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Cloud point extraction, preconcentration and spectrophotometric determination of nickel in water samples using dimethylglyoxime

Morteza Bahram[*], Somayeh Khezri and Sakineh Khezri

Department of Chemistry, Faculty of science, Urmia University, Urmia, Iran

| CHRONICLE	ABSTRACT
	A new and simple method for the preconcentration and spectrophotometric determination of trace amounts of nickel was developed by cloud point extraction (CPE). In the proposed work, dimethylglyoxime (DMG) was used as the chelating agent and Triton X-114 was selected as a non-ionic surfactant for CPE. The parameters affecting the cloud point extraction including the pH of sample solution, concentration of the chelating agent and surfactant, equilibration temperature and time were optimized. Under the optimum conditions, the calibration graph was linear in the range of 10-150 ng mL^{-1} with a detection limit of 4 ng mL^{-1}. The relative standard deviation for 9 replicates of 100 ng mL^{-1} Ni(II) was 1.04%. The interference effect of some anions and cations was studied. The method was applied to the determination of Ni(II) in water samples with satisfactory results.

1. Introduction

Nickel is a very abundant natural element and it has important roles in biological science and industry. This element is one of the essential microelements for human body. However, it can be toxic to human organisms at high concentrations. Allergic reaction, respiratory cancer and skin disorder may be caused by Ni(II) toxicity[1, 2]. Thus it is very important to develop simple, fast and reliable methods for the determination of Ni(II) in water and biological samples. Several analytical methods have been proposed for the determination of Ni(II), such as voltammetry[3, 4], ion selective electrode[5, 6], polarography[7], etc. Many of these methods are expensive or require complicated instruments and need a lot of time. Spectrophotometric methods have received considerable attention owning to their simplicity, rapidity and low cost. However, due to the presence of Ni(II) in natural water samples at low levels, a preconcentration step prior to its spectrophotometric determination is

* Corresponding author. Tel: +98 441 2972143, Fax : +98 4412776707
E-mail addresses: m.bahram@urmia.ac.ir (M. Bahram)

necessary, that can be achieved using cloud point extraction (CPE). The use of CPE process for preconcentration and extraction of metal chelates in biological and clinical samples have been reported[8-17]. This technique is based on the property of most non-ionic surfactant in aqueous solutions to form micelles and become turbid when heated to a temperature known as cloud point temperature (T_c). When the temperature is higher than T_c, the micellar solution will be separated into a surfactant-rich phase of a small volume and a diluted aqueous phase, in which the surfactant concentration is close to the critical micellar concentration (CMC). This extraction method allowed the development of an inexpensive, simple and rapid methodology for the preconcentration of metal ions. By using the surfactant in the CPE process, toxic solvent extraction has been avoided[18]. Procedures for preconcentration of metal ions using CPE has been based on the extraction of these metallic substances as sparingly water-soluble chelate complexes[19]. Several ligands such as dithizone[20], 1-(2-pyridylazo)-2-naphthol (PAN)[21], ammonium pyrolidinedithiocarbamate (APDC)[22], 1-nitroso-2-naphthol [23] and 2-amino-cyclopentene-1-dithiocarboxylic acid (ACDA)[24] have been used for cloud point extraction of Ni(II).

In the present work we report the results obtained in a study of the cloud point extraction and pre-concentration of Ni(II) after the formation of its complex with dimethylglyoxime (DMG) (Scheme 1). Triton X-114 was used as a non-ionic surfactant for CPE followed by spectrophotometric analysis extracted phase. The factors influencing the efficiency of spectrophotometric determination of Ni(II) by the proposed method were systematically studied. The method was successfully applied to determination of Ni(II) in water samples.
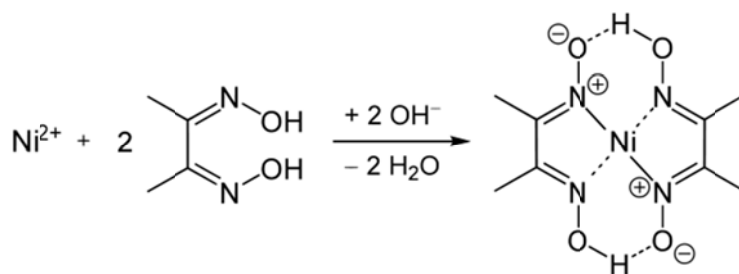
Scheme 1. The reaction of Ni $^{2+}$ with DMG to form Ni(DMG)$_2$ complex

2. Results and discussion

Absorption spectra

Fig. 1 shows the absorption spectra of the Ni(II)-DMG complex in the surfactant-rich phase after CPE procedure against reagent blank. The complex of Ni(II) with of DMG is insoluble in water. But, it has been observed that it was soluble in water by the addition of the surfactant of Triton X-114.
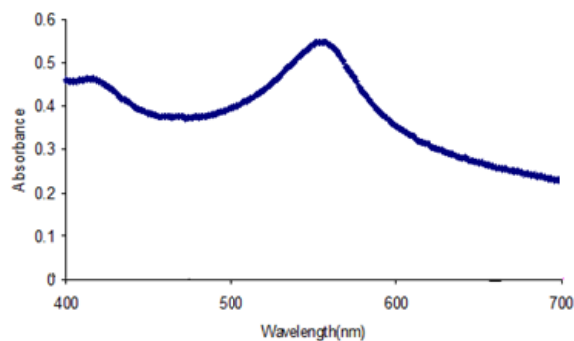

Fig. 1. Absorption spectra of Ni(II)-DMG complex after CPE at 556 nm. Conditions: 100 ng mL^{-1} Ni, 0.05 mmol L^{-1} DMG, 0.3% (V/V) Triton X-114.

Effect of pH

The extraction of metal ion by CPE method involves prior formation of a complex with sufficient hydrophobicity to be extracted into the small volume of surfactant-rich phase, in order to obtain the desired preconcentration[25]. pH plays an important role in metal-chelate formation. For this study, a pH range of 4-12 was used. Fig. 2 shows the influence of pH on the absorbance of the Ni(II)-DMG complex at 556 nm. As can be seen, at pH 10 maximum extraction efficiency was obtained. Hence, pH 10 was selected for further study.
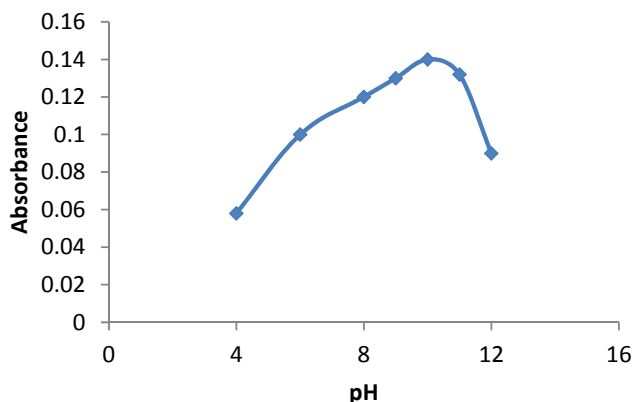

Fig. 2. Effect of pH on the absorbance of the Ni(II)-DMG complex at 556 nm. Conditions: 100 ng mL^{-1} Ni, 0.05 mmol L^{-1} DMG, 0.2% (V/V) Triton X-114.

Effect of Triton X-114 concentration

The concentration of surfactant used in the CPE is an important factor. Triton X-114 was chosen because of its commercial availability in a high-purified homogenous form, low cloud point temperature, low toxicological properties and cost. Also, the high density of the surfactant-rich phase facilitates phase separation by centrifugation[26, 27]. The effect of surfactant concentration on the extraction of Ni(II) was examined within the Triton X-114 concentration range from 0.1 to 1.0% (V/V). Fig. 3 shows that the measured absorbance of extracted solution increases as the surfactant concentration increases, and then decreases when the surfactant concentration passed the maximum extraction. Therefore 0.3% (V/V) Triton X-114 was used in order to minimize the extracted phase volume, and achieve the highest extraction efficiency.
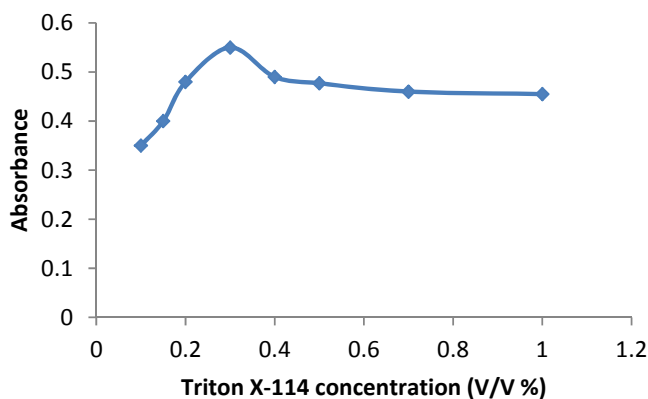

Fig. 3. Effect of Triton X-114 concentration on the absorbance of the Ni(II)-DMG complex at 556 nm. Conditions: 100 ng mL^{-1} Ni, 0.05 mmol L^{-1} DMG, pH 10.

Effect of DMG concentration

The effect of concentration of DMG on the CPE of Ni(II) was investigated in the concentration range of 0.01-0.1 mmol L^{-1}. The results were shown in Fig. 4. As it is seen for the Ni(II)-DMG complex, the signal increases up to a known concentration of DMG, reaching a plateau, which is considered as complete extraction. A concentration of 0.05 mmol L^{-1} was chosen as the optimum.
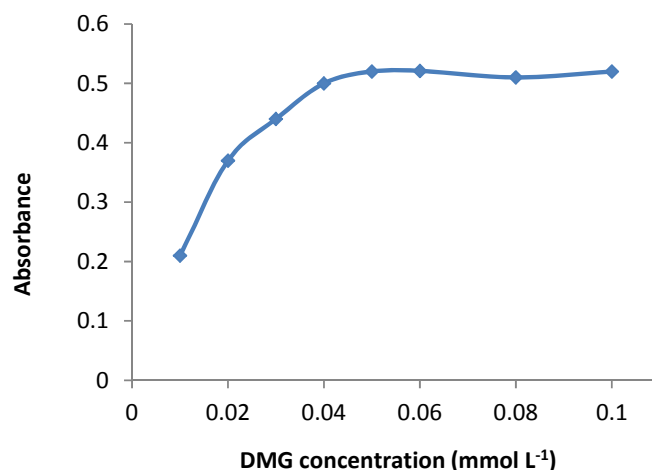

Fig. 4. Effect of DMG concentration on the absorbance of the Ni(II)-DMG complex at 556 nm. Conditions: 100 ng mL^{-1} Ni, 0.3% (V/V) Triton X-114, pH 10.

Effects of equilibration temperature and time

It was desirable to employ the shortest equilibration time and the lowest possible equilibration temperature, as a compromise between completion of extraction and efficient separation of phases. Therefore, the effect of equilibration temperature in the range of 30-80°C was studied. It was found that 50°C is adequate and sufficient to achieve complete extraction. The dependence of extraction efficiency upon equilibration time was also studied for a time interval of 5-20 min. An equilibration time of 10 min was chosen as an optimum value.

Analytical characteristics of the proposed method

Table 1 summarizes the analytical characteristics of the optimized method, Including regression equation, linear range, limit of detection and reproducibility. The limit of detection, defined as $C_L = 3$ S_B/m (where C_L, S_B and m are the limit of detection, standard deviation of the blank, and slope of the calibration graph, respectively), was 4 ng mL^{-1}. The proposed method showed an excellent repeatability (RSD < 5% for 9 replicate determinations of 100 ng mL^{-1} Ni(II)) using the optimized conditions. Because the amount of Ni(II) in 10 mL sample solution is measured after preconcentration by CPE in a final volume of 0.5 mL, the solution is concentrated by a factor of 20.

Table 1.Analytical characteristics of the proposed method

Regression equation [a]	Abs=0.0032x-0.0092
R^2 [b]	0.998
Repeatability (RSD) [C]	1.04%
LOD (ng mL^{-1})[d]	4
Linear range(ng mL^{-1})	10-150

[a] *Concentration of* Ni(II) *in* ng mL^{-1}
[b] *Squared correlation coefficient*
[c]*Relative standard deviation for 9 replicate determination of* 100 ng mL^{-1} Ni(II)
[d] *Limit of detection for S/N=3*

Interferences study

In order to study the selectivity of the proposed method, the effect of various cations and anions on the preconcentration and determination of 100 ng mL^{-1} Ni(II) was tested under the optimum conditions. The results are summarized in Table 2. An ion was considered as interferent, when it caused a variation in the absorbance of the sample greater than $\pm5\%$. The results indicate that most of the cations and anions did not interfere even when present 1000-fold excess over analyte. At pH 10, Fe^{3+} at concentrations greater than 1000 ng mL^{-1} would completely precipitated. The precipitate formed was then filtered before addition of DMG into the solution. Therefore, this cation would not interfere at higher concentrations. As can be seen in the table, a very good selectivity is achieved.

Table 2. Tolerance limit of foreign ions on the determination of 100 ng mL^{-1} of Ni(II)

Foreign ions	Tolerance ratio
Mg^{2+}, Ba^{2+}, Li^+, Na^+, K^+, CH_3COO^-, F^-, I^-, SCN^-, NO_3^-, CO_3^{2-}, Br^-, citrate, Cl^-, tartrate, urea, thiourea, oxalate	1000
Cu^{2+}, Zn^{2+}, Co^{2+}	100
Fe^{3+}	10 (1000 [a])

[a] *After filtering of the produced precipitate*

Application

In order to test the reliability of the proposed method it was applied to the determination of Ni(II) in tap water and river water samples. The water samples were analyzed after filtering through Whatman filter paper. The samples were Spiked with Ni(II) in order to validate the procedure. The results are presented in Table 3. It can be seen that the recovery of spiked samples is good. The results indicate that the proposed method is applicable for the determination of Ni(II) in real samples.

Table 3. Determination of Ni(II) in the spiked water samples by the proposed method

Sample	Added (ng mL^{-1})	Found (ng mL^{-1})	Recovery (%)
Tap water	-	<LOD	-
	100	100.5	100.5
River water	-	20	-
	100	118	98

3. Conclusion

The determination of Ni(II) in water samples was successfully performed by using cloud point extraction by applying DMG as extracting reagent. DMG is a stable and selective complexing reagent. The proposed method is simple, rapid, safe, easy to use and inexpensive. In comparison with solvent extraction methods, this procedure employs only a small amount of surfactant which from the perspective of green chemistry is environmentally-friendly materials. The method gives a very low limit of detection and good R.S.D. values, and can be applied to the determination of Ni(II) in various water samples.

Acknowledgements

Experimental

Apparatus

A Shimadzu UV-Vis 160 spectrophotometer with 1.0 cm quartz cell (0.5 ml volume) was used for recording the absorbance spectra. A Metrohm model 713 pH-meter with a combined glass electrode was used for pH measurements or adjustment. A thermostated bath maintained at the desired temperatures was used for the cloud point experiments. A centrifuge (4000 rpm, UromAzma Co., Urmia, Iran) was applied to accelerate the phase separation process.

Reagents

All chemicals used were of analytical reagent grade and distilled water was used throughout the experiments. A stock solution of nickel (500 µg mL^{-1}) was prepared by dissolving an appropriate amount of $Ni(NO_3)_2.6H_2O$ in water. Working solutions were prepared by appropriate dilution of the stock solution. A 1×10^{-3} mol L^{-1} DMG (Merck) solution was prepared by dissolving 117 mg of DMG in absolute ethanol (Merck) and diluting to 100 mL in a volumetric flask. Triton X-114 stock solution (10%, V/V) was prepared by dissolving 10 mL of concentrate solution (Merck) in hot distilled water. Buffer solution of pH 10 , 0.5 mol L^{-1} was prepared ammonia and ammonium chloride.

Procedure

For the CPE procedure, an aliquot of the solution containing 100-1500 ng Ni, 0.5 mL of DMG solution, 1 mL of pH 10 buffer solution and 0.3 mL 0f Triton X-114 solution were placed in a 15mL centrifuge tube. The solution was diluted to 10 mL with distilled water. To reach the cloud point temperature, the system was allowed to stand for about 10 min into a thermostatic bath at 50 °C. Separation of two phases was achieved by centrifugation for 10 min at 4000 rpm. The phases were cooled down in an ice bath in order to increase the viscosity of the surfactant-rich phase. The aqueous phase was easily decanted by simply inverting the tube. The surfactant-rich phase in the tube was made up to 0.5 mL by adding absolute ethanol. The absorbance was measured at 556 nm, the maximum absorbance of the complex. A blank solution was prepared in the same manner and was used as a reference.

Acknowledgment

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