

Solid-phase spectrophotometric determination of nickel in water and vegetable samples at sub- $\mu\text{g l}^{-1}$ level with *o*-carboxylphenyldiazoaminoazobenzene loaded XAD-4

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Abstract

A highly sensitive and selective solid-phase spectrophotometric method for the determination of sub- $\mu\text{g l}^{-1}$ level nickel(II) is described. Nickel(II) was sorbed on a styrene-divinylbenzene-type resin Amberlite XAD-4 as a Ni(II)–*o*-carboxylphenyldiazoaminoazobenzene (*o*-CDAA) complex. At pH 9.0, resin phase absorbances at 588 and 800 nm were measured directly with an apparent molar absorptivity of $2.95 \times 10^7 \text{ g mol}^{-1} \text{ cm}^{-1}$. The linear range of the determination was 1.2–41 $\mu\text{g g}^{-1}$ resin. The detection limit and the quantification limit were found to be 0.24 and 0.76 $\mu\text{g g}^{-1}$ resin, respectively. The relative standard deviation of 10 replicate determinations of 1.0 μg nickel(II) in 100 ml sample was of 1.5%. The tolerance limit of coexistent ions was also investigated. Most of them are in tolerable amount. For practical analyses, 1 ml acetylacetone used can eliminate the interferences caused by Cu and Fe. The procedure was validated by analysis a certified water reference material (GBW 08618 Beijing, China) and a tomato leaf certified reference material (GBW 08402 Beijing, China) with the results in agreement with the certified values. The method was applied to the determination of nickel(II) in water and vegetable samples with satisfactory results. © 2004 Elsevier B.V. All rights reserved.

Keywords: Solid-phase spectrophotometry; *o*-Carboxylphenyldiazoaminoazobenzene; Amberlite XAD-4–*o*CDAA; Water; Vegetable

1. Introduction

Nickel was long thought be essential to plants and some domestic animals [1], but not considered to be a metal of biological importance until 1975, when Zerner discovered that urease was a nickel enzyme [2,3]. Compared with other transition metals, nickel is a moderately toxic element. However, it is known that inhalation of nickel and its compounds can lead to serious problems, including cancer of the respiratory system [4]. Moreover, nickel can cause a skin disorder known as nickel-eczema [5]. Therefore, it is of importance to develop sensitive methods for determining nickel in environmental and biological samples. Spectrophotometry is the most common technique used for nickel determination using various chromogenic reagents [6–15], owing to its sim-

plicity and low cost. However, for the spectrophotometric determination of nickel(II) at sub- $\mu\text{g l}^{-1}$ level in solution is difficult due to various factors, particularly their low concentrations and matrix effects. A previous preconcentration step is often required.

The solid-phase spectrophotometry (SPS) was paid great attention recently [16–18] since it was introduced in 1976 [19]. The reason is that this technique can provide various important advantages: the sensitivity (expressed as molar absorptivity) is much higher (from 10^3 to 10^4 times) than the corresponding spectrophotometry in solution, it does not require an expensive instrumentation and the species interfering in spectrophotometry in solution can be excluded from the resin in adequate conditions. Solid-phase spectrophotometry combines the use of a solid support, such as Amberlite XAD-4, to preconcentrate the analyte with the aid of a chromogenic reagent and subsequent direct measurement of the absorbance of solid-phase [20].

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The triazene reagent as an excellent chromogenic reagent has long time been used to the determination of cadmium, nickel, mercury, etc. [21]. But it has not been put into use of SPS.

In this paper, a very sensitive and selective method for the determination of nickel(II) with a triazene reagent *o*-carboxylphenyldiazoaminoazobenzene (*o*-CDAA), was developed by using SPS. Some parameters such as pH, the resin amount, the sample volume, ionic strength, resin particle size, centrifugation rate and time and the coexistence ions were investigated in detail. The proposed method has been satisfactorily applied to the determination of nickel(II) in water and vegetable samples.

2. Experimental

2.1. Reagents

18 M Ω cm distilled de-ionized (DDI) water was purified with a Milli-Q system (Millipore, USA). Unless otherwise stated, all reagents used were of analytical grade and all solutions were prepared with DDI water. Standard labware and glassware used were throughout and repeatedly cleaned with HNO₃ and rinsed with DDI water, according to a published procedure [22].

Stock solution (1.0 g l⁻¹) of the nickel(II) was prepared as follows: 1.0 g of specpure nickel(nickel) (99.999%) was dissolved in 15 ml of 8 mol l⁻¹ HNO₃. The solution was boiled gently to expel brown fumes, cooled and diluted to 1000 ml with DDI water. The standard working solution was diluted daily prior to use. The pH was adjusted with the following buffer solutions: NaCH₃COO/CH₃COOH buffer for pH 5.0 and 6.0; Na₂HPO₄/NaH₂PO₄ buffer for pH 7.0; Na₂B₄O₇/NaOH buffer for pH 8.0–11.0; NaOH for pH 12–14.

o-Carboxylphenyldiazoaminoazobenzene solutions: solutions of various concentrations were prepared by dissolving *o*-CDAA (synthesized according to [23]), in absolute alcohol. These solutions were stored under refrigeration and in absence of light. In these conditions they were stable for at least a week.

Amberlite XAD-4 (50–400 mesh) resins (Aldrich) were used in the chloride form. It was pretreatment according to the previous procedure [24].

The water certified reference materials (GBW 08618) and the tomato leaf certified reference materials (GBW 08402) were purchased from National Research Center for Certified Reference Materials (Beijing, China).

2.2. Preparation of XAD-4-*o*-CDAA

The preparation of XAD-4-*o*-CDAA was modified from Blains' procedure [25] and described as follows: 500 mg of pretreated XAD-4 was suspended in 100 ml of 0.2% (w/v) *o*-CDAA acetone solution (in order to saturate the adsorp-

tion capability of the Amberlite XAD-4, it was largely in excess) and then 500 ml of DDI water were added dropwise to the organic solution with gently shaken at room temperature. The impregnated resins were filtered off, rinsed several times with DDI water. They were suspended in 1.0 mol l⁻¹ Na₂B₄O₇/NaOH solution for 3 days, there was no release of *o*-CDAA. Accordingly, the XAD-4-*o*-CDAA resins are suitable for SPS.

After the adsorbed resin was filtered off, the absorbance of the filtrate was measured at 430 nm and the amount of *o*-CDAA adsorbed on the resin was calculated to be about 0.35 mmol in 1 g of the resin.

2.3. Apparatus

A double beam Perkin-Elmer Lambda 35 UV-Vis spectrophotometer, from Perkin-Elmer Instruments LLC, with 1 mm quartz glass cells (10 mm × 1 mm × 45 mm, 200 μ l) was used for all spectral measurements. The spectra were obtained with a scan rate of 240 nm min⁻¹. The spectrophotometer was connected to a Legend-586 microcomputer. A model PHS-3C pH-meter (Shanghai Lida Instrument Factory, China) was used for the pH adjustments. MDS-81D microwave (CEM, USA) equipped with a Teflon-coated oven cavity and a removable 12-position sample carousel, was used for sample preparation. A model DZD-3 multifunctional shaker (Changzhou Aite Technologies Co. Ltd, China) was used for the preparation of Amberlite XAD-4-*o*-CDAA and the measurement of nickel(II) sorption equilibration. Other apparatus consisted of an Agitaser 2000 rotating bottle agitator, a Selecta Model S-240 desk centrifuge.

2.4. Absorbance measurements

The absorbance (really attenuation) of the *o*-CDAA-Ni(II) complexes on the resin was measured in a 1 mm quartz glass cell at 588 nm (corresponding to the absorption maximum of the colored species) and 800 nm (wavelength at which only the resin absorbs), compared with a 1 mm cell packed with resin equilibrated with blank solution. The net absorbance was calculated as formula below proposed by Molina-Díaz and co-workers [26].

$$A = A_{588} - A_{800}$$

2.5. General procedures

2.5.1. Procedure A

For 100 ml samples, an appropriate volume of sample containing 0.10–2.0 μ g of nickel(II) was transferred into a 1 l polyethylene bottle and then 1 ml acetylacetone, 10 ml of pH 9.0 Na₂B₄O₇/NaOH buffer solution and 60 mg of Amberlite XAD-4-*o*-CDAA were added. After levelling off to 100 ml, the mixture was shaken mechanically at 160 rpm for 20 min at room temperature and the colored resin beads

Table 1
Parameters for procedures A, B and C

Parameters	Procedures		
	A	B	C
XAD-4- <i>o</i> -CDAA (mg)	60	60	60
Nickel(II) (μg)	0.1–2.0	0.1–2.0	0.1–2.0
Acetylacetone (ml)	1	2	2
$\text{Na}_2\text{B}_4\text{O}_7/\text{NaOH}$ buffer solution (ml)	10	50	100
Final sample volume (ml)	100	500	1000
Shaking time (min)	20	60	80

were collected by filtration under suction. With the aid of a small pipette, the resin beads were packed into a 1 mm-cell together with a small volume of the filtrate. The cell was centrifuged at 3000 rpm for 3 min and a less translucent mixture was obtained. A blank solution containing all reagents except nickel(II) was prepared and treated in the same way as the sample. The absorbance difference between sample and blank, was measured as absorbance measurements, providing an estimation of the net absorbance. The calibration graphs were constructed.

Procedures B and C are described similarly with procedure A, the parameters are listed in Table 1.

2.6. Treatment of samples

2.6.1. Waters

The certified reference water was diluted to the concentration of $1 \mu\text{g l}^{-1}$ and directly determined by procedure C.

The tap waters were taken from our laboratories and the well water was collected from Shanxi Datong University (Datong, China). To oxidize organic matter such as humic acid, the samples were digested by an oxidizing UV-photolysis in the presence of 1% (v/v) H_2O_2 using a low pressure Hg-lamp which was integrated into a closed quartz vessel [27,28]. Afterwards, they were filtered through a $0.45 \mu\text{m}$ membrane filter (Millipore) and collected in a polyethylene container carefully cleaned with nitric acid. The samples were stored at 4°C until analysis. Analyses were performed with the least possible delay. The usual general precautions were taken to avoid contamination.

2.6.2. Vegetables

All vegetable samples were purchased from Huayu supermarket (Datong, China). The digested method was according to the previous procedure [29]. After digestion, each sample solution was determined by procedure A. The same pretreatment and determination methods were applied to the certified tomato leaves.

2.7. Distribution measurements

Ten milliliters of pH 9.0 $\text{Na}_2\text{B}_4\text{O}_7/\text{NaOH}$ buffer solution and 100 mg of Amberlite XAD-4-*o*-CDAA were

added to a 100 ml water solution containing 5 mg of nickel(II). After 30 min equilibration, the resin beads were separated by filtration under suction. Then, the equilibrium concentration of nickel(II) in the solution was determined by EAAS. The adsorbed resin was eluted with 1 mol l^{-1} HCl and the desorbed nickel(II) was measured with complex titration. The adsorption capacity Q_r and the distribution ratio D were calculated as the following equations:

$$Q_r = (C_0 - C_e) \frac{V}{W} \quad (1)$$

$$D = \frac{Q_r}{C_e} \quad (2)$$

where Q_r represents the quantity of the adsorbed nickel(II) (mmol g^{-1}), C_0 and C_e are the initial and equilibrium concentration of nickel(II) (mmol l^{-1}), respectively, W the mass of the resin (g), V the volume of nickel(II) solution (l) and D the distribution ratio (ml g^{-1}).

Average values of Q_r and D were of 0.24 mmol g^{-1} and $1.25 \times 10^5 \text{ ml g}^{-1}$ respectively, for three replicate determinations.

3. Results and discussion

3.1. Absorption spectra

o-CDAA reacts with nickel(II) in solution to give a 1:3 red complex [23], with an absorption maximum at 538 nm, suitable for colorimetric determination of SPS. Between pH 8.5 and 11.0 this complex is sorbed on Amberlite XAD-4-*o*-CDAA shifting the absorption maximum to 588 nm. *o*-CDAA is fixed on this resin showing an orange colour with an absorption maximum at 425 nm (430 nm in solution). The spectra of the complex in solution and resin phase are shown in Fig. 1, from which the increase of the sensitivity in the resin phase is obvious.

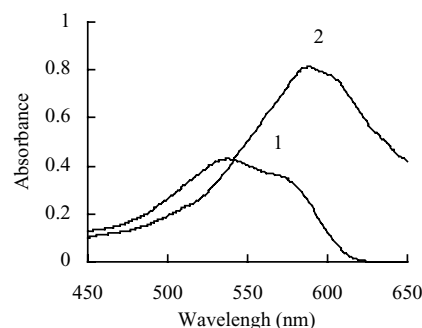


Fig. 1. Net absorption spectra of Ni(II)-*o*-CDAA species. (1) In solution: $C_{\text{Ni(II)}} 1.7 \times 10^{-6} \text{ mol l}^{-1}$, $C_{o\text{-CDAA}} 3.4 \times 10^{-5} \text{ mol l}^{-1}$, pH 9.0, 10 mm cell. (2) On resin: $C_{\text{Ni(II)}} 1.7 \times 10^{-7} \text{ mol l}^{-1}$, $C_{o\text{-CDAA}} 3.4 \times 10^{-6} \text{ mol l}^{-1}$, pH 9.0, 60 mg of resin, 1 mm cell, shaking time 20 min, V 100 ml.

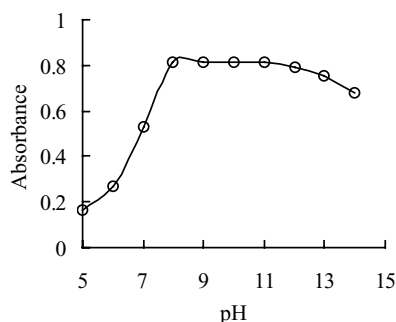


Fig. 2. Influence of pH. Conditions: $C_{\text{Ni(II)}}$ $1.7 \times 10^{-7} \text{ mol l}^{-1}$, others are the same as procedure A.

3.2. Effect of pH

This variable was studied by applying procedure A. Optimum pH for the formation and fixation of the species fell in the range 8.5–11.0 (Fig. 2). The absorbance increased rapidly with the pH value increased below pH 8.5 and decreased gradually above pH 11. Different buffer solutions were tested. The $\text{Na}_2\text{B}_4\text{O}_7/\text{NaOH}$ buffer (pH 9.0) was found to yield the best results.

With 1 mol l^{-1} HCl, the sorbed nickel(II) can be completely eluted, so the resin can be repeatedly used. But for trace analysis, the fresh resins were used for each measurement.

3.3. Effect of the amount of XAD-4-*o*-CDAA

The relationship between the absorbance and the resin amount can be derived from Beers law and the distribution ratio D as seen in Eq. (3) [30].

$$A = \frac{\varepsilon_s l_r C_0 V}{m_r + (1000V/D)} \quad (3)$$

where ε_s is the molar absorptivity of the sample species in the XAD-4-*o*-CDAA phase ($\text{g mol}^{-1} \text{ cm}^{-1}$, see Section 3.9), l_r the mean light-path length through the solid-phase (cm), C_0 the initial concentration of nickel(II) (mol l^{-1}), V the volume of sample solution (l), D the distribution ratio (ml g^{-1}) and m_r the mass of XAD-4-*o*-CDAA (g). In the case of the fraction $1000V/D = 1000 \times 0.1/1.25 \times 10^5 = 8.0 \times 10^{-4}$ g is less than one-twentieth of m_r , it can be neglected, so the Eq. (4) is obtained:

$$A = \frac{\varepsilon_s l_r C_0 V}{m_r} = \frac{K}{m_r} \quad (4)$$

According to the Eq. (4), the amount of XAD-4-*o*-CDAA has great effect on the nickel determination sensitivity. The experimental results obtained by procedure A, showed that the absorbance values significantly decreased with the amount of the resin increased. It can also be seen from Fig. 3 that the less was the resin used, the higher was the absorbance obtained. The minimum amount of dry resin required to fill the cell and facilitate handling, i.e. 60 mg,

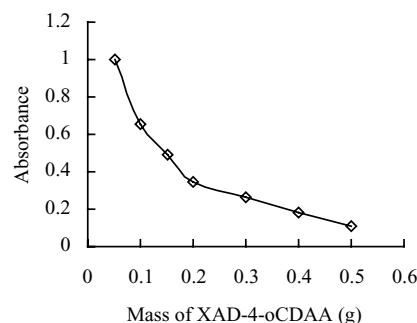


Fig. 3. Influence of the amount of XAD-4-*o*-CDAA. Conditions: $C_{\text{Ni(II)}}$ $1.7 \times 10^{-7} \text{ mol l}^{-1}$, others are the same as procedure A.

was used for all the measurements. When the measured absorbance is represented versus $1/m_r$, the Eq. (5) is obtained:

$$A = \frac{0.0487}{m_r} + 0.0157 \quad (r = 0.9994) \quad (5)$$

3.4. Effect of sample volume

According to the Eq. (4), under fixed m_r , the Eq. (6) is obtained which relates absorbance with sample volume:

$$A = \frac{\varepsilon_s l_r C_0 V}{m_r} = K' V \quad (6)$$

where $K' = \varepsilon_s l_r C_0 / m_r$ is the slope of A versus V (for V values no more than 11). The expected value for $K' = 2.95 \times 10^7 \times 0.1 \times 1.7 \times 10^{-8} / 0.06 = 0.8361 \text{ l}^{-1}$

The Eq. (6) indicates that the sample volume has significant effect on the sensitivity. The increase of absorbance with sample volume can be evaluated by measuring the absorbance of resin equilibrated with different volumes of solutions containing the same concentration of nickel(II) and proportional amounts of the other reagents. Fig. 4 shows the increase in the absorbance with sample volume. Absorbance increases according to the Eq. (7) regressed from the linear parts of the curve for V values no more than 11.

$$A = 0.813V + 0.003 \quad (r = 0.9998) \quad (7)$$

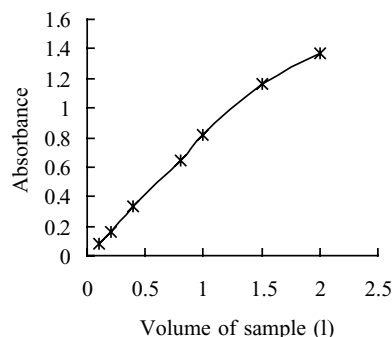


Fig. 4. Influence of the sample volume. Conditions: $C_{\text{Ni(II)}}$ $1.7 \times 10^{-8} \text{ mol l}^{-1}$, $C_{o\text{-CDAA}}$ $1.7 \times 10^{-7} \text{ mol l}^{-1}$, XAD-4-*o*-CDAA 60 mg, pH 9.0, shaking time 20–160 min.

Table 2

Comparison of R.S.D. (%) with different particle size resins and centrifugations

Centrifugation (3000 rpm)	R.S.D. (%) ^a		
	50–100 mesh	100–200 mesh	200–400 mesh
Without	16	9.4	6.7
1 min	10	6.8	4.2
2 min	8.5	4.3	2.5
3 min	6.2	3.6	1.5

^a Average of 10 measurements.

The experimental value of the slope, 0.813 l^{-1} , is in excellent agreement with the theoretical value 0.836 l^{-1} .

3.5. Effect of resin size and centrifugation conditions

The size of Amberlite XAD-4-*o*-CDAA and the centrifugation conditions have strong influence on the reproducibility of the determination. The relative standard deviations (R.S.D.) of 10 replicate measurements are shown in Table 2, using the procedure A containing $1 \mu\text{g}$ nickel(II) under conditions of various resin particle sizes and centrifugation conditions. The R.S.D. is 1.5% using 200–400 mesh Amberlite XAD-4 with centrifugation rate for 3 min at 3000 rpm, compared with 16% obtained using 50–100 mesh Amberlite XAD-4 without centrifugation, it is decreased 10 times. So the particle size 200–400 mesh and centrifugation at 3000 rpm for 3 min were recommended for this experiment.

3.6. Other experimental conditions

Absorbance was independent on ionic strength, adjusted with $\text{Na}_2\text{B}_4\text{O}_7/\text{NaOH}$ buffer solution, up to a concentration of 0.1 mol l^{-1} . For higher values, the absorbance decreased quickly as usual in SPS studies [31], probably owing to competition between the anions of the buffer for the anionic sites of the resin. The optimum shaking times were 20, 60 and 80 min for 100, 500 and 1000 ml sample volumes, respectively.

3.7. Stability and composition of the fixed complexes

The fixed complexes were stable for at least 4 h after equilibration. The composition of the fixed Ni(II)-o-CDAA complexes on XAD-4 resin was measured at the working pH 9.0 using the molar ratio [32,33] and the Job's [34] methods. The results show that the stoichiometry is $[\text{Ni(II)}]:[\text{o-CDAA}] = 1:2$ and disagree with that found in aqueous solution [23].

o-CDAA may be considered to act as a terdentate ligand having three donor atoms in a plane. Nickel(II) is coordinated through the carbonyl oxygen, the azo nitrogens of *o*-CDAA [23,35] and/or the hydroxyl group of $\text{Na}_2\text{B}_4\text{O}_7/\text{NaOH}$ solution. Therefore, the complex may be presented in resin as the form of Ni(OH)(o-CDAA)_2 instead of in the form of Ni(o-CDAA)_3 in aqueous solution.

Table 3

Effect of foreign ions on the determination of $10 \mu\text{g l}^{-1}$ of nickel(II) ($V = 100 \text{ ml}$)

Foreign ions or species	Tolerance limit ($\mu\text{g l}^{-1}$) ^a
NaCl , NaNO_3 , Na_2SO_4	50000
Ca^{2+} , Mg^{2+} , Sr^{2+} , Ba^{2+} , Br^- , F^- , SO_3^{2-} , SiO_3^{2-} , SCN^-	5000
Mn^{2+} , Sn^{2+} , Pb^{2+} , Cr^{3+} , CO_3^{2-}	2000
Al^{3+} , Fe^{3+} , $\text{C}_2\text{O}_4^{2-}$, PO_4^{3-} , NH_4^+ , CH_3COO^-	1000
Zn^{2+} , EDTA	500
Cu^{2+} , Ag^+ , S^{2-} , CN^- , Pd^{2+}	50
Hg^{2+} , Cd^{2+} , Co^{2+}	10

^a Average of three determinations.

3.8. Effect of foreign ions

The effect of various foreign ions on determination of $1.0 \mu\text{g}$ of nickel(II) was studied using procedure A. Various amounts of more than thirty foreign ions were prepared, and the procedure was followed for the determination of nickel(II) separately. With a relative error of less than $\pm 5\%$, the tolerated limits for various foreign ions are listed in Table 3. Of the ions tested, only were the interferences from Co(II) , Cd(II) and Hg(II) owing to the formation of complexes with *o*-CDAA which fixed on the solid-phase and absorbed at the working wavelength. Therefore, the proposed methods are sufficiently selective. For practical analysis, the amount of Hg(II) , Cd(II) , Co(II) is not enough to one-tenth of nickel(II). So their interferences can be neglected. The interferences come from two aspects, one derives from Cu(II) causing by complex with *o*-CDAA and the other from Fe(III) causing by hydrolysis. Their interferences are eliminated with adding 1 ml acetylacetone.

3.9. Analytical characteristics

The SPS sensitivity can be expressed as solid-phase apparent molar absorptivity ε_s and liquid-phase apparent molar absorptivity ε_l for comparison with that of the convenient spectrophotometric methods. For the former, the linear range is $1.2\text{--}41 \mu\text{g g}^{-1}$ and the least square regression equation is:

$$A = 0.8378C (\mu\text{g}/60 \text{ mg resin}) - 0.0021 \quad (r = 0.9976) \quad (8)$$

from which ε_s is $2.95 \times 10^7 \text{ g mol}^{-1} \text{ cm}^{-1}$. For the latter, they are roughly converted corresponding to the volume of sample solutions. The liquid-phase apparent molar absorptivities of the proposed methods for procedures A, B and C are listed in Table 4 compared with that of the convenient spectrophotometric procedures in literatures. It is shown that the increase in sensitivity obtained with the proposed methods is substantial, especially in relation to the solution methods using the same reagent.

The reproducibility of the proposed methods was measured for procedures A, B and C. The relative standard

Table 4
Comparison of sensitivities for determination of nickel(II)

Reagent	ε (l mol ⁻¹ cm ⁻¹)	Remarks	Reference
Diethyldithiocarbamate	6.1×10^3	Low sensitive; Bi ³⁺ , Cd ²⁺ , Cr ³⁺ , Cu ²⁺ , Fe ³⁺ , Hg ²⁺ , Mn ²⁺ , Pb ²⁺ , Zn ²⁺ interfere seriously	[6,7]
Xylenol orange	2.8×10^4	Low sensitive; Al ³⁺ , Be ²⁺ , Cd ²⁺ , Ce ³⁺ , Co ³⁺ , Cu ²⁺ , Fe ³⁺ , Hg ²⁺ , Nd ⁴⁺ , Pb ²⁺ , Ti ⁴⁺ , Zn ²⁺ interfere	[8]
Ammonium 2-amino-1-cyclohexene-1-dithiocarboate	2.8×10^4	Low sensitive; Fe ³⁺ , Cu ²⁺ , Bi ³⁺ , Ag ⁺ , Cd ²⁺ interfere seriously	[9]
1-(2-Pyridylazo)-2-naphthol	4.7×10^4	Low sensitive	[10]
<i>p</i> -Acetylsarsenazo	6.4×10^4	Low sensitive; Ba ²⁺ , Sr ²⁺ , Zn ²⁺ , Ca ²⁺ , V ⁵⁺ , Sn ²⁺ , Pb ²⁺ , Co ³⁺ , etc. interfere	[11]
2-(5-Bromo-2-pyridylazo)-5-diethylaminophenol	1.26×10^5	Long reaction time (30 min); Ba ²⁺ , Pb ²⁺ , Cd ²⁺ , Mn ²⁺ , Al ³⁺ , Zn ²⁺ , Hg ²⁺ , Cr ³⁺ , La ²⁺ , Mo ⁶⁺ , Ag ⁺ , Cu ²⁺ , Fe ³⁺ , Zr ⁴⁺ , PO ₄ ³⁻ interfere seriously	[12]
2-[2-(5-Methylbenzothiazolyl)azo]-5-dimethylaminobenzoic acid	1.26×10^5	Cu ²⁺ , Mo ⁶⁺ , Cr ³⁺ , Cd ²⁺ , V ⁵⁺ , Sn ²⁺ , Zn ²⁺ , Ag ⁺ , Co ³⁺ , Mn ²⁺ , Pb ²⁺ , Bi ³⁺ interfere	[13]
Azocalix[4]arene	1.28×10^5	High sensitive; Cu ²⁺ , Co ²⁺ interfere slightly	[10]
3,3'-Disulfodiphenylamino diazobenzene	2.09×10^5	High sensitive; Cu ²⁺ , Co ²⁺ , Cd ²⁺ interfere seriously	[14]
3-(2-Pyridyl)-5,6-diphenyl-1,2,4-triazine	2.21×10^5	High sensitive; narrow linear range; 1,2-dichloroethane and ethyl tetrabromophenolphthalene extraction	[8]
<i>p</i> -Azophenyldiazoaminoazobenzene	2.3×10^5	High sensitive, dimethylglyoxime and <i>n</i> -butylalcohol extraction	[15]
<i>o</i> -Carboxylphenyldiazoaminoazobenzene	3.3×10^5	High sensitive, sulfhydryl dextran gel adsorption	[23]
<i>o</i> -Carboxylphenyldiazoaminoazobenzene ^a	4.4×10^7	High sensitive, acetylacetone as masking reagent	Present method
<i>o</i> -Carboxylphenyldiazoaminoazobenzene ^b	2.2×10^8	High sensitive, acetylacetone as masking reagent	Present method
<i>o</i> -Carboxylphenyldiazoaminoazobenzene ^c	4.3×10^8	High sensitive, acetylacetone as masking reagent	Present method

^a Proposed method for procedure A.

^b Proposed method for procedure B.

^c Proposed method for procedure C.

deviations were 1.5, 1.8 and 2.5% for 10 replicate measurements each containing 1 μ g nickel(II).

The standard deviations (S.D.) of the blanks, necessary for calculating the detection limit defined by IUPAC [36,37], measured as the average of 10 determinations and expressed as SD units, were 0.002, 0.003 and 0.005 for procedures A, B and C, respectively. The detection limits of the proposed methods are similar to those obtained by other sensitive techniques such as EAAS, AFS and ICP-AES (Table 5). The

accuracy and precision of the proposed SPS methods are also similar to the ones obtained by the techniques indicated above.

3.10. Analytical applications

A certified water reference material (GBW 08618) and a certified tomato leaf reference material (GBW 08402) were used for method validation. The results shown in Tables 6 and 7 were compared with the certified values using the *F*-criterion and the *t*-test at 95% confidence limits [38]. Good agreement was obtained between the estimated content by the proposed method and the certified values for nickel(II).

The proposed method has been applied to the determination of nickel(II) in tap water and well water and also applied to rape leaves, celery leaves and spinach leaves. The determination of nickel(II) was performed using the standard calibration graph method, since no matrix effect was observed (Tables 6 and 7). The results were compared with those found by EAAS, which were in excellent agreement in both cases.

Table 5
Analytical parameters for SPS nickel(II) determination

Parameters	Procedures		
	A	B	C
Linear range (μ g l ⁻¹)	0.48–25	0.14–4.9	0.048–2.5
Detection limit (μ g l ⁻¹)	0.14	0.017	0.012
Quantification limit (μ g l ⁻¹)	0.48	0.053	0.041
R.S.D. (%) (<i>n</i> = 10)	1.5 (10) ^a	1.8 (20) ^a	2.5 (10) ^a

^a Nickel(II) concentration (μ g l⁻¹) used for the determination of reproducibility.

Table 6
Determination of nickel(II) in water samples ($\mu\text{g l}^{-1}$)^a

Samples	Certified value	Found by proposed method	Found by EAAS method ^b
Certified water ^c	1000 \pm 1	1050 \pm 3	
Tap water 1	–	0.46 \pm 0.04	0.42 \pm 0.03
Tap water 2	–	0.78 \pm 0.03	0.74 \pm 0.02
Tap water 3	–	0.94 \pm 0.02	0.96 \pm 0.03
Well water	–	1.6 \pm 0.03	1.63 \pm 0.04

^a Average of three determinations \pm standard deviation.

^b Electrothermic atomic absorption spectroscopy.

^c National Research Center for Certified Reference Materials GBW 08618 (Beijing, China).

Table 7
Determination of nickel(II) in vegetable samples ($\mu\text{g g}^{-1}$)^a

Samples	Certified value	Found by proposed method	Found by EAAS method ^b
Tomato leaves ^c	0.35 \pm 0.05	0.37 \pm 0.03	
Rape leaves ^d	–	0.84 \pm 0.02	0.86 \pm 0.03
Celery leaves ^d	–	0.47 \pm 0.03	0.48 \pm 0.02
Spinach leaves ^d	–	0.60 \pm 0.02	0.63 \pm 0.02

^a Average of three determinations \pm standard deviation.

^b Electrothermic atomic absorption spectroscopy.

^c National Research Center for Certified Reference Materials GBW 08402 (Beijing, China).

^d Purchased from Huayu Supermarket (Datong, China).

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