Asian Journal of Chemistry Vol. 18, No. 3 (2006), 2185–2193

Synthesis of a New Hydroxytriazene Derivative and Its Application for Selective Extraction-Spectrophotometric Determination of Nickel(II)

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A new hydroxytriazene derivative (3-hydroxy-3-phenyl-1-*o*-trifluorophenyl triazene, triazene-I) was synthesized and investigated as a selective complexing ligand for the extraction- spectrophotometric determination of Ni^{2+} ions. The yellowish Ni(II)-triazene-I complex was extracted from an aqueous solution (pH = 8.5) into a chloroform layer and its absorbance was measured at 410 nm (λ_{max}). The absorbance obeyed Beer's law over the range of 2.0×10^{-6} to 8.0×10^{-5} M, with a molar absorptivity of about 1.8×10^{4} L mol^{-1} cm^{-1}. The limit of detection was found to be 5.0×10^{-7} M of Ni^{2+} ion. The influence of pH, shaking time, volume ratio, concentration of the complexing ligand, ionic strength, temperature and the effect of diverse ions on the extraction and determination of Ni^{2+} ions were investigated. Job's method was applied for indicating the stoichiometry of the complex. Also, K_f and ΔG of the complex were estimated. The proposed method was successfully applied to the extraction and determination of Ni^{2+} ion in soil samples.

Key Words: Hydroxytriazene, Nickel(II), Extraction, Spectrophotometric determination.

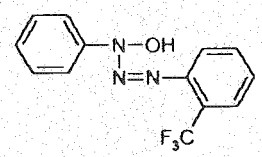
INTRODUCTION

Nickel is an important metal ion in the environment, marine and aquatic chemistry, in food and in biological samples, because of its possible interaction with the environmental compartments and biota[1].

Several methods have been developed for the determination of nickel, such as AAS[2], ET-AAS[3], XRF[4], ICP-AES[5], DPV-HMDE[6] and spectrophotometry[7]. A fewer number of colorimetric regents such as 8-hydroxyquinoline[8], *o*-phenanthroline[9], *o*-hydroxyacetophenone hydrazone[10], *o*-diketonedioxime[11] and furfural-2-benzothiazolyl hydrazone[12] are available for the spectrophotometric determination of nickel. Liquid-liquid extraction of nickel using diethyldithiocarbamate[13], dithizone[14], alamine 336[15], oxo-pyrazole derivatives[16], bis-2-ethylhexyl phosphoric acid[17], 1-(2-pyridylazo)-2-naphthol (PAN)[18] and 4-(2-pyridylazo) resorcinol (PAR)[19] as complexing agents has been performed only for the separation of nickel. However, reports on extractive-spectrophotometric determination of nickel are rare in the literature.

The application of hydroxytriazenes as analytical reagents is quite established[20, 21] during the last decades. These compounds are well known chelating agents, having been widely used as complexometric and spectrophotometric reagents for the extraction and determination of transition metal ions. Moreover, some attempts have been made to study the biological activity of hydroxytriazenes[22]. Recently, a

number of hydroxytriazenes have been screened for their insecticidal, antifungal and antimicrobial activities[23]. In the present investigation, 3-hydroxy-3-phenyl-1-*o*-trifluorophenyl triazene is synthesized and explored as a new reagent for the extraction and spectrophotometric determination of Ni^{2+} ion.



3-Hydroxy-3-phenyl-1-*o*-trifluorophenyl triazene (Triazene I)

EXPERIMENTAL

Analytical reagent-grade chloroform, dichloromethane and carbon tetrachloride (from Merck) were used without any further purification. The materials for synthesis (nitrobenzene and 2-aminobenzotrifluoride) were purchased from Fluka and used as received. All acids and bases were of the highest purity available from Merck. Reagent-grade nickel(II) nitrate and other salts were of the highest purity available and were dried in vacuum over P_2O_5 before use. Doubly distilled deionized water was used throughout. Acetate-acetic acid, NaH_2PO_4-NaH_2PO_4 and KCl-NaOH-borate buffer solutions were used in order to adjust the pH to different values. The standard stock solution of Ni^{2+} ions (0.02 M) was prepared by dissolving appropriate amount of nickel(II) nitrate in 2.0 mL of concentrated nitric acid and diluted to 100 mL with water. Working solutions were prepared by appropriate dilution of the stock solution.

Absorbance measurements were carried out with a Shimadzu UV-1650PC double-beam spectrophotometer and a 1 cm quartz cell at 410 nm (λ_{max}). A Shimadzu AA6650 atomic absorption spectrometer equipped with a GFA-EX7 graphite furnace and an ASC-6100 autosampler was utilized for the determination of remaining nickel in the aqueous phase and testing of the real samples. A Jenway 4030 digital pH-meter equipped with a combined glass-calomel electrode was used for pH adjustments. A Gallenkamp SGL-700-010 V shaker was used to shake the solutions.

Synthesis of Triazene-I

The synthesis of hydroxytriazenes was reported using three different methods. The first method involves reduction of nitrosobenzenes or substituted nitrosobenzene with phenyl or substituted phenylhydrazenes[24]. In the second method, an alkyl or arylhydroxylamine is coupled with diazonium salt at 0–5°C in 1 : 1 molar proportion to give the corresponding hydroxytriazenes[25]. The third method involves oxidation of diazoaminobenzene with peroxy benzoic acid under mild pH condition[26].

Because of better yield and ease of preparation, the second method is preferred over the other two methods. Thus, 3-hydroxy-3-phenyl-1-*o*-trifluorophenyl triazene was synthesized using second method, *i.e.*, coupling phenyl hydroxylamine with 2-benzotrifluoride diazonium chloride at 0–5°C in 1 : 1 molar proportion, in acetate buffer medium (pH = 5.0). The structure and purity of the

synthesized compound was confirmed using CHN elemental analyzer, IR, ^{1}H NMR and ^{13}C NMR.

General procedure

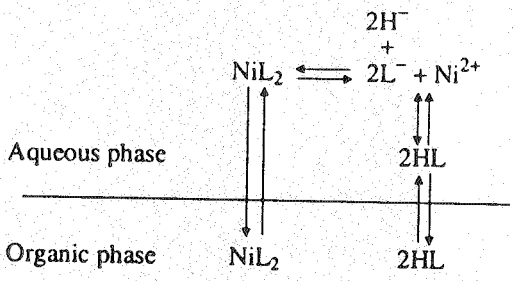
A 10 mL aliquot of the sample solution containing 1×10^{-4} M of Ni^{2+} (pH = 8.5, KCl-NaOH-borate buffer) was transferred to a separatory funnel. After addition of 10 mL chloroform containing 1×10^{-3} M of triazene-I, the resulting mixture was shaken for 10 min. The two phases were allowed to settle and separate completely. Then, the yellow-colored organic phase was separated, and its absorbance was measured at 410 nm against a reagent blank solution.

Determination of nickel in soil samples

Three soil samples from different zones of the flowerbeds of Lorestan University were collected, mixed and ground after drying in oven for 12 h at 250°C. Then, 0.5 g of each sample was weighed precisely and dissolved in a 10 mL portion of aqua-regia (HNO_3 /HCl mixture, 1 : 3). After addition of 20 mL of double distilled water, the solutions were filtered and diluted to the mark with water in a 50 mL volumetric flask after adding buffer solution to adjust the pH to 8.5. Finally, a 10 mL portion of each sample was taken and the proposed liquid-liquid extraction and spectrophotometric determination method was performed.

RESULTS AND DISCUSSION

Some preliminary experiments showed that triazene-I solution in chloroform can extracts Ni^{2+} from aqueous solutions. The proposed extraction mechanism can be explained as:



in which HL, L^- and NiL_2 are the ligand, deprotonated ligand and Ni(II)-triazene-I complex respectively. The absorption spectra of the triazene-I and Ni(II)-triazene-I complex in chloroform are shown in Fig. 1.

It is clear from the spectrum that the λ_{max} of the complex in the organic phase is 410 nm, whereas triazene-I did not show any absorbance at this wavelength. Thus 410 nm was selected for absorbance measurements.

The optimum extraction conditions were established by the studies of the effects of pH, shaking time, volume ratio of organic to aqueous phase, ligand concentration, temperature and ionic strength.

Effect of pH

In order to investigate the influence of pH on the liquid-liquid extraction of Ni^{2+} ions using triazene-I, the pH of aqueous solutions was varied over the range of 5.0–10.0, by using different buffer solutions (acetate-acetic acid: pH = 5.0–5.6;

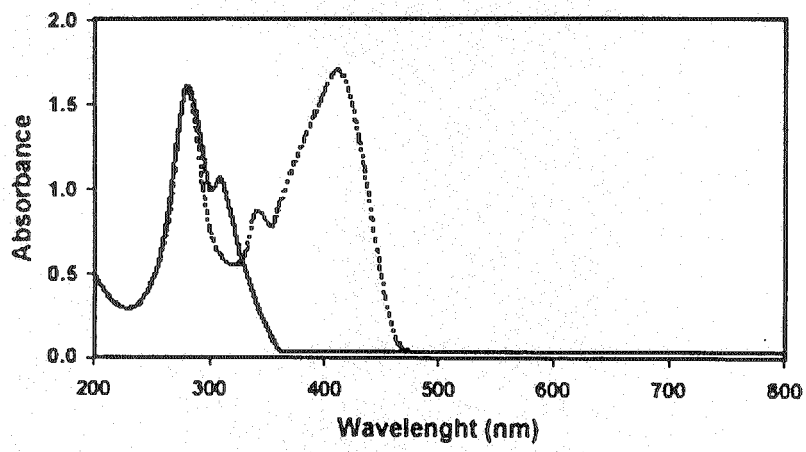


Fig. 1. Absorption spectra of triazene-I (—) and Ni(II)-triazene I complex (---) in chloroform. Conditions: 10 mL of 1.0×10^{-4} M Ni^{2+} in aqueous solution was extracted using 10 mL of 1.0×10^{-3} M triazene-I in chloroform

phosphate: pH = 5.6–7.8; Borate-KCl-NaOH: pH = 7.8–10.0) and the proposed extractive-spectrophotometric procedure was followed. The results (Fig. 2) show that the highest extraction per cent was obtained at pH 8.5. In acidic medium,

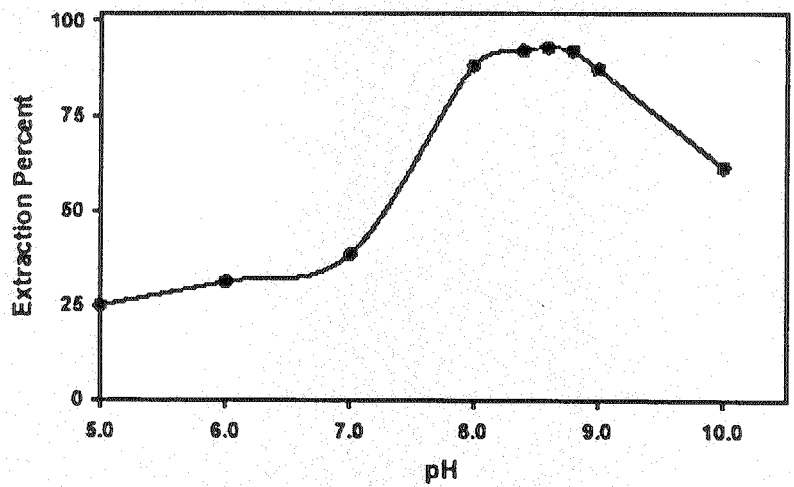


Fig. 2. Effect of pH on the extraction per cent of Ni^{2+}. Conditions: 10 mL of 1.0×10^{-4} M Ni^{2+} sample solution was extracted using 10 mL of 1.0×10^{-3} M triazene-I in chloroform

triazene-I has two tautomeric forms related to the resonance of proton between the O and N atoms, which inhibits complex formation through electron pairs of them, as the donor sites. Thus, at pH lower than 7 the extraction per cent of Ni^{2+} ion decreases. On the other hand, in basic medium (pH > 7.0) deprotonation of the hydroxyl group occurs and the resulting negative charge on the O atom facilitates the complex formation. Decrease of the extraction per cent in strong basic conditions (pH > 9.0) is probably due to the formation of Ni(II)-hydroxide. Hence, 8.5 was selected as the optimum pH for further studies.

Effect of shaking time

Varying the shaking time over the range of 2–25 min showed (Fig. 3) that at least 10 min shaking time is needed for the quantitative extraction of Ni(II)-triazene-I

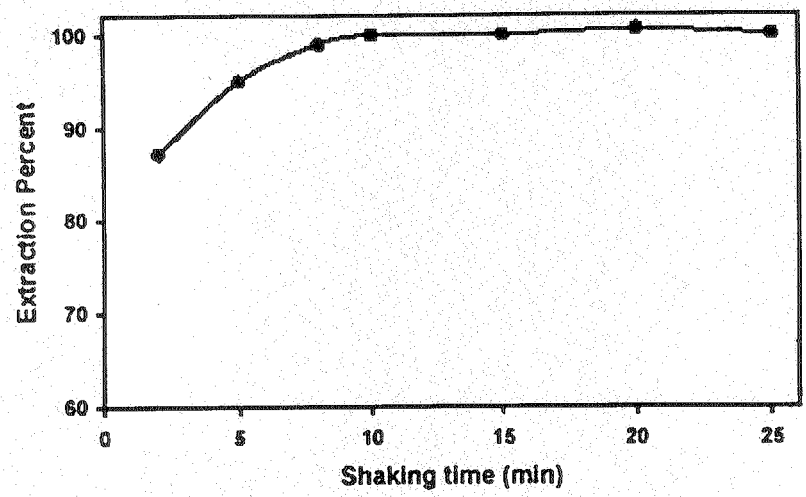


Fig. 3. Effect of shaking time on the extraction per cent of Ni^{2+}. Conditions: 10 mL of 1.0×10^{-4} M Ni^{2+} in aqueous solution (pH = 8.5) was extracted using 10 mL of 1.0×10^{-3} M triazene-I in chloroform

complex using proper organic phase. Prolonged shaking time up to 25 min (maximum examined time) had no significant effect on the extraction per cent.

Effect of volume ratio

In order to evaluate the preconcentration ability of the extraction system, the volume ratio of organic phase to aqueous phase was varied from 1 : 1 (10 mL of organic phase and 10 mL of aqueous phase) to 1 : 5, and the proposed method was carried out. The results revealed that over the range studied, the volume ratio had no significant effect on the extraction per cent and in all cases a quantitative recovery was obtained. Thus, to access the higher preconcentration factor and reduce the organic solvent consumption it is recommended to use 1 : 5 ratio.

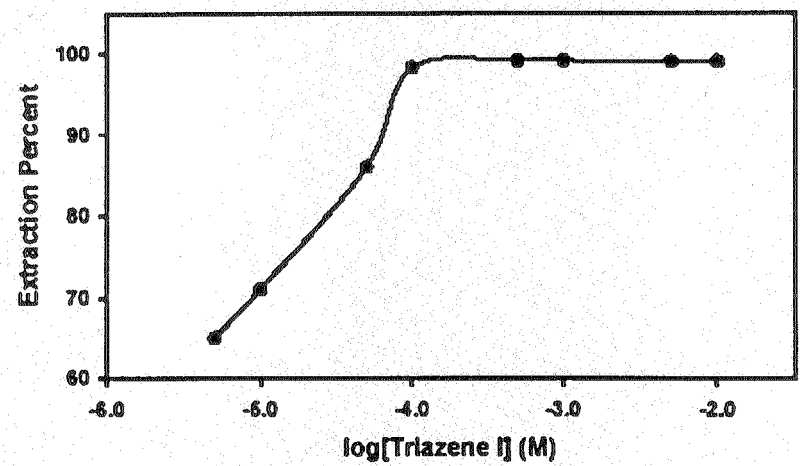


Fig. 4. Effect of triazene-I concentration on the extraction per cent of Ni^{2+}. Conditions: 10 mL of 1.0×10^{-4} M Ni^{2+} in aqueous solution (pH = 8.5) was extracted using 10 mL of chloroform containing triazene-I; shaking time: 10 min

Effect of Triazene-I concentration

To investigate the effect of triazene-I concentration on the extraction per cent of Ni^{2+} ion, its concentration was varied over the range of 5.0×10^{-6} to 1.0×10^{-2}

M (Fig. 4). It was found that by using triazene-I concentrations greater than 1.0×10^{-4} M, the extraction of Ni^{2+} ion was quantitative. Increasing the concentration of triazene-I to 1.0×10^{-2} M had no significant effect on the extraction per cent. Thus, to access a reliable quantitative extraction at different concentrations of Ni^{2+}, 1.0×10^{-3} M of triazene-I was selected, as the optimum concentration, for further studies.

Effect of ionic strength

Liquid-liquid extraction of Ni^{2+} ion using triazene-I from aqueous solutions with different ionic strengths was studied. For this purpose, the concentration of $NaNO_3$ in the aqueous phase was varied over the range of 0.0–1.0 M and the recommended procedure was conducted. The results (Fig. 5) show that increasing of the concentration of $NaNO_3$ to 0.6 M does not affect the extraction per cent of Ni^{2+} ion, while at higher concentrations of $NaNO_3$ the extraction per cent decreases

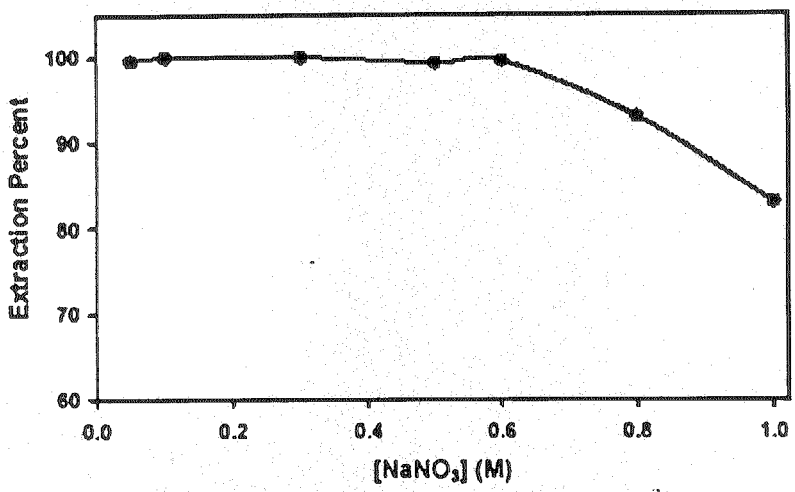


Fig. 5. Effect of $NaNO_3$ concentration on the extraction per cent of Ni^{2+}. Conditions: 10 mL of 1.0×10^{-4} M Ni^{2+} in aqueous solution (pH = 8.5) was extracted using 10 mL of 1.0×10^{-3} M triazene-I in chloroform; shaking time: 10 min

Effect of temperature

To study the effect of temperature on the extraction of Ni^{2+} ion using triazene-I, the liquid-liquid extraction experiments were performed at different temperatures over the range of 20–40°C. The results showed that temperatures greater than 27°C cause a little decrease in shaking time, probably due to increase of molecular collisions, resulting in faster complex formation between Ni(II) and triazene-I.

Stoichiometry of Ni(II)-Triazene I complex

The stoichiometry of Ni(II)-triazene I complex was studied using continuous variation (Job's) method[27, 28]. For this purpose, varying volumes of the two stock solutions of Ni(II) and triazene-I, with the same concentrations of 1.0×10^{-4} M, were taken and mixed in constant volumes. The absorbance of the formed complex for each solution was recorded at 410 nm (λ_{max}) and all points plotted *vs.* the mole ratio of Ni(II). As can be seen (Fig. 6), the plot shows a distinct break at the mole ratio of about 0.33, emphasizing the successive formation of 2 : 1 (triazene-I to Ni(II)) species in solution (Ni(II)-2 triazene-I or NiL_2).

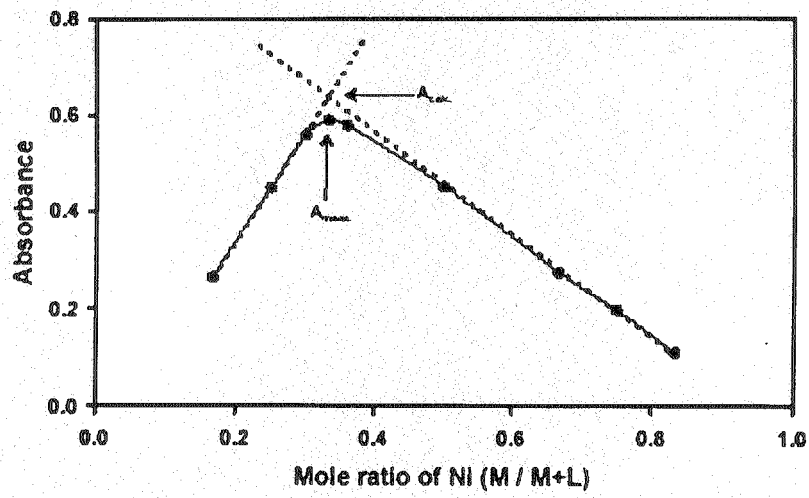


Fig. 6. The absorbance-mole ratio plot for the formation of Ni(II)-triazene-I complex: experimental (—), calculated (---)

Thus, the degree of dissociation (a) can be estimated from the following formula:

$$a = A_{calc} - A_{meas} / A_{calc}$$

where $A_{meas.}$ is the measured absorbance of deflected point (the break point of the mole ratio plot) and A_{calc} is the calculated absorbance of deflected point (the cross point of the two tangent lines). The dissociation constant (or instability constant, $K_{inst.}$) can be derived as follows:

$$ML_2 \rightleftharpoons M + 2L$$

$$K_{inst} = [M][L]^2/[ML_2] = C\alpha(2C\alpha)^2/C(1 - \alpha)$$

$$K_{inst} = 4C^2\alpha^3/1 - \alpha$$

$$K_f = 1/K_{inst} = 1 - \alpha/4C^2\alpha^3$$

where C is the initial concentration of the complex and K_f is the formation constant. Otherwise, total changes in Gibb's free energy (ΔG) can be estimated from the formation constant (K_f) as follows:

$$\Delta G = -2.303\ RT \log K_f$$

The estimated K_f and ΔG at the room temperature were 2.6×10^{10} and 59.8 kJ mol^{-1}, respectively.

Analytical performance

For constructing a calibration curve for the proposed spectrophotometric method, different concentrations of Ni^{2+} ion were examined under the optimal conditions. It was found that the absorbance of Ni(II)-triazene-I complex at 410 nm (λ_{max}) obeyed Beer's law over the concentration range of 2.0×10^{-6} to 8.0×10^{-5} M of Ni^{2+} ion. Molar absorptivity of the coloured complex was found 1.8×10^4 L mol^{-1} cm^{-1}. The regression equation was $A = 18213 \times C - 0.012$ with $r = 0.997$, where A is the absorbance and C is the concentration (M) of nickel. The limit of detection obtained from 3σ of the blank was 5.0×10^{-7} M.

In order to investigate the selective liquid-liquid extraction and determination

of Ni^{2+} ion using triazene-I in the presence of other metal ions, an aliquot of aqueous solution (10 mL) containing 1.0×10^{-4} M of Ni^{2+} ion and different amounts of some other cations were taken and the proposed method was performed. The results (Table-1) showed that Ni^{2+} ion in the binary mixtures were extracted almost completely, even in the presence of up to 10 mg of some cations.

TABLE-1
EXTRACTION AND DETERMINATION OF Ni^{2+} ION FROM BINARY MIXTURES USING TRIAZENE-I[a]

Diverse ion	Amount taken (μg)	Recovery of Ni^{2+} ion (%)	Diverse ion	Amount taken (μg)	Recovery of Ni^{2+} ion (%)
Na^+	10000	97.9 (0.3)[b]	Co^{2+}	3000	99.4 (0.2)
K^+	10000	99.5 (0.2)	Zn^{2+}	3000	99.5 (0.2)
Ca^{2+}	5000	96.1 (0.5)	Pb^{2+}	3000	97.1 (0.1)
Mg^{2+}	5000	95.4 (0.3)	Cd^{2+}	3000	97.1 (0.1)
Ba^{2+}	5000	99.2 (0.1)	Fe^{3+}	100	97.4 (0.4)
Sr^{2+}	3000	98.5 (0.3)	Al^{3+}	100	98.5 (0.3)
Cu^{2+}	3000	98.9 (0.1)	Cr^{3+}	100	96.9 (0.1)
Mn^{2+}	3000	96.7 (0.2)			

[a]10 mL of aqueous solution (pH = 8.5) containing 1.0×10^{-4} M Ni^{2+} and different amount of other cations were extracted using 10 mL of 1.0×10^{-3} M Triazene I in chloroform, shaking time: 10 min.
[b]RSD% based on three replicate analyses.

To evaluate the application of the proposed method to real samples, it was applied to the extraction and determination of Ni^{2+} in three agriculture soil samples. The results are summarized in Table-2. As can be seen, a satisfactory agreement exists between the data obtained by the proposed method and those reported by electrothermal atomic absorption spectrometry (ET-AAS).

TABLE-2
LIQUID-LIQUID EXTRACTION AND SPECTROPHOTOMETRIC DETERMINATION OF Ni^{2+} ION IN FLOWER-BED SOIL SAMPLES USING TRIAZENE-I[a]

Sample	Ni^{2+} determined (μg g^{-1})	
	Proposed method	ET-AAS
Soil sample 1	75.4 (2.8)	78.9 (1.8)[b]
Soil sample 2	156.7 (3.1)	160.2 (2.0)
Soil sample 3	201.3 (2.2)	198.1 (1.6)

[a]0.5 g of each sample was dissolved in aqua-regia, filtered and diluted to 50 mL (pH = 8.5), and 10 mL of it was extracted using 10 mL of 1.0×10^{-3} M triazene-I in chloroform, shaking time: 10 min.
[b]RSD % based on three replicate analyses.

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(*Received*: 8 October 2005 ; *Accepted*: 3 March 2006) AJC-4701