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Method for Determination of Trace Nickel(II) with Ethylhexyl Benzoxazole Sulphide

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Synthesis and application of ethylhexyl benzoxazole sulphide (EHBS), as a new chromogenic reagent for the determination of nickel has been described. Highly sensitive, selective and fast method for determination of nickel based on its rapid reaction with ethylhexyl benzoxazole sulphide and the solid phase extraction of the coloured complex on a nonpolar resin DIAION HP20 has been developed. In the presence of pH 4.7 acetic acid-sodium acetate buffer solution and sodium dodecyl sulfate (SDS) medium, ethylhexyl benzoxazole sulphide reacted with nickel to form coloured complex of nickel-to-EHBS molar ratio of 1:2. The complex was enriched by the solid phase extraction with the DIAION HP20 cartridge. The complex was eluted from the cartridge with dimethyl formamide (DMF) and enrichment factor of 100 was achieved. In DMF medium, molar absorptivity of the complex was 1.03×10^5 L mol^{-1} cm^{-1} at 600 nm. Beer's law was obeyed in the concentration range 0.01-0.7 μg mL^{-1}. The relative standard deviation for eleven replicate samples at the 0.6 μg L^{-1} level was 2.8 %. In the original sample detection limit was 0.08 μg L^{-1}. This method was applied to the determination of trace nickel in water samples with good result.

Key Words: Ethylhexyl benzoxazole sulphide, Nickel, Solid phase extraction, Spectrophotometry.

INTRODUCTION

Nickel is a moderately toxic element as compared with other transition metals. However, it is known that inhalation of nickel and its compounds can lead to serious health problems, including respiratory system and cancer. Moreover, nickel can cause a skin disorder known as nickel-eczema[1]. Several sophisticated techniques, such as inductively coupled plasma atomic emission spectrometry (ICP-AES), inductively coupled plasma mass spectrometry (ICP-MS), atomic absorption spectrometry, *etc*., have been applied widely to the determination of nickel[2-10]. The spectrophotometric method still has the advantages in respect to simplicity and low operating costs. For this reason, a wide variety of spectrophotometric methods for the determination of nickel have been reported; each chromogenic system has its advantages and disadvantages with respect to sensitivity, selectivity and rapidity. There is a vast range of reagents which can be used, including 5-(6-methoxy-2-benzothiazoleazo)-8-aminoquinoline[11], 2-[2-(6-methylbenzothiazolyl)azo]-5-(Nethyl-N-carboxylmethyl)aminobenzoic acid[12], *p*-acetylarsenazo[13], sulfonated-1-(2-pyridylazo)-2-naphthols[14], calixarene[15], *etc*. However, the routine spectrophotometric methods are often not sensitive enough to determine low concentrations of nickel ions in water samples at a μg L^{-1} levels. For the determination of low concentrations of nickel ions, a pre-concentration step is usually required.

In this paper, the colour reaction of ethylhexyl benzoxazole sulphide (EHBS) with nickel and the solid phase extraction of Ni(II)-EHBS complex on the DIAION HP20 cartridge has been described. Based on this, a highly sensitive, selective and rapid method for the determination of nickel in water samples has been developed.

EXPERIMENTAL

All reagents were of the highest available purity (at least of analytical grade). All the solutions were prepared with ultra-pure water obtained from a UPHW-1-90 reagent water system (Ulupure corporation, China). A 3.0×10^{-3} mol L^{-1} EHBS solution was prepared by dissolving EHBS with 95 % ethanol. A stock standard solution of nickel (1.0 mg mL^{-1}) was obtained from the Chinese Standard Material Center and a work solution of 0.2 μg mL^{-1} was prepared by diluting the stock standard solution. Sodium dodecyl sulfate (SDS) solution, 3 % (w/v) in water, was used. Acetic acid-sodium acetate buffer solution (pH 4.7) was prepared as usual.

Synthesis of ethylhexyl benzoxazole sulphide (EHBS): EHBS was synthesized according to the following procedure: 2-mercaptobenzoxazole (30.2 g, 0.2 mol), ethanol (160 mL) and NaOH (8.0 g, 0.2 mol) were put in a round-bottom fitted with a mechanical stirrer and condenser and the mixture was heated for about 10 min 2-ethylhexyl bromide (38.6 g, 0.2 mol) was then added gradually with stirring through a dropping funnel and the reaction mixture was refluxed for 4 h. The residual solid was filtered after cooling down and the ethanol was removed by distillation. The organic phase was diluted with ether (50 mL), washed with water two times and dried with anhydrous Na_2SO_4. The ether was evaporated and ethylhexyl benzoxazole sulphide was obtained. Its structure (Fig. 1) was verified by elemental analysis, ^1H and ^{13}C NMR. The results of elemental analysis are: $C_{15}H_{21}NOS$, calcd. (found.) (%), C 68.39 (68.56), H 8.04 (7.91), N 5.32 (5.46); ^1H NMR (300 MHz, $CDCl_3$) δ 7.61 (d, $J = 7.4$ Hz, 1H), 7.43 (d, $J = 8.0$ Hz, 1H), 7.30-7.20 (m, 2H), 3.41-3.34 (m, 2H), 1.79-1.73 (m, 1H), 1.55-1.34 (m, 8H), 0.99-0.88 (m, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.60, 151.82, 142.07, 124.16, 123.66, 118.31, 109.73, 39.02, 36.53, 32.34, 28.72, 25.63, 22.90, 14.05, 10.80 ppm.

A UV-2550 spectrophotometer (Shimadzu, Japan) equipped with 10 mm microcell (0.5 mL) was used for all absorbance measurements. pH was measured using a PHS-3C precision pH meter (REX Instrument Factory, Shanghai, China).

DIAION HP20 was purchased from Mitsubishi Chemical Corporation (Tokyo, Japan). DIAION HP20 resin is an aromatic type adsorbent. It is based on crosslinked polystyrenic matrix. Its surface area is 600 m^2 g^{-1}. DIAION HP20 is widely used in different industrial fields[16]. It was washed successively with methanol, water, 1 mol L^{-1} HNO_3 in acetone, water, 1 mol L^{-1} NaOH and water, sequentially.

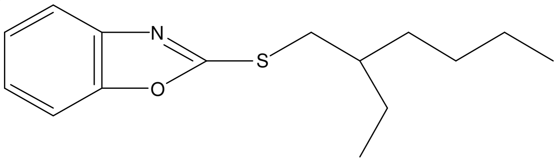

Fig. 1. Structure of ethylhexyl benzoxazole sulfide (EHBS)

General procedure: To either standard or sample solution containing no more than 0.7 μg of Ni(II) in a 100 mL calibrated flask, 7.0 mL of acetic acid-sodium acetate buffer solution, 5 mL 3×10^{-3} mol L^{-1} EHBS solution and 5 mL 3 % SDS solution were added. The mixture was diluted to the mark and mixed well. After 4 min the solution was passed through the DIAION HP20 cartridge at the flow rate of 10 mL min^{-1}. After the enrichment step was completed, the retained complex was eluted from the cartridge with 1 mL of DMF at the flow rate of 1 mL min^{-1} in reverse direction. The volume of the eluent was adjusted to 1 mL in a 1 mL calibrated flask by adding microamount of DMF with a 200 μL syringes. Absorbance of this solution was measured at 600 nm in a 10 mm microcell (0.5 mL) against the reagent blank prepared in a similar way without nickel.

Sample preparation: For biological samples, 0.20 g of the sample (GBW09101) was weighted accurately into the 60 mL Teflon high-pressure microwave acid-digestion bomb to which, 4 mL of concentrated nitric acid and 1 mL of 30 % hydrogen peroxide was added. The bombs were sealed tightly and then positioned in the carousel of the microwave oven (WX-4000, 1000W, Preekem Scientific Instruments corporation, Shanghai, China). The system was operated at full power for 6 min. The digested material was evaporated to incipient dryness. Then, 20 mL of 6 mol L^{-1} HCl was added to the beaker and the mixture was heated to dryness. This last step was repeated twice to ensure total elimination of HNO_3. The residue was diluted with 0.1 mol L^{-1} HCl solutions. Afterwards, sample solution was cooled and filtered using the filter paper. The filtrate was collected into a 50 mL of calibrated flask quantitatively and the nickel contents were analyzed according to the general procedure.

For water samples, river water sample was collected from Yangzong river (Yuxi, P.R. China). Lake water sample was collected from Yangzong hai lake (Yuxi, P.R. China), Tap water sample was freshly collected from our laboratory. All water samples were immediately acidified by adding several drops of nitric acid and filtrated with 0.45 μm filter. Then the preconcentration procedure given above was applied to the samples.

RESULTS AND DISCUSSION

Absorption spectra: Absorption spectra of EHBS and Ni(II)-EHBS complex were recorded. Maximum absorbance of EHBS and Ni(II)-EHBS complex were measured at 450 and 600 nm, respectively. The wavelength of 600 nm was chosen for further quantitative analysis (Fig. 2).

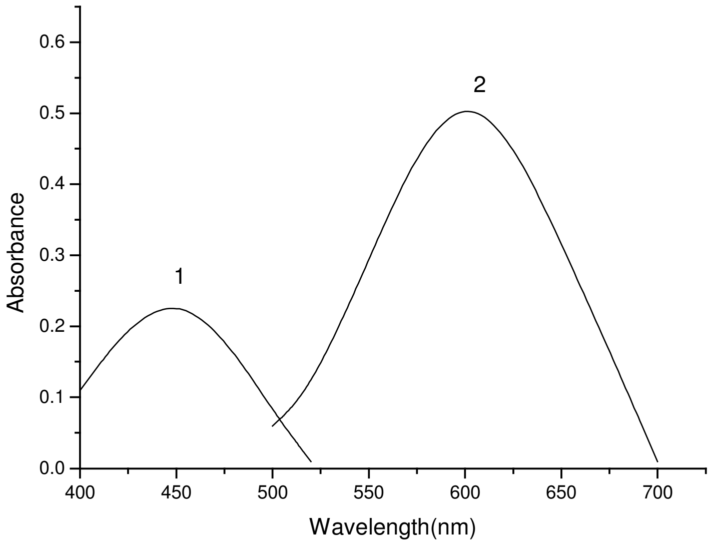

Fig. 2. Absorption spectra of EHBS and Ni(II)-EHBS: (1) EHBS-SDS blank against water; (2) EHBS-SDS-Ni(II) complex against reagent blank. The concentration of Ni^{2+} is 5.11×10^{-6} mol L^{-1}

Effect of acidity: The experiments showed that the optimal reaction pH values for nickel with EHBS is in the ranges 3.6-5.6. Acetic acid-sodium acetate buffer solution of pH 4.7 was recommended to control pH. As the use of 6.0-8.0 mL of the buffer solution (pH 4.7)/100 mL of final solution gives maximum and constant absorbance. Therefore, 7 mL of the buffer was chosen.

Effect of surfactants: The effects of various surfactants were studied. In the presence of anionic or nonionic surfactants, the absorption of the Ni(II)-EHBS chromogenic system increases markedly. The order of increase in absorbance is sodium dodecyl sulfate (SDS) > sodium dodecyl benzenesulfonate (SDBS) > polyoxyethylene nonylphenol ether (emulsifier-OP) > Tween-20 > Tween-80 > Triton X-100, whereas in the absence of surfactants, each of the chromogenic systems gives low absorption. When cationic surfactants such as cetyltrimethylammonium bromide (CTAB) and cetylpyridinium chloride (CPC) were added, the system gave about the same absorption as obtained without adding any surfactants. Thus, cationic surfactants have no sensitivity on Ni(II)-EHBS complex. Therefore, SDS is the most appropriate surfactant. For the systems, the increase in absorbance is constant when 4-6 mL of 3 % SDS is added. Use of 5 mL is recommend.

Effect of EHBS concentration: For up to 0.7 μg of Ni(II), the use of about 3-7 mL of a 3×10^{-3} mol L^{-1} EHBS solution was found to be sufficient for complete reaction. Accordingly, 5 mL EHBS solution was added in all further measurement.

Solid phase extraction: It has been shown that EHBS forms stable complex with Ni(II) in the weakly acidic medium. To meet the requirement of metal complex enrichment by solid phase extraction in the weakly acidic medium, the DIAION

HP20 cartridge was used. The flow rate was set to 10 mL min^{-1} during enrichment and to 1 mL min^{-1} during elution. It has been found experimentally that EHBS and its Ni(II) complex are quantitatively retained on the cartridge in the weakly acidic medium.

0.1 g of the DIAION HP20 sorbent was placed in the conical flasks (one cartridge of the DIAION HP20 contained 1 g of the sorbent). Stock solution of Ni(II), SDS and EHBS were added to the flask. Acidity of the solution was adjusted to pH 4.7 using acetic acid-sodium acetate buffer solution. The solutions were mixed thoroughly in a mechanical shaker. Concentration of Ni(II) was measured by GFAAS as soon as the equilibrium was reached. The maximum adsorption capacity of the DIAION HP20 cartridge was 8.52×10^{-4} mol g^{-1} for Ni(II).

Since the maximum amount of Ni(II) in the performed experiments was only 1.19×10^{-8} mol, the cartridge (1 g) had more than enough capacity to enrich the Ni(II)-EHBS complex.

In order to choose an appropriate eluent for the retained Ni(II)-EHBS complex, after extraction of 1.19×10^{-8} mol of nickel from the solution, nickel ions were eluted with different eluting agents, such as dimethyl formamide (DMF), ethanol, methanol, acetonitrile, isopentyl alcohol and acetone. Their elution efficiency decreased in the following sequence: DMF > ethanol > methanol > isopentyl alcohol > acetone > acetonitrile. Finally, DMF was selected as the appropriate eluent. Quantitative recovery (> 98 %) was obtained using 1 mL of DMF at the flow rate of 1 mL min^{-1}. In the subsequent experiments, 1 mL of DMF was used as the eluent to desorb the Ni(II)-EHBS complex.

Stability of the chromogenic system: After mixing the components, the absorbance reaches its maximum within 4 min at room temperature and remains stable for 8 h in aqueous solution. After having been extracted into DMF, the complex was stable for at least 10 h.

Calibration curve and sensitivity: The calibration curve show that Beer's law is obeyed in the concentration range of 0.01-0.7 μg Ni(II)/mL in the measured solution. The linear regression equation obtained was: $A = 1.75C$ (μg mL^{-1}) + 0.0102 ($r = 0.9991$). The molar absorptivity was calculated to be 1.03×10^{5} L mol^{-1} cm^{-1} at 600 nm. The detection limit, based on 3 times the relative standard deviation of the blank, was 0.08 μg L^{-1} in the original sample. The relative standard deviation at the concentration level of 0.6 μg L^{-1} of Ni(II) (11 repeats) was 2.8 %.

Composition of the complex: The composition of the complex was determined by the continuous variation and the molar ratio method. Both showed that the molar ratio of Ni(II) to EHBS is 1:2.

Interference: The selectivity of the proposed method is shown in Table-1 for the determination of 0.3 μg/100 mL of Ni(II) in the presence of various ions with a relative error of ± 5 %. It is evident that most common ions do not interfere with the determination. This method has high selectivity.

TABLE-1
TOLERANCE LIMITS FOR THE DETERMINATION OF
0.3 μg of Ni(II) WITH EHBS (RELATIVE ERROR ± 5 %)

Ion added	Tolerate (mg)
F^-, K^+, Ca^{2+}	12.00
Na^+, ClO_3^-, Br^-	9.00
SO_4^{2-}, IO_3^-, I^-, NO_3^-	7.00
Al^{3+}, SO_3^{2-}	4.00
Ba^{2+}, BrO_3^-, $S_2O_3^{2-}$	3.00
Rh^{3+}, Ir^{3+}	0.80
Pt^{4+}	0.50
Mg^{2+}, Ag^+	0.40
Pd^{2+}, Fe^{3+}	0.10
Cu^{2+}, Zn^{2+}, Co^{2+}	0.04

Applications of the presented procedure: In order to establish the validity of the proposed procedure, the method has been applied to the determination of nickel in standard reference materials (GBW09101). The results are given in Table-2.

TABLE-2
DETERMINATION OF Ni (μg g^{-1}) IN THE CERTIFIED REFERENCE MATERIAL
AFTER APPLICATION OF THE PRESENTED PROCEDURE (n = 5)

Sample	Certified value (μg g^{-1})	Our value (μg g^{-1})
GBW09101	3.71 ± 0.4	3.80 ± 0.5

The proposed method is applied to determine of nickel in water samples. The results for water samples are given in Table-3. The results indicate that the recoveries in the range of 93-107 % are reasonable well for trace analysis.

TABLE-3
DETERMINATION OF Ni (μg L^{-1}) IN WATER SAMPLES (n = 5)

Samples	GFAAS (μg L^{-1})	Found (μg L^{-1})	RSD (%)	Recovery (%) (Add 2 μg L^{-1} Ni)
River water	2.5	2.6	3.8	93-99
Lake water	3.9	3.8	2.6	99-107
Tap water	1.8	1.7	5.8	100-106

Conclusion

EHBS is a sensitive and selective spectrophotometric reagent for determination nickel. Molar absorptivity of the complex reaches 1.03×10^5 L mol^{-1} cm^{-1}. Ni(II)-EHBS complex in 100 mL solution can be concentrated up to 1 mL, representing enrichment factor of 100, when solid phase extraction on DIAION HP20 cartridge is applied. Detection limit reaches 0.08 μg L^{-1} in original samples and nickel in water samples can be determined directly. Most foreign ions do not interfere during determination. The method is a simple, sensitive, precise, reliable and accurate technique. Therefore, proposed method can be applied to routine analysis.

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