

Solid phase extraction of nickel as methylthymol blue complex on naphthalene adsorbent and flame atomic absorption spectrometric determination

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Abstract

A solid-phase extraction procedure has been developed for the determination of nickel prior to its analysis by flame atomic absorption spectrometry (FAAS). The method is based on the adsorption of nickel as a methylthymol blue complex on naphthalene-methyltrioctyl ammonium chloride adsorbent, elution by nitric acid and subsequent determination by FAAS. The effect of different variables such as pH, methylthymol blue concentration, eluent and diverse ions on the recovery of the analyte was investigated. A preconcentration factor of 50 was achieved using the optimum conditions. The calibration graph is linear in the range 10-500 ng mL⁻¹ of nickel in the initial solution with $r=0.9993$. Detection limit based on the $3S_b$ criterion was 3.6 ng mL⁻¹ and 2.4 ng mL⁻¹ for 100 and 150 mL of sample solution, respectively. The relative standard deviation (RSD) was 2.9 and 2.3 % for 100 and 250 ng mL⁻¹ of nickel ($n=7$). The method was applied to the determination of nickel in ore and water samples.

Keywords: Nickel, methylthymol blue, solid-phase extraction, naphthalene adsorbent, flame atomic absorption spectrometry

Résumé

Nous avons développé une procédure d'extraction phase solide pour la détermination du nickel avant son analyse par spectrométrie d'absorption atomique avec flamme (FAAS). La méthode est basée sur l'adsorption du nickel comme complexe de bleu de méthylthymol sur

l'adsorbant de chlorure de naphthalène-méthyltrioctyle ammonium, suivi d'une élution par l'acide nitrique et la détermination subséquente par FAAS. Nous avons étudié l'effet de différentes variables comme le pH, la concentration de bleu de méthylthymol, l'éluant et les divers ions, sur le recouvrement du nickel. Un facteur de préconcentration de 50 a pu être atteint avec les conditions optimales. La droite de calibration était linéaire dans la gamme 10-500 ng mL⁻¹ de nickel dans la solution initiale, avec une valeur de $r = 0.9993$. La limite de détection basée sur le critère $3S_b$ était de 3.6 ng mL⁻¹ et 2.4 ng mL⁻¹ pour 100 et 150 mL de solution de départ, respectivement. L'écart type relatif était de 2.9 et 2.3 % pour 100 et 250 ng mL⁻¹ de nickel ($n=7$). La méthode a été utilisée pour la détermination du nickel dans des échantillons de minerai et d'eau avec de bons recouvrements.

Introduction

Determination of toxic elements in environment samples is one of the most important tasks in analytical chemistry (1). One of these elements is nickel, which is toxic and carcinogenic. Moreover, nickel can cause a skin disorder known as nickel-eczema. This is a considerable health problem particularly among women. Determination of nickel could be carried out by flame atomic absorption spectrometry (AAS) (2, 3), electrothermal atomic absorption spectrometry (ETAAS) (4) and inductively coupled plasma atomic emission spectrometry (ICP-AES) (5). In spite of improvements in sensitivity due to modern analytical techniques, direct determination of metal ions at trace levels is limited due to their low concentration and matrix interference and usually a preconcentration step is required. Conventional separation

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methods such as ion exchange (6) co-precipitation (7) and solvent extraction (8) are frequently used to remove the analyte from matrix elements and improve detection limits through preconcentration of the analyte. In recent years solid-phase extraction has become a preferred method for concentrating the analyte prior to its analysis by FAAS or other techniques. Different solid phases such as polyurethane (9), Amberlite XAD-2 functionalized with *o*-aminophenol (10), XAD-4 functionalized with *o*-aminobenzoic acid (11), cellulose (12), molecularly imprinted polymers (13) and styrene divinyl benzene embedded with 5,7 dichloroquinone-8-ol (14) have been prepared and used for preconcentration of nickel and other elements. Microcrystalline naphthalene (15-17) and benzophenone (18) have also been used as solid phases for adsorptive extraction of metal ion complexes.

In this work we propose a solid-phase extraction method for the determination of nickel by flame atomic absorption spectrometry. Nickel complex with methylthymol blue can be adsorbed on methyltrioctyl ammonium chloride supported on naphthalene used as an adsorbent column. The nickel complex adsorbed on the naphthalene column is eluted with nitric acid solution and its nickel content is determined by flame atomic absorption spectrometry.

Experimental

Instrumentation

A Varian Techtron AA6 flame atomic absorption spectrometer was used for the determination of nickel. It was equipped with a nickel hollow cathode lamp and air – acetylene burner. The instrumental parameters were: wavelength = 232 nm, lamp current = 5 mA, and bandpass = 0.5 nm.

All pH measurements were made by a Metrohm digital pH meter equipped with a combined glass electrode. A Shimadzu rotary oil vacuum pump type SA18 was also used.

Reagents

All reagents were analytical grade and used as purchased. Double distilled water was used to prepare all the solutions. The stock solution of 1000 $\mu\text{g mL}^{-1}$ of nickel was prepared by dissolving 0.5181 g of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Merck) in water, adding 2 mL of concentrated nitric acid and diluting to 100 mL in a volumetric flask. The required concentration of nickel solution was prepared by appropriate dilution of the stock solution. A 1.0 mol L^{-1} of nitric acid solution was prepared by diluting 6.4

mL of HNO_3 (Merck, 70 %, $d=1.42$) to 100 mL in a volumetric flask.

Buffer solution of pH = 9 was prepared by the addition of 10 % of hydrochloric acid to 50 mL of NH_3 (17%, $d = 0.88$) and adjusting the pH to 9 using a pH meter. Methylthymol blue solution of 1.18×10^{-3} mol L^{-1} was prepared by dissolving 0.1 g of methylthymol blue (Merck) in water and diluting to 100 mL in a volumetric flask.

The naphthalene adsorbent solution was prepared by dissolving 10 g of naphthalene and 1 g of methyltrioctyl ammonium chloride in 25 mL of acetone on a hot-plate stirrer at 40°C in a beaker. This solution was transferred to 1000 mL of water while stirring the solution at room temperature. It was stirred for 1-2 h and allowed to stand for 30 min. The supernatant solution of naphthalene coprecipitated with methyltrioctyl ammonium chloride was drained off by decantation and washed twice with water in same way. This adsorbent slurry was stored in a bottle for further use.

General Procedure

A glass column with a very fine bore was used as a preconcentration column. It was filled with the adsorbent and it was slightly pressed in the column with a flat glass rod. 100 mL of the solution containing 10-500 ng mL^{-1} of nickel, 3 mL of 1.18×10^{-4} mol L^{-1} methylthymol blue and 3 mL of ammonium buffer solution (pH = 9) was passed through the column at a solution flow rate of 15 mL min^{-1} . The metal complex was eluted with 3 mL of HNO_3 solution (1.0 mol L^{-1}) and the nickel content of the eluent was determined by FAAS. A blank solution was also run under the same analytical conditions.

Results and Discussion

Methylthymol blue has 4 negative sites (COO^- groups) and therefore it forms negative complexes with metal ions, which are capable of forming ion pairs with the methyltrioctyl ammonium cation on the adsorbent site. The negatively charged complex formed between nickel and methylthymol blue was used for the preconcentration of nickel on the naphthalene-methyltrioctyl ammonium chloride adsorbent.

Effect of pH

The effect of pH on the recovery was evaluated by performing the solid phase extraction at different pH values. The pH values of the sample solutions were adjusted in the range of 3-10 using buffer solutions with

the corresponding pH. According to the results shown in Fig. 1, maximum recoveries were obtained at pH values between 9-10. Therefore, pH = 9 was selected as optimum and an ammonia-ammonium chloride buffer with pH = 9 was used to maintain this pH.

Effect of methylthymol blue concentration

The effect of methylthymol blue concentration on the retention of the nickel methylthymol blue complex on the adsorbent was also investigated. The concentration of methylthymol blue was varied in a series of 100 mL volumetric flasks containing 250 ng mL⁻¹ of nickel and the general procedure was followed. The results shown in Fig. 2 indicate that the highest recovery was obtained at methylthymol blue concentration of 3.54×10^{-5} mol L⁻¹ in the final solution. Therefore, this concentration was selected as optimum. 3 μ L of 0.118 mol L⁻¹ was added to 100 mL of sample solution to achieve this concentration.

Effect of eluent concentration and volume

Nitric acid was found to be an effective eluent for the elution of the adsorbed analyte complex. When using hydrochloric and sulfuric acid, the recovery of nickel determined in the eluents by FAAS was about 60 and 75 % respectively, whereas that of nitric acid was about

90 %. Therefore, the effect of nitric acid concentration on the absorption signal of nickel was examined. As shown in Fig. 3 the recovery increased as the HNO₃ concentration was increased up to 1 mol L⁻¹, at which point the recovery then remained constant. The concentration of nitric acid selected for subsequent studies was 1.0 mol L⁻¹. Different volumes of the 1.0 mol L⁻¹ nitric acid were used to strip the complex. The highest recovery was obtained when 3 mL of nitric acid was used. Hence, 3 mL was chosen for the elution of complex in subsequent studies.

Effect of sample and eluent flow rates

The flow rate of the sample solution and eluent through the column are very important parameters because they control the time of adsorption and elution, hence the analysis time can be greatly affected. The effect of sample and eluent flow rates on the recovery of nickel was examined in the range of 2-15 mL min⁻¹. It was found that the retention and elution of the nickel complex was not affected by the flow rates and a flow rate of 15 mL min⁻¹ was selected to decrease the analysis time.

The effect of amount of methyltrioctyl ammonium chloride

The amount of methyltrioctyl ammonium chloride

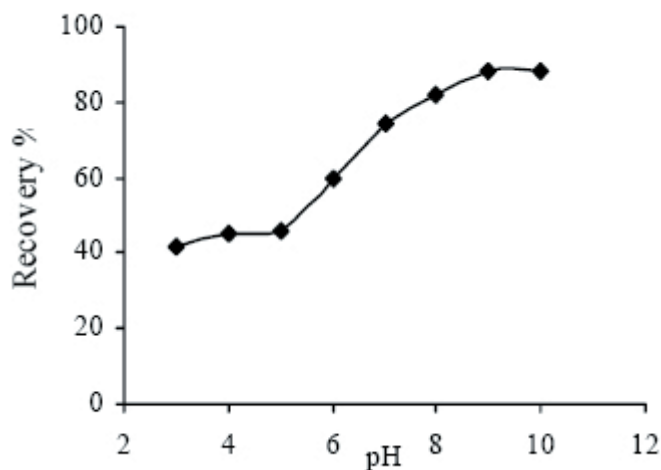


Figure 1. The effect of pH on the recovery of 250 ng mL⁻¹ of Ni. Conditions: volume of the sample = 100 mL, methylthymol blue concentration = 3.54×10^{-5} mol L⁻¹.

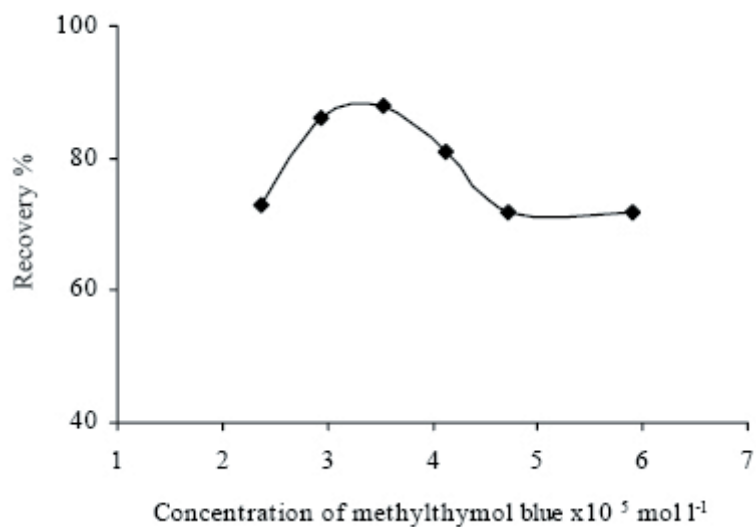


Figure 2. The influence of methylthymol blue concentration on the recovery of 250 ng mL^{-1} of Ni. Conditions: volume of the sample = 100 mL, pH = 9.

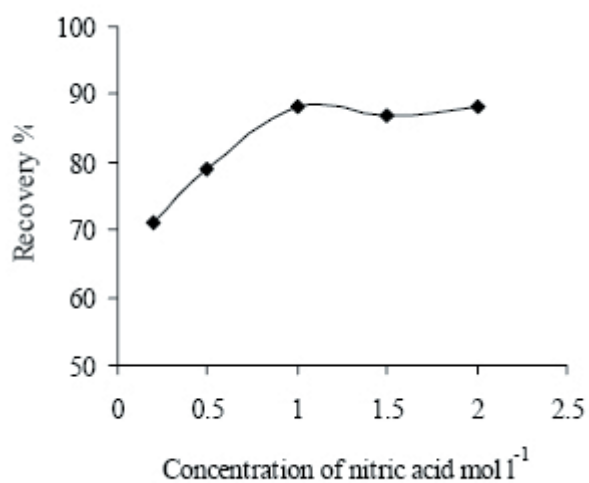


Figure 3. Effect of nitric acid concentration on the recovery of 250 ng mL^{-1} of Ni. Conditions: volume of the sample = 100 mL, pH = 9, methylthymol blue concentration = $3.54 \times 10^{-5} \text{ mol L}^{-1}$.

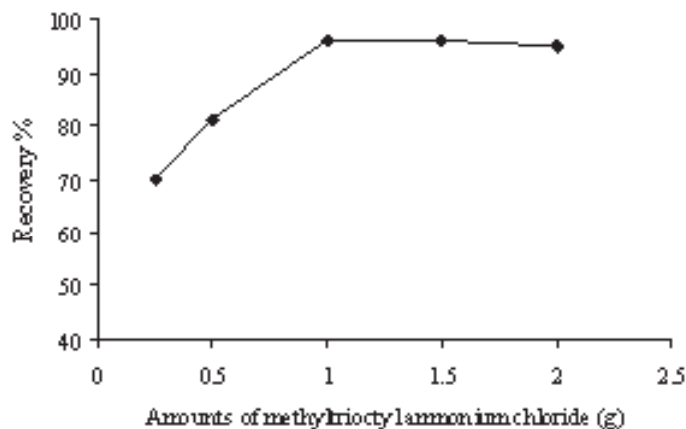


Figure 4. The effect of the amount of methyltriethyl ammonium chloride loaded on the column on the recovery of 250 ng mL⁻¹ of Ni,. Conditions: volume of the sample = 100 mL, pH = 9, methylthymol blue concentration = 3.54×10^{-5} mol l⁻¹.

loaded on naphthalene was optimized and the results are shown in Fig. 4. The recovery of the nickel increased up to a loading of 1 g of methyltriethyl ammonium chloride on 10 g of naphthalene, and above that value the recovery remained constant. Therefore, 1 g of loading was chosen as optimum.

Effect of sample volume

For the analysis of real samples by first using a pre-concentration step, the volume of the sample is one of the important parameters for obtaining a high pre-concentration factor. It was found that the recovery was constant when up to 150 mL of the sample was used. At higher volumes the recovery decreases. The pre-concentration factor was calculated by the ratio of highest sample volume, 150 mL, to the eluent volume, 3 mL. Therefore, a pre-concentration factor of 50 could be achieved.

Analytical performance

The calibration graph is linear in the range 10-500 ng mL⁻¹ of nickel in the initial solution. The equation of the line is $A = 9 \times 10^{-4}C - 5 \times 10^{-4}$ with $r=0.9993$ where A is the absorbance and C is the concentration of nickel in ng mL⁻¹ (or 0.2-10 μ g mL⁻¹ in the final solution after pre-concentration with the equation of $A = 3.7 \times 10^{-2}C - 5 \times 10^{-4}$). Detection limit based on the $3S_b$ criterion was 3.6 ng mL⁻¹ when 100 mL of solution was used. It was

decreased to 2.4 ng mL⁻¹ when 150 mL of the solution was used. The relative standard deviation (RSD) for 100 and 250 ng mL⁻¹ of nickel was 2.9 and 2.3 % (n=7), respectively.

Interference studies

The interference due to co-existing ions in the determination of 250 ng mL⁻¹ of nickel was studied by applying the general procedure described in the experimental section. Any deviation of ± 5 % or more from the standard absorbance value was taken as interference. The results are shown in Table 1.

Applications to real samples

The accuracy of the method was investigated by determining nickel in an ore sample, drinking water and water from the river. 10 mL of concentrated nitric acid was added to 1 g of ore sample and was heated on a hot plate. Then, it was cooled and filtered, and diluted to 100 mL in a volumetric flask. 25 mL of this solution was treated using the general procedure. The results for the ore are given in Table 2 and are compared with those obtained by direct FAAS. As can be seen, there is a good agreement between the two methods. The results for spiked water samples are given in Table 3. The recoveries obtained revealed that the proposed method produces accurate results.

Table 1. Effect of interfering ions on the determination of nickel.

Interfering Ion	Tolerance ratio
Ba ²⁺ , Pd ²⁺ , Bi ³⁺ , Na ⁺ , Cr ³⁺ , Fe ³⁺ , Al ³⁺ , K ⁺ , Au ³⁺ , Sn ²⁺ , I, CH ₃ COO ⁻ , F ⁻ , SO ₄ ²⁻ , NO ₂ ⁻ , Ca ²⁺ , Cd ²⁺ , Ti ⁴⁺ , Hg ²⁺	1000
Sr ²⁺ , Cu ²⁺ , Zn ²⁺ , Mn ²⁺ , Pb ²⁺	100
	10

Table 2. Determination of nickel in an ore sample.

Proposed Method ^a	[Nickel] (µg/g)	Relative error %
	Direct FAAS Method ^a	
1.15 ± 0.03	1.18 × 0.03	2.54

a. $\bar{x} \pm ts/\sqrt{n}$ at 95% confidence (n = 5)

Table 3. Determination of nickel in water samples.

Sample	Nickel added (ng/mL)	Nickel found ^a (ng/mL)	Recovery %
tap water	0	ND	
	50	48 ± 1	96
	250	245 ± 3	98
river water	0	30 ± 1	-
	100	126 ± 3	97
	250	266 ± 4	95

^a $\bar{x} \pm ts/\sqrt{n}$ at 95% confidence (n = 5)

Conclusion

The results of the present investigation show that solid phase extraction using naphthalene as an adsorbent provides a simple and sensitive method for preconcentration of trace amounts of nickel. The precision based on replicate analysis is less than 5 % for the analytes and is as quantitative for spiked and ore samples as compared with direct FAAS. The detection limit achieved is lower than some of the previously reported methods (6,9,11,12).

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