

# Research Journal of Pharmaceutical, Biological and Chemical Sciences

## Determination of Nickel by Flame Atomic Absorption Spectrometry after Dispersive Liquid-Liquid Microextraction

Sánchez Rojas F\*, Bosch Ojeda C and Cano Pavón JM

Department of Analytical Chemistry, Faculty of Sciences, University of Málaga, E-29071, Málaga, Spain.

### ABSTRACT

In this article, a new method was developed for the determination of nickel ion by combining dispersive liquid-liquid microextraction preconcentration with flame atomic absorption spectrometry. 1, 5-bis (di-2-pyridyl) methylene thiocarbonylhydrazide (DPTH) was used as chelating agent, and chloroform and methanol as extraction and dispersive solvent. Several factors that may be affected on the extraction process, like, extraction solvent, disperser solvent, the volume of extraction and disperser solvent, pH of the aqueous solution and extraction time were optimized. Under the optimal conditions, the calibration curve was linear in the range of  $10 \text{ ng mL}^{-1}$  to  $0.5 \text{ } \mu\text{g mL}^{-1}$  of nickel and detection limit based on three times the standard deviation of the blank ( $3S_b$ ) was  $5 \text{ ng mL}^{-1}$  in original solution. The relative standard deviation for seven replicate determination of  $0.2 \text{ } \mu\text{g mL}^{-1}$  nickel was  $\pm 2.3\%$ . The developed method was validated by the analysis of one certified reference material and applied successfully to the determination of nickel in water, plant and food samples with satisfactory analytical results. The proposed method was simple, rapid, cost-efficient and sensitive.

**Keywords:** Nickel; dispersive liquid-liquid microextraction; flame atomic absorption spectrometry; water and food samples

*\*Corresponding author*

Email: fsanchezr@uma.es



## INTRODUCTION

In recent years, pollution of the environment by toxic elements has been dramatically increased; therefore, the determination of toxic metals such as nickel in environmental samples is a very important task. Nickel is a chemical element present in trace amounts in natural water samples and is a nutritionally essential trace metal for at least several animal species, microorganisms, and plants, therefore either deficiency or toxicity symptoms can occur when too little or too much Ni is taken up [1]. Interest in the determination of nickel has been increased over the last few years because of its influence on human body. Adverse effects of water soluble inorganic nickel species occur when contact with the skin. After inhalation, it causes nickel dermatitis, respiratory tract irritation and asthma. The presence of this metal in elevated levels causes a skin disorder known as “nickel-eczema” [2, 3].

Due to the low concentration of nickel in environmental samples and the matrix interferences, the direct determination of nickel in environmental samples by atomic spectrometric techniques, e.g. flame and graphite furnace atomic absorption spectrometry (FAAS and GFAAS) or inductively coupled plasma-optical emission spectrometry (ICP-OES), is usually difficult, and an initial sample pretreatment, such as preconcentration of the analyte and matrix separation, is often necessary. Recently, dispersive liquid–liquid microextraction (DLLME) has been developed as a new mode of liquid-phase microextraction and attracted increasing attention for its simple operation, high enrichment factor, rapidness, and high extraction efficiency [4].

FAAS is more advantageous than common techniques, since it presents desirable characteristics, such as low costs, operational facilities, high analytical frequency, and good selectivity for determination of trace and toxic metals in different environmental samples [5]. In this way, Khani and Shemirani developed a method for the determination of nickel and manganese by ionic liquid based DLLME coupled to FAAS detection [6]. Other published determinations of nickel by DLLME are combined with GFAAS [7-10].

This article presents the development of a procedure for the preconcentration of nickel from different samples and its determination by FAAS. This procedure is based on DLLME after complexing this metal with 1,5-bis(di-2-pyridylmethylene) thiocarbonohydrazide (DPTH).

## MATERIALS AND METHODS

### Instrumentation

Phase separation was achieved with a centrifuge Selecta Centromix in 10 mL calibrated conical tubes.

A Varian Model SpectrAA 50 (Mulgrave, Victoria, Australia) flame atomic absorption spectrometer was used for the analysis with the appropriate nickel hollow cathode lamp. The operating parameters were set as recommended by the manufacturer. Atomic absorption

measurements were carried out in an air-acetylene flame. The following conditions were used: absorption line Ni: 232.0 nm; slit widths: 0.2 nm; and lamp currents: 4 mA.

### Reagents and samples

High purity water (resistivity 18.2MΩcm) obtained by a Milli-Q® water purification system (Millipore, Bedford, MA, USA) was used throughout this work. 1000 mg L<sup>-1</sup> stock solutions of nickel (E. Merck, Darmstadt, Germany). Working standard solution was obtained daily by stepwise dilution of the standard stock solution. DPTH solution in DMF was prepared by dissolving solid reagent samples prepared and purified by the authors [11].

The accuracy of the method for determination of nickel content was checked by analyzing the reference standard material BCR 176 “City waste incineration ash”; for this the certified nickel content was 123.5±4.2 mg kg<sup>-1</sup>. The sample was first prepared in accordance with the instructions on the analysis certificate, after which an accurately weighed amount (50.4 mg) was subjected to microwave digestion. The solution obtained was then adjusted to the optimum pH and, finally, the sample was diluted to 100 mL with de-ionized water in a calibrated flask.

The proposed method was also evaluated by analysis of nickel in several spiked food samples. The Ni concentrations in all the original samples were below the detection limit. For this purpose, standard solutions containing nickel were added to 0.3–1.2 g of diverse food and the resulting materials were mineralized by microwave digestion, adjusted pH and diluted at convenient volume.

Natural waters were collected in polypropylene bottles previously cleaned by soaking for 24 h in 10% (v/v) nitric acid and finally rinsed thoroughly with ultra-pure water before use.

### Dispersive liquid-liquid microextraction procedure

For DLLME under optimum conditions, 10 mL analyte solution containing nickel, 2 mL acetate buffer solution pH 5.4, 1 mL of 0.05% DPTH solution as chelating agent was placed in a 10 mL screw cap glass test tube. Then, 1 mL of methanol (as disperser solvent) and 0.5 mL of chloroform (as extraction solvent) was rapidly injected into a sample solution by using a microsyringe. A cloudy solution was formed in the test tube and separation of the phases was achieved by centrifugation at 3800 rpm for 5 min. After this process, a small droplet of organic phase was sedimented in the bottom of conical test tube. After removal of the whole aqueous solution, the extraction phase was aspirated into the FAAS.

## RESULTS AND DISCUSSION

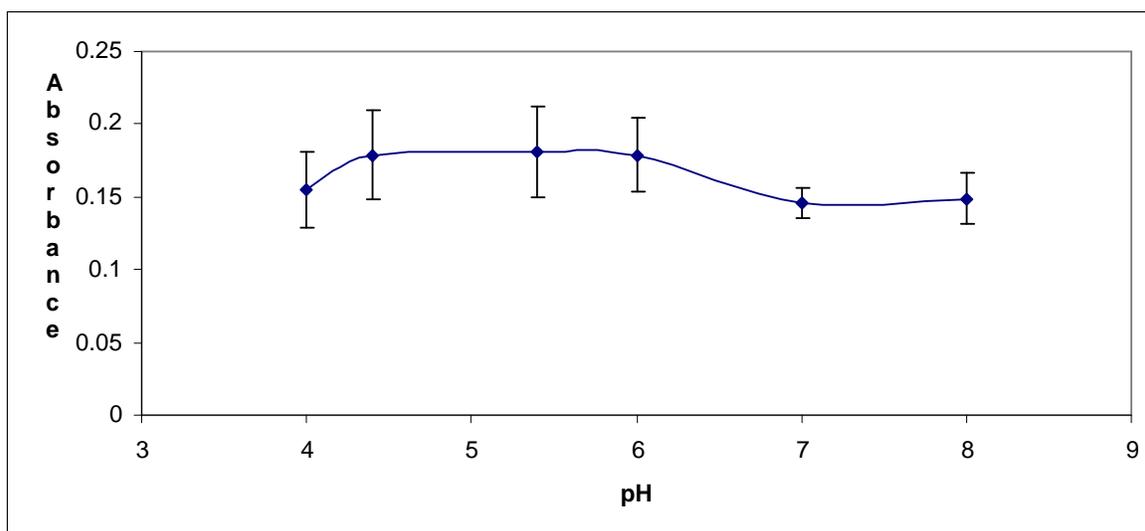
For higher sensitivity, selectivity and precision for metal determination with the DLLME method, the effect of the main parameters, like the type of disperser and extraction solvent,

sample, sample acidity, amount of chelating agent, and extraction time, were studied and optimized thoroughly. All analyses were carried out in triplicate.

### Effect of pH

It is well known that the pH of the sample solution was one of the important factors affecting the formation of complexes. Fig. 1 displayed the effect of pH on the signal intensity of nickel. As can be seen, the signal intensity of Ni was constant from pH 4.4 to 6.0. Therefore, a pH 5.4 was selected for further study.

Figure 1: Influence of pH on the DLLME procedure

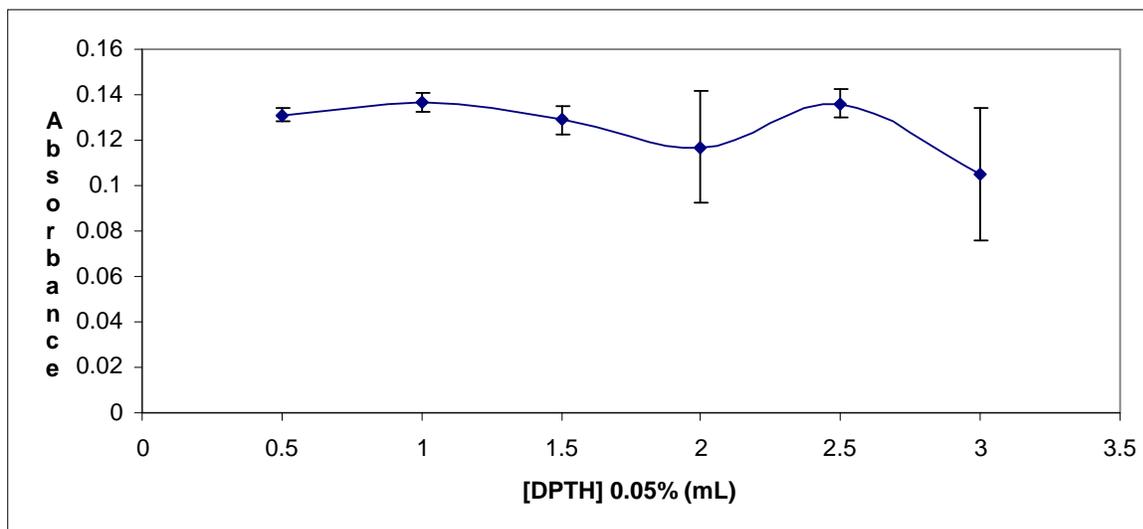


Also, the influence of acetate buffer solution amount was investigated for variation of volume added from 1 to 5 mL. The extraction efficiency was stable in all studied range. A volume of 2 mL was selected as optimum value for subsequent work.

### Effect of DPTH concentration

Concentration is a critical variable to be optimized in extraction methods based on a chelating agent such as DPTH. In order to determine the optimal reagent concentration, an experiment was carried out in which all other experimental variables, except reagent concentration, remained constant. The variation of the analytical signal as a function of the concentration of DPTH in the range of  $2.5 \times 10^{-3}$ – $1.5 \times 10^{-2}$ % (w/v) was studied, and the experimental results in figure 2 demonstrated that the signal intensity of the analyte was practically constant by DPTH at concentrations up to about  $1.5 \times 10^{-2}$ % (w/v). A  $5 \times 10^{-3}$ % (w/v) DPTH was selected for further research.

Figure 2: Effect of [DPTH] on the DLLME procedure



### Effect of ionic strength

The influence of ionic strength was examined by studying the extraction efficiency for NaCl concentration in the range 0-3%. Ionic strength had a negative effect upon percent recovery and sensitivity.

### Effect of disperser solvent and its volume

In DLLME, selecting an appropriate disperser solvent is important, since disperser solvent should be miscible with both extraction solvent and aqueous sample. For the sake of acquiring the most suitable disperser solvent, three kinds of disperser solvents: acetone, acetonitrile, ethanol and methanol were studied. The best results were achieved with methanol.

The influence of the volume of disperser solvent methanol on the absorbance of Ni was also examined. Results showed that there was no significant difference among absorbances obtained by the volume studied (0.5 to 2 mL). So, in further experiments, 1 mL of disperser solvent volume was selected.

### Effect of extraction solvent and its volume

The extraction solvent was selected based on higher density than water, extraction capability for the compounds of interest, and low solubility in water [12]. Several solvents such as chloroform, dichloromethane, carbon tetrachloride, were tested to choose a suitable extraction solvent. Results showed that the maximum extraction recovery was obtained by using chloroform.

To examine the effect of extraction solvent volume, solutions containing different volumes (0.3-0.7 mL) of chloroform were subjected to the same DLLME procedure. When the volume of extraction solvent was increased, the volume available for the measurement also increased, but the enrichment factors decreased. Thereby, in the following studies, the optimum volume of 0.5 mL was selected for the extraction solvent although for samples with less nickel amount 0.3 mL chloroform can be used in order to obtain higher preconcentration factor.

### Analytical features

Under optimum conditions, the calibration curves were observed as linear in the concentration range of 10–500 ng mL<sup>-1</sup> Ni by using 10 mL of the solution. The correlation coefficients of the calibration curve equations were above of 0.994, which indicates that a good linear regression was established between the absorbances and the concentrations. The detection limit was calculated according to three times the standard deviation of the blank signals with the preconcentration step. The precision were expressed as a relative standard deviation (RSD) for seven replicate measurements of different Ni(II) concentrations. Finally, the enrichment factors were calculated by the ratio of slope of preconcentrated samples to those obtained without preconcentration. The results were given in Table 1.

**Table 1: Analytical features of the proposed method**

	With different types and volumes of extractant		
	0.5 mL chloroform	0.3 mL chloroform	0.5 mL dichloromethane
Dynamic range	10–500 ng mL <sup>-1</sup>	10–500 ng mL <sup>-1</sup>	10–500 ng mL <sup>-1</sup>
Regression equation	$y = 0.0002x + 0.031$	$y = 0.0008x + 0.0658$	$y = 0.0006x + 0.2066$
Correlation coefficient (R) <sup>2</sup>	0.9943	0.9978	0.9952
Detection limit	5 ng L <sup>-1</sup>	-	-
R.S.D. (%) (n=7)	2.8 (for 50 ng mL <sup>-1</sup> ) 2.3 (for 200 ng mL <sup>-1</sup> ) 1.4 (for 500 ng mL <sup>-1</sup> )	-	-
Preconcentration factor	20	80	60

### Effect of foreign ions

In order to evaluate the effect of other metal ions in the preconcentration procedure, a 10 mL volume of sample solution containing 200 ng mL<sup>-1</sup> of Ni in the presence of various amounts of other ions was prepared and analyzed by the proposed method. The tolerance limit was defined as the concentration of added ion that caused less than ± 5% relative error in the determination of Ni<sup>2+</sup>. About 500-fold excess of Fe<sup>3+</sup>, Ca<sup>2+</sup>, Ba<sup>2+</sup>, Mn<sup>2+</sup>, K<sup>+</sup>, I<sup>-</sup>, F<sup>-</sup>, SO<sub>4</sub><sup>=</sup> and HCO<sub>3</sub><sup>-</sup> do not affect Ni signal. Cd<sup>2+</sup>, Hg<sup>2+</sup>, Cr<sup>3+</sup> and Al<sup>3+</sup> do not interfere at 100-fold excess. Cu<sup>2+</sup>, Bi<sup>3+</sup>, Zn<sup>2+</sup> and Co<sup>2+</sup> can be tolerated at 50-fold excess.

## Analysis of standard reference material

In order to assess the accuracy and validity of the presented procedure, the method was applied to the determination of nickel in a certified reference material (BCR-176 “City Waste Incineration Ash”), which was analyzed according to the proposed method. It was found that analytical results were in good agreement with the certified values (Table 2).

**Table 2: Determination of nickel in real samples**

Sample	Added (ng mL <sup>-1</sup> )	Found (ng mL <sup>-1</sup> ) <sup>a</sup>	Recovery (%)
Tap water	20	20.0 ± 1.0	100.0
Well water	20	20.0 ± 1.2	100.0
	Added (µg g <sup>-1</sup> )	Found (µg g <sup>-1</sup> ) <sup>a</sup>	
Apple	13.2	12.2 ± 0.3	92.4
Rice	10.7	10.9 ± 0.5	101.7
Lentil	24.2	24.4 ± 1.1	100.9
Lettuce	23.5	23.5 ± 0.3	100.0
Liver	41.4	44.8 ± 0.6	108.2
Chick-pea	10.3	10.2 ± 0.1	99.0
Fish	12.5	12.3 ± 0.8	98.4
Bignonia leaves	20.8	22.2 ± 0.6	106.7
Pinus leaves	22.3	22.4 ± 1.2	100.4
	Certified value (mg kg <sup>-1</sup> )	Found value (mg kg <sup>-1</sup> ) <sup>a</sup>	
BCR 176	123.5 ± 4.2	125.5 ± 6.6	101.6

<sup>a</sup>. mean ± standard deviation (n=3)

## Determination of nickel in food, plant and water samples

In view of the application of the method to the determination of nickel in food and plant samples, the ability to recover nickel from different samples spiked with nickel was investigated. All food samples were arbitrarily selected and acquired from a local superstore. For this purpose, standard solutions containing different quantities of nickel were added to samples and the resulting material was prepared as described under Experimental. Standard additions method was used in all instances and the results were obtained by extrapolation. The results of these analyses are summarised in Table 2, and indicated excellent recoveries in all instances.

In the laboratory, before the preconcentration procedure, all the water samples were filtered through a 0.45 µm pore-size membrane filter to remove suspended particulate matter and were stored at 4 °C. The optimized methodology was applied for the determination of nickel in different water samples and the analytical results along with the recovery are given in Table 2. As can be seen, good recoveries were obtained in the spiked real samples analysis.



## CONCLUSION

A method of DLLME coupled to FAAS has been developed for the sensitive determination of nickel in different samples. The method significantly improved the performance of the FASS detection for nickel. DLLME offers advantages over traditional liquid-liquid extraction, such as elimination of handling large volumes of organic solvents. The method has been validated by the analysis of standard reference material.

## ACKNOWLEDGEMENT

The authors thank to the Ministerio de Ciencia e Innovación for supporting this study (Projects CTQ2009-07858) and also the Junta de Andalucía.

## REFERENCES

- [1] Cempel M and Nikel G. Pol J Environ Stud 2006; 15:375.
- [2] Christensen JM, Kristiansen J, Nielsen NH, Menne T and Byrialsen K. Toxicol Lett 1999; 108:185.
- [3] Kristiansen J, Christensen JM, Henriksen T, Nielsen NH and Menne T. Anal Chim Acta 2000; 403:265.
- [4] Ojeda CB and Rojas FS. Chromatographia 2009; 69: 1.
- [5] Pereira MD and Arruda MAZ. Microchim Acta 2003; 141:115.
- [6] Khani R and Shemirani F. Clean – Soil Air Water 2010; 38: 1177.
- [7] Jiang H, Qin Y and Hu B. Talanta 2008; 74: 1160.
- [8] Shirkhanloo H, Rouhollahi A and Mousavi HZ. J Chinese Chem Soc 2010; 57: 1035.
- [9] Sereshti H, Khojeh V and Samadi S. Talanta 2011; 83:885.
- [10] Mizzaei M, Behzadi M, Abadi NM and Beizaei A. J Haz Mat doi: 10.1016/j.jhazmat.2010.12.080. 2010.
- [11] Abascal JB, Torres AG and Pavon JMC. Microchem J 1983; 28:132.
- [12] Jahromi EZ, Bidari A, Assadi Y, Hosseini MRM and Jamali MR. Anal Chim Acta 2007; 585:305.