoming increasingly important. Methods such as flame atomic absorption spectrometry (FAAS) [3], electrothermal atomic absorption spectrometry (EAAS) [4], inductively coupled plasma atomic emission spectrometry (ICPAES) [5], differential pulse cathodic stripping voltammetry (DPCSV), fast neutron radiochemical activation analysis (NRA) [6], and spectrophotometry have been used for the determination of zinc (II). Among these technologies, FAAS is reliable down to about 0.2 mg/L and, hence, is not suitable for the analysis of zinc (II) in solution samples. EAAS, ICP-AES, DPCSV, and NRA are generally used to determine zinc (II) at low concentrations; but, in order to meet the requirements of accuracy and precision, some preconcentration steps must be used. Spectrophotometric methods are simple and economical. However, a sensitive, selective, and stable chromogenic reagent is acid, p-chlorobenzenediazoaminoazobenzene, and 2-hydroxy-5-nitrophenyldiazoaminoazobenzene. Among these reagents, the reagents mentioned in [7] have a low sensitivity and so are not suitable for the determination of nickel in solution samples. The reagents in [8] have a higher sensitivity. However, preconcentration steps are required. The

reagents in [9] have a high sensitivity and simplicity reaction conditions, but they have only been applied to determine nickel in alloy samples. required. The main reagents to determine nickel reported in the literature are p-acetylarsenazo, 2,4-dibromobenzenediazoaminoazobenzene, 4-(2-pyridylazo)-resorcinol, butanedione oxime, diethyldithiocarbamate, 1-(2-pyridylazo)-2-naphthol, α -furildioxime, ammonium-2-amino-1-cyclohexene-1-dithiocarboate, 2-[2-(5-methylbenzothiazoly)-azo]-5-dimethyl aminobenzoic acid, p-chlorobenzenediazoaminoazobenzene, and 2-hydroxy-5-nitrophenyldiazoaminoazobenzene. Among these reagents, the reagents mentioned in [10] have a low sensitivity and so are not suitable for the determination of zinc (II) in solution samples. The reagents in [11] have a higher sensitivity. But, preconcentration steps are required. The reagents in [12] have a high sensitivity and simple reaction conditions, but they have only been applied to determine zinc (II) in alloy samples. Triazene is a very sensitive chromogenic reagent. There are many research reports on using it to determine cadmium and mercury [13]. A new triazene reagent (ABHPT) for the determination of zinc (II) in solution samples has been synthesized in our laboratory. It has a high sensitivity and simple reaction conditions. Thus, ABHPT was used for the spectrophotometric determination of trace zinc (II) in solution samples in the Surkhandarya region following work.

2. Experimental part

Materials. Absorbances were measured on a Lambda 35UV/Vis spectrophotometer (PerkinElmer, United States) with a 1-cm cell. The pH values were measured with a model PHS-3C meter (Shanghai Leici Analytical Instrument Factory, China). A standard stock solution of zinc (II) (1.0 mg/mL) was prepared by dissolving 0.1000 g of high purity zinc (II) (99.99%) in 15 mL of 8 M nitric acid. The solution was boiled gently to expel brown fumes, then the solution was cooled and diluted to 100 mL with deionized water. A standard working solution (5.0 μ g/mL) was prepared by dilution with water.

Methods.

Synthesis of ABHPT. Here, 0.05 mol (10 g) of p-aminoazobenzene was added in 30 mL 2 : 1 HCl and stirred well. Sodium nitrite solution (dissolve 3.45 g NaNO_2 in 40 mL of H_2O) was added dropwise while maintaining a reaction temperature below 5°C . After 200 g/L of sodium carbonate solution were added to the above solution, the pH was adjusted to 3–4. Next, 5.5 g of 2-amino-3-hydroxypyridine solid was dissolved in 50 mL of ethanol and then added dropwise to the above diazotized solution. The pH was adjusted to 6–7 with absolute sodium acetate. After 2 h, the precipitate was filtered and washed with deionized water and 50% ethanol, respectively, then dried under the infrared lamp. Next, 2.4 g of ABHPT was obtained, with a yield of 75.5%

General procedure. No more than 15 μ g of zinc were transferred into a 25 mL of calibrated flask, 2.0 mL of borax buffer solution (pH 10.0), 2.0 mL of 2.0% (m/v) Triton X-100, and 1.0 mL of 0.02% ABHPT were added successively, and the solution was diluted to the mark with water and mixed well. The absorbance at 530 nm in a 1-cm cell was measured against the reagent blank. The reagent blank was prepared in a similar manner, but without zinc (II). All measurements were performed at room temperature.

RESULTS AND DISCUSSION

Absorption spectra. Under the experimental conditions, the absorption spectra of ABHPT and the ABHPT-Zn(II) complex were scanned, the absorption curves are shown in Fig. 1.

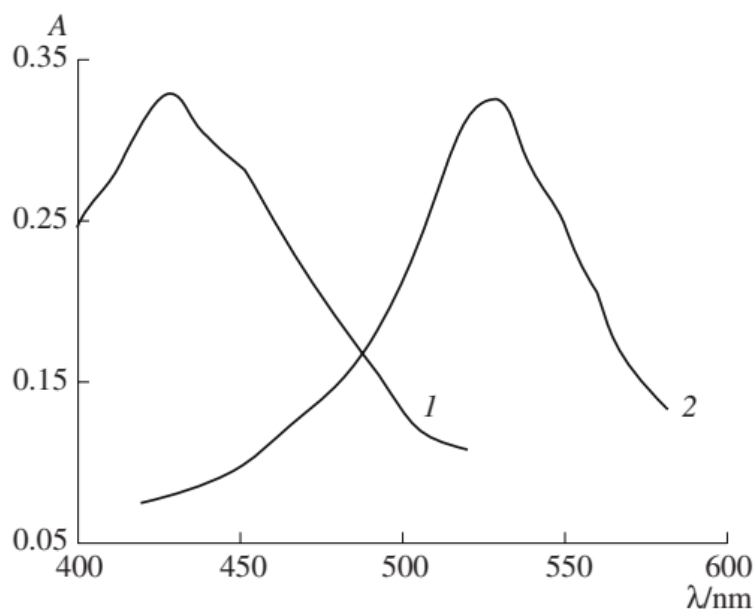


Fig. 1. Absorption spectra of (1) ABHPT against water and (2) ABHPT–Ni(II) against the reagent blank. $\Delta\lambda = 100$ nm.

The absorption maximum of ABHPT is at 430 nm and the ABHPT–Zn(II) complex gives an absorption peak at 530 nm. The difference between the two peaks is 100 nm, and is easy to distinguish. Therefore, a wavelength of 530 nm was chosen for the spectrophotometric determination of nickel in the following study.

The effect of acidity. The effects of various pH values on the ABHPT–Zn(II) complex formation reaction were tested. It was found that the absorbance of the complex is almost unchanged in the pH value range of 9.0–11.0. Therefore, a pH-10.0 borax buffer solution was used. The effect of the volume of the pH-10.0 borax buffer solution was tested. The absorbance increased sharply with an increasing volume of buffer solution up to 1.0 mL, and then tended to remain constant within the range 1.0–3.0 mL. Above 3.0 mL, the absorbance decreased slowly. Thus, the addition of 2.0 mL of borax buffer solution (pH 10.0) was recommended.

The characteristics of the complex. The color complex could be formed immediately at 0–20°C. The absorbance of the complex could be stable for at least 48 h under 20°C. The composition ratio of the Zn(II)–ABHPT complex obtained using Job’s method and the mole ratio methods was 1:2. According to the structure of ABHPT, we think that it is a plane conjugate system and it has a Cs symmetry. We optimized the structure of ABHPT with the AM1 half experiential method [14], and calculated the Mulliken charge for all of the atoms. The result shows that the oxygen atom (O) and the nitrogen atoms (N1, N2) have the highest charge density, and so they are ready to bond to Zn(II). The probable structure of ABHPT–Zn(II) is thus suggested in Fig. 2, which is similar with the complex studied in.

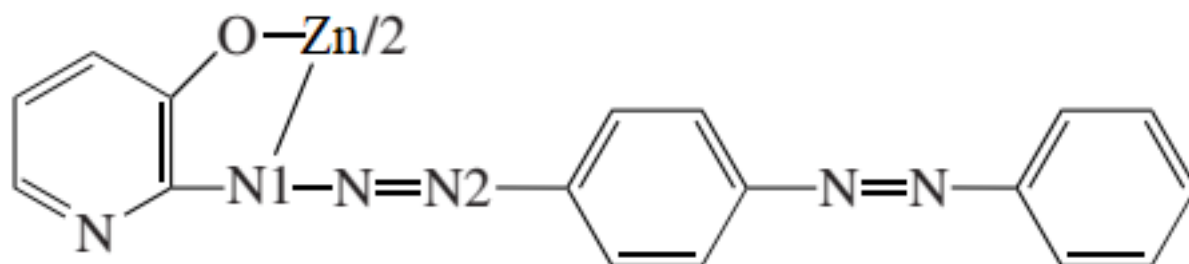


Fig. 2. Structure of the ABHPT–Zn(II) complex

Analytical characteristics. The calibration graph was constructed according to the usual procedure. Beer's law was obeyed for 0–15 μg of zinc in 25 mL solution at 530 nm. The apparent molar absorptivity of the complex was 2.6×10^5 L/(mol cm). The limit of detection as defined by IUPAC [29] and the limit of quantification [30] were found to be 0.25 and 0.74 ng/mL, respectively. The relative standard deviation was 1.0% for 11 determinations of 5.0 μg Zn(II) in 25 mL solution. The simple linear regression calibration equation is $A = 0.172C$ ($\mu\text{g}/25\text{mL}$) + 0.026 with a correlation coefficient of 0.9997.

Adsorbent characteristics of the sulfhydryl dextran gel for metal ions. Sulfhydryl dextran gel has an excellent sorption ability to heavy metal ions such as Ag^+ , Hg^{2+} , Cu^{2+} , Sn^{2+} , Zn^{2+} , Pb^{2+} , Cd^{2+} , Co^{2+} , and Ni^{2+} . However, when the acidity was adjusted to 1.0 M HCl, only Ag^+ , Hg^{2+} , Cu^{2+} , Ni^{2+} , and Pb^{2+} can be adsorbed quantitatively with sulfhydryl dextran gel, and zinc is not adsorbed when held in a water solution. Hence, first, the acidity of the solution was adjusted to 1.0 M HCl with a concentrated HCl, and, next, 0.1 g sulfhydryl dextran gel was added. Ag^+ , Hg^{2+} , Cu^{2+} , Zn^{2+} , and Pb^{2+} were adsorbed completely, and, thus, their effect on the determination of zinc would be eliminated.

Conclusion

The chromogenic reaction was immediately completed and the formed complex was stable for at least 48 h at 0–20°C. The proposed method is sensitive, and the molar absorptivity is 2.6×10^5 L/(mol cm). The sensitivity is higher than that of FAAS. Compared with other reagents for the spectrophotometric determination of zinc. The proposed method is very selective in the Surkhandarya region.

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