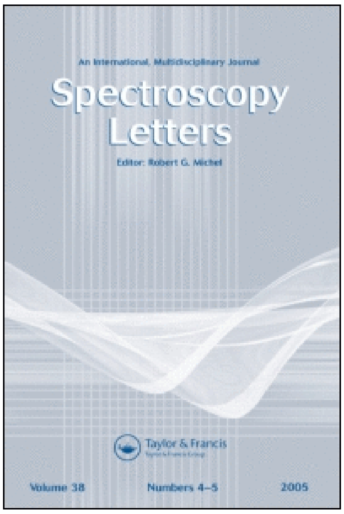

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Solvent Extraction-Spectrophotometric Determination of Nickel(II) in Natural Waters Using DI-2-Pyridyl Ketone Benzoylhydrazone

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SOLVENT EXTRACTION-SPECTROPHOTOMETRIC DETERMINATION OF NICKEL(II) IN NATURAL WATERS USING DI-2-PYRIDYL KETONE BENZOYLHYDRAZONE

Keywords: DPKBH, Nickel; Extraction; Spectrophotometry.

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ABSTRACT

A new analytical method using the reagent di-2-pyridyl ketone benzoylhydrazone (DPKBH) as a colorimetric chelating agent for the spectrophotometric determination of Ni(II) in natural water samples was established. This method involves a liquid-liquid extraction and was developed for determination of trace amounts of Ni(II).

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Under the established optimal conditions Ni(II) can be quantitatively extracted with DPKBH in chloroform. The yellow Ni(II)-complex exhibits one maximum absorbance at 406 nm.

The chelated nickel(II) obeys the Beer's law and the method is suitable in the concentration range from 0.3 to 9.4 μg/L. In order to validate the method, Ni(II) concentration was determined in a water sample and the result was compared with the value obtained by AAS method. The results are in good agreement. When the spectrophotometric method was used, fluoride ions were added in order to mask the presence of iron, which can be present in water samples and is the principal interferent. The advantages of the proposed method are the short time required, high sensitivity, good precision and the use of non-expensive instrumentation.

INTRODUCTION

Nickel(II) is an important metal in the environmental, marine and aquatic chemistry, in food and in biological samples, because of its possible interaction with the environmental compartments and biota.

Nickel occurs in aquatic systems as soluble salts adsorbed, or associated with organic particles. It may be deposited in sediments by processes as precipitation, adsorption or complexation on clay particles. Because of the changes in physical and chemical parameters or due to the microbial activity, sorption processes may be reversed leading to release of nickel from the sediments[1].

Nickel concentrations of 0.228-0.693 μg.L^{-1}, determined for a vertical open ocean water profile, were considered to reflect the actual nickel concentration in this medium[2]. Concentrations of nickel in freshwater systems[3] are generally less than 10 μg.L^{-1}.

A variety of methods have been used to determine nickel concentrations in different media as biological materials[4-7], water[2,7-12], soil[13,14], air[3], food[7,15] and other materials as steel[16-18]. Analysis for nickel in natural water is frequently performed by EAAS with preconcentration factors providing detection limits as low as 10 ng.L^{-1} in sea-water analysis[2,7,10]. Nickel concentrations as low as 60 ng.L^{-1} can be determined in natural waters by inductively-coupled plasma atomic emission spectroscopy (ICP-AES)[11]. Pihlar et al.[7] presented the DPV-HMDE method with prior chelate adsorption at the Hg electrode as a procedure for the determination of nickel levels in natural waters and waste water. Particle-induced X-ray emission makes possible the detection of various trace metals in water at the ng/L level[19]. The analysis of Ni(II) aqueous solutions in the 1-2 μg.L^{-1} region is possible by extracting the Ni-heptoxime-chelate and carrying out a differential pulse polarographic determination of the extracted compound in a supporting electrolyte of tolueno/methanol/LiCl [20].

In spite of the number of disposable methods, little information is available on nickel distribution and speciation in natural water because its determination in such low concentrations is very difficult. In this way, new analytical methods should be developed to make easier the speciation of nickel compounds in environmental media, biological materials, workplaces, and atmospheric emissions.

This paper describes a new sensitive method for the extractive spectrophotometric determination of Ni(II) from aqueous solution using di-2-pyridyl ketone benzoylhydrazone(DPKBH). The liquid-liquid extraction step where chloroform and water are used is based on the higher solubility of Ni(II)-DPKBH complexes in chloroform than in water. The water/chloroform ratio used in the extraction procedure was 35. This ratio is a compromise between the need for the highest ratio possible (most effective preconcentration) and the solubility of chloroform in water [21].

DPKBH is a sensitive reagent used for the spectrophotometric determination of trace amounts of many transition metal ions and has been used for the spectrophotometric determination of iron(II)[22], iron(II) and iron(III)[23], cobalt(II)[24], palladium(II)[25] and nickel(II)[26]. The concentrations of Fe(II) and Fe(III) were simultaneously determined in cloudwater samples by spectrophotometric technique employing di-2-pyridyl ketone benzoylhydrazone as a dual chelating agent[21]. In the present work this chelate agent was used in order to develop a simple, suitable, sensible and cheap analytical method to determine Ni(II) in a very low concentration similar to the present in natural waters. It is important to consider that the principal interference caused by the presence of iron ions in water samples can be masked with addition of fluoride ions.

EXPERIMENTAL

Apparatus - All spectrophotometric measurements were carried out on a double-beam U-3000 model Hitachi spectrophotometer using 1.00 and 5.00 cm quartz cells. All atomic absorption measurements were performed on a Varian Model AA1275 atomic absorption spectrometer, under the following operation conditions: wavelength 232 nm and acetylene flow.

Reagents and Solutions - All reagents and solvents were of analytical-reagent grade. The synthesis of DPKBH was performed according to the procedure outlined by Garcia-Vargas et al.[27]. 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 chloroform. Ni(II) sulphate hexahydrated salt was dissolved in water acidified with perchloric acid ($pH \cong 1$) and standardized by EDTA titration [28].

Water Collection - The natural water samples were collected in polyethylene bottles at a site near from Alfenas, city located at the south of Minas Gerais, a Brazilian State.

The samples were collected and preserved, according with the procedures from Standard Methods [29], in order to avoid any changes.

Spectral Characteristics of Ni(II)/DPKBH in Chloroform - In order to obtain the absorption spectrum of the complexes, 350 mL of Ni(II) aqueous solution 2.04×10^{-6} M was prepared, and added to 10 mL of DPKBH 7.20×10^{-2} M in chloroform. The bottles of blank and sample were shaken for 5 min. to ensure a complete extraction by the chelation of Ni(II) in the organic phase. The water was

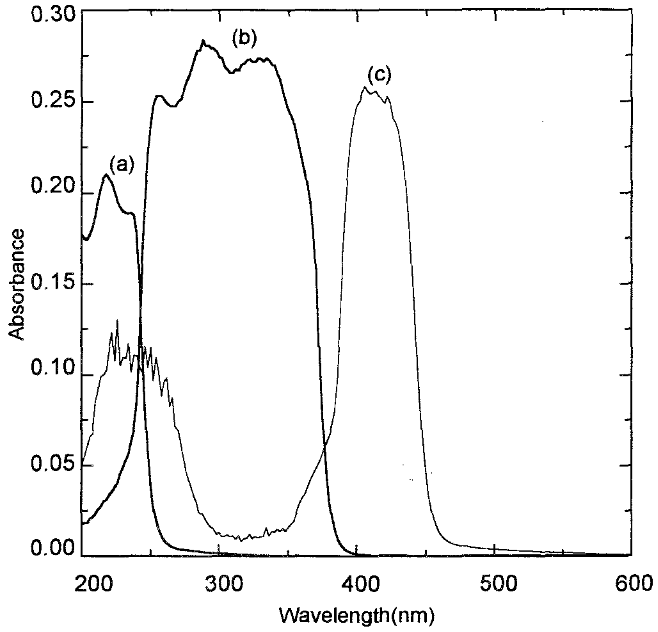

FIG. 1 - Absorption spectra for:
(a) $CHCl_3$
(b) 2.70×10^{-4} M DPKBH in chloroform
(c) Ni(II) = 1.3×10^{-7} M and DPKBH = 7.20×10^{-2} M
5 min. agitation time (shaker). pH≅6. Pathlength = 1cm.

decanted, and the remaining water-chloroform mixture was separated using a separatory funnel. The water phase was discarded and the chloroform phase was saved for the spectrophotometric analysis. No buffer was used in the liquid-liquid extraction, since the pH of the chloroform phase was ≅ 6 and this value belongs to the best range of pH for a complete coordination of Ni(II) by DPKBH[27].

Absorption spectra were obtained in order to verify the behavior of all reagents as chloroform, DPKBH, and Ni(II)/DPKBH complexes. The maximum absorbance of the Ni(II)-DPKBH complexes was found to be 406 nm as shown in Figure 1. DPKBH and chloroform absorb in a wavelength range that is different from the Ni(II)/DPKBH complex as shown in Figure 1.

RESULTS AND DISCUSSION

Analytical Parameter - The influence of different shaking modes was verified. For the ligand, chloroform (10 mL) containing DPKBH $2.7X10^{-3}$ M was added to 350 mL of distilled water and the mixture was shaken for 5 min.. The remaining water-chloroform mixtures were separated from the water phase and the absorption spectra of DPKBH were obtained for the following different kinds of shaking: a) magnetic; b) mechanical; c) shaking table. The behavior of the Ni(II)/DPKBH complexes was also studied by using different kinds of shaking: a) manual; b) magnetic; c) mechanical; d) shaking table. Volumes of 350 mL of $9.95x10^{-7}$ M Ni(II) solution and 10.0 mL of $6.70x10^{-3}$ M DPKBH in chloroform, were shaken for 5 min.. The remaining water-chloroform mixtures were separated from the water phase and used to the spectrophotometric analysis.

The effect of different shaking types were observed for the reagent and the Ni(II)/DPKBH complexes. DPKBH showed the same behavior and all of the obtained spectra for different shaking modes were similar to that found in Figure 1-b. For Ni(II)/DPKBH complexes, the same study was carried out in order to verify the efficacy of the extraction front to the agitation type. In the case of the ultrasound, after a 2 min. shaking period, a perturbation was observed probably due to the decomposition of the reagents. The obtained results showed the same efficacy to make the extraction, whether shaking table, mechanic, magnetic, or manual agitations were used.

The stability of the Ni(II)/DPKBH complexes were determined by preparing 350 mL of 2.04×10^{-6} M Ni(II) solution, adding 10.0 mL of 3.60×10^{-2} M DPKBH in chloroform and shaking for 5 min. The absorbance of the extracted chloroform phase was measured at 406 nm every 15 min. in a 12-hour period.

The study about the stability of the complex showed that the color was almost instantaneously attained and it was constant for at least 12 hours. This stability permits us to conclude that in absence of sided reactions which could cause modifications in natural samples, several samples may be prepared and later measured in a 12-hour period.

The effect of the excess of DPKBH was studied for two Ni(II) concentrations, 2.04×10^{-6} and 4.20×10^{-7} M, and by using the shaking table. From each metal aqueous solution, 350 mL were taken and added to 10.0 mL of DPKBH solution in different concentrations. The mixtures (aqueous and chloroform solutions) were shaken for 5 min.. The absorbance of the chloroform phase was measured at 406 nm.

The variation in the reagent excess showed a dependence between the absorbance of Ni(II)/DPKBH complexes and the reagent concentration. The effect of the DPKBH excess was studied with a Ni(II) constant concentration equal to 2.04×10^{-6} M. The same procedure was used as written before but using different concentrations of DPKBH. A 5 min. magnetic shaking period was used. After the

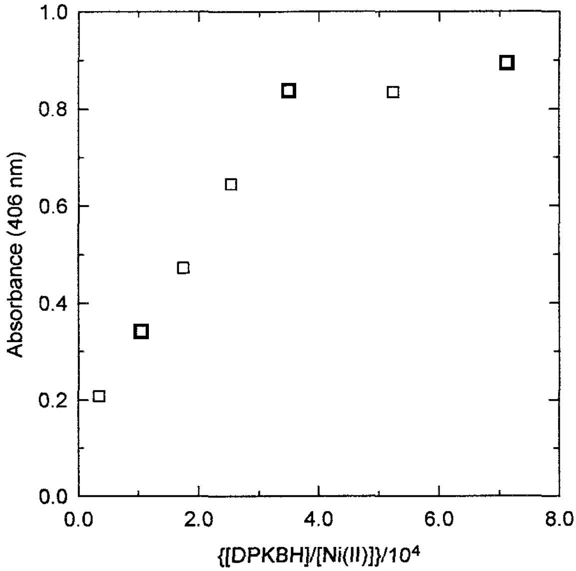

FIG. 2 - Absorbance (406 nm) of Ni(II)/DPKBH system as a function of the DPKBH/Ni(II) molar ratio. Ni(II) = 4.20×10^{-7} M. Shaking period of 5 min. (shaker), extracion in $CHCl_3$. pH≅6. Pathlength=1 cm.

liquid-liquid extraction, the absorbance of the chloroform phase was measured at 406 nm. The absorbance did not present significant changes for ligand/metal ratios higher than 1.8×10^4 : 1. In respect to the use of the shaking table the same behavior was observed showing an equal efficacy in the extractive process.

When the concentration of Ni(II) was reduced to 4.20×10^{-7} M, a higher DPKBH/Ni(II) molar ratio, 3.00×10^4 M, was necessary to reach the higher absorbance as shown in Figure 2.

The influence of the shaking time was observed by using 350 mL of aqueous 2.42×10^{-7} M Ni(II) and 10 mL of 3.00×10^{-2} M DPKBH solutions. The absorbances were measured at 406 nm after 2, 3, 5 and 10 minutes-shaking periods and the respective values are 0.327; 0.370; 0.514 and 0.515. As it can be observed after 5 min. the absorbance did not change. In this way, the 5 min. period was adopted.

As the net charge of the complexes is not known the use of an electrolyte as a counter-ion may or may not show a better extraction coefficient. In this way the influence of the sodium chloride electrolyte in the liquid-liquid extraction was studied by using 350 mL of 2.42×10^{-7} M Ni(II) solution. Sodium chloride (2.0g) was added and 10 mL of 3.00×10^{-2} M DPKBH in chloroform was mixed. Different shaking times (2, 3, 5, 10 min.) were used and the absorbance values are 0.127; 0.159; 0.239 and 0.241. It is clear that the addition of NaCl was not favorable because the absorbances were lower than in the absence of NaCl and did not attain a constant value before 10 min.. This suggests that probably the complex is an uncharged chelate and the ratio Ni(II)/DPKBH is 1:2.

Reproductibility - The reproductibility of the extraction technique was investigated carrying out ten replicates for the extraction process. Two different concentrations of standard Ni(II) solution were used, 8.62×10^{-9} and 7.41×10^{-8} M. The average of the results and the standard deviations are $(6.3 \pm 0.5) \times 10^{-9}$ and $(8.2 \pm 0.4) \times 10^{-8}$ with 8% and 5% as the relative errors for 8.62×10^{-9} and 7.41×10^{-8} M of Ni(II), respectively. The proposed method presents a very good reproducibility for such low concentrations of Ni(II).

Analytical Curve - In order to obtain the analytical curve, spectrophotometric measurements were carried out with several mixtures prepared according to the procedure: 560 mL of Ni(II) solution in different concentrations were added to 16 mL of 3.00×10^{-2} M DPKBH, in chloroform. After a 5 min. shaking period in a shaking table and the separation of the phases, the absorbances were measured at 406 nm and a linear relationship was observed to the absorbance and the concentration of Ni(II) within the 5.6×10^{-9} - 1.6×10^{-7} M range or 0.3 to 9.4 μg/L. The ratio between the ligand and the metal concentrations for the higher concentration of nickel (II) is 10^{5}, and this is enough to the quantitative chelation of Ni(II) in the full range of the analytical curve. The parameters of the linear equation and the respective standard deviations are: $(1.39 \pm 0.96) \times 10^{-2}$ for the intercept and $(6.08 \pm 0.12) \times 10^{6}$ for the slope. The correlation coefficient is 0.987. The molar absorptivity of the extracted metal chelates is 175 times lower than the experimental angular coefficient 6.08×10^{6}, due to the preconcentration factor of 35 and the use of a 5 cm cell. In this way the actual molar absorptivity of the Ni(II)/DPKBH complex is 3.47×10^{4} $mol^{-1}.L.cm^{-1}$.

Determination of Nickel in natural waters - The present method was used in the determination of nickel in a natural water sample and the result was compared with AAS results.

In order to eliminate the interference of iron, sodium fluoride was used as a masking agent. To 110 mL of the samples, 1.5 g of the salt was added. The volume was completed up to 560 mL with deionized water and this final solution was added to 16 mL of 3.00×10^{-2} M of DPKBH in chloroform.

The concentrations of Ni(II) were obtained by using the here presented liquid-liquid extraction with DPKBH in chloroform associated to the spectrophotometric techni and the AAS reference method. The results are, respectively, 25.9 μg/L and 30.0 μg/L. Both results are in a very good agreement with a difference of 14% which is very suitable for natural water analysis.

CONCLUSION

In this way a simple, sensible and cheap analytical method can be used to determine Ni(II), using DPKBH as chelating agent. The same ligand was applied before to determine Ni(II) in ethanol-water solution without preconcentration. A linear response was attained within the nickel concentration range equal to 8.50×10^{-7}-1.72×10^{-5} M [26]. With the new method using a liquid-liquid extractive process, Ni(II) in aqueous solutions can be determined in a hundredth of the concentration when compared to the ethanol method. A very complete study of the possible interference ions was carried out and like the ethanol method[26] the same principal interferents can be attributed to the chloroform method.

The present method can be used to determine nickel in several water samples like waste-water, drinking-water and freshwater among others. The liquid-liquid extraction process is very sensitive and reproducible and can be used associated to other experimental techniques as DPV-HMDE due to the adsorptive properties observed for the Ni(II)/DPKBH complexes or EAAS. It is important to emphasize that except ultrasound, any kind of agitation can be used with equal and excellent efficacy.

Fluoride ions were added and the interference of iron was efficiently masked making possible and exact the spectrophotometric determination of Nickel(II).

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