On-line preconcentration of nickel on activated carbon prior to its determination by vapor generation associated to inductively coupled plasma optical emission spectrometry

S. Cerutti,[ab] S. Moyano,[a] J. Marrero,[c] P. Smichowski[d] and L. D. Martinez*[ab]

[a] Departmento de Química Analítica, Facultad de Química, Bioquímica y Farmacia, Universidad Nacional de San Luis, Chacabuco y Pedernera, P.O. Box 375, 5700 San Luis, Argentina

[b] Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Rivadavia 1917, CP C1033 AAJ Ciudad de Buenos Aires, Argentina. E-mail: ldm@unsl.edu.ar; Fax: +54-2652-430224

[c] Comisión Nacional de Energía Atómica, Unidad de Actividad Química, Centro Atómico Constituyentes, Av. General Paz 1499, 1650 Buenos Aires, Argentina

[d] Comisión Nacional de Energía Atómica, Unidad Proyectos Especiales de Suministros Nucleares, Av. Libertador 8250, 1429 Buenos Aires, Argentina

An on-line nickel preconcentration system implemented with chemical vapor generation associated to inductively coupled plasma optical emission spectrometry (VG-ICP-OES) was studied. Trace amounts of nickel were preconcentrated by sorption on a minicolumn packed with activated carbon at pH 5.0. The analyte retained was removed from the minicolumn with 0.3 mol l^{-1} hydrochloric acid. After that, volatile species of nickel were generated by merging the acidified sample and sodium tetrahydroborate(III) in a continuous flow system. The gaseous analyte was subsequently introduced via a stream of Ar carrier into the inlet tube of the inductively coupled plasma torch. For the preconcentration procedure, an enrichment factor of 36-fold for a sample volume of 25 ml was obtained. The detection limit (DL) obtained was 0.06 µg l^{-1}. The precision (RSD) for ten replicate determinations at a level of 0.5 µg l^{-1} was 4.0%. Potential interfering effects on the Ni signal were examined.

1. Introduction

Hydride generation techniques have expanded in scope in recent years in response to the reports of the successful generation of a number of "unconventional" volatile species.[1–8]

In this sense, Guo et al.[9] and Smichowski et al.[4] reported the generation of volatile species of nickel by reaction in an aqueous solution with sodium or potassium tetrahydroborates.

Considering the low content of nickel in environmental samples, sensitive analytical techniques are required to obtain low detection limits (DLs). Inductively coupled plasma optical emission spectrometry (ICP-OES) is widely recognized as a suitable technique for the determination of nickel.[10,11] However, the low level of nickel in waters is not compatible with the DL of this technique.

Preconcentration is an effective means of extending the DLs of the ICP-OES technique. Because of its sorption characteristics, activated carbon (AC) has been widely used in the preconcentration procedures of several metal ions, and the enrichment of trace metals using AC has been performed with very high concentration factors in different matrices.[10,12–14]

In the present work, for first time, an on-line preconcentration procedure has been coupled to nickel vapor generation.

2. Experimental

2.1. Reagents

The 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 30 min, then with 10% v/v nitric acid for 20 min and finally washed with deionized water until neutral pH was reached].

Nickel standard solution was prepared by appropriate dilutions of a 1000 mg l^{-1} stock solution (Merck, Darmstadt, Germany) 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.

Sodium tetrahydroborate(III) solution, 1% m/v, was prepared by dissolving NaBH$_4$ powder (Sigma–Aldrich, St. Louis, USA) in ultra-pure water. Solutions were stabilized in 0.1% m/v NaOH (Merck) and filtered before use through Whatman No. 42 paper to eliminate turbidity. The solution was stored in a polyethylene flask at 4 °C.

Welding argon from Praxair (Buenos Aires, Argentina) was found to be sufficiently pure for Ni determination.
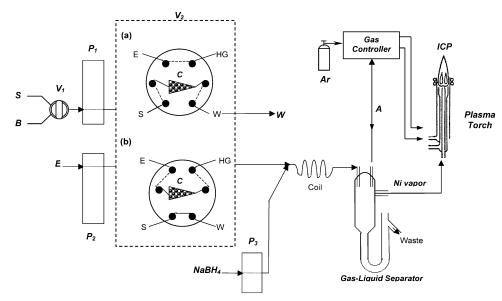
All the solutions containing the potentially interfering ions were prepared by adding appropriate amounts of stock solutions made from Merck Titrisol or their chloride salts in 0.3 mol l^{-1} hydrochloric acid.

Ultrapure water (18 MΩ cm) was obtained from an EASY pure RF (Barnstead, Dubuque, IA, USA).

All other solvents and reagents were of analytical-reagent grade or better, and the presence of nickel was not detected in the working range.

2.2. Apparatus

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 hydride unit used was a PS Analytical Ltd. hydride generator and the flow speeds of the reagents were controlled by a Watson-Marlow 303X peristaltic

Fig. 1 Schematic diagram of the instrumental setup. S, Sample (flow rate: 17 ml min^{-1}); B, buffer diluted (flow rate 2 ml min^{-1}); E, eluent (flow rate: 2.0 ml min^{-1}); NaBH$_4$ solution (flow rate 2 ml min^{-1}); W, waste; C, minicolumn packed with AC; HG: hydride generator; A, argon; P$_1$, P$_2$, P$_3$, peristaltic pumps; V$_1$, two way valve; V$_2$, injection valve Valve positions: (a) sample loading; (b) injection.

pump. The Ni vapor generated was swept out by Ar connected directly to the inlet tube of the plasma torch. The transfer line was short enough to avoid transport losses. The operating 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, four-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 carry the sample, reagent and eluent. The 221.647 nm spectral line was used and FI system measurements were expressed as peak height emission, which was corrected against the reagent blank. The temperature was controlled by means of a water bath, Polyscience (Polytemp Corporation, Niles, IL, USA).

2.3. Sample preparation

The drinking water samples were filtered through 0.45 μm pore size membrane filters immediately after sampling, adjusted to pH 5.0 with acetic acid solution and stored at 4 °C in bottles (Nalgene; Nalge, Rochester, NY, USA).

Table 1 Instrumental parameters employed for nickel determination

Plasma	
Forward power	1.0 kW
RF generator	40.68 MHz
Plasma gas flow rate	8.5 l min^{-1}
Auxiliary gas flow rate	1.0 l min^{-1}
Carrier gas flow rate	0.5 l min^{-1}
Observation height	15 mm
Hydride generation	
Samples and reagents flow rate	2.0 ml min^{-1}
Sample acidity (hydrochloric acid)	0.3 mol l^{-1}
NaBH$_4$ concentration	1.0% m/v
Temperature	60 °C

2.4. Analytical procedure

Before loading, the conical minicolumn was conditioned for preconcentration at the correct pH (5.0) with the 1.0 mol l^{-1} acetic acid buffer solution, valve V$_1$ in position B (Fig. 1). The nickel solution was then loaded on to 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).

After the loading time, the sample still present in the lines and the conical minicolumn was removed with a further washing with buffer diluted solution, with valve V$_1$ again on position B. After that, peristaltic pump P was stopped, the injection valve V$_2$ was switched to the injection position, (b), and the retained metal was eluted with 0.3 mol l^{-1} hydrochloric acid at a flow rate of 2.0 ml min^{-1}. The acidified sample solution was merged with the reductant into the vapor generator in a continuous flow system at 2.0 ml min^{-1} using a peristaltic pump. The volatile nickel compound generated was separated from the solution by means of a U-tube separator and swept by Ar (0.55 l min^{-1}) into the bottom of the quartz torch. The operating system measurements were expressed as peak-height emission, which was corrected against the reagent blank.

3. Results and discussion

The analytical parameters such as pH, activated carbon conditions, column design, size of activated carbon particles, sample loading rate, interferents, and preconcentration system performance, were studied. In addition, physical and chemical parameters affecting the overall efficiency of Ni vapor generation were evaluated.

3.1. Experimental conditions

All the optimized parameters are in agreement with those reported in previous works.[4,9,10] The selected pH was 5.0; the flow rate of sample through the conical minicolumn was 17 ml min^{-1}.

A NaBH$_4$ concentration of 1% m/v and a 0.3 mol l^{-1} concentration of HCl were selected as the most convenient for the nickel vapor generation. In the same way, the most suitable Ar flow rate used to transport nickel volatile compounds into the gas–liquid separator and then into the plasma torch was about 0.55 l min^{-1}.

In addition, we evaluated the effect of different flow rates on Ni signal. Low rates of 2.0 ml min^{-1} for the acidified samples and tetrahydroborate solution were the best choice to generate efficiently volatile compounds of nickel. Above or below this value, Ni vapor production decreases. In order to provide sufficient delay for completion of the reaction of nickel vapor generation, a reaction coil of 500 µl was adopted for subsequent studies: the reaction coil was immersed in a water bath at 60 °C.

In order to obtain a high transfer efficiency between the gas–liquid separator and the ICP-torch, a transfer line of 0.45 m length was the best option.

3.2. Interference studies

We studied two kinds of interferences: elements that could affect the preconcentration of Ni and those related to the vapor generation.

In the first case, the effects of representative potential interfering species at the concentration levels at which they might occur in the sample studied were tested. Thus, Cu(II), Zn(II), Pb(II), Co(II), Mn(II) and Fe(III) could be tolerated up to at least 2500 µg l^{-1}. Commonly encountered matrix components, such as alkali and alkaline earth elements, are not retained on activated carbon.

With respect to the nickel vapor generation, the effect of 50 mg l^{-1} and 250 mg l^{-1} concentrations of different elements were evaluated. No variation of Ni signal was observed when Al(III), As(III), Cd(II), Cr(III), Ge(IV), Mn(II), Sb(III), Sn(IV), Zn(II), Te(IV), Ti(IV), V(V), Bi(III), Co(II), Cu(II), Fe(III), Mn(II), Pb(IV) and Se(IV) were tested. These results show that the generation of Ni vapor is highly selective.

3.3. Performance of the system

The overall time required for the preconcentration of 25 ml of solution (1.47 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 (approximately 0.5 min, at a flow rate of 2.0 ml min^{-1}) and conditioning (0.4 min, at flow rate of 1.2 ml min^{-1}) was about 4.14 min. Thus, the throughput was about 14 samples per hour. A total enrichment factor of approximately 36-fold for a sample volume of 25 ml was obtained with respect to nickel determination by ICP-OES without preconcentration.

Owing to the association of the on-line preconcentration procedure with the nickel vapor generation, a detection limit value (calculated as the amount of Ni required to yield a net peak that was equal to three times the standard deviation of the background signal (3σ)) of 0.06 µg l^{-1} was obtained. The precision for 10 replicate determinations at the 0.5 µg l^{-1} Ni level was 4.0% relative standard deviation, calculated from the peak heights obtained.

Recovery studies on a real sample have demonstrated that the proposed method is adequate for nickel determination; the recoveries were in the range 97–100.5%. 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 27.4 ± 0.8 µg kg^{-1}. Using the proposed methodology, the content of Ni determined in this SRM was 27.0 ± 0.3 µg kg^{-1}.

Finally, the results of the method applied to nickel determination in drinking water samples analyzed over 4 weeks were in the range 3.2–4.1 µg l^{-1}.

4. Conclusions

This study has demonstrated for the first time the possibility of associating an on-line preconcentration procedure using activated carbon as sorbent with the generation of volatile species of nickel. This coupling could be applied to other elements which form "unconventional" volatile species.

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