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# Nickel determination in saline matrices by ICP-AES after sorption on Amberlite XAD-2 loaded with PAN

Sérgio L.C. Ferreira *, Cristiane F. de Brito, Alailson F. Dantas, Neyla M. Lopo de Araújo, A.C. Spinola Costa

*Instituto de Química, Universidade Federal da Bahia, Campus Universitário da Federação, Salvador, Bahia 40170-290, Brazil*

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**Abstract**

In the present paper, a solid phase extraction system for separation and preconcentration of nickel (ng $g^{-1}$) in saline matrices is proposed. It is based on the adsorption of nickel(II) ions onto an Amberlite XAD-2 resin loaded with 1-(2-pyridylazo)-2-naphthol (PAN) reagent. Parameters such as the pH effect on the nickel extraction, the effect of flow rate and sample volume on the extraction, the sorption capacity of the loaded resin, the nickel desorption from the resin and the analytical characteristics of the procedure were studied. The results demonstrate that nickel(II) ions, in the concentration range 0.10–275 μg $l^{-1}$, and pH 6.0–11.5, contained in a sample volume of 25–250 ml, can be extracted by using 1 g Amberlite XAD-2 resin loaded with PAN reagent. The adsorbed nickel was eluted from the resin by using 5 ml 1 M hydrochloric acid solution. The extractor system has a sorption capacity of 1.87 μmol nickel per g of Amberlite XAD-2 resin loaded with PAN. The precision of the method, evaluated as the R.S.D. obtained after analyzing a series of seven replicates, was 3.9% for nickel in a concentration of 0.20 μg $ml^{-1}$. The proposed procedure was used for nickel determination in alkaline salts of analytical grade and table salt, using an inductively coupled plasma atomic emission spectroscopy technique (ICP-AES). The standard addition technique was used and the recoveries obtained revealed that the proposed procedure shows good accuracy. 

*Keywords:* Nickel preconcentration; Solid phase extraction; Inductively coupled plasma atomic emission spectroscopy; Alkaline salts

## 1. Introduction

The determination of nickel traces in saline matrices by inductively coupled plasma atomic emission spectrometry (ICP-AES) is difficult, because the aspiration of solutions with high salt concentrations in the plasma can cause problems such as blockage of the nebulizer, considerable background emission, and transport and chemical interferences with a consequent drop in sensitivity and precision [1–4]. Thus, trace determination in saline solutions always needs a prior separation.

* Corresponding author. Tel: +55-71-2375784/2375785; fax: +55-71-2355166/2374117; e-mail: slcf@ufba.br.

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Several papers on this subject have appeared in the literature [5–9]. The process involving extraction in the solid phase has received more acceptance due to a number of possible advantages including availability of the solid phase, getting large preconcentration factors, and the facility for enrichment using systems with continuos flow, besides this they dispense with the need of organic solvents which are usually toxic [10].

A chelating sorbent loaded with dithizone [5] was obtained by chemical reaction with styrene-DVB (5%) copolymer as matrix. It was used for the preconcentration of nickel and other metals. A column containing silica loaded with 8-hydroxyquinoline [6] was used for preconcentration and determination of nickel, iron, zinc and copper by GFAAS. A procedure [7] for preconcentration of nickel, cadmium, cobalt, copper, manganese, lead and zinc was developed. In it, the metal cations were complexed with diethyldithiocarbamate, adsorbed on a $C_{18}$ column and eluted with methanol. Amberlite XAD-2 chemically modified with alizarin red-S [8] and pyrocatechol violet [9] was recommended for the preconcentration and determination of nickel and other metals by spectrometric techniques.

This paper proposes an analytical procedure for the preconcentration and determination of nickel in alkaline salts, using atomic emission spectrometry with inductively coupled plasma, after chelation onto a column containing Amberlite XAD-2 resin loaded with 1-(2-pyridylazo)-2-naphthol (PAN).

Amberlite XAD-2 (polystyrene-divinylbenzene polymer) is a resin very used in preconcentration procedures. In our laboratory, it has been used in the preconcentration and simultaneous determination of zinc and copper in natural waters [11].

PAN is a chromogenic reagent proposed several times for spectrophotometric determinations of metal cations [12]. It reacts with the nickel (II) cation, forming a stable complex of composition 1:2 nickel(II)–PAN. The complex formed has a red color.

## 2. Experimental

### 2.1. Apparatus

An Applied Research Laboratories model 3410 minitorch sequential inductively coupled plasma spectrometer with an IBM PC-AT computer was used. The emission measurements were made using the conditions given in Table 1. A nickel calibration graph (0–2.0 μg $ml^{-1}$) was obtained using solutions prepared from 1 mg $ml^{-1}$ stock solution. The limit of detection and the background equivalent concentration (BEC) were 16

Table 1
Operating parameters for the inductively coupled plasma spectrometer

| | |
|---|---|
| Spectrometer | 1 m, Czerny-Turner, vacuum |
| Grating | 2400 grooves $mm^{-1}$, holographic |
| Bandwidth | 13 pm, 1st order<br>7 pm, 2nd order |
| Slit widths | 20 μm |
| PMT | R955 Hamamatsu |
| RF generator | Crystal controlled solid state exciter, class AB2 amplifier, 27.12 MHz |
| Forward power | 650 W |
| Reflected power | <5 W |
| Torch | 3-Tube minitorch (ARL) |
| Observation height | 9 mm Above load coil |
| Nebulizer | Meinhard concentric glass |
| Spray chamber | Conical glass 45 ml volume, impact sphere |
| Pump | Peristaltic, Gilson Minipuls2 |
| Sample uptake | 2.5 ml $min^{-1}$ |
| Outer argon flow | 7.5 l $min^{-1}$ |
| Intermediate argon flow | 0.8 l $min^{-1}$ |
| Carrier argon flow | 0.8 l $min^{-1}$ |
| Wavelength | 221.646 nm |
| Signal integration time | 5 s |
| Integration for determination | 3 |

and 98 μg $l^{-1}$, respectively. The correlation coefficient was 0.9994.

An Ismatec peristaltic pump model Reglo furnished with tygon tubes were employed to propel the sample solutions. A 300 ANALYSER pH meter was used to measure the pH values.

### 2.2. Reagents

All reagents were of analytical reagent grade unless otherwise stated. Double distilled water was used for the preparation of solutions. The nitric acid and hydrochloric acid were of suprapur quality (Merck). The laboratory glassware was kept overnight in a 5% nitric acid solution. Before use, the glassware was washed with deionized water and dried in a dust-free environment.

The nickel solution (10.00 μg $ml^{-1}$) was prepared by diluting a 1000 μg $ml^{-1}$ nickel solution (atomic absorption, Aldrich) using a 5% hydrochloric acid solution. The PAN solution (0.10%) was prepared by dissolving 0.25 g PAN (Aldrich) in 250 ml ethanol. The hexamine buffer solution (pH 6.5) was prepared by dissolving 56.0 g hexametilenetetramine in 1000 ml deionized water and the pH adjusted with 5% hydrochloric acid solution.

### 2.3. Preparation of the Amberlite XAD-2 column loaded with PAN

XAD-2 was treated with an ethanol–hydrochloric acid–water (2:1:1) solution over night. Later, the resin was rinsed with deionized water until it was pH neutral, being dried in an oven at a temperature of 110°C for 3 h.

The packing of the column must be done using ethanol as eluent because with water the grains of resin float. The resin is saturated with the reagent by elution of 10 ml of a 0.10% PAN solution in ethanol at a flow rate of 0.50 ml $min^{-1}$. Later it is rinsed with water until the complete elimination of excess reagent occurs. All experiments were done in glass columns with a 0.80 cm i.d. and length of 15 cm, containing 1g XAD-2. Before the sample elution the column must be preconditioned by passing a buffer solution.

### 2.4. Procedure for the sorption of nickel(II) on the Amberlite XAD-2

Transfer 25–200 ml of the sample solution containing nickel in the concentration range 0.10–275 μg $l^{-1}$ to a 250 ml beaker, add 10 ml of buffer solution pH 6.5. This solution must be passed through the column at a flow rate of 0.60 ml $min^{-1}$. After passing this solution, the column was rinsed with 10 ml of deionized water. The adsorbed nickel(II) on the column was eluted with 5 ml 1 M hydrochloric acid solution, at a flow rate of 0.60 ml $min^{-1}$. The eluent was collected in a 10-ml volumetric flask with dilution using 1 M hydrochloric acid solution and the nickel determinate by the ICP-AES technique.

## 3. Results and discussion

### 3.1. pH effect on the nickel sorption onto Amberlite XAD-2 resin

The effect of pH on the sorption of nickel(II) ions was studied and the results demonstrated that it is maximum and quantitative ($>95\%$) in the pH range 6.0–11.5, as can be seen in Fig. 1. pH control was done using an acetate buffer with pH 4.0–6.0, a hexamine buffer with pH 6.5, a borate buffer pH 8.0 and an ammonium buffer with pH 10.0. For pH 11.5 a solution of sodium hydroxide was used. In the proposed procedure, a hexamine buffer with pH 6.5–7.0 is recommended because at alkaline pH the PAN reagent reacts with other metallic ions.

### 3.2. Effect of flow rate and sample volume

The effect of flow rate on nickel retention was examined by varying the flow rate from 0.30 to 2.50 ml $min^{-1}$ under optimum conditions. The results demonstrated that the retention of nickel on the resin is quantitative ($>95\%$) only for a flow rate lower than 0.60 ml $min^{-1}$. The effect of the sample volume on the nickel extraction was investigated by passing 25, 50, 100, 200 and

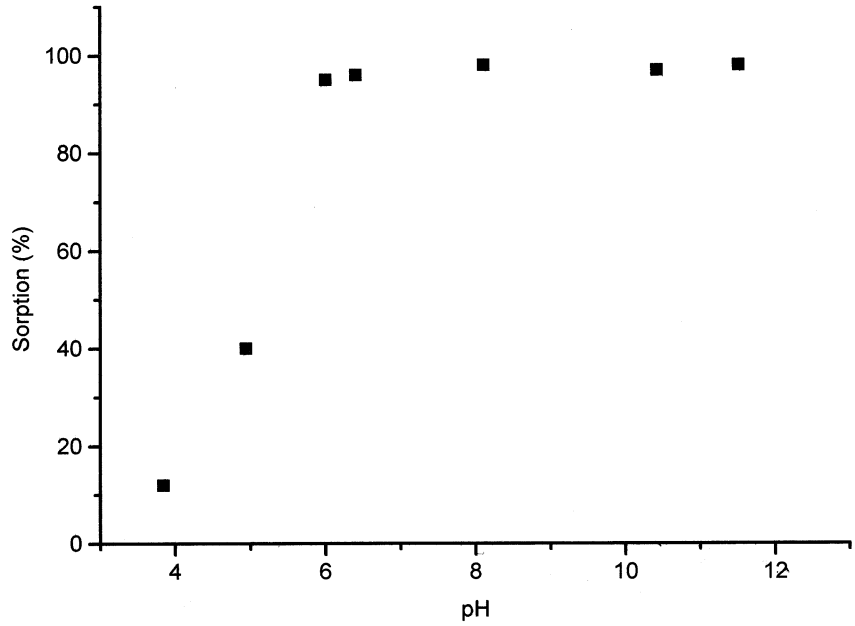


Fig. 1. Effect of pH on the nickel sorption on the XAD-2 column.

250 ml through the column at a constant flow-rate of 0.60 ml $min^{-1}$. In all cases the recovery obtained was higher than 95%.

### 3.3. Effect of electrolytes on the sorption of the nickel

The influence of electrolytes on the sorption of nickel(II) ions in the proposed system was also studied. The results demonstrated that the extraction is quantitative ($>95\%$) even in the presence of 200 ml 30% sodium chloride solution or 200 ml 30% potassium nitrate. The salts used in this experiment were of suprapur quality (Merck).

### 3.4. Sorption capacity

The sorption capacity of the Amberlite XAD-2 resin loaded with PAN for the extraction of nickel was also determined. Increasing amounts of nickel were added to a column containing 1.0 g of loaded resin. The results demonstrated that the resin has a sorption capacity of 1.87 μmol nickel per g XAD-2 resin. Under conditions of maximum adsorption the distribution coefficient was higher than $1.0 \times 10^4$ l $kg^{-1}$.

### 3.5. Nickel desorption from XAD-2 resin

In order to determine the nickel desorption from resin 5.0 ml solutions of hydrochloric acid with concentrations of 0.10, 0.50, 1.0 and 2.0 M were tested. The results demonstrated that the desorption is acceptable ($>95\%$) for solutions with concentrations $\geq 1$ M. In this procedure a concentration of 1 M is recommended.

### 3.6. Application

The proposed procedure can be applied to the preconcentration and separation of nickel, in the concentration range 0.10–275 μg $l^{-1}$, contained in a solution volume of 25–250 ml, by using of 1 g Amberlite XAD-2 resin loaded with PAN reagent.

The precision of the method, evaluated as the R.S.D. obtained after analyzing a series of seven replicates, was 3.9% for nickel in a concentration of 0.20 μg $ml^{-1}$.

The method proposed was applied for nickel determination in alkaline salts and table salt. A volume of 200 ml of the sample solution at a

Table 2
Determination and recovery of nickel in alkaline salt samples

| Sample | Concentration added (ng $g^{-1}$ salt) | Nickel found * (ng $g^{-1}$ salt) | Recovery (%) |
|---|---|---|---|
| NaCl | 0 | $34 \pm 2$ | – |
| | 500 | $504 \pm 16$ | 94 |
| $NaNO_3$ | 0 | $49 \pm 8$ | – |
| | 500 | $526 \pm 10$ | 95 |
| $KNO_3$ | 0 | $38 \pm 3$ | – |
| | 500 | $523 \pm 14$ | 97 |
| KCl | 0 | $39 \pm 4$ | – |
| | 500 | $554 \pm 14$ | 103 |
| Table salt | 0 | $78 \pm 8$ | – |
| | 500 | $548 \pm 16$ | 94 |

* At 95% confidence level.

concentration of 30% was used during the analyses. The standard addition technique was applied and the recoveries obtained revealed that the proposed procedure has good accuracy. The results are described in Table 2.

## 4. Conclusions

The present paper is opportune considering the analytical problem of trace determination in saline matrices by ICP-AES, and the fact that nickel is frequently present at trace levels in these substances.

The great advantages of this procedure are: (i) preparation of the extractor system is simple and fast; (ii) the elution step does not involve the use of organic solvents as in other procedures; (iii) during the nickel desorption the PAN reagent remains in the resin, allowing use of the column several times; (iv) the proposed procedure can be adapted easily for preconcentration and determination of nickel by the flow injection analysis technique.

The recovery obtained, measured by the standards addition technique, revealed that the proposed procedure shows good accuracy.

The procedure proposed was applied for nickel determination in alkaline salts by using ICP-AES, however it can be used for other samples and using other analytical methods such as AAS and GFAAS.

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