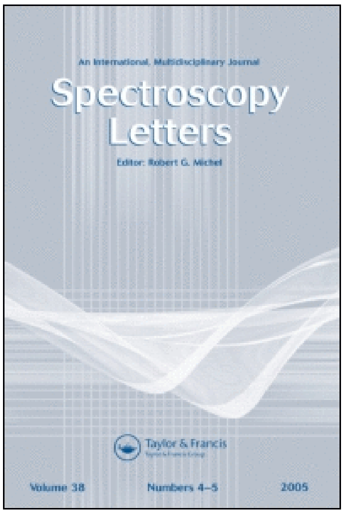

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A New Spectrophotometric Method with Di-2-Pyridyl Ketone Benzoylhydrazone for Determination of Nickel(II)

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A NEW SPECTROPHOTOMETRIC METHOD WITH DI-2-PYRIDYL KETONE BENZOYLHYDRAZONE FOR DETERMINATION OF NICKEL(II)

KEY WORDS: Nickel(II), Di-2-Pyridyl Ketone Benzoylhydrazone, Spectrophotopmetric Determination

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ABSTRACT

Nitrogen-containing heterocyclic hydrazones have been used as analytical reagents, mainly to metallic ion spectrophotometric determinations in natural water samples. Using the reagent di-2-pyridil ketone benzoilhydrazone (DPKBH) we

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(*) To whom correspondence should be addressed. e-mail: maevsiha@usp.br have developed a spectrophotometric method for the determination of Ni(II) in samples of several sources. DPKBH was used in excess in order to coordinate Ni(II) and the highest sensitivity was obtained in 50% v/v ethanol solutions when ammonium acetate buffer was added to maintain pH≅6.

Analysis for Ni(II) in natural water is frequently performed by EAAS following preconcentration involving solvent extraction. While these methods are sensitive, they also require relatively expensive instrumentation and are generally time-consuming. In contrast, the advantages of the proposed method are the use of simple instrumentation and the possibility of its application in the field. The method is fast, shows high sensitivity, good precision and several samples can be prepared and measured until 10 hours later .

The best order for the addition of reagents, stability of the complex, effect of the reagents excess and foreign ions besides composition of the complex are here reported. A linear behavior was observed between absorbance and nickel concentration. The favorable range is 8.50×10^{-7} to 1.72×10^{-5} mol.L^{-1}. The correlation coefficient is 0.997. The intercept of the linear curve is 3.55×10^{-3} and the slope is 4.00×10^{4} cm^{-1}.mol^{-1}.L. The standard error of the intercept and slope is 3.73×10^{-3} and 4.48×10^{-4}, respectively.

INTRODUCTION

The knowledge of heavy element content in waters is an important factor because water is an important source of minerals or many diseases are caused by an unbalance in the supply of mineral needs of both man and animals. Although nickel has been considered an essential element for animal nutrition[1], it also belongs to the very toxic metal group[2]. Therefore this metal needs comprehensive ecochemical and ecotoxicological investigations on its fate and behaviour in ecosystems of the terrestrial and aquatic environment. However, very little information is available on nickel distribution and speciation in water because its determination is difficult due to the very low concentrations. More reliable analytical procedures for the determination of trace amounts of nickel are therefore required.

Nickel is an ubiquitous trace metal and occurs in the soil, water, air, and in the biosphere. It is the fifth most abundant element by weight after iron, oxygen, magnesium, and silicon, and the 24th most abundant element in the earth's crust[3]. The average content in the earth's crust is about 0.008%[4].

The primary sources of nickel emissions into the ambient air are the combustion of coal for heat or power generation, the incineration of waste and sewage slude, nickel mining and primary production, steel manufacture, electroplating, and miscellaneous sources, such as cement manufacturing.

Nickel is introduced into the aquatic by removal from the atmosphere, by surface run-off, by discharge of industrial and municipal waste, and natural erosion of soils and rocks. Nickel occurs in aquatic systems as soluble salts adsorbed on clay particles or organic matter, or associated with organic particles, such as humic and fulvic acids and proteins. In natural waters, over a pH range of 5-9 , the hydrated divalent ion Ni(II) as $[Ni(H_2O)_6{}^{2+}]$ is the dominant form. In that pH range, nickel may also be adsorved on iron and manganese oxides, or form complexes with inorganic ligands (OH^-, SO_4^{2-}, Cl^- or NH_3)[5]. Most nickel compounds are relatively soluble at pH values < 6.5, whereas nickel exists predominantly as insoluble nickel hydroxides at pH values > 6.7.

Acid rain has a pronounced tendency to mobilize nickel from soil and increase nickel concentrations in ground water, leading eventually to increased uptake and potential toxicity for microorganisms, plants, and animals[3]. In the organism from the environment the nickel toxicity varies considerably according to species and abiotic factors[5].

Nickel from various industrial processes and other sources reaches waste - water. Residues from waste-water treatment are disposed of by deep well injection, ocean dumping, land treatment, and incineration. Industrial and municipal waste and atmospheric fallout contribute with 0.37×10^7 Kg/year and 2.5×10^7 Kg/year, respectively[5].

A new method is here described for spectrophotometric determination of Ni(II) using excess of di-2-pyridyl ketone benzoylhydrazone (DPKBH) as a colorimetric chelating agent without preconcentration. The DPKBH is a sensitive reagent for the spectrophotometric determination of trace amounts of many transition metal ions[6] and has been used for the spectrophotometric determination of iron(II)[7], iron(II) and iron(III)[8], cobalt(II)[9] and palladium(II)[10]. In a previous study[11], the concentrations of Fe(II) and Fe(III) were successfully and simultaneously determined by spectrophotometric technique in cloudwater samples employing di-2-pyridyl ketone benzoylhydrazone as a dual chelating agent.

Having in mind to develope an analytical method to determine Ni(II) in natural waters, a spectrophotometric study was carried out. This paper reports a detailed study to optimize the analytical parameters for a sensible determination of nickel.

EXPERIMENTAL

Reagents and solutions

All reagents and solvents were of analytical-reagent grade. The synthesis of DPKBH (Fig. 1) was performed according to the procedure outlined by Garcia-Vargas et al.[6]. Equimolar amounts of di-2-pyridyl ketone and benzoylhydrazide were mixed in ethanol, and a few drops of concentrated hydrochloric acid were added. The mixture was refluxed for 1h, and after cooling, distilled water was added to a 1+3 volume ratio (volume of ethanol to volume of water). Several drops of sodium hydroxide solution were added to the refluxed solution to increase the pH $\cong$ 5. The resulting precipitate was collected on a Büchner funnel and recrystallized twice from an ethanol-water solution. After synthesis, the melting point of the product (136 - 138°C) and the absorption spectrum of its complex with Ni(II) were checked. Solutions of DPKBH were prepared by dissolving the reagent in ethanol. Ni(II) sulphate hexahydrated salt was dissolved in water. The solution (1.00×10^{-2} mol.L^{-1}) was acidified with perchloric acid (pH$\cong$1) and standardized by EDTA titration[12].

A 25% m/v (g per 100 mL) ammonium acetate solution was added in order to increase the pH of the measured solutions to $\cong$ 6.

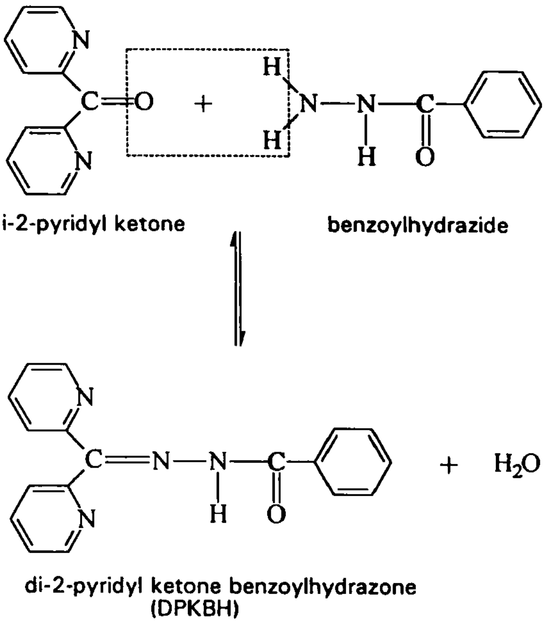

FIG. 1 - Reaction involved in the synthesis of DPKBH and its structure.

Apparatus

All spectrophotometric measurements were carried out on a Hewlett-Packard (HP) diode-array spectrophotometer 8452 A using 1.00 cm quartz cells. The pH measurements were carried out with a metrohm 654 pH meter and a combination glass electrode (Ag/AgCl as reference electrode).

RESULTS AND DISCUSSION

Absorption Espectra

Some absorption espectra were obtained in order to verify the behavior of all reagents such as ethanol, ammonium acetate, DPKBH and Ni(II)/DPKBH complexes. Solutions containing Ni(II) 7.64×10^{-6} mol.L^{-1} and DPKBH 1.66×10^{-3} mol.L^{-1} were prepared in ethanol 50% v/v and NH_4Ac solution. The maximum absorbance of the Ni(II)-DPKBH complexes was found at 390 nm as shown in Fig. 2. Ethanol and ammonium acetate do not absorb in this wavelength.

Reagent addition order

The order used to mix all of the reagents has often a marked effect on the colour reaction and on the rate of the colour development[13]. Several studies were made in ethanol-water solution (50% v/v) in order to investigate the stability of the system Ni(II)/DPKBH as a function of the time using different orders of reagent addition. Fig. 3 shows the behavior of the system Ni(II)/DPKBH for the best four orders of reagent addition at a period of two hours. According to the obtained results the following order was adopted as the most favorable: Ni(II), ethanol, DPKBH and NH_4Ac. The reason for this choice was the better stabilization as a function of the time.

Stability of the complex

The stability of the Ni(II)/DPKBH complexes was determined by preparing a 1.06×10^{-5} mol.L^{-1} Ni(II) solution in presence of excess of DPKBH (1.40×10^{-3} mol.L^{-1}). The absorbance was measured as a function of time at 390 nm. Table 1 shows that a stable colour of the Ni(II)/DPKBH complex was attained within 15 minutes after the addition of DPKBH reagent, and the intensity remained constant for at least 10 hours. During the first 8 hours the measured values presented a difference not higher than 0.5%. After this period a increase of

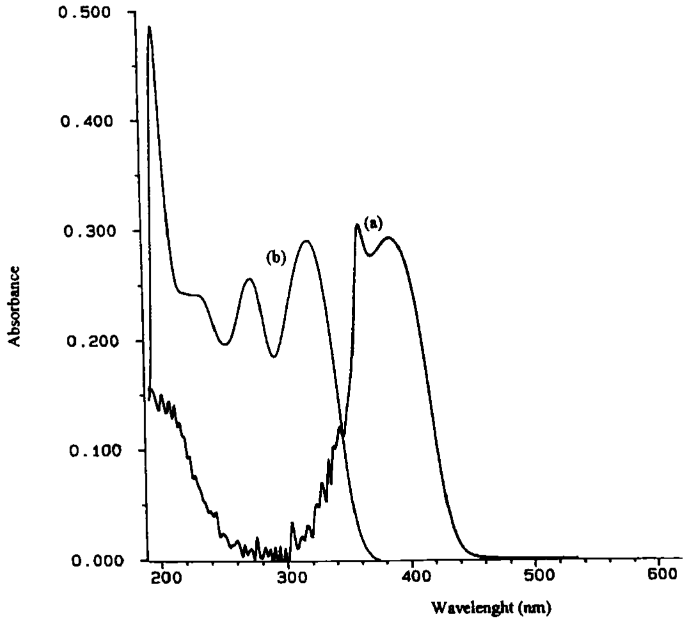

FIG. 2 - Absorption spectra in ethanol (50% v/v) and pH ≅ 6.
(a) Ni(II) = 7.64x10^{-6} mol.L^{-1} and DPKBH = 1.66x10^{-3} mol.L^{-1}.
(b) DPKBH = 1.00x10^{-5} mol.L^{-1}. Pathlength = 1cm.

1% in values of absorbance was observed. This permits to conclude that in absence of sided reactions which can make modifications in natural samples, several samples may be prepared and later measured into a 10 hour period.

Effect of excess of reagent

The absorbance of Ni(II) complexes exhibit dependence on the reagent concentration. The effect of the DPKBH excess was studied at 390 nm and pH ≅ 6 in the presence of 50% v/v ethanol. It was observed that keeping the Ni(II) concentration constant at 1.53x10^{-5} mol.L^{-1} the absorbance increased when the

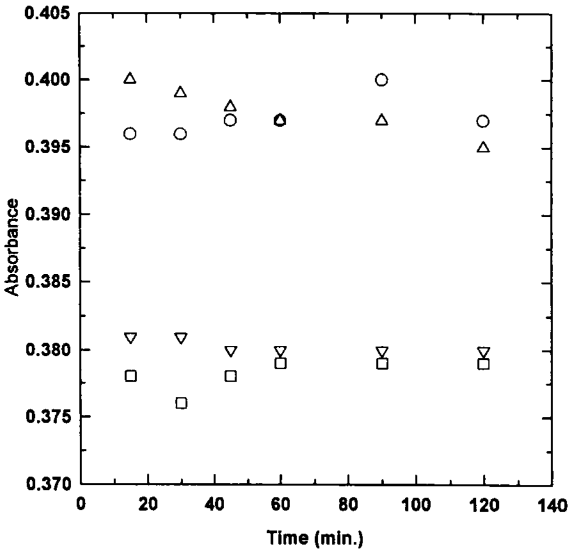

FIG. 3 - Absorbance (390 nm) *vs* time to several orders of addition of the reagents:
O Ni(II), Ethanol , NH_4Ac and DPKBH
∇ Ni(II), Ethanol, DPKBH and NH_4Ac
□ Ethanol, Ni(II), DPKBH and NH_4Ac
Δ Ethanol, Ni(II), NH_4Ac and DPKBH
Ni(II) = 1.06×10^{-5} mol.L^{-1}, DPKBH = 1.40×10^{-3} mol.L^{-1}.
Ethanol 50% v/v. pH $\cong$ 6. Pathlength = 1cm.

ratio Ni(II):DPKBH was varied up to a 1:5. Beyond this ratio any further increasing in the DPKBH concentration did not affect the absorbance (Fig. 4).

Analytical Curve

Spectrophotometric measurements were made with several solutions prepared according to the procedure: 5 mL of Ni(II) solution (pH $\cong$ 1); 4.2 mL of ethanol; 0.8 mL of DPKBH 2.09×10^{-2} mol.L^{-1} and 0.1 mL of a 25% m/v (g per 100mL)

TABLE 1
Absorbance as a Function of the Time. Each Absorbance is a Four Read Value Average.
Ni(II) = 1.06 x10^{-5} mol.L^{-1} and DPKBH = 1.40x10^{-3} mol.L^{-1}.
pH ≅ 6. λ= 390 nm. Pathlength of 1-cm.

Time (minutes)	Absorbance	Time (minutes)	Absorbance
15	0.381	240	0.379
30	0.381	300	0.380
45	0.380	360	0.380
60	0.380	420	0.380
90	0.380	480	0.380
120	0.380	540	0.385
180	0.378	600	0.385

solution of ammonium acetate were mixed. The absorbances were measured at 390 nm and a linear relationship was obtained between the absorbance and the concentration of Ni(II) within the range 8.50x10^{-7} - 1.72x10^{-5} mol.L^{-1}. The intercept of the linear curve is 3.55x10^{-3} and the slope is 4.00x10^{4} cm^{-1}.mol^{-1}.L. The standard error of the intercept and slope is 3.73x10^{-3} and 4.48x10^{-4}, respectively. The correlation coefficient is 0.997.

Effect of foreign ions

In the study of interfering ions, several cations in the form of chlorides, nitrates or sulfates and anions as potassium or sodium salts were added separately and the effects of each one on the control absorbance were observed at 390 nm. The Ni(II) concentration was fixed at 1.53x10^{-5} mol.L^{-1}. The results obtained are presented in

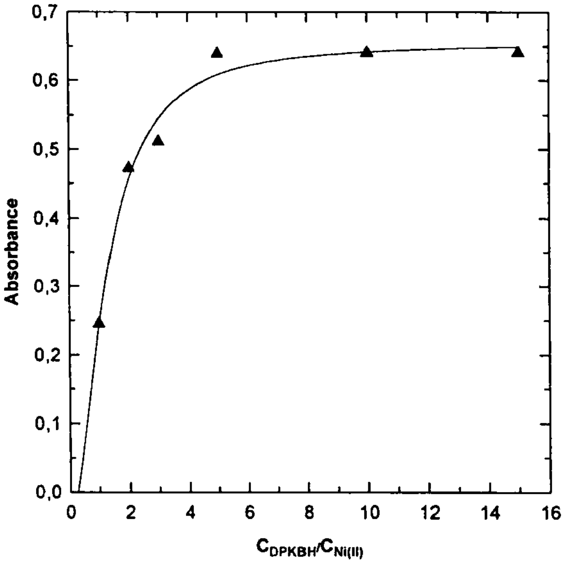

FIG. 4 - Absorbance (390 nm) of Ni(II)/DPKBH system as a function of the DPKBH/Ni(II) molar ratio. Ni(II) = 1.53×10^{-5} mol.L^{-1}. Ethanol 50%v/v. pH ≅ 6 (ammonium acetate). Pathlength = 1cm.

Table 2. A difference of ± 2% in the absorbance was considered acceptable. Among 30 available ions tested, only Fe(II), Fe(III), Zn(II) and Cu(II) interfere seriously and should be absent. Other ions could interfere because they probably react with DPKBH forming strongly colored complexes. These ions include Cd(II), Co(II) and Hg(II). However, the concentrations of these metals in most water systems are several orders of magnitude lower than Ni(II) and thus are unlikely to cause interferences[14]. On the other hand, a 10.000 time weight excess of other metal ions and common anions did not show any interference.

TABLE 2

Effect of Foreign Ions on Determination of 1.53×10^{-5} mol.L^{-1} of Ni(II).

Tolerance limit Ion/Ni(II)	Ions
> 10.000	Na^+, Cl^-, K^+, NO_3^-, Mg^{2+}, SO_4^{2-}, Ba^{2+}, Ca^{2+}, HCO_3^-, Br^-, I^-, SCN^- e HCHO
> 1000	CO_3^{2-}(a), HPO_4^{2-}(a), SO_3^{2-}(a), F^-(a) e AsO_2^-
> 100	Al^{3+} e NO_2^-
> 10	$C_2O_4^{2-}$, Mn^{2+} e Cr^{3+}
> 1	Cu^{2+}, Zn^{2+}, Co^{2+}, Fe^{2+}, Fe^{3+}(b), Hg^{2+} e Cd^{2+}

(a) - Formation of precipitate has been observed for a ratio > 10000 .

(b) - in presence of excess fluoride, the interference of Fe(III) at concentrations up to 100 times larger than Ni(II) was eliminated.

Composition of the complex

Job's method[15] of continuous variations was used to evaluate the stoichiometric ratio of metal to ligand in the complex. The results showed a 1:2 ratio of Ni(II) to DPKBH (Fig. 5), suggesting that DPKBH may act as a tridentate ligand coordinating to metal ions probably through two nitrogen and one oxygen atoms, resulting an uncharged complex.

CONCLUSIONS

Nickel has not been considered as a broad scale global contaminant; however, ecological changes, such as decreases in the number and diversity of species, have been observed near nickel-emitting sources. Microecosystem studies have shown that addition of nickel to soil disturbs the nitrogen cycle[5].

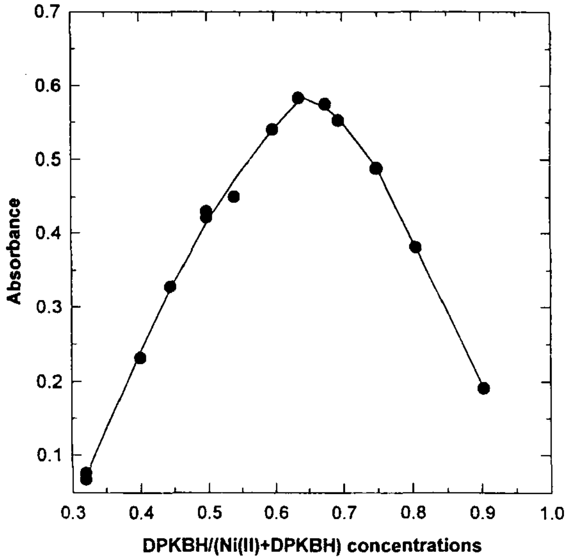

FIG. 5 - Absorbance (390 nm) *vs* DPKBH/(Ni(II)+DPKBH) concentrations in ammonium acetate pH ≅ 6, ethanol 50% v/v. The sum ([Ni(II) + [DPKBH]) is constant and equal to $5x10^{-5}$ mol.L^{-1}. Pathlength = 1cm.

Analysis for Ni(II) in natural water is frequently performed by EAAS following preconcentration involving solvent extraction. While these methods are sensitive, they also require relatively expensive instrumentation and are generally time-consuming.

Adsorption stripping voltametry is also widely recognised as one of the most sensitive technic. Many examples of electrochemical stripping analysis of nickel(16-22) can be found and they are based on the preconcentration achieved by adsorption of some complexes on a mercury electrode surface. All these methods have advantages such as sensitivity, non destructive and specificity. However, for some kind of samples, like natural waters, they are not enough sensitive or they require long deposition times. In contrast, the advantages of the proposed method are the use of simple instrumentation and the possibility of its application in the field. The method is fast, shows high sensibility, good precision and several samples can be prepared and measured until 10 hours later.

Effluents from waste-water treatment plants have been reported to contain up to 3.41×10^{-6} mol.L^{-1} [5]. As the results obtained in the present study had shown favorable absorbances for Ni(II) concentrations within the range 8.50×10^{-7} - 1.72×10^{-5} mol.L^{-1}, the here presented method can be used to determine Ni(II) in those kind of samples.

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