

The determination of nickel(II) after on-line sorbent preconcentration by inductively coupled plasma atomic emission spectrometry using Borassus Flabellifer inflorescence loaded with coniine dithiocarbamate

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Abstract

A procedure was developed for the determination of nickel(II) in water samples by inductively coupled plasma atomic emission spectrometry (ICP-AES) after preconcentration on coniine dithiocarbamate (CDC) supported by Borassus Flabellifer inflorescence. The sorbed element was subsequently eluted with 0.4 M nitric acid and the acid eluates are analysed by ICP-AES. The influence of various parameters such as pH, flow rate of sample, eluent concentration, volume of the sample and volume of eluent were investigated. Under the optimal conditions, nickel in aqueous sample was concentrated about 100-fold. Nickel recovery was obtained using the proposed method in range of 98.9–99.9%. This method is also applied for the analysis of spiked and natural water samples. The results provide strong evidence to support the hypothesis of an adsorption mechanism.

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1. Introduction

Nickel is a moderately toxic element compared to other transition metals. However, it is known that inhalation of nickel and its compounds can lead to serious problems, including respiratory system cancer [1,2]. Moreover, nickel can cause a disorder known as nickel-eczema [3]. Other studies [4–6] show diseases characterised as occupational disease [6], increased in patients who consume food and beverage rich in nickel. Environmental pollution monitoring requires determination of toxic heavy elements in trace levels. The inductively coupled plasma atomic emission spectrometry (ICP-AES) technique, which offers fast multi-elemental analysis suffers from a poor sensitivity in the determination of heavy elements present in environmental samples like river water, tap water, natural and spiked water samples. This drawback can be rectified by a combi-

nation of a suitable on-line preconcentration technique with subsequent ICP-AES determination.

On-line separation and preconcentration techniques have received considerable attention during recent years and is widely applied for the selectivity and the sensitivity enhancement. Various methods of preconcentration of analytes prior to determination with atomic absorption spectrometry are based on solvent extraction [7]. Chelating ion exchange [8,9], co-precipitation method [10,11], various chromatographic techniques [12] and sorbent extraction [13,14] have been developed and discussed in the literature. The methods like solvent extraction, co-precipitation and chromatographic techniques are tedious, time-consuming, provide low detection limits and also help to avoid interferences in the analysis of real samples. Chelating ion exchangers are commonly available, but commercially high cost and their preparation are not easy. Extraction of the dithiocarbamate complexes of metals into isobutylmethylketone (IBMK) and subsequent determination has been widely applied in the determination of metals in natural waters. However, this sample solvent extraction concentration procedure cannot be combined with ICP-AES because of difficulties of introducing

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organic solvents into the plasma of an ICP spectrometer [15,16]. Antanasova et al. [17] and Arpadjan et al. [18] have reported preconcentration of metals on solid support impregnated with sodium diethyl-dithiocarbamate (Na-DDTC) and ammonium hexamethylene dithiocarbamate (HMDC) and subsequent determination of ICP-AES. In these methods, they used propanol and methanol for elution of metals from the sorbent. Since the organic solvents cannot be directly nebulized into the argon plasma, they further diluted the eluents with water and then analysed the elements by ICP-AES. Activated carbon has proven to be an excellent collector for numerous metal ions. Some of them are collected owing to their irreversible adsorption and others are adsorbed as metal chelates using organic ligands such as dithiozone, 8-hydroxy quinoline, dithiocarbamate α -diphenylglyoxime [19] and pyrogallol red [20,21]. The prepared activated carbon filter (sorbent) is used only for analysis.

In this paper, authors report a new on-line column separation and preconcentration method for determination of Ni(II). The column loaded with BFI material and used for several times without destruction and sorbed elements were sequentially eluted with 0.4 M nitric acid. The acid eluates were further analysed by ICP-AES. Elution of metals with HNO₃ enabled their direct nebulization into the argon plasma of ICP-AES. The sorbent used in present studies is selective for Ni(II) at the pH selected, other cations cannot occupy the site of the ligand on the supported solid phase.

2. Experimental

2.1. Instrumentation

Atomic emission spectrometer (ICP-AES Varian, Liberty Series 11, Australia) was used. The plasma was run at 700 V with 15 l/min argon. The operating conditions and wavelength of the emission line examined are listed in Table 1.

The analyte on-line preconcentration was selected on the basis of net and background intensities as well as their freedom from spectral overlaps. An Elico model Li-129 pH meter with combination glass and calomel electrode was used for pH measurements.

The schematic diagram of the on-line preconcentration method is shown in Fig. 1. The hardware of the system comprises a 32-channel I/O card (PCL-720; Pentasoftware, India),

Table 1
ICP-AES operating parameters

Photomultiplier tube voltage (V)	700
Incident power (kW)	1.1
Plasma gas flow (min/l)	15.0
Auxiliary gas flow (min/l)	1.5
Observation height (mm)	14.0
Pump rate (rpm)	15.0
Sample uptake time (s)	25.0
Wavelength of element Ni(II)	221.647

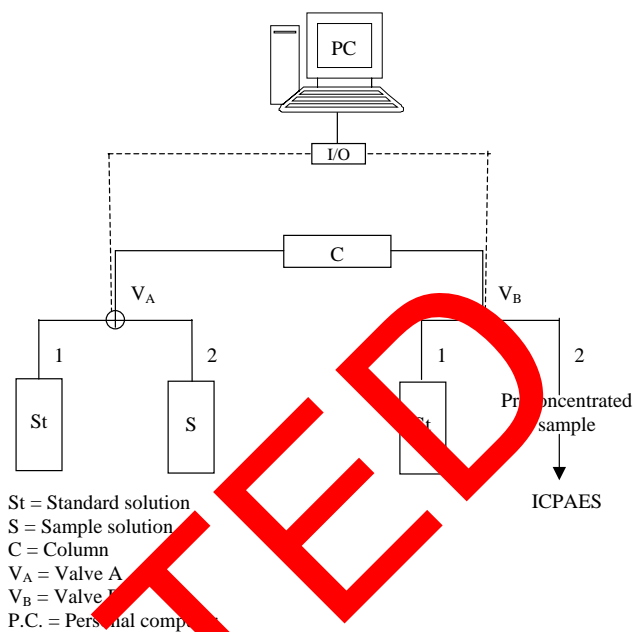


Fig. 1. Schematic diagram for preconcentration of Ni(II).

which was a power relay module to convert the output of I/O card to 220 V a.c., a peristaltic pump (IS matiec, ISM 404) through 220 V electrical valves. Silicon rubber tubing pump (1 mm i.d.) and a pc computer, Pentium IV. A program was written in Borland C++.

In the on-line preconcentration procedure, the sample was pumped through the 20 ml medical syringe via position 1 of valve A (Fig. 1), where nickel(II) ions were retained in the column by forming a complex with conicine dithiocarbamate (CDC). In this case, valve B was in the waste position. When the sample was eluted completely, position 1 of valve A was closed automatically, valve B was switched to the preconcentration sample and position 2 of valve A was opened when 0.4 M nitric acid was passed through the column to elute the Ni(II) ions by breaking the complex. The eluted preconcentrated sample was analysed by ICP-AES.

2.2. Chemicals

All chemicals used were of analytical reagent grade. Deionized doubly distilled water was used throughout the experiment. A nickel(II) standard solution was prepared by appropriate dilution of ICP standards (Merck, Germany) of Ni(II). Working standards of (0.1, 0.2, 0.5 and 1.0 $\mu\text{g/ml}$) were prepared by appropriate dilution with deionized distilled water. Conicine dithiocarbamate solution (0.01%) was prepared by dissolving 0.01 g of the reagent in 100 ml of doubly deionized distilled water. Samples were filtered through a cellulose membrane of pore size 0.45 μm .

Buffer solution of pH 7.0 ± 0.2 was prepared by adding concentrated H₂SO₄ (3.4 ml) to 250 ml distilled water in a 500 ml flask. The mono sodium dihydrogen phosphate monohydrate (25 g) was added and the flask shaken until

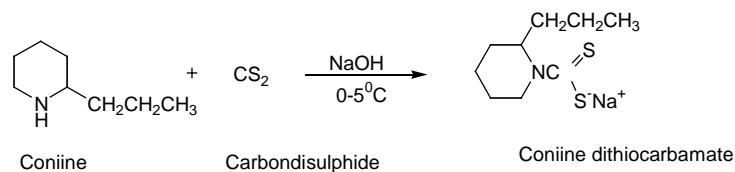


Fig. 2. Synthesis of coniine dithiocarbamate reagent.

dissolution was completed. The solution was then diluted to 500 ml.

2.3. Column preparation

A medical syringe (20 ml) was used as column. The support was prepared from *Borassus Flabellifer* inflorescence in following manner: 1 cm thick segments with diameter of 2.5 cm were cut. The segments were soaked in 0.4 M nitric acid for 12 h, washed in deionized doubly distilled water and dried prior to use. The syringes were then filled with the air-dried segments. The column consists of seven to eight separate segments. Then, 3.0 g of solid coniine dithiocarbamate was introduced between the segments. This amount of the complex forming agent was necessary to retain the 100 µg of each element in the 200 ml sample.

2.4. Synthesis of coniine dithiocarbamate reagent

Carbon disulphide (80 g) was slowly added to a solution of coniine (85 g) in 25 ml of water at 5 °C with constant stirring, followed by 40 g of sodium hydroxide dissolved in 20 ml of water to form coniine dithiocarbamate as shown in Fig. 2. The product was warmed to room temperature and washed repeatedly two to three times with purified acetone. The reaction product was purified by crystallization in acetone. The purified compound has a melting point of 303–308 °C at 740 mm pressure.

3. Procedure

The method was tested with model solutions before its application to real samples. A 200 ml 0.040 µg/ml Ni(II) solution buffered at pH 7.0 ± 0.2 with phosphate buffer was passed through the column by opening the position 1 of valves A and B at flow rate of 7.0 ml/min. After finishing the solution, position 1 of the valves A and B is closed automatically and position 2 of valves A and B is opened. Therefore, 5 ml of 0.4 M nitric acid was passed through the column to elute the Ni(II) ions with a flow rate of 1 ml/min. The acid eluents were collected into a metal free polyethylene bottle and nebulized into the plasma of ICP-AES. The percent of metal ions adsorbed on the column for known concentration of Ni(II) was calculated as:

$$\frac{\text{amount of Ni(II) ions in the initial sample}}{\text{amount of Ni(II) ions eluted from column}}$$

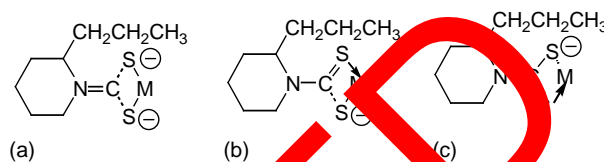


Fig. 3. Resonance hybrid of the coniine dithiocarbamate with metal.

4. Results and Discussion

Coniine dithiocarbamate is a sensitive, selective and specific complexing ligand for analytical determination of Ni(II) at pH 7.0 ± 0.2. Crystallization of water is less in coniine dithiocarbamate when compared with other dithiocarbamate, therefore, the extractability of the complex become easier. The metal salt of this reagent is a resonance hybrid of the structures, which contributed to stability of metal complexes as shown in Fig. 3. This proposed method was employed for the present natural water samples collected from Swarnamukhi river belt (Chandragiri), Kalyanidam reservoir and Ghajulamandayam area. The samples were used directly to measure the Ni(II) contents by the proposed method after filtered with cellulose membrane of pore size 0.45 µm. For each sample, 200 ml was passed through the column as explained by the recommended procedure and results were tabulated in Table 2. Then, spiked water samples were prepared with 2 l of distilled water by adding known amounts of Ni(II), preconcentrated and determined by the standard procedure discussed earlier and percentage recoveries of Ni(II) were presented in Table 3 and detection limits for determination of Ni(II) by ICP-AES after on-line preconcentration on BFI loaded with coniine dithiocarbamate are 0.002 ng/ml.

4.1. Influence of pH

pH effect on the preconcentration of metal on *Borassus Flabellifer* inflorescence loaded with coniine dithiocarbamate was studied by on-line determination of 20 µg of

Table 2
Analytical results of nickel(II) in the natural water samples

Sl. no.	Sample	Ni(II) found (ng/ml) ^a (n = 4)
1	Swarnamukhi river belt (Chandragiri)	10.69 ± 0.8
2	Kalyanidam reservoir	17.20 ± 0.5
3	Ghajulamandayam area	25.32 ± 0.8

^a For four determinations.

Table 3

Recovery of nickel(II) from different concentrations of spiked water samples after preconcentration on *Borassus Flabellifer* inflorescence loaded with coniine dithiocarbamate

Concentration of nickel(II) added (ng/l)	
20	
Found (ng/l)	19.78
Recovery (%)	98.90
R.S.D. ^a (%)	±2.54
40	
Found (ng/l)	39.72
Recovery (%)	99.30
R.S.D. ^a (%)	±2.63
60	
Found (ng/l)	59.78
Recovery (%)	99.63
R.S.D. ^a (%)	±2.70
80	
Found (ng/l)	79.91
Recovery (%)	99.88
R.S.D. ^a (%)	±2.89

^a Recovery (%) and R.S.D. (%) for four determinations.

Ni(II) in the pH range of 1.0–8.0 and by introducing 1.0 g of coniine dithiocarbamate between inflorescence segments. The elution was performed with 0.4 M HNO₃. The data corresponding to pH effect were shown in Fig. 4. At pH 7.0 ± 0.2, the maximum recovery was obtained.

4.2. Chromatographic support

The optimum amount of the coniine dithiocarbamate ensuring quantitative sorption of the Ni(II) was 3.0 g. It depends on the volume and rate of sample passing through the column. Experiments were carried out with solid coniine dithiocarbamate (1.0–10 g) spread between the *Borassus Flabellifer* inflorescence segments. It was established that 3.0 g of solid coniine dithiocarbamate was enough to provide quantitative retention of 100 µg of Ni(II) in a 200 ml water sample at pH 7.0 ± 0.2 and subsequent elution was

Table 4

Effect of sample volume on the elution of metal

Sl. no.	Volume of water (ml)	Recovery (%) of nickel(II) ions ^a
1	50	99.0 ± 1.0
2	100	99.6 ± 1.1
3	200	99.9 ± 0.2
4	300	99.5 ± 0.7
5	400	99.1 ± 0.7
6	500	98.8 ± 1.1

^a Recovery (%) for four determinations

carried out with 0.4 M HNO₃. The column can be regenerated and used several times until the saturation of the *Borassus Flabellifer* inflorescence material.

4.3. Efficiency of elution

The choice of selecting an eluent was a difficult problem because of the limitation of the ICP to tolerate organic solvent. In addition, an eluent should not destroy the *Borassus Flabellifer* inflorescence as a solid support in the column. Hence, for the simultaneous determination of the preconcentrated element by ICP-AES, the elution was performed with 0.15–0.5 M HNO₃ and is dependent on the concentration of HNO₃ as shown in Fig. 5. Quantitative multi-element elution was achieved for 0.4 M HNO₃. Hence, 5 ml of 0.4 M HNO₃ was chosen as the optimum eluent for the Ni(II) determination and recoveries were 100%.

4.4. Effect of volume of a sample on elution

The effect of the sample volume on the extraction of Ni(II) was studied by taking different volumes of water samples in the range of 50, 100, 200, 300, 400 and 500 ml. The extraction was carried out as described in procedure and results were reported in Table 4. In this case, the recovery obtained was higher than 99.99 at 200 ml volume. However, the efficiency of recovery slightly decreases when the sample

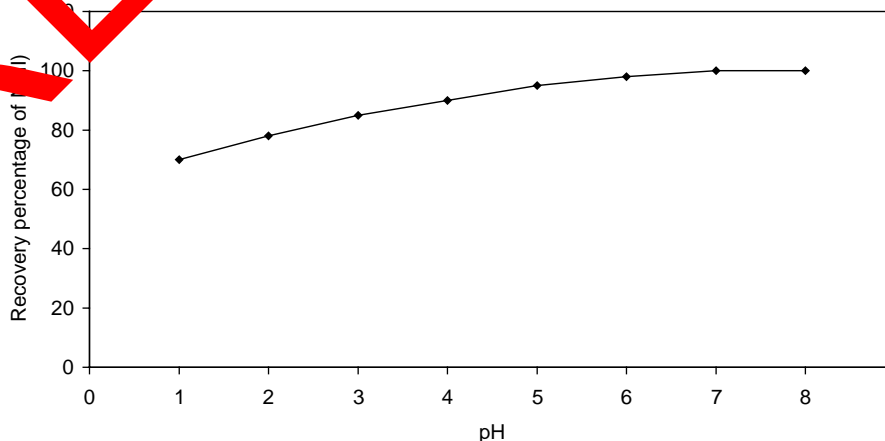


Fig. 4. Effect of pH on complexation of Ni(II)-CDC.

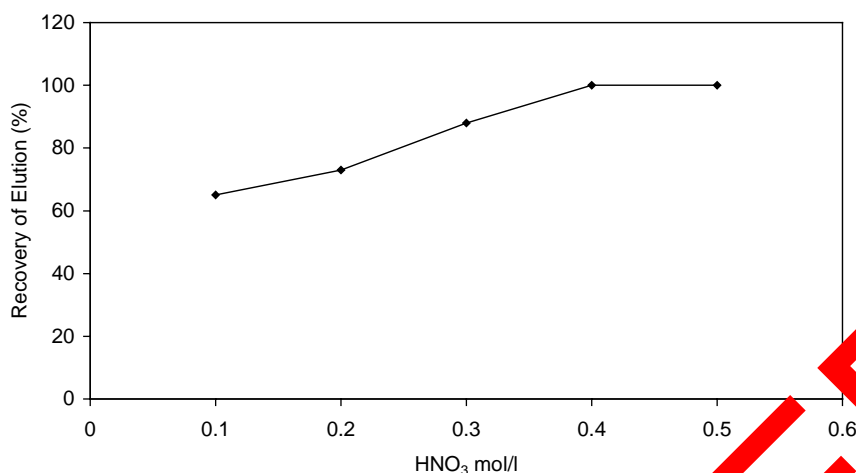


Fig. 5. Effect of HNO₃ concentration on elution of Ni(II).

volume is more than 200 ml. Hence, 200 ml of water sample was chosen for the present study.

4.5. Influence of matrix ions

The influence of matrix ions in water samples on the recovery of nickel(II) ions was also investigated. It indicates that Co²⁺, Cu²⁺ (50 µg/ml), Cr³⁺, Cu²⁺ (100 µg/ml), Mg²⁺, Mn²⁺ (200 µg/ml), Ca²⁺ (400 µg/ml), IO₃⁻, BrO₃⁻, Cd²⁺, Zn²⁺, Pb²⁺ (800 µg/ml) and Na⁺, K⁺, CS⁺, NO₃⁻, PO₄³⁻, Cl⁻, Br⁻, I⁻ (1000 µg/ml), in turn, do not show interference in ordinary condition during the present study.

4.6. Effect of volume of an eluent on percentage of elution of Ni(II)

The effect of volume of an eluent on elution of Ni(II) from various water samples on BFI material measured at 30–35 °C was shown in Table 5. It can be observed that the elution of Ni(II) gradually increases with increase of volume of eluent to certain extent. After increasing the volume of an eluent, the elution percentage slightly decreases. Thus, 5 ml of HNO₃ was chosen for 100% recovery of Ni(II) ions.

Table 5
Effect of volume of eluent on percent elution of Ni(II) ions

Sl. no.	Volume of eluent (ml)	Elution (%) of Ni(II) ions ^a
1	1.0	60.5 ± 2.3
2	2.0	80.3 ± 1.6
3	3.0	90.6 ± 1.7
4	4.0	95.7 ± 1.9
5	5.0	99.9 ± 0.6
6	6.0	98.6 ± 0.6
7	7.0	86.3 ± 2.1

^a Elution (%) of four determinations.

5. Conclusion

The newly developed method is simple, selective, sensitive and reproducible for pre-concentration and determination of trace levels and ultra trace levels of Ni(II). The modified BFI material is stable for several treatment of sample solution. The method is used for pre-concentration of Ni(II) at a level of 0.002 ng/ml with the help of coniine dithiocarbamate. The relative standard deviation for four independent determination reached values of 2.54–2.89% for Ni(II) solution of different concentrations. The recovery of Ni(II) from spiked water samples was in the range of 98.9–99.9%.

Coniine dithiocarbamate possesses a high electric dipole moment. The propyl substituent on C₂ carbon of coniine ring being influences the +I effect, leads to the free-electron-releasing tendency of the N-group into sulphur atoms, therefore, the electron donating capacity of coniine dithiocarbamate increases, permitting the formation of strong complexes with metal ions.

The Ni(II) present in different sources were containing different values due to:

- (i) Natural decomposition of Ni(II) from river bed sediments.
- (ii) The catchment area of Swarnamukhi is the Seshachalam Hills, where the weathering process of parent rock and soil erosion lead to the contribution of Ni(II).
- (iii) Pioneer alloys casting, sugar factory, electro plating industries whose industrial effluent are directly let out into the stream of Swarnamukhi (water is not treated) causes high concentrations of Ni(II) at the Ghajulamandyam area.
- (iv) The agricultural by-product BFI acts as an additional adsorbent for solid support of CDC for specific adsorption of Ni(II) from water samples.

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