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Online Copper Removal for Selenium Determination by Hydride Generation-Inductively Coupled Plasma Optical Emission Spectrometry

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Abstract: Selenium determination in samples with a high copper content by hydride generation–inductively coupled plasma optical emission spectrometry (HG-ICP-OES) after online copper removal and selenium (VI) reduction is described. An activated carbon minicolumn was used for the retention of copper and its subsequent separation of Se. Se(VI) was then online reduced by heating into a PTFE coiled

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reactor with 12 M HCl. The analyte was introduced into a water stream containing sodium tetrahydroborate (NaBH_4) in order to generate selenium hydride (H_2Se). The detection limit (DL) obtained was $0.8 \mu\text{g L}^{-1}$, and the precision, expressed by the relative standard deviation (RSD), was 2.5% ($n = 10$; $10 \mu\text{g L}^{-1}$ selenium level). The current method was applied to the Se determination in two copper reference materials, MBH-39DK 3601 (with a Se content of 90 mg kg^{-1}) and MBH-39 DK 3604 (with a Se content of 15 mg kg^{-1}).

Keywords: Activated carbon, continuous flow, HG-ICP-OES, online Cu removal, Se determination, Se(VI) prereduction

INTRODUCTION

The hydride generation (HG) technique in combination with inductively coupled plasma–optical emission spectrometry (ICP-OES) is a routine methodology for the determination of selenium.^[1,2] The HG-ICP-OES technique minimizes spectral interference problems caused by other matrix components. However, there remain other types of interferences such as those affecting the HG process. It is well-known that the interference caused by copper is a serious problem for the determination of selenium by HG-ICP-OES or hydride generation atomic absorption spectrometry (HG-AAS),^[3–5] because this interference results in the inhibition of selenium hydride formation.^[6–8]

Removal of Cu has been attempted by addition of different masking agents.^[9–12] However, the interference caused by copper could not be totally eliminated when its concentration was more than 200 mg L^{-1} .

On the other hand, several procedures for separating selenium from the matrix by means of coprecipitation with lanthanum hydroxide,^[13] liquid–liquid extraction with APDC-chloroform,^[14] or isolating it by means of ion exchange in a batch system have been carried out.^[11,14,15] Nevertheless, they have the disadvantage of being tedious and labor dependent on operator skills.

As well, flow injection (FI) hydride generation coupled to ICP-OES^[16–18] or ICP-MS^[19] has been used to reduce the interference effect caused by some transition metals in the determination of selenium.

Online separation techniques have become increasingly popular for the determination of trace elements in different types of samples. Cationic or anionic resins have been used in continuous-flow injection systems for the elimination of interferences such as copper, nickel, and iron.^[20–23]

In previous works, we described some online procedures concerning interference removal. In all these systems, a flow injection approach was needed to improve the coupling between the separation technique and the hydride generation.^[14,17,20,21,23]

Activated carbon (AC) has been widely used for many purposes both in laboratory and industrial settings, due to its ability to adsorb organic compounds and inorganic metal complexes. Since its introduction in

analytical chemistry, enrichment of trace metals using AC has been favorably performed with very high concentration factors in different matrices.^[24–27]

The mechanism of sorption on AC is still under investigation, and the adsorption of metals on activated carbon could be explained using Langmuir and Freundlich equations. The adsorption equilibrium studies have revealed that pH is the dominant parameter controlling the adsorption.^[28]

This paper reports a simple online system for the generation of selenium hydride, in which the interference of copper has been online removed using a minicolumn packed with activated carbon. As well, online prereduction of Se in a continuous-flow system has been carried out. Moreover, an important advantage of this work is the quantitative Cu retention on AC at high sample loading rates. This fact is particularly important due to existence of a good agreement with the optimal hydride generation flow rate (9 mL min^{-1}) without the use of a flow injection system. The interference separation procedure allowed the determination of selenium by HG-ICP-OES in high copper content samples.

MATERIALS AND METHODS

Reagents

An 0.6% (w/v) sodium borohydride solution (>98% Aldrich Chemical Co., Milwaukee, WI, USA) was prepared in 0.5% (w/v) sodium hydroxide solution and was filtered through Whatman no. 42 filter paper to remove undissolved solids. This solution was prepared daily.

Standard solution of selenium was prepared by dissolution of suitable amounts of the oxide (99.999% pure, Johnson Matthey Chemicals, Karlsruhe, Germany) in small volumes of nitric acid, followed by dilution with ultrapure water. The activated carbon (Merck, Darmstadt, Germany, 50–70 mesh) was used after pretreatment with acid [activated carbon was heated with 10% (v/v) hydrochloric acid for 30 min and then with 10% (v/v) nitric acid for 20 min and finally washed with deionized water until neutral pH was reached].

Ultrapure water ($18 \text{ m}\Omega \text{ cm}$) was obtained from EASY pure RF (Barnstedt, Dubuque, Iowa, USA). All reagents were of analytical reagent grade, and the presence of selenium was not detected in the working range.

Instrumentation

The measurements were performed with a sequential ICP spectrometer (BAIRD ICP 2070; Bedford, MA, USA). The ICP operating conditions are listed in Table 1. The FI system used is shown in Fig. 1. A Minipulse 3 peristaltic pump (Gilson Villiers-Le-Bell, France) was used. Sample and eluent line

Table 1. ICP-OES instrumental parameters employed for selenium determination

Forward power	1.0 kW
RF generator	40.68 MHz
Coolant 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
Solution uptake rate	1.5 mL min ⁻¹
Observation height (above load coil)	15 mm

ICP-OES, inductively coupled plasma optical emission spectrometry.

were selected using a Reodyne (Cotai, CA, USA) model 50, four-way rotary valve. The hydride unit used was a hydride generator (PS Analytical Ltd., Orpington, Kent, UK) and the flow rate of the reagents was controlled by a Watson-Marlow (Falmouth, Cornwall, UK) 303X peristaltic pump. The coiled reactor (150 cm length, 0.7 mm i.d.) was prepared using PTFE tubing. A microbore glass column (100 mm length, 3 mm i.d.) fitted with porous 25- μ m glass beads was used as the activated carbon holder. Tygon-type pump tubing (Ismatec, Cle-Parmer, Vernon Hills, IL, USA) was employed to propel the sample, reagent, and eluent. The Se 196.026-nm spectral line was used.

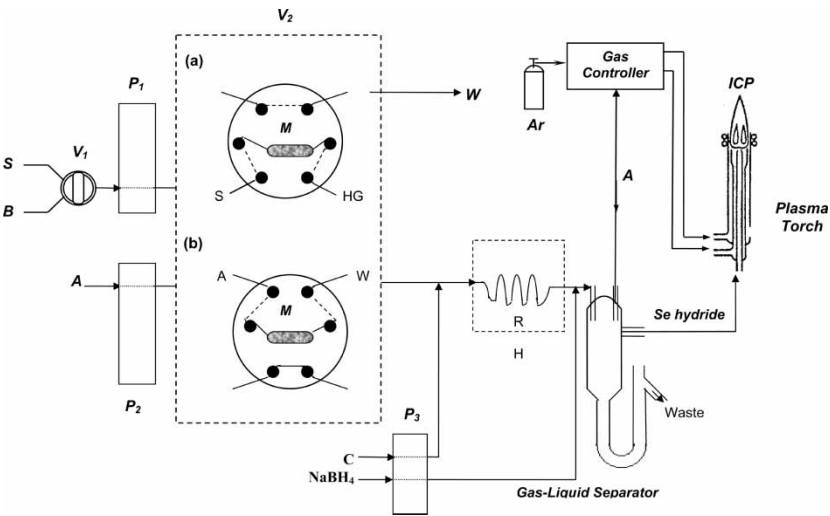


Figure 1. Schematic diagram of the instrumental setup. S, sample (flow rate 1.5 mL min⁻¹); A, 2 mol L⁻¹ HNO₃ (flow rate 1.5 mL min⁻¹); C, 12 mol L⁻¹ HCl (flow rate: 4.5 mL min⁻¹); M, minicolumn; R, reactor; H, boiling water bath; W, waste; P, peristaltic pump; V₁, two-way valve; and V₂, six-port valve. Valve positions: (a) Cu retention; (b) Cu elution.

Column Preparation

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

Dissolution of Copper Metal Reference Materials

A sample of 0.125 g of copper metal was digested with approximately 10 mL of a nitric and hydrochloric acid mixture (1 + 3). The resulting solution was heated to near dryness, taken up with 30.0 mL of 2 mol L⁻¹ NH₃/NH₄⁺ solution at pH 9.0, and made up to 250 mL with ultrapure water. The solution was then ready for analysis.

Method Development

Selenium Determination

The manifold showed in Fig. 1 was used for removal of Cu and reduction of Se. The minicolumn (M) packed with activated carbon was conditioned during 15 s with diluted NH₃/NH₄⁺ buffer at pH 9.0 at a flow rate of 8 mL min⁻¹; valve V₁ in B position and valve V₂ in position (a). After that, the sample was pumped (P₁) at 4.5 mL min⁻¹ through the minicolumn in order to achieve the copper removal with V₁ in S position and V₂ in position (a); and 12.0 mol L⁻¹ HCl (C) was pumped (P₂) at 4.5 mL min⁻¹ through the reactor (R) placed in a boiling water bath (95°C) (H) in order to reduce Se(VI) to Se(IV).

After that, two-way valve, V₂, was switched to position (b) and the interferences were eluted using 20% (v/v) nitric acid (A), which was pumped during 60 s through the minicolumn at a flow rate of 2 mL min⁻¹. Then, the minicolumn was washed with ultrapure water. After the clean-up period, the conditioning step was carried out, and a new cycle was repeated.

Standard solutions, requiring no copper isolation, were pumped (S) through the valve V₂ (b), bypassing the minicolumn. The HG manifold and solvents, 12.0 mol L⁻¹ HCl (C) and 0.6% (w/v) NaBH₄ (flow rate 3 mL min) ran continuously throughout the procedure, independently of the matrix isolation unit operation. The operating conditions were established and the determination was subsequently carried out.

It was verified that the same minicolumn packed with activated carbon can be used at least 200 cycles without any loss of its performance.

RESULTS AND DISCUSSION

Interference Removal Conditions

The proposed separation/determination system permitted to separate copper from selenium by using an activated carbon minicolumn, online reduction of Se(VI) by means of HCl and heating conditions, and subsequent HG-ICP-OES determination.

Figure 2 shows the results for the determination of selenium in some synthetic samples with high copper content. It can be concluded that in samples in which the selenium content is low (trace level) and copper is found as a major interfering component, necessarily a separation technique must be used.

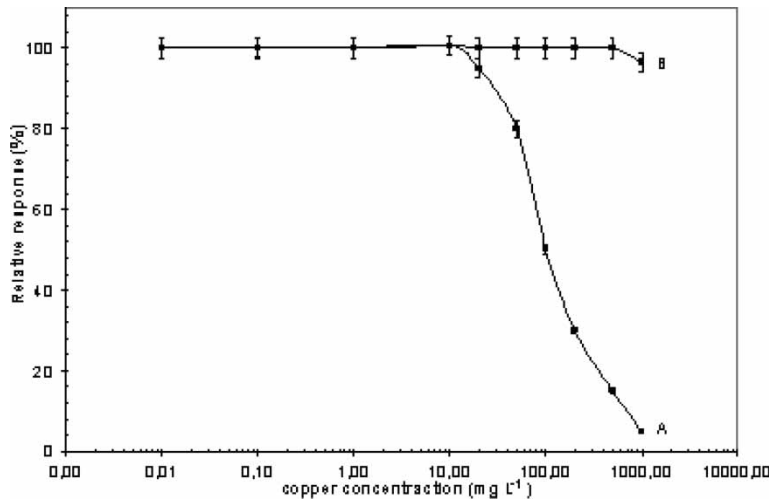


Figure 2. Effect of copper concentration on the response of Se(IV) (10 $\mu\text{g L}^{-1}$). A, Approach not including an activated carbon minicolumn prior to Se determination by HG-ICP-OES. B, Approach including an activated carbon minicolumn prior to Se determination.

Effect of pH and Column Length on Cu Retention

In order to optimize the retention sorption conditions for the retention of Cu on AC, the Cu copper signal was monitored by measuring it with ICP-OES while changing the pH of the solution (1000 mg L^{-1} Cu level) that passes through the minicolumn (10-cm length) packed with AC. Figure 3 shows that the optimum pH value for Cu retention on AC was 9.0. At lower pH values, the recovery decreases.

On the other hand, the minicolumn length was tested by measuring the Cu retention signal on AC by ICP-OES. Solutions containing a

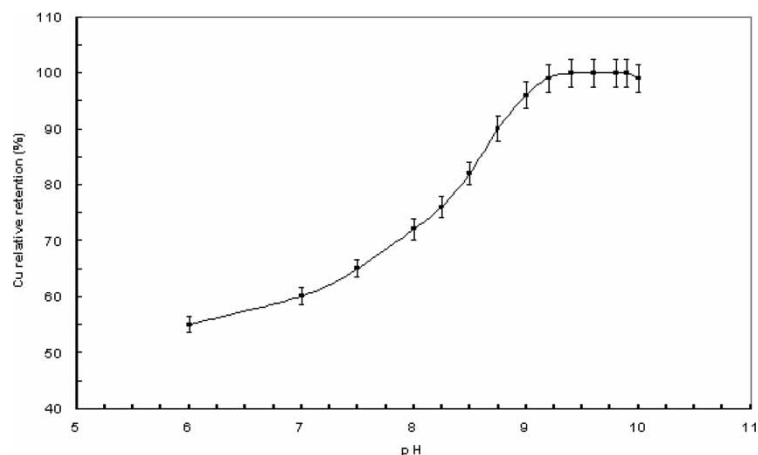


Figure 3. Effect of pH on the retention of copper. Sample flow rate 4.5 mL min^{-1} at 1000 mg L^{-1} Cu level.

1000 mg L^{-1} Cu concentration buffered at pH 9 were passed through different AC minicolumn lengths. As seen in Fig. 4, the retention decreased at lengths shorter than 8.0 cm. Accordingly, the chosen minicolumn length for subsequent experiments was 10 cm.

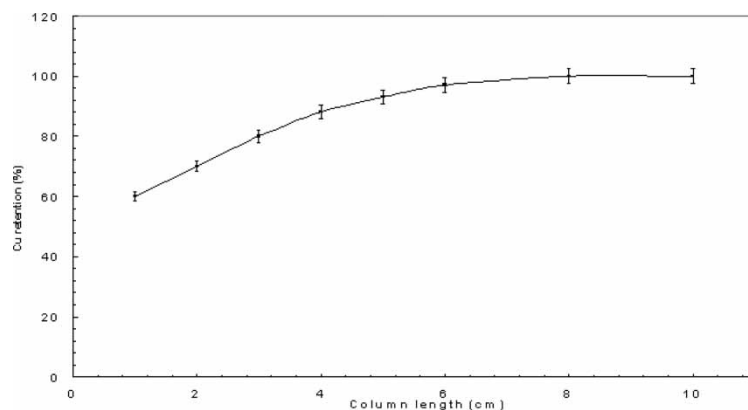


Figure 4. Effect of column length on the retention of copper. Sample flow rate, 4.5 mL min^{-1} ; pH = 9.0; and Cu concentration, 1000 mg L^{-1} .

Effect of the Sample Loading Rate on Cu Retention

The evaluation of the effect of sample flow rate on Cu % recovery was performed by following a batch procedure: an aqueous solution containing

Cu analyte (500 mg L^{-1}) buffered to pH 9.0 was passed through the column packed with AC at flow rates between 1 and 10 mL min^{-1} during 1.5 min. Finally, the retained metal was eluted with 20% (v/v) nitric acid into a 100-mL volumetric flask. The concentrations of Cu were determined by ICP-OES. Recovery was calculated against the theoretical concentration. After these experiments were carried out, we could verify that with flow rates up to 8 mL min^{-1} , there is no effect on the Cu retention, while at higher loading flow rates the recovery decreases.

However, in order to satisfy the optimal hydride generation sample flow rate (9 mL min^{-1}) requirement, a compromise decision was made. Taking into account the HCl flow rate (4.5 mL min^{-1}), a 4.5 mL min^{-1} sample loading flow rate was chosen. Accordingly, the hydride generation requirements were accomplished without sacrificing the necessary conditions to attain an optimal copper separation.

Effect of Se-Hydride Generation Conditions

The optimal sample flow rate into the conventional hydride generation system was found to be 9 mL min^{-1} . In previous reported works,^[14,17,20–23] a loop sample had always been employed in order to make compatible the interference elimination flow rate with the optimal hydride generation flow rate. Because the Cu elimination flow rate could be high enough for online coupling both steps, separation and hydride generation, the system proposed is able to run continuously.

This system enabled us to separate copper using the activated carbon mini-column at a 4.5 mL min^{-1} flow rate. Subsequently, online reduction of Se(VI) was carried out by introducing the sample into an HCl stream (at a 4.5 mL min^{-1} flow rate) following the introduction in the coiled reactor (95°C).

Evaluation of the System Performance

The relative standard deviation (RSD; $n = 10$, at 95% confidence level) was 2.5% (at $25 \text{ } \mu\text{g L}^{-1}$ selenium level), calculated using the obtained emission signal. The detection limit (DL) was calculated as the amount of selenium required to yield a neat signal equal to three times the standard deviation of the background signal (3σ). The value of the DL obtained was $0.8 \text{ } \mu\text{g L}^{-1}$.

Method Validation

To check the proposed method for selenium determination, a recovery study was carried out on synthetic samples. The recoveries were found to be in the range 98.0–100.5%. Finally, the method was applied to the selenium

Table 2. Results of the analysis of copper in two reference materials

Sample	Certified value Se (mg kg ⁻¹)	Se found (mg kg ⁻¹)
MBH-39 DK 3601	90 ^a	90.5 ± 1.3 ^b
MBH-39 DK 3604	15 ^a	14.8 ± 1.5 ^b

^aRecommended values.

^b95% confidence interval (n = 10).

determination in two copper reference materials, MBH-39 DK 3601 and MBH-39 DK 3604, and the results are shown in Table 2.

CONCLUSIONS

The results obtained for the analysis of two reference materials show that it is possible to determine selenium precisely and accurately in samples with a high copper content by HG-ICP-OES. The copper was online removed by means of a rapid and simple solid-phase extraction procedure using activated carbon like adsorbent. In the system proposed, the pH adjustment by means of ammonia buffer suffices to retain the copper ions on activated carbon. As well as, a flow injection system was unnecessary to achieve the main purpose of the current work, copper separation from Se, subsequent online Se reduction, and its determination by HG-ICP-OES.

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REFERENCES

1. Nakahara, T. Applications of hydride generation techniques in atomic absorption, atomic fluorescence and plasma atomic emission spectroscopy. *Prog. Anal. At. Spectrosc.* **1983**, 6, 163–223.
2. Nakahara, T. Hydride generation techniques and their applications in inductively coupled plasma atomic emission spectrometry. *Spectrochim. Acta Rev.* **1991**, 14, 95–109.

3. Meyer, A.; Hofer, C.; Tolg, G.; Raptis, S.; Knap, G. Cross-interferences by elements in the determination of traces of selenium by the hydride-AAS procedure. *Fresenius Z. Anal. Chem.* **1979**, 327, 337–344.
4. Weltz, B.; Melcher, M. Mechanisms of transition metal interferences in hydride generation AAS. *Analyst* **1984**, 109, 577–579.
5. D'Ulivo, A.; Ginfranceschi, L.; Lampugnani, L.; Zamboni, R. Masking agents in the determination of selenium by hydride generation technique. *Spectrochim. Acta* **2002**, 57 (B), 2081–2094.
6. Thompson, M.; Pahlavanpour, B.; Walton, S.; Kirbright, G. Simultaneous determination of trace concentrations of arsenic, antimony, bismuth, selenium, and tellurium in aqueous solution by introduction of the gaseous hydrides into an inductively coupled plasma source for emission spectrometry. II. *Analyst* **1978**, 103, 705–713.
7. Campbell, A. D. A critical survey of hydride generation techniques in atomic spectroscopy. *Pure Appl. Chem.* **1992**, 64, 227–244.
8. Bax, D.; Agterdenbos, J.; Worrell, E.; Beneken Kolmer, J. The mechanism of transition metal interference in hydride generation atomic absorption spectrometry. *Spectrochim. Acta* **1988**, 43 (B), 1349–1354.
9. Wickstrom, T.; Lund, W.; Bye, R. Determination of arsenic and tellurium by hydride generation atomic spectrometry: minimizing interference from nickel, cobalt, and copper by using an alkaline sample solution. *Analyst* **1995**, 120, 2695–2698.
10. Wickstrom, T.; Lund, W.; Bye, R. The masking effect of iron(III) on the interference from nickel and copper in the determination of tellurium by hydride generation/atomic absorption spectrometry. *Anal. Chim. Acta* **1988**, 208, 347–350.
11. Bye, R.; Engvik, L.; Lund, W. Thiourea as a complexing agent for reduction of copper interference in the determination of selenium by hydride generation/atomic absorption spectrometry. *Anal. Chem.* **1983**, 55, 2457–2458.
12. Nakahara, T.; Kikui, N. Determination of trace concentrations of selenium by continuous hydride generation-inductively coupled plasma spectrometry. *Spectrochim. Acta* **1985**, 40B, 21–28.
13. Bedard, M.; Kerbyson, J. Determination of arsenic, selenium, tellurium, and tin in copper by hydride evolution atomic absorption spectrophotometry. *Can. J. Spectrosc.* **1976**, 21, 64–68.
14. Martinez, L. D.; Bucells, M.; Pelfort, E.; Roura, M. Removal of iron interference in the determination of selenium in geological samples by continuous glow hydride generation ICP-AES. *Fresenius J. Anal. Chem.* **1996**, 354, 126–127.
15. Hershey, J.; Keliher, P. Some atomic absorption hydride generation inter-element interference reduction studies utilizing ion exchange resins. *Spectrochim. Acta* **1989**, 44 (B), 329–337.
16. Bolea, E.; Laborda, F.; Castillo, J. R.; Sturgeon, R. E. Electrochemical hydride generation for the simultaneous determination of hydride forming elements by inductively coupled plasma-atomic spectrometry. *Spectrochim. Acta* **2004**, 59 (B), 505–513.
17. Martinez, L. D.; Saidman, E.; Marchevsky, E.; Olsina, R. A. Determination of selenium in geochemical samples by flow injection hydride generation inductively coupled plasma atomic emission spectrometry following on-line removal of iron interference by anion exchange. *J. Anal. At. Spectrom.* **1997**, 12, 487–490.

18. Machat, J.; Otruba, V.; Kanicky, V. Spectral and non spectral interferences in the determination of selenium by inductively coupled plasma-atomic emission spectrometry. *J. Anal. At. Spectrom.* **2002**, *17*, 1096–1102.
19. Sieniawska, C.; Mensikov, R.; Delves, H. Determination of total selenium in serum, whole blood and erythrocytes by ICP-MS. *J. Anal. At. Spectrom.* **1999**, *14*, 109–112.
20. Moyano, S.; Gásquez, J.; Marchevsky, E.; Olsina, R.; Martinez, L. D. The determination of Se by flow injection hydride generation ICP-OES using anion exchange for on-line removal of copper. *Atomic Spectros.* **1997**, *18*, 152–155.
21. Martinez, L. D.; Bucells, M.; Pelfort, E.; Roura, M.; Olsina, R. Selenium determination by HG-ICP-ES: elimination of iron interferences by means of an ion-exchange resin in a continuous flow system. *Fresenius J. Anal. Chem.* **1997**, *357*, 850–852.
22. Offley, S. G.; Seare, N. J.; Tyson, J. F.; Kibble, H. A. B. Elimination of copper interference by continuous flow matrix isolation in the determination of selenium by flow injection hydride generation atomic absorption spectrometry. *J. Anal. At. Spectrom.* **1991**, *6*, 133–138.
23. Stripeikis, J.; Tudino, M.; Troccoli, O.; Wuilloud, R.; Olsina, R.; Martinez, L. D. On-line copper and iron removal and selenium(VI) pre-reduction for the determination of total selenium by flow-injection hydride generation-inductively coupled plasma optical emission spectrometry. *Spectrochim. Acta* **2001**, *56* (B), 93–100.
24. Narim, I.; Soylak, M.; Elci, L.; Dogan, M. Determination of trace metals ions by AAS in natural water samples after preconcentration of pyrocatechol biolett complexes on activated carbon column. *Talanta* **2002**, *52*, 1041–1046.
25. Cerutti, S.; Silva, M.; Gásquez, J.; Olsina, R.; Martinez, L. D. On-line preconcentration/determination of cadmium in drinking water on activated carbon using 8-hydroxyquinoline in a flow injection system coupled to an inductively coupled plasma-optical emission spectrometer. *Spectrochim. Acta* **2003**, *58* (B), 43–50.
26. Yunes, N.; Moyano, S.; Cerutti, S.; Gásquez, J.; Martinez, L. D. On-line preconcentration and determination of nickel in natural water samples by flow injection-inductively coupled plasma-optical emission spectrometry (FI-ICP-OES). *Talanta* **2003**, *59*, 943–949.
27. Gil, R.; Cerutti, S.; Gásquez, J.; Olsina, R.; Martinez, L. D. On-line preconcentration and determination of chromium in parenteral solution by inductively coupled plasma-optical emission spectrometry. *Spectrochim. Acta* **2005**, *60* (B), 531–535.
28. Chen, J.; Lin, M. Surface charge and metal ion adsorption on an H-type activated carbon: experimental observation and modeling simulation by the surface complex formation approach. *Carbon* **2001**, *39*, 1491–1504.