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Separation and Preconcentration of Trace Amounts of Nickel in Environmental and Biological Samples by Flotation Using Dimethyl glyoxime

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A simple and selective method for separation and preconcentration of nickel has been developed. The method is based on the flotation of a complex of nickel and dimethyl glyoxime at the aqueous solution of *n*-hexane interface. The floated layer was then dissolved in 5 mL of 1 mol L^{-1} nitric acid for the subsequent spectrometric determination. The quantitative flotation of the complex was possible in the pH range of 9-12. The method is simple and free from the interference of all cations and anions and has a wide linear range. The procedure was successfully applied to the determination of trace amounts of nickel in well water and waste water in coating plant. The method's accuracy was investigated by using standard reference material alloys (NIST 864) and by spiking the samples with different amounts of Ni^{2+}.

Key Words: Flotation, Spectrometry, Dimethylglyoxime, Nickel.

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 problems, including respiratory system cancer[1]. Nickel is an important constituent of several steel alloys. Its determination is required to control both raw material and industrial products[2].

Nickel is easily accessible to atomic absorption spectrometry determination and is routinely analyzed by this method in many laboratories. However, interferences have been observed in several matrices including silver alloys, steel ores and copper based materials. Enhancement, depression and absence of interference are reported and some of these finding conflicts with one another[3]. Furthermore, ultra trace determination of nickel is not possible by flame atomic absorption spectrometry.

Thus, due to complex matrices and low concentrations of most heavy metals including nickel in environmental and biological samples, their sensitive determination necessitates the use of separation and preconcentration methods. Liquid-liquid extraction methods are frequently used for the separation and preconcentration of nickel[4,5]. However, classical extraction methods usually required large volumes of high-purity solvents and a large preconcentration factor is not possible. These drawbacks may be partly avoided by a flotation technique, which allows the handling of large volumes of samples and considerable savings in reagents and time[6-9].

Dimethyl glyoxime is widely used, for the spectrophotometric determination of nickel[10,11] also it has been used for separation and perconcentration of nickel by liquid-liquid extraction[5] or solid phase extraction[12-14] but all of these separation methods suffer from lack of selectivity.

For example, metal ions such as Ni(II), Pb(II), Mn(II), Bi(III), Co(II), Cd(II), Zn(II) and Fe(II) could interfere at concentrations higher than 5 mg L^{-1} in solid phase extraction of Ni^{2+} using dimethyl glyoxime as a complexing agent[14].

This paper deals with a selective and simple method for separation and perconcentration of nickel with dimethyl glyoxime by flotation method.

Primary investigations showed that none of the two usual complexes of nickel and dimethyl glyoxime could not float completely in interface of liquid and organic phase due to solubility in water and organic phase of $Ni(Dm)_3^{2-}$ and $Ni(HDm)_2$, respectively.

Thus, a different complex of nickel and dimethyl glyoxime was studied. As it observed, in more basic pHs, a different complex could be formed that is floated in interfaces of two phases.

This complex is formed very fast and metal ions (*e.g.*, Fe^{2+}, Co^{2+} and Cu^{2+}) which form coloured, water-soluble

complexes with dimethyl glyoxime do not interfere in this condition. Sensitive spectrometric determination of trace amounts of nickel in complex environmental and biological samples by dimethyl glyoxime could be possible after preconcentration and separation of Ni(II) with this method.

EXPERIMENTAL

The solutions were prepared with freshly deionized water and chemicals of analytical reagent grade. The 1 g L^{-1} nickel standard stock solution was prepared by dissolving 6.73 g $(NH_4)_2Ni(SO_4)_2 \cdot 6H_2O$ (Merck, Germany) in water containing 2 mL of conc. H_2SO_4 and completing the volume to 1 L with water.

The 2 % (m/v) dimethyl glyoxime solution was prepared by dissolution an appropriate amount of reagent in 250 mL of a 2 mol L^{-1} NaOH solution.

Sodium borate-boric acid buffer (pH = 10). This solution was prepared by dissolving 12.78 g of sodium borate (Merck) in 100 mL of water, followed by the addition and dissolution of 6.18 g of boric acid (Merck) and was diluted to 1000 mL. The standard reference material with certified values was the NIST 864 (New York, USA) Inconel 600. The materials were dissolved in concentrated HCl and HNO_3 acids[16].

Sample preparation for real samples: Analysis of water sample was performed as follow. The 400 mL of sample was poured in a beaker and 8 mL conc. HNO_3 and 3 mL of H_2O_2 of (30 %) for elimination and decomposition of organic compound were added. The samples, while stirring was heated to one-tenth volume. After adjustment of samples pH to desired value the flotation was performed according to the recommended procedure.

Homogenized soil sample 20 g or blood sample 20 mL was weighed accurately and in a 200 mL beaker was digested in the presence of an oxidizing agent with the addition of 10 mL concentrated HNO_3 and 2 mL 70 % $HClO_4$ was added and heated for 1 h. The content of the beaker was filtered through a Whatman No. 40 filter paper and diluted to 150 mL with distilled water. Then its pH was adjusted to 8.5 and the recommended procedure was applied[16].

A Varian AA-220 (Sydney, Australia) atomic absorption spectrometer equipped with deuterium correction and nickel hollow cathode lamp as the radiation source was used. All absorption measurements were performed under the following operation conditions: wavelength: 232 nm; band pass: 0.5 nm; current: 15 mA and using an air-acetylene flame. A pH meter, Metrohm744A, was used for pH measurements.

Procedure: To the solution containing not more than 50 µg of Ni, 5 mL of 0.02 mol L^{-1} EDTA solution and 10 mL of boric acid/sodium borate buffer was added. The solution was transferred to a 250 mL separating funnel; then 2 mL dimethyl glyoxime (2 % (w/v)) and 10 mL *n*-hexane were added sequentially. The funnel was stoppered, vigorously shaken for 2 min, then left to rest for a few minutes. As soon as the floating layer had settled at the organic interface, both the upper organic and lower aqueous layers were discarded by slowly opening the cock of the funnel. The floated layer was completely separated by adhering to the inner walls of the funnel was then dissolved in 5 mL of 1 mol L^{-1} nitric acid. Finally, its absorbance was measured by FAAS at the wavelength of 322 nm, against a reagent blank, which was prepared in the same manner.

RESULTS AND DISCUSSION

The reaction between nickel and dimethyl glyoxime is a well-established process. Dimethylglyoxime reacts with nickel ions in a neutral or ammoniacal medium to form a pink, flocculent precipitate which has been the basis of the well-known gravimetric method for determining nickel. The nickel dimethylglyoximate chelate is soluble in $CHCl_3$ and other non-polar organic solvents. The extraction of $Ni(HDm)_2$ is primarily important in the separation of nickel, but relatively large quantities of nickel have been determined by of the pale yellow chloroform solution of $Ni(HDm)_2$. Also in an alkaline medium and in the presence of oxidants, nickel forms a brown-red, water soluble dimethyl glyoxime complex which is the basis of the popular method for determining nickel. In this complex, nickel is in the IV oxidation state and the anionic complex[3] has the formula $Ni(Dm)_3^{2-}$. Primary investigation showed that any of each two complexes could not float completely in the interface of liquid and organic phase because of solubility in water and organic phase of $Ni(Dm)_3^{2-}$ and $Ni(HDm)_2$, respectively. Thus a different complex of nickel and dimethyl glyoxime was studied. As it was observed, in more basic pHs and with dimethyl glyoxime which dissolved in NaOH solution a different complex could be formed that is floated in interfaces of two phases.

$$Ni^{2+} + 2\ DH_2 \longrightarrow Ni(DH)_2 + 2H^+$$

$$Ni(DH)_2 + 2OH^- \longrightarrow [NiD_2]^{2-} + 2H_2O \text{ (in alkaline solution)}$$

$$Ni^{2+} + 2DH_2 + 2OH^- \longrightarrow [NiD_2]^{2-} + 2H^+ + 2\ H_2O$$

Though the spectroscopic evidence indicated the presence of various nickel-dimethyl glyoxime complexes with different ratios of metal to ligand (1:2 and 1:4) in solution, the difficulties still encountered in the identification of a 'metastable' complex are not clearly understood[17].

The various parameters such as pH, shaking times and the concentration of the ligand, which influence the flotation of nickel-dimethyl glyoxime complex, were optimized.

Optimization: The effect of the pH on the flotation of the complex was investigated by varying the pH of Ni(II) solution (8.5×10^{-7} mol L^{-1}) in the range from 4 to 12 before the addition of the organic phase. The results in Fig. 1, indicates that the maximum absorbance occur at the pHs above 9.

The decrease in absorbance at lower pH values was attributed to the protonation of the weakly basic coordination group of ligand, also in neutral pHs $Ni(HDm)_2$ could be formed, which is dissolved somewhat in *n*-hexane. In the subsequent work, pH 10 was selected.

Fast formation of Ni-DMG complex and no solubility of complex in *n*-hexane are depending to kind of dimethyl glyoxime solvent.

If dimethyl glyoxime had solved in ethanol, efficiency of flotation would be low but flotation efficiency increase in more basic solvents because of increasing polarity of Ni-DMG c omplex. The effect of the agitation time on the flotation was studied by varying the shaking time between 10 and 180 s. The result of the investigation indicates that the time of 60 s is

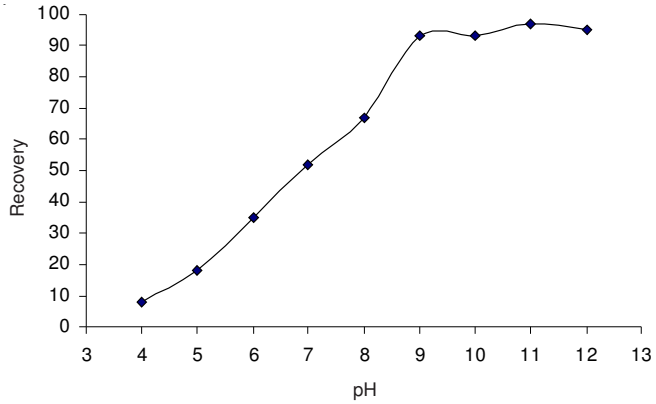

Fig. 1. Effect of pH on the flotation process at the conditions where: $C_{Ni(II)} = 8.5 \times 10^{-7}$ mol L^{-1} and $C_{DMG} = 4 \times 10^{-4}$ mol L^{-1}

sufficient for the quantitative formation and flotation of the complex.

The effect of the dimethyl glyoxime concentration on the flotation of the complex was studied over the concentration range of 0.1×10^{-5} to 1×10^{-3} mol L^{-1}. As shown in Fig. 2, maximum absorbance occurs to dimethyl glyoxime concentrations above 2×10^{-4} mol L^{-1}. Since by increasing the concentration of Ni(II) ions, a greater amount of dimethyl glyoxime was required, a solution with 4×10^{-4} mol L^{-1} dimethyl glyoxime was chosen for further investigations.

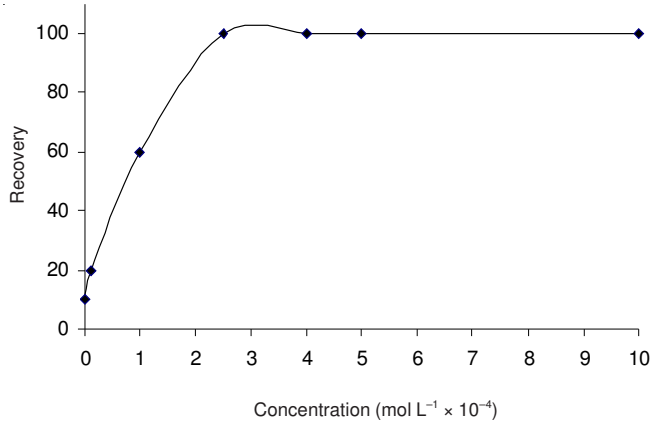

Fig. 2. Effect of dimethyl glyoxime concentration on the determination of Ni(II) at the conditions where: pH = 10 and $C_{Ni} = 8.5 \times 10^{-7}$ mol L^{-1}

Flotation of the complex was investigated with several organic solvents. It was found that the absorbance depends on the solvent. For example, at the optimum conditions, the absorbance values for the flotation of 8.5×10^{-7} mol L^{-1} Ni(II) with cyclohexane, *n*-heptane and *n*-hexane were 0.438, 0.462 and 0.486, respectively. In addition, quicker separation between the phases was observed using *n*-hexane. Moreover, it was chosen for the further investigations. Also the complex is dissolved somewhat in solvent such as, toluene, xylene and chloroform.

A possible concern was whether a high enrichment factor could be realized.

This was investigated by carrying the flotation processes and varying the volume of the aqueous solution between 20 and 250 mL, while maintaining the amounts of nickel and the organic-phase constant. It was found that the flotation process was quantitative over the range of 20-150 mL of the aqueous phase.

A higher volume, however, resulted in a decrease in the efficiency of the flotation process.

Precision and detection limit: The relative standard deviation (10 replicate analyses) at 50 μg L^{-1} for nickel cation was 2.1 % and corresponding to detection (based on 3s) was 2 μg L^{-1}.

Interferences: The most significant interferences for the nickel determination with dimethyl glyoxime are Cu^{2+}, Co^{2+} and Fe^{2+} that produce stable complexes with the organic reagent.

Fortunately, in this flotation method, the complex with dimethyl glyoxime could not be floated in interface of two phases and have not any interference in the determination of Ni^{2+}. However, 5 mL of 0.02 M EDTA solution was added to prevent the formation of insoluble compounds in the alkaline medium.

Application: To validate the methodology, the proposed method was applied to different environmental and biological samples for nickel determination. The wastewater was collected from an electroplating plant. Along with the samples, several known amounts of Ni(II) were spiked to examine the reliability of the method (Table-1).

TABLE-1
DETERMINATION OF NICKEL IN REAL SAMPLES

Sample	Added (μg L^{-1} or μg g^{-1})	Measured[a] (μg L^{-1})	R.S.D. (%)	Recovery (%)
Soil	0	N.D.[b]	–	–
	100	96.2	2.7	96
	200	194.5	2.9	97
Blood	0	37.4	3.1	–
	100	132.4	3.0	97
	200	231.5	3.2	96
Well water	0	N.D.[b]	–	–
	100	94.4	2.1	94
	200	191.8	2.2	95
Wastewater	0	114.6	2.5	–
	100	208.5	2.6	97
	200	303.4	2.6	96

[a]The results are reported as the average value from five sample measurements; [b]Not Detected.

Furthermore, the accuracy of the method was investigated by analysis of standard reference material alloys (NIST 864) by flotation spectrometry method. The certified nickel was 73.10 % and nickel found was 73.07 ± 0.08 %, in good agreement with the certified value at the 95 % confidence level.

Conclusion

This work has demonstrated the ability of nickel determination in the real samples with a good accuracy and selectivity. The AAS method, which is established as an accepted method for the determination of silver traces, exhibits insufficient sensitivity and poor detection limit for direct determination of, especially in the presence of some ions, such as Fe, Ag and Cu at high level, furthermore, the accuracy is endangered[3].

In comparison with the extraction-spectrophotometric methods in which the organic solvents are usually harmful to

environment, the organic solvent used in this method does not polluted and can be used repeatedly without any purification process. Consequently, this method can be carried out easily without any sophisticated devices, especially for the aquatic solutions.

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