ANALYTICAL APPLICATION OF THE REACTION SYSTEM ALIZARINE-HYDROGEN PEROXIDE IN BORATE BUFFER MEDIA FOR THE SPECTROPHOTOMETRIC KINETIC DETERMINATION OF Ni(II)

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A rapid, simple, sensitive and selective new spectrophotometric kinetic method for Ni(II) traces determination at room temperature was elaborated in this paper. It is based on the catalytic effect of nickel ions upon the oxidation of alizarine (AL) by hydrogen peroxide in borate buffer (BUF) solution. The method was confirmed by determination of Ni(II) traces in fresh water samples. The obtained results were compared to those obtained by ICP-OES method and good agreement of the results was found.

Keywords: Ni(II) determination, catalyst, spectrophotometric kinetic method

Introduction

No doubt, nickel is one of the most interesting heavy metals today. It is abundant in lithosphere and biosphere so that natural deficiency does not occur. Nickel is an important alloying element for steel and cast iron. It is incorporated in electrodes, coins, ships, magnets, turbines, etc. Because of its permanence in air, nickel is also adequate for iron and brass plating. It is an essential trace element and micro nutrient in humans, as well as in number of animals and plants: nearly 40 ng/ml of Ni(II) is required for normal metabolism of many living organisms. Normal human plasma contains about 0.012 to 0.085 ppm of Ni(II). Nickel is the cofactor of some biologically important enzymes and when bound to ribonucleic acid it has a special affinity to bones and skin and plays a significant role in pigmentation. On the other hand, higher amounts of nickel, both in the form of inorganic salts and some soluble organic complexes are well known as carcinogens of living organisms and serious environmental pollutants: nickel can bind to the cell membrane and hinder the transport process through the cell wall. So, the development of new methods for Ni(II) determination is of continuing scientific interest and it is also very important for the better eco systems monitoring in future.

There are different published methods for Ni(II) determination. Atomic absorption spectrometry (AAS) methods, like flame (FAAS) [1-3], electrothermal (ET AAS) [4], high resolution continuum source graphite furnace (HR-CS GF AAS) with a previous extraction from the original matrix [5] are very interesting. Also, inductively coupled plasma (ICP) methods like ICP-MS [6,7] and ICP-OES [8,9] are in expansion. Various classes of organic reagents, especially hydrazones,

have been described as spectrophotometric reagents for Ni(II) determination [10-13]. After the cloud-point extraction and preconcentration procedure, the authors determined nickel as the complex with 2-amino-cyclopentene-1-dithiocarboxylic acid (ACDA), using Triton-X-114 as surfactant [10]. Saritha and Sreenivasulu Reddy formed the green complex of Ni(II) and 5-bromo-2-hydroxyl-3-methoxybenzaldehyde-4-hydroxy benzoic hydrazone with the absorption maximum at 440 nm [11], while other Indian authors built the nickel complex with pyridine 2,3 dicarboxylic acid [12].

Laser induced breakdown spectroscopy (LIBS) [14]; X-ray fluorescence techniques [15] and spectro-fluorimetric method [16] for nickel traces determination are also reported.

Nickel was determined in different samples like meteorites [14], soils [5,17,18,19], garnets [9], alloys [11], a dry skin membrane and larva slough of some animals which are used as medicines [8], in plants and vegetable oil [11], bean seed [1], food [2], canned tomato paste [4], biological materials, human serum, urine and hair [6,15], alcoholic beverages [7,5], drinking water [2,3,10,11,13], sea, rain, marine, fresh and ground water [2,14,20,21], synthetic samples [12], etc.

Experimental

Apparatus

Spectrophotometric measurements were performed on UV-VIS spectrophotometer Shimadzu UV- VIS 1650 PC (Shimadzu, Japan). ICP-OES measurements were

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performed on ICP-OES, model ICAP 65000 Duo (Thermo Scientific, UK). Cylindrical cells were thermostated at 20.00 ± 0.02 °C using thermo-circulating bath (Julabo MP-5A). pH measurements were performed using a Hach H260G pH-meter with a non-glass pH probe PH77SS (Hach, USA).

Reagents and Chemicals

Analytical grade reagents provided by Merck, Germany, unless indicated otherwise, and ultrapure water (18.2 M Ω) (water purification system Thermo Fisher Scientific Smart 2 Pure Standard) were utilized for the preparation of the solutions. Adequate polyethylene vessels were used for storage of the solutions. Borate buffer solutions were prepared by mixing the sodium tetraborate solution with HCl and NaOH solutions according to the rule, and their pH values were checked using a pH-meter. A stock Ni(II) solution ($1 \cdot 10^{-4}$ g cm $^{-3}$) was prepared by dissolving the exactly measured NiCl $_2 \cdot 6$ H $_2$ O in deionized water. The concentration of the stock solution was checked complexometrically. The alizarine solution (0.002 mol dm $^{-3}$) was prepared by dissolving the exactly measured substance in NaOH solution (0.1 mol dm $^{-3}$). This solution was stable for five days. All polyethylene containers and the glassware were washed with diluted hydrochloric acid (1:1), the solution of potassium hydroxide in ethanol and then repeatedly well rinsed by tap water, distilled and deionised water. All concentrations described here are the initial concentrations in the reaction mixture at time zero after mixing. Each kinetic result is the average of five determinations.

Procedure

In order to obtain good mechanical and thermal stability, the instruments were run for ten minutes before the first measurement. Selected volumes of reactants and deionized water were poured separately in the reaction mixture vessel with four compartments (Budarin vessel) up to a pre-determined total volume of 10 cm 3 . The solution of Ni(II) was measured into one leg of the Budarin vessel for catalytic reaction and the same volume of deionized water was measured for non-catalytic reaction. After thermo-stating for ten minutes, the reagents were mixed and simultaneously the stopwatch was turned on. The solution was immediately added to a properly rinsed spectrophotometer cell with a path length of 10 cm, and the absorbance was measured every 15 seconds, starting from the 45 th second of the reaction up to ten minutes of the reaction. Spectrophotometric measurements were performed at the wavelength of 460 nm, and at working temperature of 20 ± 0.02 °C.

The reaction was tested by examining the influence of each component of the reaction mixture upon the reaction rate of catalytic and non-catalytic reaction. The concentration of each component was changing consecutively, while the concentrations of other components, as well as the working temperature, were kept constant.

Results and discussion

While the reaction proceeds, the initial violet color of the solution fades and a pale yellow reaction product is formed. Neither the exact mechanism of the reaction nor the chemical nature of the products was of major interest in the investigation. Spectrophotometric measurements were performed at the wavelength of the absorption maximum of alizarine (460 nm) in borate buffer media (Figure 1). The logarithm of absorbance-time curves is linear during the first five to ten minutes of the reaction for different Ni(II) concentrations, so all kinetic results were treated by the integral variant of the tangent method [22]. The rate of the reaction was obtained using the slope of the kinetic curves of the absorbance - time plot.

Figure 1. Absorption spectra of alizarine in borate buffer. Initial conditions: AL $8.0 \cdot 10^{-5}$ mol dm $^{-3}$; 20 ± 0.02 °C; pH: 1- 10.6 ; 2- 9.1 ; 3- 8.5

Hence, the influence of the pH value of the selected borate buffer solutions on the rate of both the catalytic and non-catalytic reactions was examined in the pH interval of about 7.7 to about 9.0 (Figure 2). The value of 8.46 was selected as the most appropriate one, because it provides difference of the reaction rates of the catalytic and non-catalytic reactions and good reproducibility of absorbance measurements in the absorbance area of the least error for spectrophotometric measurements, for both reactions very well. The same principles were used for the selection of optimal conditions in all further investigations. The borate buffer pH 8.46 was used in subsequent examinations.

The rates of both the catalytic and non-catalytic reaction show the first order dependence on the buffer concentration (Figure 3) within the range of $5.2 \cdot 10^{-3}$ to $7.8 \cdot 10^{-3}$ mol dm $^{-3}$, and the concentration of $6.5 \cdot 10^{-3}$ mol dm $^{-3}$ was selected as the optimal concentration of the borate buffer for further measurements.

Figure 2. Dependence of the reaction rate on pH. Initial conditions: AL $8.0 \cdot 10^{-5}$ mol dm⁻³; BUF $5.85 \cdot 10^{-3}$ mol dm⁻³; H₂O₂ $0.2 \cdot 10^{-3}$ mol dm⁻³; Ni(II) $4.0 \mu\text{g cm}^{-3}$; 20 ± 0.02 °C. A-catalytic reaction, B-non-catalytic reaction.

Figure 3. Dependence of the reaction rate on the BUF concentration. Initial conditions: pH 8.46; AL $8.0 \cdot 10^{-5}$ mol dm⁻³; H₂O₂ $0.2 \cdot 10^{-3}$ mol dm⁻³; Ni(II) $4.0 \mu\text{g cm}^{-3}$; 20 ± 0.02 °C. A-catalytic reaction, B-non-catalytic reaction.

Figure 4. Dependence of the reaction rate on the AL concentration. Initial conditions: pH 8.46; BUF $6.5 \cdot 10^{-3}$ mol dm⁻³; H₂O₂ $0.2 \cdot 10^{-3}$ mol dm⁻³; Ni(II) $4.0 \mu\text{g cm}^{-3}$; 20 ± 0.02 °C. A-catalytic reaction, B-non-catalytic reaction.

The dependence of the rate of the catalytic and non-catalytic reactions on the reducing agent concentration was monitored within the concentration range of $4.0 \cdot 10^{-5}$ to $10.0 \cdot 10^{-5}$ mol dm⁻³ AL. Within this interval, both catalytic and non-catalytic reaction rates show a first order dependence of the AL concentration (Figure 4). The concentration of $8.0 \cdot 10^{-5}$ mol dm⁻³ AL was selected as optimal.

At last, the influence of the concentration of the oxidant was tested (Figure 5). Within the investigated concentration range of H₂O₂ of $0.2 \cdot 10^{-3}$ to $0.8 \cdot 10^{-3}$ mol dm⁻³, both catalytic and non-catalytic reaction rates show a first order dependence of the oxidant concentration. H₂O₂ concentration of $0.4 \cdot 10^{-3}$ mol dm⁻³ was selected as adequate for further work because it provides a good difference of the reaction rates of catalytic and non-catalytic reactions.

Hence, the optimal conditions were found to be: pH 8.46, cBUF = $6.5 \cdot 10^{-3}$ mol dm⁻³, cAL = $8.0 \cdot 10^{-5}$ mol dm⁻³, cH₂O₂ = $0.4 \cdot 10^{-3}$ mol dm⁻³.

Under the optimal conditions, the dependence of the catalytic reaction rate on the Ni(II) concentration was observed at three temperatures: 20 ± 0.02 , 23 ± 0.02 and 25 ± 0.02 °C. The linear dependence of calibration curves falls within the range of $7.0 \cdot 10^{-7}$ to $8.0 \cdot 10^{-6}$ g cm⁻³ Ni(II).

The adequate equations of calibration curves for 20 ± 0.02 °C (Eq. 1), 23 ± 0.02 °C (Eq. 2), and 25 ± 0.02 °C (Eq. 3), were calculated as follows:

$$\text{Slope} = (0.01027 \pm 0.00001) \cdot c + (0.01495 \pm 0.00017) \dots \dots \dots (1)$$

$$\text{Slope} = (0.01234 \pm 0.00003) \cdot c + (0.01811 \pm 0.00015) \dots \dots \dots (2)$$

$$\text{Slope} = (0.01325 \pm 0.00002) \cdot c + (0.02246 \pm 0.00011) \dots \dots \dots (3)$$

where: c is Ni(II) concentration in $\mu\text{g cm}^{-3}$.

The accuracy and precision of the method were checked for three different Ni(II) concentrations within the range of the calibration curve. Five repeated measurements were performed for each concentration. Satisfactory results were obtained. For Ni(II) concentrations of $5.0 \cdot 10^{-6}$ g cm⁻³, $6.0 \cdot 10^{-6}$ g cm⁻³ and $7.0 \cdot 10^{-6}$ g cm⁻³, RSD values were found to be 4.6%, 3.2%, and 2.7%, respectively.

The selectivity of the method was established by interference studies: selected ions were separately added in the reaction mixture. The tolerance limit was estimated as the concentration of the added ion that gives up to a 3% relative error in the determination of nickel. Cations were added as chlorides or nitrates and anions were added as sodium or potassium salts. Each ion was added in six known concentration ratios (0.01:1, 0.1:1, 1:1, 10:1, 100:1 and 1000:1) against the constant Ni(II) concentration of $1.0 \mu\text{g cm}^{-3}$. The measurements were performed at 20 ± 0.02 °C, and about 30 most frequently used cations and anions were tested (Na⁺, Ag⁺, Ca²⁺, Sr²⁺, Ba²⁺, Mg²⁺, Zn²⁺, Cu²⁺, Pb²⁺, Pd²⁺, Co²⁺, Hg²⁺, Sn²⁺, Bi³⁺, Fe³⁺, Al³⁺, As³⁺, Sb³⁺, Au³⁺, acetates, tartarates,

oxalates, molybdates, wolframates, Br⁻, I⁻, NO₃⁻, SO₄²⁻, CO₃²⁻, PO₄³⁻). The results presented in Table 1 reveal that proposed methods for nickel determination have a very good selectivity.

Table 1. Selected results of interference studies for nickel determination, initial conditions: pH 8.46; AL $8.0 \cdot 10^{-5}$ mol dm⁻³; BUF $6.5 \cdot 10^{-3}$ mol dm⁻³; H₂O₂ $0.4 \cdot 10^{-3}$ mol dm⁻³; Ni(II) 1.0 µg cm⁻³; 20±0.02 °C

Added ion	Ion ratio: Ni(II)	Nickel determination
Co(II)	1000	catalyzes
Pb(II)	1000	inhibits
Hg(II)	100	catalyzes

Only the presence of Co²⁺, in the ratio 1000:1, and Hg²⁺, in the ratio 100:1 against the nickel concentration, catalyzes the determination of nickel, while the presence of Pb²⁺, in the ratio 1000:1, inhibits the determination of nickel by the proposed method. The ions that interfere the determination of nickel can be easily removed by standard analytical methods like masking, precipitation, etc., depending of different samples nature.

By application of spectrophotometric technique, at the wavelength of 460 nm, a limit of quantification (LQ) of 119 ng cm⁻³ Ni(II) was reached, and the limit of detection (LD) of 31 ng cm⁻³ Ni(II) was obtained. LQ was defined as the ratio signal : noise = 10:1 and LD was defined as signal 3:1 against the blank.

The method was successfully applied to Ni(II) determination in fresh water samples. The samples were analyzed by application of both, the presented spectrophotometric kinetic method and ICP-OES method. As presented in Table 2, there is a good agreement of the results.

Table 2. Ni(II) determination in fresh water samples, initial conditions: pH 8.46; AL $8.0 \cdot 10^{-5}$ mol dm⁻³; BUF $6.5 \cdot 10^{-3}$ mol dm⁻³; H₂O₂ $0.4 \cdot 10^{-3}$ mol dm⁻³; 20±0.02 °C

Sample	Spectrophotometric-kinetic determination ^a µg cm ⁻³	Recovery %	Determination by ICP-OES ^a µg cm ⁻³	Recovery %
1	3.84±0.04	95.1	3.99±0.02	99.8
2	3.97±0.06	96.4	4.12±0.02	99.6
3	5.85±0.03	97.3	5.98±0.02	99.8
4	5.97±0.02	97.7	6.25±0.02	99.7

^aThe mean value of five measurements ± 2SD

Conclusions

The proposed spectrophotometric kinetic method for the determination of Ni(II) shows a very good selectivity and provides a rapid and easy performance at room temperature (20 °C) by using available equipment and cheap chemical substances. The obtained results are precise and reproducible. The RSD value was found to be in the range 2.7 - 4.6% for the investigated concentration range of Ni(II).

On the grounds of the obtained results, the new spectrophotometric kinetic method is recommendable for the

determination of Ni(II) in fresh water samples and potentially also in other samples from the industrial processes and the environment. The results suggest that it could also be a good basis for further investigations of spectrophotometric kinetic methods for the heavy metals trace analysis.

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Izvod

PRIMENA REAKCIONOG SISTEMA ALIZARIN- H_2O_2 U BORATNOM PUFERU ZA SPEKTROFOTOMETRIJSKO KINETIČKO ODREĐIVANJE NIKLA

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Predložena spektrofotometrijska kinetička metoda za određivanje Ni(II) pokazuje vrlo dobru selektivnost i lako se i brzo izvodi na sobnoj temperaturi (20 °C). Uz korišćenje dostupne opreme i jeftinih supstanci, postižu se precizni i reproduktivni rezultati. Spektrofotometrijskim merenjem, na talasnoj dužini od 460 nm, postignuta je granica kvantifikacije (LQ) od 119 ng cm⁻³ Ni(II), kao i granica detekcije (LD) od 31 ng cm⁻³ Ni(II). LQ je definisana kao odnos signal : šum = 10:1 and LD kao signal 3 : 1 u odnosu na slepu probu. RSD vrednosti se nalaze u rasponu od 2,7 – 4,6% za ispitivanu oblast koncentracija Ni(II). Na osnovu dobijenih rezultata se može zaključiti, da je nova kinetička spektrofotometrijska metoda pogodna za određivanje Ni(II) u prirodnim vodama, a potencijalno i u drugim uzorcima iz proizvodnih procesa i životne sredine. Takođe, rezultati ispitivanja ukazuju na to da ona može da bude dobra osnova za dalja istraživanja u oblasti razvoja novih spektrofotometrijskih kinetičkih metoda za analizu teških metala.

Ključne reči: određivanje Ni(II), katalizator, spektrofotometrijska kinetička metoda