Determination of Nickel in Natural Water Samples by Flow Injection-Inductively Coupled Plasma Optical Emission Spectrometry

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An on-line nickel preconcentration and determination system implemented with inductively coupled plasma optical emission spectrometry associated to flow injection was studied. Trace amounts of nickel were preconcentrated by sorption on a conical mini-column packed with activated carbon modified with a Schiff's base *bis*(2-hydroxyphenylamino)glyoxime at pH 5.0. The nickel was removed from the minicolumn with 20 % nitric acid. An enrichment factor of 80-fold for a sample volume of 50 mL was obtained. The detection limit value for the preconcentration method proposed was 70 ng L^{-1}. The precision for 10 replicate determinations at the 0.6 µg L^{-1} Ni level was 2.2 % relative standard deviation, calculated from the peak heights obtained. The calibration graph preconcentration method for nickel was linear with a correlation coefficient of 0.9996 at levels near the detection limits up to at least 120 µg L^{-1}. The method was successfully applied to the determination of nickel in natural water samples.

Key Words: ICP-OES, Flow injection, On-line preconcentration, Nickel, *bis*(2-Hydroxyphenylamino)glyoxime.

INTRODUCTION

Nickel is a siderophile element, its abundance in average crustal rocks is 75 µg g^{-1}. Additionally, nickel is a good pathfinder of its deposits in practically all types of surveys using most sampling media[1]. In residual soil samples, nickel is an important guide to underlying Ni-sulfides[2]. Nickel is a chemical element present in trace amounts in natural water samples, is possible to find very low nickel concentration levels in river waters, in the order[1,3] of 1.5 µg L^{-1}. This value is taken as the base value for prospective studies. The use of Ni in prospective studies of river water is limited to the determination of low concentrations close to the base value. On the other hand, international regulations on water quality are lowering the maximum permissible levels of potentially toxic metals in human. Thus, the guideline value of Ni in drinking water[4] is 20.0 µg L^{-1}. Hence, the analytical control of nickel in drinking water is becoming very important.

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Considering the low content of nickel in environmental samples, sensitive analytical techniques are required to obtain low detection limits. Atomic absorption spectrometry with flame (FAAS)[5-10] and electrothermal atomization (ETAAS)[11] become the most appropriate techniques for its determination, but the detection limits in these methods is not sufficient when the concentrations are too low.

Inductively coupled plasma optical emission spectrometry (ICP-OES) is widely recognized as a suitable technique for the determination of nickel amounts[12]. However, the low level of nickel in natural waters is not compatible with the detection limit of this technique. In order to achieve accurate, reliable and sensitive results, pre-concentration and separation are needed when the concentrations of analyte elements in the original material or the prepared solution are too low to be determined directly by ICP-OES.

Preconcentration is an effective means for extending the detection limits of ICP-OES technique. However, when practiced manually in the batch mode, the operations are usually tedious to be compatible with the ICP-OES measurements. Stringent control of the laboratory environment is also required to avoid sample contamination if ultra-trace determinations in the ng mL^{-1} range are to be attempted. This situation has been improved significantly by using flow injection coupled with ICP-OES[13-15]. Some methodologies used for nickel preconcentration have been developed with ionic exchanger resins[16] and knotted reactors[17].

Activated carbon has been widely used for many purposes both in laboratory and industrial settings, due to its ability to adsorb organic and inorganic compounds[18]. Since its introduction in analytical chemistry, enrichment of trace metals using activated carbon has been favourably performed with very high concentration factors in different matrices[19-21]. The mechanism of sorption on activated carbon is still under investigation. Adsorption equilibrium studies have revealed that pH is the dominant parameter controlling the adsorption[22]. Generally, sorption of dissolved metal ions on activated carbon can be improved in the presence of chelating or precipitating agents[23-29]. In this study, an on-line procedure for preconcentration and determination of nickel at low concentration levels by ICP-OES using a conical mini-column packed with activated carbon is proposed. Nickel was retained by sorption on activated carbon in absence of complexing reagent. The pH adjustment of the solution suffices to retain nickel ion.
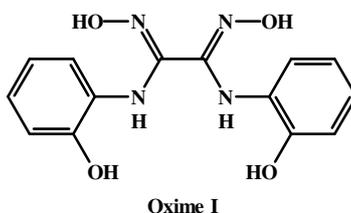
Oxime I

Base *bis*(2-hydroxyphenylamino)glyoxime

EXPERIMENTAL

Activated carbon (Merck, Darmstadt, Germany, 50-70 mesh) was used after pretreatment with acid [activated carbon was heated to 60 °C with 10 % (v/v) hydrochloric acid for 0.5 h and then with 10 % (v/v) nitric acid for 20 min and finally washed with deionized water until neutral pH was reached].

Schiff base, *bis*(2-hydroxyphenylamino)glyoxime (oxime I) was synthesized and purified as follows: 40 mL of *ortho*-aminophenol was dissolved in a mixture of 40 mL methanol and 67 mL ethanol and 27 mL of double distilled water was added. Then, 20 mmol dichloroglyoxime dissolved in 20 mL methanol was added instantly and the obtained solution was stirred. A white brown precipitated product appeared slowly after 5 min. After addition of 20 mmol sodium bicarbonate, the mixture was stirred for 3 h. Finally, the precipitated product, was filtered out, washed with cold ethanol and recrystallized from water/methanol (3:1) mixture. The structure of the compound was confirmed by NMR and FT-IR spectrometry[30].

A solution of oxime I was prepared as follow: to a solution of 0.2 g of oxime I in 10 mL of ethanol, 5 drops of 1 M NaOH were added, dissolved and its volume adjusted to 50 mL with water. Preparation of admicell column: to 40 mL of water containing 1.5 g of alumina, 10 mL of the above oxime I solution was added. The pH of the suspension was adjusted to 2.0 by addition of 4 M HNO_3 and stirred by mechanical stirrer for 20 min. Then the top liquid was decanted (and discarded) and the remained alumina was washed three times with water, then with 5 mL of 4 M HNO_3 and again three times with water.

Nickel standard solution was prepared by appropriate dilutions of a 1000 mg L^{-1} stock solution (Merck) immediately before use. Buffer solution was prepared by diluting a 1.0 mol L^{-1} acetic acid solution adjusted to pH 5.0 with sodium hydroxide solution. Ultrapure water (18 MΩ cm^{-1}) was obtained from an EASY pure RF (Barnstedt, Dubuque, IA, USA). All other solvents and reagents were of analytical-reagent grade.

The measurements were performed with a sequential ICP spectrometer [Baird (Bedford, MA, USA) ICP2070]. The 1 m Czerny-Turner monochromator had a holographic grating with 1800 grooves mm^{-1}. The ICP conditions are listed in Table-1. The FI system used is shown in Fig. 1. A Minipuls 3 peristaltic pump [Gilson (Villiers-Le-Bel, France)] was used. Sample injection was achieved using a Rheodyne (Cotati, CA, USA) Model 50, 4-way rotary valve. A home-made conical minicolumn (40 mm length, 4.5 mm internal upper-diameter and 1.5 mm internal lower-diameter) was used as the activated carbon holder. Pump tubes-Tygon type (Ismatec, Cole-Parmer Instrument Company, Niles, IL, USA) were employed to propel the sample, reagent and eluent. The 221.647 nm spectral line was used and flow injection system measurements were expressed as peak height emission, which was corrected against the reagent blank.

TABLE-1
ICP-OES INSTRUMENTAL PARAMETERS
EMPLOYED TO NICKEL DETERMINATION

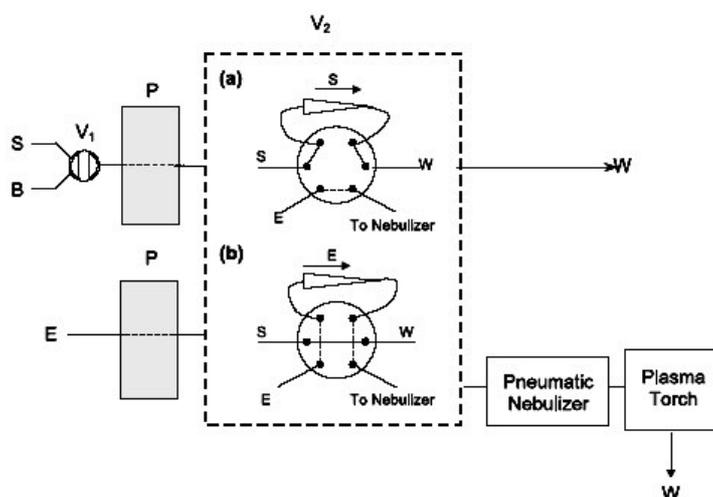| 1.0 kW	Forward power	1.0 L min^{-1}	Auxiliary gas flow rate
40.68 MHz	RF generator	0.5 L min^{-1}	Carrier gas flow rate
Glass, Meinhard	Nebulizer	1.5 mL min^{-1}	Solution uptake rate
8.5 L min^{-1}	Plasma gas flow rate	15 mm	Observation height

Fig. 1.   Schematic diagram of the instrumental setup. S, sample (flow rate: 17 mL min^{-1}); E, eluent (flow rate: 1.5 mL min^{-1}); A, Ar (flow rate: 0.7 l min^{-1}); W, waste; P, peristaltic pump; C, minicolumn packed with activated carbon; V, injection valve, valve positions: (a) sample loading; (b) injection

Column preparation: The conical minicolumn was prepared by replacing 100 mg of activated carbon into an empty column using the dry packing method. To avoid loss of activated carbon when the sample solution passes through the conical minicolumn, a small amount of quartz wool was placed at both sides of the conical minicolumn The column was then connected to a peristaltic pump with PTFE tubing to form the preconcentration system.

Sample preparation: The natural waters samples were filtered through 0.45 mm pore size membrane filters immediately after sampling and were adjusted to pH 5.0 with acetic acid solution and stored at 4 °C in bottles (Nalgene; Nalge, Rochester, NY, USA). All the glassware and plasticware used were previously washed with a 10 % (v/v) HNO$_3$/water solution and then with ultrapure water.

Preconcentration step: Before loading, the conical minicolumn was conditioned for preconcentration at the correct pH (5.0) with the 1.0 mol L^{-1} of acetic acid buffer solution, valve V$_1$ in position B (Fig. 1). The nickel solution was then loaded on the activated carbon at a flow rate of 17.0 mL min^{-1} with valve V$_1$ in position S and valve V$_2$ in load position (a).
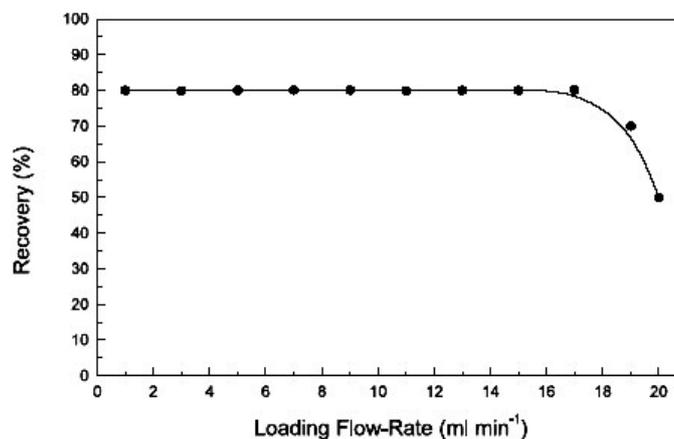
Fig. 2.   Dependence of Ni preconcentration with pH of loading solutions. Sample loading volume was 50 mL; loaded flow rate was 17 mL min^{-1}; elution flow rate was 1.5 mL min^{-1} and Ni concentration was 0.5 µg L^{-1}

Design of the column: The column design strongly influences the performance of preconcentration systems[31]. The proposed method was applied to a classical column of 3.0 mm internal diameter and 50 mm length and a conical mini-column of 4.5 mm internal upper-diameter and 1.5 mm internal lower-diameter, both columns packed with the same activated carbon mass. From present studies, it is verified that the conical minicolumn performance was much better than that of the classical column, the improvement being of 90 % with respect to the enrichment factor.

Effect of size particles: In the present work a size of activated carbon of 50-70 mesh was considered adequate for the preconcentration procedure in the conical mini-column. Smaller activated carbon particles could have improved retention capacity, but this would have increased back-pressure of the minicolumn and the flow rate ought to have been reduced, with the subsequent increase in preconcentration time. On the other hand, with particles sizes greater than 50 mesh the recovery decreased.

Effect of eluent: In order to elute nickel adsorbed on the activated carbon, nitric acid was adopted as eluent. Nickel was completely eluted with 1.0 mL of 20 % (v/v) nitric acid. The optimum eluent flow rate was 1.5 mL min^{-1}.

Performance of the system: The overall time required for preconcentration of 50 mL of solution (2.94 min, at a flow rate of 17 mL min^{-1}); washing (0.30 min, at a flow rate of 1.2 mL min^{-1}); eluting (*ca.* 0.5 min, at a flow rate of 1.5 mL min^{-1}) and conditioning (0.4 min, at flow rate of 1.2 l min^{-1}) was about 4.14 min, the throughput being about 14.5 samples *per* hour. A total enrichment factor of *ca.* 80-fold for a sample volume of 50 mL was obtained with respect to the nickel determination by ICP-OES without preconcentration.

TABLE-3

CONCENTRATIONS OF NICKEL IN DRINKING WATER AND
RIVER WATER SAMPLES (95 % CONFIDENCE INTERVAL, n = 6)

Ni concentration (μg L^{-1})	Sample (tap water)	Ni concentration (μg L^{-1})	Sample (river water)
3.217 ± 0.09	A (1st week)	1.517 ± 0.08	A
4.266 ± 0.08	B (2nd week)	1.826 ± 0.07	B
3.895 ± 0.08	C (3rd week)	1.495 ± 0.08	C
3.106 ± 0.07	D (4th week)	1.604 ± 0.07	D

The drinking water samples were collected at different times in our laboratory and the tap water samples were collected in different sectors of the Saveh Tehran, Iran.

Comparatively, Packer *et al.*[16] reported an EF of *ca.* 30-fold and the throughput was 20 samples per hour; while Ivanova *et al.*[17] reached an EF of 21-fold, the throughput being 26 samples per hour. The detection limit value for the preconcentration method calculated as the amount of Ni required to yield a net peak that was equal to 3 times the standard deviation of the background signal (3s) was 70 ng L^{-1}. The precision for 10 replicate determinations at the 0.6 μg L^{-1} Ni level was 2.2 % relative standard deviation, calculated from the peak heights obtained. The calibration graph preconcentration method for nickel was linear with a correlation coefficient of 0.9996 at levels near the detection limits up to at least 120 μg L^{-1}. The accuracy of the method was evaluated by analyzing a standard reference material, NIST SRM 1640 'trace elements in natural water', with a Ni content of 27.49/0.8 μg kg^{-1} and a density of 1.00159 ± 0.0005 g mL^{-1} at 22 °C. Using the proposed method the content of Ni determined in this SRM was 27.09 ± 0.3 μg kg^{-1}.

Finally, the results of the method applied to nickel determination in water samples are given in Table-3.

Conclusion

The main difficulty in the determination of nickel in natural waters is its low concentration level. The procedure here developed using an online preconcentration system with a FI-ICP-OES method has shown adequate sensitivity, besides being simple and economical, as only activated carbon is used for preconcentration of Ni without complexation.

The almost instantaneous release of adsorbed metal during the elution phase and the dimensional stability of the activated carbon are ideal properties for its exploitation in on-line FIA-ICP-AES systems. The recovery studies using the standard addition method showed that the proposed method can be used for the determination of nickel in natural water samples.

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