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EXTRACTION-SPECTROPHOTOMETRIC DETERMINATION OF NICKEL AT MICROGRAM LEVEL IN WATER AND WASTEWATER USING 2-[(2-MERCAPTOPHENYLIMINO)METHYL]PHENOL

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ABSTRACT. An extraction-spectrophotometric method for determination of nickel at sub ppm level using 2-[(2-mercaptophenylimino)methyl]phenol (MPMP) as the new extractant is described. The reagent reacts with nickel(II) at pH > 10 and form a 1:2 brown complex, which is extracted into chloroform. The complex has a maximum absorption at 421 nm with the molar absorptivity of 2.41×10^5 M^{-1} cm^{-1}. Beer's law is obeyed over the range of 0.011-0.30 μg mL^{-1}. The Sandell's sensitivity for 0.001 absorbance unit is 5.34×10^{-4} μg cm^{-2}. The relative standard deviation at 0.018 μg mL^{-1} is 1.1 % (n = 8). The procedure was successfully applied to determination of nickel in wastewater and standard alloy and the accuracy was determined by recovery experiment, independent analysis by furnace-AAS, and analysis of a certified reference martial.

KEY WORDS: Ni determination, Liquid-liquid extraction, Schiff bases, Spectrophotometry

INTRODUCTION

Nickel is widely used in electroplating, the manufacture of Ni-Cd batteries, rods for arc welding, pigments of paints, ceramic, surgical and dental prostheses, magnetic tapes and computer components and nickel catalysts. Nickel enters waters from dissolution of industrial processes and waste disposal [1]. Nickel was thought to be essential for plants and some domestic animals [2], but not considered to be a metal of biological importance until 1975, when Zerner discovered that urease was a nickel enzyme [3]. Nickel is essential constituent in plant urease. Jack beans and soybeans generally contain high concentration of nickel [1]. Compared with other transition metals, nickel is moderately toxic element, and still at low concentration produces a general toxic effect on the human organism, causing nasopharynx and lung diseases, malignant tumors and dermatological discase [4]. Nickel-containing sewage is harmful after ingress into water. This fact explained the importance of the monitoring of nickel concentration in natural and waste water samples. Flame and graphite furnace atomic absorption spectrometry and spectrophotometric methods provides accurate and rapid determination of nickel in natural and waste waters [5]. However, very frequently a direct determination can not be applied due to low concentration of analyte or matrix interferences.

The most widely used techniques for the separation and preconcentration of nickel are liquid-liquid extraction [6], precipitation [7], and chelating resin [8]. The large distribution ratios attainable in some solvent extraction systems allow the analytes determination at trace levels.

An advantage of solvent extraction is that both separation and preconcentration which are often required; can be obtained in the same step [9]. Historically the first instance of chemical analysis of metal ions was combination of liquid extraction and spectrophotometric methods, in which the analysis was performed on the extracting phase. Nevertheless, the solvent extraction of nickel is still an important process and is used in several plants to recover and separate nickel from wastewaters [10, 11]. Many classical ligands such as dimethylglyoxime, dithizone, and sodium-diethyldithiocarbamate are known as an extractant for extraction/spectrophotometric determination of nickel [12, 13].

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In this work the capability of 2-[(2-mercaptophenylimino)methyl]phenol (MPMP, Figure 1) for the extraction and spectrophotometric determination of nickel is investigated. MPMP is a tridentate Schiff base, derived from salicylaldehyde (salen). Schiff bases are known to form stable complexes with metal ions [14, 15]. There are some reports dealing with the analytical application of this type of ligands as ion carrier in construction of membrane electrode [16], and modifier in solid phase extraction [17, 18]; we also recently find that octadecyl silica membrane disk modified by MPMP has the capability of retention of silver from aqueous sample [19]. However, the use of Schiff bases as extractant in liquid extraction is rare [20, 21]. So it was appropriate to consider the capability of Schiff base for the separation and preconcentration of metal ions by liquid-liquid extraction. Studies confirmed the reliability of MPMP as an extractant of Ni and a rapid, sensitive and efficient extraction/spectrophotometric method for determination of nickel at trace level in water and wastewater samples was developed.

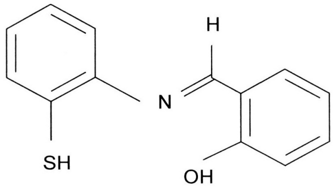

Figure 1. Structure of the Schiff base MPMP.

EXPERIMENTAL

Reagents

All reagents and solvents were of analytical reagent grade. 2-[(2-Mercaptophenylimino)methyl]phenol was synthesized and purified as described else where [22, 23]. Doubly-distilled deionized water was used throughout this work. Methanol and chloroform (both from Merck, Germany) were of extra pure grade and were used as received. The stock solution of nickel (1 x 10^{-2} M) was prepared by dissolving an appropriate amount of $Ni(NO_3)_2.6H_2O$ in 1 mL of nitric acid in a 100 mL volumetric flask, and diluted to the mark with water. Standard solutions of nickel were prepared by appropriate dilution of stock solution. The ammonium buffer (pH ~ 10.5 ± 0.5) was prepared by dissolving 6.75 g of ammonium chloride in 500 mL of doubly distilled water, adding 57 mL of concentrated ammonia and diluting to one litter with water.

Apparatus

A Jenway Model 6300 UV-Visible spectrophotometer (England) with a 1 cm optical path tubular glass cell was used for all absorbance measurements. The UV-Visible spectra were recorded with a JASCO Model 7800 double-beam spectrophotometer (Japan) with a 1 cm quartz cell. For measurement of nickel in the aqueous phase, a Buck scientific atomic absorption spectrometer (model 210, VGP, USA) equipped with a nickel hallow cathode lamp was used. pH values were determined with a Metrohm model 694 pH meter (Swiss) equipped with a combined glass-calomel electrode.

Procedure

To an aliquot of a solution containing not more than 30 µg of nickel 10 mL of ammonium buffer (pH ≈ 10.5) was added and was dilute to 100 mL. The solution was transferred into a 150 mL separatory funnel. The mixture was extracted with 5 mL of 1 x 10^{-3} M of MPMP in chloroform by shaking the funnel vigorously for 10 min, allowed the phases to separate and the absorbance of the organic phase was measured at 421 nm against a reagent blank.

RESULTS AND DISCUSSION

In the preliminary study it was confirmed that 2-[(2-mercaptophenylimino)methyl]phenol form a chloroform extractable complex with nickel. MPMP has one nitrogen, one oxygen and one sulfur donating group in its structure and is soluble in organic solvent but not in water at neutral pH. Therefore it can act as tridentate ligand and from a neutral metal chelate with nickel(II), which extracts into non-polar solvents such as chloroform. The absorption spectra of the complex of nickel with MPMP showed a maximum at 421 nm with a molar absorptivity of 2.4 x 10^5 M^{-1} cm^{-1}, whereas the ligand has a negligible absorbance at this wavelength. Thus 421 nm was selected for the absorbance measurements.

Effect of pH

The extraction of nickel with MPMP was carried out over the pH range of 2-12. It was found that the extraction efficiency is highly dependent on sample pH and quantitative extraction was achieved at pH greater than 10. The extraction of nickel from aqueous phase decrease progressively at lower pH. This is probably due to protonation of the ligand which cause a decrease in the stability of its complex with Ni^{2+} ions. Although nickel may precipitate in aqueous phase at high pH, but it will dissolve in the presence of MPMP complexing agent, and in this experiment no precipitate was observed.

Effect of MPMP concentration

It was found that at a MPMP concentration of greater than 8 x 10^{-4} M, maximum extraction is achieved and level off at higher concentration of ligand. Thus, an optimum concentration of 1 x 10^{-3} M of MPMP in chloroform was selected for the study.

Effect of shaking time

The extraction of nickel under the concentration recommended in the procedure is rapid. Varying the shaking period from 2 to 14 min showed that 6 min shaking is sufficient for quantitative extraction of nickel. Thus the kinetic of complex formation and extraction of nickel and MPMP is fast.

Composition of the extraction species

The stoichiometry of the complex of Ni(II)-MPMP was confirmed by performing spectrophotometric measurements using Job and slope ratio method [24].

In Job's method the amount of nickel in aqueous phase and MPMP in the organic phase were varied so that their sum was equal to 1 x 10^{-4} mmol. The pH was kept constant at 10.5 by ammonium buffer solution. The maximum absorbance value corresponds to a mole ratio [Ni^{2+}]/[MPMP] of 1:2 which supports a NiL_2 stoichiometry.

In the slope ratio method two series of experiments were performed. In the first series the concentration of the ligand in the organic phase was kept constant (1×10^{-4} M) while the concentration of nickel in aqueous phase was varied from 1×10^{-5} - 8×10^{-5} M. In the second series the concentration of nickel in aqueous phase was kept constant at 1×10^{-4} M while [MPMP] was varied (1×10^{-5} - 8×10^{-5} M). Two straight lines, with a slope ratio of 2:1 were obtained, which suggest again that the complex has the formula of NiL_2.

Analytical performance

In order to quantify nickel at low level (µg level) the preconcentration capability of the extraction system was investigated by extracting 17 µg of nickel from different volume of water (5-150 mL) according to the recommended procedure. The results showed that up to 130 mL, the extraction was quantitative. Thus based on the consideration of the ratio of aqueous phase (130 mL) to the organic phase (5 mL), a preconcentration factor of 26 was obtained for the method.

Performance characteristic of the developed technique was obtained by extracting standard solution of nickel. For an aqueous volume of 100 mL the calibration graph exhibited linearity over the range of 0.01-0.30 µg mL^{-1} with a correlation coefficient of 0.9998 ($A = 4.1225\ C - 0.0012$ where A is the absorbance and C is concentration of nickel in µg mL^{-1}). The Sandell's sensitivity [25] for 0.001 absorbance was 5.34×10^{-4} µg cm^{-2}. The relative standard deviation (95 % confidence level) for 0.17 µg mL^{-1} of nickel was found to be 1.1 % (n = 8).

Table 1. Effect of foreign ions in determination of nickel (3×10^{-4} mmol) from 100 mL of aqueous samples.

Foreign ion	Mole ratio [M^{n+}/Ni^{2+}]	Recovery (%)
Ag^{+}	400	99.2 ± 0.5
CO_3^{2-}	400	97.2 ± 0.4
Sr^{2+}	300	98.8 ± 0.5
Zn^{2+}	300	97.6 ± 0.3
Na^{+}	300	98.9 ± 0.2
K^{+}	300	97.3 ± 0.4
Cs^{+}	300	96.9 ± 0.6
SO_4^{2-}	300	95.5 ± 0.5
NO_3^{-}	300	96.9 ± 0.4
PO_4^{3}	300	95.2 ± 0.2
Mg^{2+}	250	98.2 ± 0.3
Ca^{2+}	250	98.4 ± 0.5
Al^{3+}	250	97.1 ± 0.4
CH_3COO^{-}	250	96.4 ± 0.6
Mn^{2+}	200	97.7 ± 0.2
I^{-}	200	95.2 ± 0.3
Br^{-}	200	96.6 ± 0.4
Pb^{2+}	50	98.6 ± 0.5
Cd^{2+}	50	95.5 ± 0.6
Cu^{2+}	20	97.1 ± 0.4
Co^{2+}	20	95.6 ± 0.3
Pt^{2+}	20	96.2 ± 0.2
Fe^{2+}	20	95.3 ± 0.5
Hg^{2+}	20	95.8 ± 0.4
Cr^{3+}	20	96.1 ± 0.3

The effect of various ions on the determination of nickel with MPMP at a fixed concentration of nickel (0.17 µg mL^{-1}) and in the presence of different amounts of foreign ions was studied. An error of ± 5 % in absorbance was considered tolerable. The results are summarized in Table 1 and indicate that at the given level there is no significant interference with the extraction and spectrophotometric determination of nickel. Thus the system has a high selectivity for nickel ions.

Furthermore, a comparison of analytical parameter obtained by this method and with that reported by several other extraction spectrophotometric methods for determination of nickel is given in Table 2. As could be seen, the presented method has high molar absorptivity and is more sensitive; thus it is suitable for trace analysis of nickel in the sample type examined.

Table 2. Comparison of the present method with other reported spectrophotometric methods.

Reagent	pH	λ_{max} (nm)	Molar absorbtivity $M^{-1}cm^{-1}$	M:L	Linear range (µg mL$^{-1)}$	Sandall's sensitivity (µg cm^{-2})	Remarks	Ref.
Thiazole-2-carbaldehyde 2-quinolyl hydrazone	8.7 - 9.5	522	7.17 x 10^4	1:2	0.7	8.6 x10^{-4}	Poor selectivity several metal ion interfere at mole ratio of greater than one	[26]
Dimethylglyoxime	12	470			0.26-2.1		Poor sensitivity	[27]
N-Ethyl-3-carbazolecarboxaldehyde-3-thiosemicarbazone	6.0	400	1.114 x 10^4	1:1	1.2-5.6	5.29 x 10^{-3}	Moderate sensitivity	[28]
2-Hydroxy-4-isopropoxyacetophenone thiosemicarbazone	9.0	400	8.4 x 10^2	___	16.44	___	Very poor sensitivity	[29]
7-Methyl-2-chloroquinoline-3-carbaldehyde thiosemicarbazone	6.0	410	1.67 x 10^2	___	4.0	___	Ce(III), Al(III) and Ga(III) interfered, very poor sensitivity	[30]
2,4-Dihydroxy acetopheneone thiosmicarbazone	7.0 - 8.0	385	8.2 x 10^3	1:1	1.0-8.0	___	Poor sensitivity	[31]
2-[(2-mercaptophenylimino)-methyl]phenol	>10	421	2.41 x 10^5	1:2	0.011-0.30	5.34 x 10^{-4}	Sensitive and selective	This work

Application of the proposed method

To confirm the usefulness of the proposed method, it was applied to the determination of nickel in well water and wastewater samples. For this purpose the samples were first filtered through a Millipore 0.45 µm pore-size membrane into previously cleaned polyethylene bottles and were then treated according to the given procedure. Reliability of the method was checked by the spiking experiments and comparing the results with the data obtained by GFAAS. As shown in Table 3, the results obtained with the proposed method agree well with the data obtained by furnace atomic absorption analysis, and the recovery of spiked samples is good, suggesting that the procedure is reliable for the sample type examined.

Furthermore, the above procedure was applied to the determination of nickel in a standard reference alloy C12X3500 (MBH Analytical Limited, U.K.) with composition of (C = 0.18 %, P = 0.029 %, Cr = 0.31 %, Co = 0.005 %, Si = 0.45 %, Mn = 0.70 %, Mo = 0.10 %, Sn = 0.03 %, W = 0.29 %, Ti = 0.054 %, V = 0.002 %, Ag = 0.07 %, S = 0.032 %, Ni = 0.18 %, Cu = 0.15 % and Al = 0.35 %). The concentration of nickel in the sample was found to be 0.178 % which is in good agreement with the value of 0.18 % reported by MBH Analytical Limited for the above mentioned standard. This further confirmed the reliability of the method for analysis of a wide range of samples.

Table 3. Determination of nickel in well water and waste water samples.

Sample	Added ($\mu g\ L^{-1}$)	Found[a] ($\mu g\ L^{-1}$)	Recovery (%)	GF-AAS[a] ($\mu g\ L^{-1}$)
Well water		ND[b]		5.3 ± 0.2
	15.0	14.8 ± 0.2	98.7	
Waste water		74.2 ± 0.9		73.8 ± 2.9
	15.0	88.7 ± 1.3	96.7	
Waste water		57.3 ± 1.2		57.8 ± 1.8
	15.0	72.2 ± 1.6	99.3	

[a]Mean and standard deviation of three determinations. [b]ND = not detected.

CONCLUSIONS

In this study for the first time it was shown that the Schiff bases could be used as a ligand for liquid-liquid extraction and spectrometric determination of traces of metal ions. The important features of the method are simplicity, freedom from interferences, high selectivity, with separation ability of MPMP for nickel at trace level. The preconcentration factor of the method is high and it is judged that the procedure have considerable potential for determination of nickel in wastewater samples.

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