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Determination of scandium in acid mine drainage by ICP-OES with flow injection on-line preconcentration using oxidized multiwalled carbon nanotubes



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ABSTRACT

An on-line scandium preconcentration and determination system implemented with inductively coupled plasma optical emission spectrometry associated with flow injection was studied. Trace amounts of scandium were preconcentrated by sorption on a minicolumn packed with oxidized multiwalled carbon nanotubes, at pH 1.5. The retained analyte was removed from the minicolumn with 30% (v/v) nitric acid. A total enrichment factor of 225-fold was obtained within a preconcentration time of 300 s (for a 25 mL sample volume). The overall time required for preconcentration and elution of 25 mL of sample was about 6 min; the throughput was about 10 samples per hour. The value of the detection limit was 4 ng L^{-1} and the precision for 10 replicate determinations at 100 ng L^{-1} Sc level was 5% relative standard deviation, calculated from the peak heights obtained. The calibration graph using the preconcentration system was linear with a correlation coefficient of 0.9996 at levels near the detection limits up to at least 10 mg L^{-1} . After optimization, the method was successfully applied to the determination of Sc in an acid drainage from an abandoned mine located in the province of San Luis, Argentina.

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1. Introduction

Scandium, a predominantly soil-associated trace element, can be under some circumstances released into the environment from new technologies development, mine activity, and industrial waste; among others [1–6]. This element has been used as a marker of environmental pollution produced by some radionuclides present in the particulate material adhered to environmental matrices (plants, natural waters, etc.) [7–9]. In addition, the massive development and use of new technologies has released certain elements to the environment, so that rare earth elements and Sc have been reported above the usual levels [10,11].

On the other hand, pollution from abandoned mining sites has caused water and soil contaminations in many parts of the world [12,13]. This environmental polluting phenomenon is produced with oxidation of sulfide minerals e.g. pyrite and pyrrhotite [14,15]. Consequently, acidification would increase the dissolution of toxic metals from tailings, waste rock piles, and open pits [13]. Therefore, soil and water ecosystems would be contaminated [16,17]. Certainly, as rainfall water infiltrates into the underground

soil/rock, it can cause pore-water flow into the pore space of the soil/rock. When the pore-water becomes in contact with the soil/rock, it can react chemically with the mine waste and other soil minerals, dissolving metals and other compounds at the mine site. Since the dissolved analytes can be transported through pore-water advection, convection, and solute diffusion/dispersion [18], they can contaminate both the land and the groundwater at the mine site [13].

Acid minesoils are found extensively over large areas (Spain, Portugal, developed on abandoned mine lands of the Iberian Pyrite Belt, including the world-renowned mining districts of Riotinto, Tharsis and Aljustrel) [13]. Mining activity was very popular a few centuries ago in the province of San Luis, Argentina. Nowadays, the mines have been abandoned, but there are many drainages coming out from them, which are affecting the river water and soil quality of the surrounded inhabited areas. Studies have already demonstrated the presence of some rare earths elements-enriched zones [19,20] and, due to the acidity characteristics of the soil and drainages, Sc could be present at levels above usual, considering that the concentration level of this element in natural waters can be very low [21].

Although enrichment, sensitive analytical techniques are required for Sc determination. Powerful methodologies with sufficient detection capability such as neutron activation analysis (INAA) [1–3]

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have been used for its detection. However, this method is time-consuming – approximately 3 weeks – and routine analysis of numerous samples is laborious. INAA also requires sophisticated instrumentation that may be not available in most of the analytical laboratories. Another interesting technique for Sc determination is inductively coupled plasma-mass spectrometry (ICP-MS), but the isotopic nature of the element makes it susceptible to polyatomic interferences [22]. Moreover, this technique has a Sc detection limit of $0.05 \mu\text{g L}^{-1}$; so its capability is insufficient for scandium determination in natural water samples.

In the same way, if conventional inductively coupled plasma optical emission spectrometry (ICP-OES) is used, the low level of scandium concentration in environmental matrices is not compatible with the determination limit of the technique. Consequently, in order to achieve accurate, reliable, and sensitive results, preconcentration and separation approaches are normally proposed when the levels of the studied analytes in the original material or the prepared solution are too low to be determined directly by ICP-OES.

Because of its sorption characteristics, carbon nanotubes (CNTs) have been proposed as a novel solid phase extractant for various inorganic and organic compounds [23–29], thus they have come under intense multidisciplinary study because of their unique physical and chemical properties and applications [30–33]. A large specific surface area and sorption capacity linked to developed internal pore structures and the presence of a wide variety of surface functional groups are some of the advantages of this material [34–36]. The primary adsorption mechanism of metal ions to CNTs is perceived to be surface complexation with functional groups, so the performance is mainly determined by the nature and the concentration of these groups, which could be different due to the modification and functionalization of the surface [26–29]. Nowadays, work has progressed in developing diverse chemical varieties of CNTs, which suggests a wide range of possible SPE materials (e.g. single and multiwalled carbon nanotubes (SWCNTs and MWCNTs), functionalized, non-functionalized, etc.), including different chemical possibilities and applications in SPE methods [30–32].

Taking into account the properties of the carbon nanotubes and the sensitivity of ICP-OES coupled to a flow injection system, a study was undertaken to develop a method to determine Sc at ultra-trace levels. To this aim, a novel, rapid, and sensitive method

for the preconcentration and determination of scandium in acid mine drainage (AMD) samples using multiwalled carbon nanotubes as sorbent material was proposed. Scandium was retained without the need of a complexing reagent, pH adjustment sufficed to achieve a quantitative adsorption, making the proposed system simpler and economical. The on-line determination was performed using ICP-OES. The flexibility of adopting diverse sample loading times to attain different enrichment factors was one of the advantages of the proposed method.

2. Experimental

2.1. Standards and reagents

All solutions were prepared with Ultrapure water (18 M Ω cm) obtained from a Mili-Q, EASY pure RF (Barnsted, Iowa, USA). For pH adjustment, hydrochloric acid and sodium hydroxide purchased from Merck (Germany) were used. Nitric and sulfuric acids were obtained from Sigma-Aldrich (Germany). Sc stock standard solution, from metallic scandium (8625 h, Colbrook, Koch-Light Laboratories, England, purity > 96%), was prepared. Aqueous working standard solutions were made by stepwise dilution from the stock solution. Multiwalled carbon nanotubes were purchased from Sun Nanotech Co. Ltd., (Jiangxi, China). All glasses and other lab materials were cleaned by soaking in 10% HNO₃ and rinsing with ultrapure water. All other solvents and reagents were of analytical reagent grade or better and the presence of scandium was not detected in the working range.

2.2. Instrumentation

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 FI system used is shown in Fig. 1. The ICP operating conditions are listed in Table 1. A Minipuls 3 peristaltic pump [Gilson (Villiers-Le-Bell, France)] was used. Sample injection was achieved using a Rheodyne (Cotati, CA, USA) Model 50, four-way rotary valve. The conical minicolumn was prepared by placing 150 mg of oxidized multiwalled carbon nanotubes (Ox-CNTs) into an empty conical tip using the dry packing method. To avoid filling losses when the

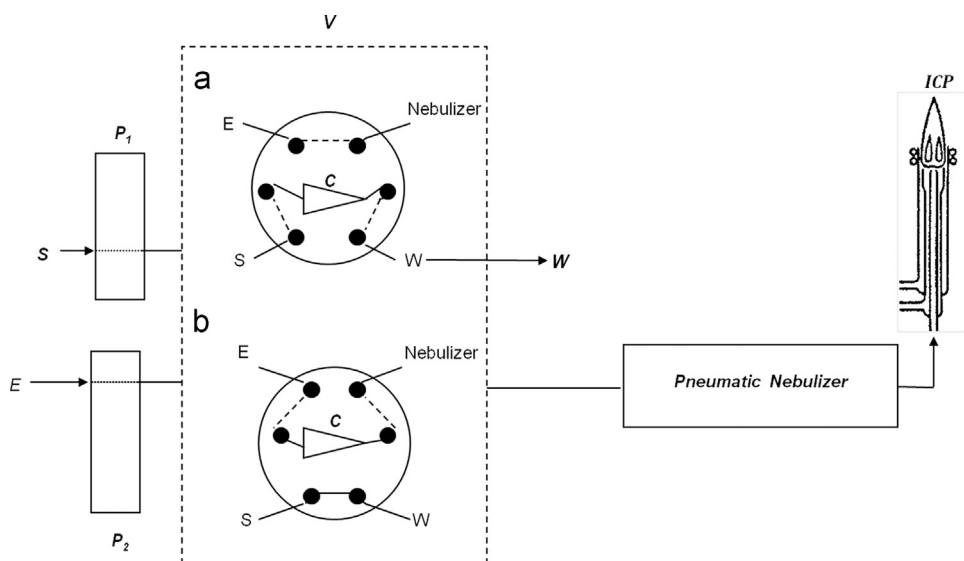


Fig. 1. Schematic diagram of the instrumental setup. S: sample (flow rate: 5.0 mL min^{-1}); E: eluent (flow rate: 1.5 mL min^{-1}); W: waste; P₁, P₂: peristaltic pumps; C: Ox-CNTs-minicolumn; V: injection valve. Valve positions: (a) sample loading; (b) injection.

sample solution passed through the conical minicolumn, a small amount of quartz wool was placed at both the ends. The column was then connected to a peristaltic pump to form the preconcentration system. Prior to use, a 5% nitric acid solution was passed through the CNTs minicolumn. After that, the column was washed with ultra-pure water until reaching neutral pH. Tygon-type pump tubing (Ismatec, Cole-Parmer, Vernon Hills, IL, USA) was employed to propel the sample and eluent. Measurements were expressed as peak height emission, which was corrected against the reagent blank.

2.3. CNTs oxidation procedure

Commercial MWCNTs were treated as reported previously [37]. The followed approach allowed the generation of –COOH and –OH groups onto the CNTs surface, improving their solubility. As mentioned in the literature, the CNTs oxidation reaction is easy to start at the end caps because of the heavy strain of the hexagon–heptagon pairs [25,31]. Thus the end caps are quickly removed leaving open-ended tubes, functionalized with carboxylic acid groups [27,33]. The obtained Ox-CNTs were filtered and washed repeatedly with ultrapure water until complete elimination of the residual acid. The resultant powder was packed into a conical minicolumn.

2.4. Sample collection

La Carolina abandoned mine is located approximately 80 km north of San Luis city, specifically on the bottom of the Tomolasta hill (Fig. 2). According to the 2010 national census, the population of La Carolina village was approximately 250 people. The climate

of this region has been classified as semi-arid with average minimum and maximum temperatures ranging from $-12\text{ }^{\circ}\text{C}$ to $30\text{ }^{\circ}\text{C}$ during winter and summer seasons; respectively. La Carolina village was founded around 1792 when gold mining activities began in the nearby. From this date, the mine underwent three exploitation phases: (a) 1794–1810 by Spain, (b) 1860–1890 by an English company and, (c) 1920–1955, by an Argentinean company. Currently, no mining actions are being carried out, but the past actions have left hundreds of abandoned tunnels with their ventilation shafts producing significant amounts of AMD. Previous research [38] has shown that effluent water samples had low pH (from 2.6 to 5.5); for this study, a pH value of 3.5 was determined in the AMD samples. In addition, several minerals such as quartz veins with auriferous pyrite, native gold, chalcopyrite, sphalerite, and galena, accompanied by abundant clay material, product of the alteration of the host rocks, have been observed. Due to this kind of mineralization, high concentrations of sulfate and iron can be determined in all extension of the stream and nearby areas. The presence of these minerals in large quantities shows that AMD generation is very active at La Carolina gold mine. Furthermore, Zn-related to the gold mineralization anomalous levels have been reported in the river streams near to La Carolina [38].

2.5. Sample preparation

Immediately after collection, the acid mine drainage samples were filtered through $0.45\text{ }\mu\text{m}$ pore size membrane filters, acidified with nitric acid, and stored to $4\text{ }^{\circ}\text{C}$ in Nalgene bottles. Samples' pH was determined in the field using a portable pH-meter (Orion Research, Inc., Orion 230 A, Beverly, MA, USA) equipped with a 9107 BN Orion glass electrode.

2.6. Preconcentration step

Scandium concentration of the AMD samples was determined using an on-line system composed of flow injection (FI) and a packed minicolumn associated with inductively coupled plasma optical emission spectrometer. Thus, 25 mL of aqueous sample solution (pH adjusted to 1.5) containing scandium, at a flow rate of 5.0 mL min^{-1} , were on-line passed through the Ox-CNTs minicolumn; valve V in load position (a) (Fig. 1). Finally, the peristaltic pump P_1 was stopped, the injection valve V was switched to the

Table 1
ICP instrumental parameters for Sc determination.

Conditions	
RF generator power (kW)	1.0
Frequency of RF generator (MHz)	40.68
Outer gas flow rate (L min^{-1})	8.5
Auxiliary gas flow rate (L min^{-1})	1.0
Observation height (mm)	15
Sc spectral line (nm)	361.364

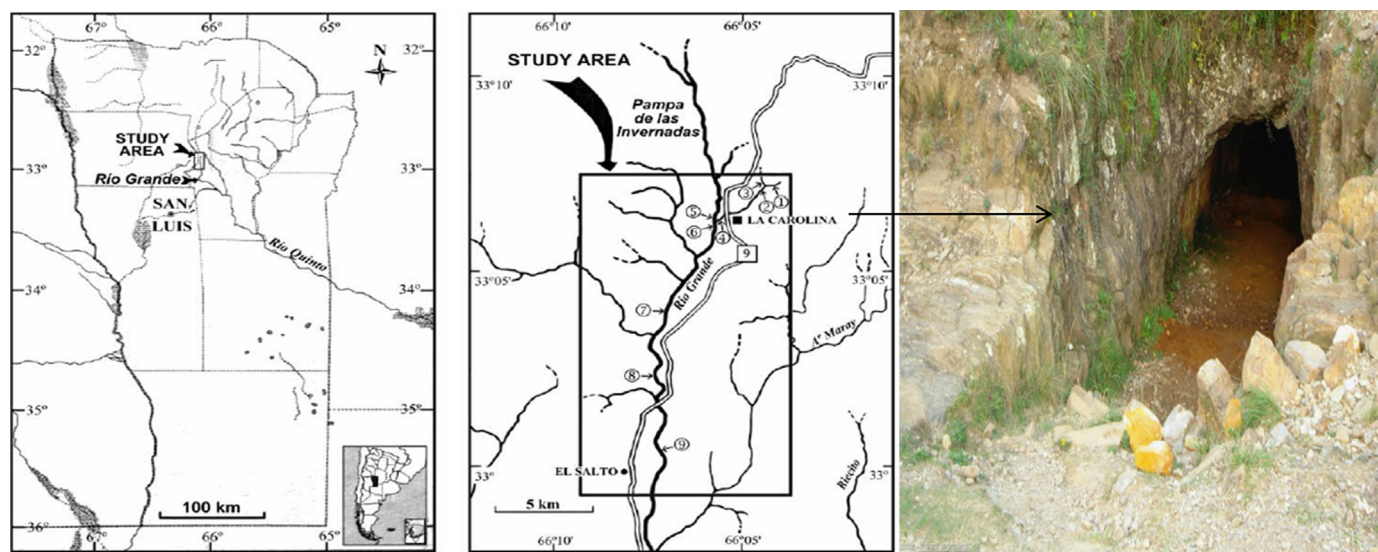


Fig. 2. Location of the source of the mine acidic water associated with the gold deposit of La Carolina, San Luis, Argentina.

injection position (b) and the retained metal was eluted with 30% (v/v) nitric acid at a flow rate of 1.5 mL min^{-1} , directly into the ICP-OES. The operating conditions were established and the determination was carried out.

3. Results and discussion

The preconcentration system, allowed the lowering of the ICP-OES detection limits to values compatible with the Sc content in the acid mine drainages.

3.1. Effect of pH on adsorption

The pH value plays an important role with respect to the adsorption of different ions on CNTs [26,32,39]. The surface charge depends on the pH of the surrounding electrolyte. The oxidation of CNTs with concentrated acids lead to the surface functionalization with oxygen-containing groups and the isoelectric point (IEP) of MWNTs shifts to the lower pH values [39]. When the pH of the solution is higher than the IEP of the Ox-CNTs, the negative charge on the surface provides electrostatic attractions that are favorable for adsorbing cations. The decrease of pH leads to the neutralization of surface charge, so the adsorption of cations onto CNTs decreases quickly.

In order to optimize the sorption conditions for the retention, the scandium signal was monitored by ICP-OES while changing the pH of the solution that passed through the minicolumn. Thus a series of Sc sample solutions were adjusted to different pH values (between 1.0 and 10.0) and processed according to the procedure described in the preconcentration step section. As it can be seen in Fig. 3, the optimal Sc adsorption was achieved at pH values between 1 and 2. These results were in agreement with others reported for the retention of several rare earth elements (Eu, Gd, Ho, La, Sm, Tb, Yb) onto carbon nanotubes [40]. Consequently, a pH value of 1.5 was selected for further experiments.

3.2. Effect of CNTs type

The retention behavior of Sc on Ox-CNTs and unmodified (native) CNTs was evaluated. Quantitative adsorption was achieved (> 95%) when Ox-CNTs were employed as sorbent material. It is evident that the appearance of oxygen-containing groups on the CNTs surface is the main responsible for the retention of Sc. The same behavior has been observed and reported for several metals [37,41,42]. Accordingly, Ox-CNTs were selected as the best alternative for further experiments.

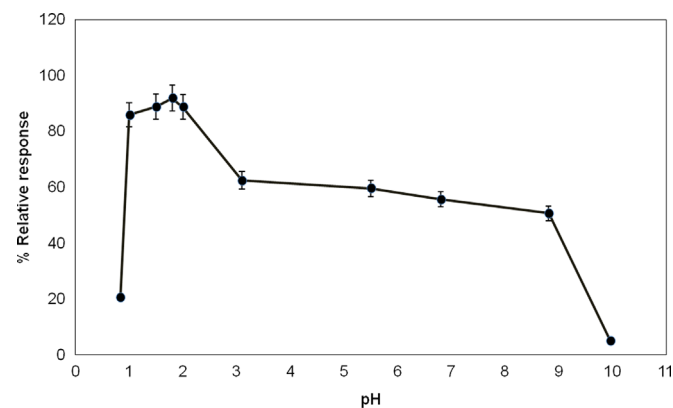


Fig. 3. Effect of the sample pH on the Sc retention on the Ox-CNTs minicolumn.

3.3. Evaluation of parameters affecting the preconcentration performance

3.3.1. Sample loading flow rate

Sample flow rate controls the time of analysis and influences the contact time between the analyte and the active sites. In this study, the influence of the sample loading rate on the analytical response obtained was studied between 3 and 12 mL min^{-1} . It was verified that the analytical signal diminished progressively when the loading flow rate was increased above 5 mL min^{-1} , whilst it remained constant at lower flow rates (Fig. 4). With the objective of achieving greater retention and avoiding tight packing of the filling material, a 5.0 mL min^{-1} sample loading flow rate was selected.

3.3.2. Evaluation of the sample loading time

In order to obtain a high enrichment factor, different sample loading times were used for preconcentration. It was observed that the enrichment factor value increased linearly with preconcentration until at least 300 s (Fig. 5). This behavior gave an indication of the capacity and active sites of the preconcentration system. The flexibility of adopting different sample loading times to attain different enrichment factors can be considered as one of the advantages of the proposed method. A sample loading time of 300 s (25 mL of sample volume) was fixed in order to attain an enrichment factor of 225-fold.

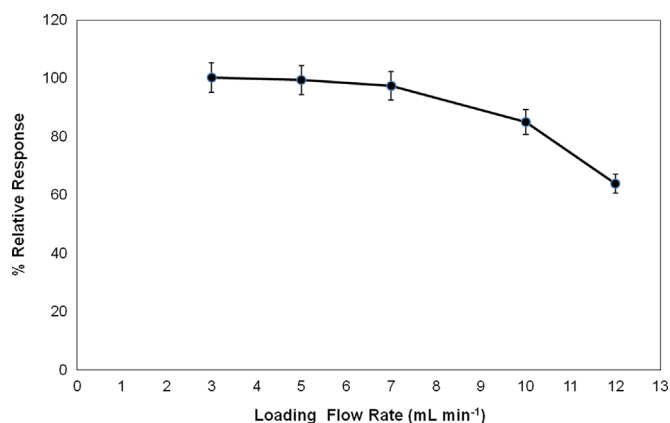


Fig. 4. Effect of the sample loading flow rate on the response of the analyte.

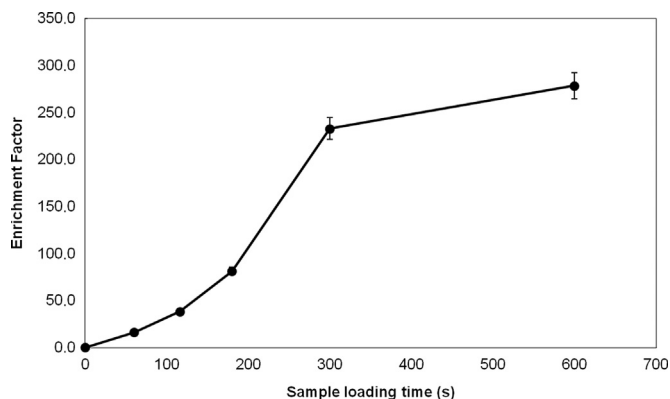


Fig. 5. Influence of the sample loading time on the enrichment factor obtained. Loading flow-rate: 5.0 mL min^{-1} ; elution flow-rate: 1.5 mL min^{-1} ; Sc concentration: 0.1 mg L^{-1} .

3.3.3. Optimization of the elution conditions

The elution step involves an exchange between analyte ions and H^+ [43]. A satisfactory eluent should effectively release the analyte in a discrete volume in order to obtain the best recovery. Nitric and hydrochloric acid have turned out to be good eluents in many carbon nanotubes-based on-line preconcentration systems. Both acids were tested at different concentrations in order to evaluate and compare the Sc desorption from the Ox-CNTs minicolumn. Nitric acid turned out to be the best eluent for the retained metal. A minimum concentration of 30% (v/v) was needed to obtain the best analytical response. In addition, elution flow rate was also a parameter to be optimized for two main reasons: (1) it is known to be an ionic exchange process that needs enough contact time to occur and, (2) elution rate must be compatible with the ICP-OES inflow rate. Thus several flow rates were evaluated and no significant signal changes were observed with rates up to 1.5 mL min^{-1} . Accordingly, a flow rate of 1.5 mL min^{-1} was selected assuring repeatability of the elution steps.

3.4. Column re-use

Stability and regeneration of the minicolumn were investigated. The column can be re-used after regeneration with 2 mL of the nitric acid used for elution and then with a few milliliters of distilled water. The columns showed to be stable up to 400 adsorption cycles without either deterioration or decrease in Sc recovery.

3.5. Interferences

The effects of potentially interfering species (at the concentration levels at which they may occur in the sample concerned) were tested under the corresponding optimum preconcentration conditions. Thus, some commonly encountered ions were evaluated, and they could be tolerated without observing an effect in the system's performance up to at least the following levels: Fe^{+3} : 30 mg L^{-1} ; Ni^{+2} ; Cu^{+2} , Al^{+3} , and Pb^{+2} : 3 mg L^{-1} ; and Zn^{+2} : 15 mg L^{-1} . Commonly encountered matrix components such as alkali and alkaline earth elements were not retained on the CNTs minicolumn under the herein proposed working conditions [44–46].

3.6. Analytical performance

The overall time required for preconcentration of 25 mL of sample (5 min, at flow rate of 5 mL min^{-1}), and elution, including washing time, (approx. 1 min, at flow rate of 1.5 mL min^{-1}) was about 6 min; the throughput was about 10 samples per hour. A sensitive enhancement factor of 225-fold was obtained for a preconcentration time of 300 s. The precision for 10 replicate determinations at 100 ng L^{-1} Sc concentration was 5% relative standard deviation (RSD), calculated from the peak heights obtained. The calibration graph using the preconcentration system for scandium was linear with a correlation coefficient of 0.9996 at levels near the detection limits up to at least 10 mg L^{-1} . The detection limit (DL) was calculated as the concentration of scandium required to yield a net peak that was equal to three times the standard deviation of the blank signal (3s). The value of DL obtained for the preconcentration of 25 mL of sample solution was 4 ng L^{-1} .

3.7. Method validation and application

Water-based reference materials with a certified value for Sc do not exist. However, a recovery study is considered as a validation method [47]. Therefore, in order to demonstrate the validity of the

Table 2

Recovery study (acid mine drainage) (95% confidence interval; $n=6$).

Aliquots	Quantity of Sc added ($\mu\text{g L}^{-1}$)	Quantity of Sc found ($\mu\text{g L}^{-1}$)	Recovery (%) ^a
1–6	0.0	1.5 ± 0.1	–
7	2.0	3.4	95.0
8	4.0	5.5	100.0
9	6.0	7.7	103.3
10	8.0	9.4	98.8

^a $100 \times [(\text{found} - \text{base})/\text{added}]$.

proposed methodology, 250 mL of AMD sample was collected and divided into 10 portions of 25 mL each. The proposed preconcentration method was applied to six diluted (1:50, v/v) portions and the average quantity of scandium obtained was taken as a base value. Then, increasing quantities of scandium were added to the other aliquots of sample and scandium was determined by the same preconcentration method (Table 2). Finally, the results of the method applied to the determination of Sc in the acid drainage of La Carolina mine are shown in Table 2. The levels found were in good agreement with those reported previously [12]. It is important to notice that the concentration levels determined were above the average values reported for this metal in river waters [48,49]. This fact can be explained due to the water acidity conditions capable of increasing the dissolution of metals from tailings, waste rock piles, and open pits; among others.

4. Conclusions

The main difficulty found in the determination of scandium in environmental matrices is related to its low concentration levels. In the present work, satisfactory sensitivity, reliability, speed of analysis was attained using an online preconcentration system based on Ox-MWCNTs with a FI-ICP-OES detection approach. Thus the obtained results demonstrated for the first time the possibility of quantitatively retaining/preconcentrating Sc onto Ox-MWCNTs without the need of any complexing agent, which made the method simpler and economical. In addition, the rapid uptake of Sc, other than usually interfering cations, its almost instantaneous release during the elution step, and the possibility of column re-using for ~ 400 cycles without being detrimental to performance were ideal properties. Therefore, the preconcentration system associated with ICP detection allowed the determination of Sc at sub-trace levels in acid mine drainage samples and could be applied to the determination of this analyte in other environmental samples.

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