



Determination of the total and extractable fraction of Ni in lake sediments and natural waters of San Luis (Argentina) by FAAS using a simple solid phase extraction system

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ABSTRACT

An on-line nickel preconcentration and determination system implemented with flame atomic absorption spectrometry (FAAS) was developed. The nickel was retained on the inner walls of a column filled with ethyl vinyl acetate (EVA). The EVA was used as sorbent material for on-line solid-phase extraction (SPE) in the absence of complexing agent. The effects of sampling volume, elution conditions, sample pH and flow rate on the Ni extraction were studied. The analytical efficiency parameters obtained with this methodology were: enrichment factor (EF) of 46 times for a preconcentration time of 120 s, the limit of detection (LOD) was $3.78 \mu\text{g L}^{-1}$, and the precision for six replicate determinations (repeatability conditions) at $20 \mu\text{g L}^{-1}$ Ni concentration was 4.38% relative standard deviation. The sampling frequency for the proposed system was about 20 samples/h. The optimized procedure was applied to the determination of Ni in natural water and lake sediment samples.

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1. Introduction

Nickel is an element that is often found in water as it is used in a number of industrial processes. The exposition to this element may take place by air, soil, drinking water, food samples and mainly by skin contact. In small quantities, nickel is considered an essential element but in excess is reported as toxic. The intake in higher concentrations than permitted, can cause damage to lungs, kidneys, gastrointestinal problems, pulmonary fibrosis, and skin dermatitis, etc. [1].

The Ni determination at trace level is an important topic for the environmental defense, human health, etc. [2]. Ni is normally present at trace level concentration, as a consequence its determination i.e. in water could be carried out directly by electrothermal atomic absorption spectrometry (ETAAS) [3–5] or by inductively coupled plasma mass spectrometry (ICP-MS) [6–9], which has usually enough sensitivity. However, inductively coupled plasma optical emission spectrometry (ICP-OES) [10–20] and flame atomic absorption spectrometry (FAAS) [21–33], in order to obtain an appropriate level of sensitivity, preconcentration/separation procedures are required. In this sense solid phase extraction (SPE) takes an important role in the preconcentration step, due to its simplicity, ease of use, economical nature, environmental friendliness, determination of volatile nickel species by CVG-atomic fluorescence spectrometry (AFS) [34], etc.

The control of the sediments is very important due to its role as final receptors of contaminants in aquatic ecosystems [35]. Furthermore, the use of different digestion methods in the determination of low concentration of Ni in sediments may lead to different results and consequently to different environmental considerations [36], even if these methods are not related to the anthropic fraction of elements.

The dissolution of sample is one of the most crucial steps prior to trace element determination in solid materials. Sample preparation techniques such as hot plate and microwave digestion have widely been used for this purpose and over the years have become established standard methods (i.e.: EPA 3050 standard 3050 B, EPA 3051 standard 3051 A & B [37], ISO standard 11466 [38], The Community Bureau of Reference (BCR) of the Commission of the European Communities [39]) for trace element dissolution from a large number of matrices. The digestion techniques, however, require the use of concentrated mineral acids, high temperatures and, in the case of microwave applications, high pressures. Moreover, the overall sample preparation is basically the most time-consuming part of elemental analysis. Therefore, considerable interest has been expressed for simple and fast sample preparation procedures. The digestion methods generally provide information on the total content of trace elements in sediment without discriminating for the contribution and the level of anthropogenic pollution.

In the recent years sequential extraction procedures have been increased in attention [40]. Some authors defend simple extractions with dilute hydrochloric acid [41–43] for sediment and soil, because

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they focused on the mobile or labile phase which is related with the bio-accumulation and bioavailability. In addition dilute hydrochloric acid leach can be used as a first step to recognize and identify trace metal pollution. Thus, the use of dilute HCl acid is low cost, fast, does not require acids as HClO_4 and HF, considerable reduction of time of analysis in comparison with other extractions and more meaningful than a total digestion. In fact the use of 0.5 M HCl has been recommended and the result obtained with this is comparable with other sequential extractions. A weak acid attack removes loosely bonded metal, absorbed on clay particles (minerals) or other minerals with large surface area (i.e. Fe and Mn oxides) and metal precipitated as its salt.

The aim of the current work was to develop a simple analytical methodology for the preconcentration using solid phase extraction for on-line determination of Ni by FAAS. The effect of the chemical and physical variables on the preconcentration, including pH, sample flow rate, buffer concentration and flow rate, and eluent concentration and flow rate were evaluated and optimized. For the preconcentration of the analyte a column filled with ethyl vinyl acetate (EVA) was used.

The optimized methodology was applied to natural sample waters, lake sediments and certified reference material, (CRM) VKI QC METAL LL1 and lake sediment TRAP-LRM, from IJS. The digestion of the sediment was carried out by partial extraction using 1 M HCl and total digestion using microwave assisted digestion with nitric acid and hydrogen peroxide to compare (EPA standard 3051 A).

2. Experimental

2.1. Standards and reagents

All solutions were prepared with ultrapure water (18 M Ω cm) obtained from an EASY pure RF (Barnstead, Iowa, USA). All the glasses and plastic materials were cleaned by soaking in a 10% HNO_3 and were rinsed with distilled water prior to use.

Hydrochloric acid, puriss. p.a. ACS (Sigma-Aldrich), was used as eluent in the flow injection system and prepared by appropriate dilution with distilled water from the concentrated acid. To alkalize solutions, NaOH (Merck, Germany) was used.

Working standard solutions of the metal were prepared by a dilution of a 1000 mg L $^{-1}$ Ni(II) atomic spectroscopy standard solution Trace CERT® (Fluka, Switzerland.)

Buffer solution was prepared from sodium tetraborate puriss p.a. standard substance (Riedel-de Haën, Seelze, Germany) adjusted to the appropriate pH (9.00) by adding a diluted hydrochloric acid or sodium hydroxide solution. Fresh buffer solution was prepared daily.

2.2. Instrumentation

Experiments were performed using a Shimadzu Model AA-6800 atomic absorption spectrophotometer (Tokyo, Japan) equipped with a deuterium background corrector. Nickel hollow-cathode lamps (Hamamatsu, Photonics K., Japan) were employed as the radiation sources. The wavelength used was 221.47 nm for Ni. The FAAS instrumental and operating conditions are listed in Table 1. A Minipulse 3 peristaltic pump Gilson (Villiers-Le-Bell, France) was also used. Sample injection was

achieved using a Rheodyne (Cotati, CA, USA) Model 50, four-way and of six ports, two positions, and rotary valves.

Microwave-assisted acid digestion was carried out in a microwave oven Milestone START D (Milestone, Bergamo, Italy), equipped with high pressure digestion rotor in segmented format (maximum pressure 100 bar or 1440 psi) and direct temperature monitoring and control up to 300 °C in a reference vessel. Installed power 1.200 W and the operating frequency is 2.5 GHz. Tetrafluorometoxil (TFM) reaction vessels were used in all digestion procedures. The reaction vessels were cleaned by using 5 mL of concentrated nitric acid before each digestion.

2.2.1. Microwave digestion

For microwave digestion 0.25 g of each sample was transferred to 100 mL Teflon vessels. Samples were digested by making use of HNO_3 , $\text{HCl}/\text{H}_2\text{O}_2$ (3:1) acid mixtures in a microwave digestion system. Blank digest was carried out in the same way.

2.3. Sampling

The samples were collected in two stations (A, B) affected to different degrees by the rivers, located along the mouths of the La Florida lake, San Luis, Argentina.

La Florida lake, situated in the central part of Argentina, is a semi-enclosed lake that stores 105 million cubic meters of water, irrigates an area of 10,000 ha and creates a significant hydraulic power take for the city of San Luis and Villa Mercedes, while attenuates the big floods of the rivers.

It is exposed mainly to the presence of two affluent rivers, Trapiche and Grande rivers respectively.

In this work two sampling points of different degrees of potential pollution were considered, they are in the mouths of the lake. Surface sediments, the first 10 cm layer, free of animal, were taken from these points and then put into polyethylene containers, after that each sample was hand ground to a powder and dried at room temperature.

With respect to the natural water samples, immediately after collection, the samples were filtered using 0.45 μm pore diameter membrane filters. After that, the water samples were acidified to pH 2 with nitric acid and stored in glass bottles at 4 °C.

2.4. Microwave digestion

In order to determine the total metal concentration in sediments with conventional acidic digestion, we applied the EPA standard 3050 (A). An acid mixture of 69% HNO_3 (6 mL), and 30% H_2O_2 (2 mL) was added to 0.25 g of sample put into PTFE vessels and submitted to the temperature program, with the following parameters: 10 min up 200 °C ramp–10 min at 200 °C step. Finally the samples or CRMs were diluted to 100 mL and transferred to polyethylene tubes. The procedure was applied in triplicate. For each digestion, reagent blanks were obtained. The blanks were prepared in the same conditions as the samples without the sediments and CRMs.

2.5. Column preparation

Ethyl vinyl acetate is a flexible (rubbery), transparent polymeric material with good low temperature flexibility, chemical resistance (to acids, alkalis, and alcohols) and high friction coefficient properties. EVA-polymer pellets (containing 28 wt.% vinyl acetate) (LAQUIMAR, Buenos Aires, Argentina) were used to create the preconcentration minicolumn as follows: the minicolumn was prepared by placing 100 mg approximately of EVA turnings (small shaving with a media length of 1.5 mm and a media wide of 0.45 mm) into an empty cylindrical EVA tubing using the dry packing method. Small amount of quartz wool was placed on both ends of the minicolumn. Finally, the column was connected with PTFE tubing to the peristaltic pump to form the preconcentration system.

Table 1
Operating FAAS conditions.

FAAS instrumental operating conditions	
Spectral bandpass	0.2 nm
Lamp current	8.0 mA
Slit width	7.0 mm
Flow rate gas	1.8 L min $^{-1}$
Wavelength of Ni	231.91 nm
Background correction	Deuterium lamp
Sample flow rate	4.5 mL min $^{-1}$

2.6. On-line preconcentration system for nickel determination

A diagram of the on-line preconcentration system is shown in Fig. 1. The flow system consisted of two peristaltic pumps (P_1 & P_2) fitted with Tygon tubes, a four-way valve (V), and a column (C) packed with EVA is coupled to the FAAS. The flow system was operated in a time-based mode. Before loading, the minicolumn was conditioned for the preconcentration at the correct pH value with buffer solution. The sample (S) and buffer (B) solutions were loaded at 5.0 mL min^{-1} and 2.5 mL min^{-1} respectively, with a peristaltic pump (P_1) through the column. The sample and buffer were mixed about 1 cm from the column inlet while a 20% (v/v) hydrochloric acid (E) solution passing directly throughout the manifold to the detection system used a peristaltic pump (P_2). The precipitate, which is formed instantaneously after the mixing point, was collected on the EVA contained in the column with the valve (V) in load position (a). The effluent emerging from the column was discarded (W). Finally, peristaltic pump was stopped, and the injection valve was switched at the injection position (b), and the precipitated analyte was eluted from the EVA with 20% hydrochloric acid at flow rate of 4.5 mL min^{-1} directly into the nebulizer and the FAAS.

3. Results and discussion

With the aim of evaluating the sorption conditions for the nickel retention, several experimental variables affecting the preconcentration system were studied. The analytical parameters as pH, sample loading rate, selection of eluent, and preconcentration system performance, were optimized. A $20 \mu\text{g L}^{-1}$ Ni solution was used for all the measurements and three independent experiments were carried out for each optimized variable. In all figures, the points were connected in order to achieve a better visualization of the experimental trends, but these trends do not represent any mathematical function.

Ni preconcentration in natural water samples was necessary because its concentration is too low to be compatible with DLs by FAAS.

3.1. Retention of the analyte on the minicolumn

The retention of the analyte on the EVA, depends mainly on the surface characteristics, i.e. hydrophobic nature, electrostatic interaction

between the surface charge and the precipitate of the analyte and physic adsorption.

The scanning electron microscopy (SEM) image of the EVA turnings before and after preconcentration step is illustrated in Fig. 2 and shows the coverage of EVA surface by a precipitate.

3.2. pH studies

Between the chemical variables, pH is a critical parameter for effective precipitate and retention on the column. In order to evaluate the effect of pH on the preconcentration, the pH of the sample solutions containing $20 \mu\text{g L}^{-1}$ of nickel ions was adjusted between the range of 2.0 to 12.0 and the proposed method was applied. Nickel signal was monitored by measuring it with FAAS while changing the pH of the solution that passes through the column. Fig. 3 shows that the optimal pH values were in the range 8.5–12. At lower pHs (<8.0) the effective retention on the column decreased. Considering these results, the selected pH was 9.0.

3.3. Effect of buffer concentration

To investigate the optimum concentration of the buffer solutions on the quantitative preconcentration/separation of methodology, some experiments were developed by increasing the amount of the buffer concentration from 0.01 to 0.2 mol L^{-1} . Quantitative recoveries for the analytes were obtained after 0.1 M of sodium tetraborate. Subsequent studies for further experiments were carried out with 0.1 M of sodium tetraborate.

3.4. Buffer flow rate

The buffer flow rate through the column is another step that needs to be optimized in the proposed system. In this study we have verified that with flow rates of up to 3.0 mL min^{-1} there was no effect on analyte recovery, which under optimum conditions was close to 100%. At higher flow rates, the preconcentration and recovery showed an obvious decrease with a diminishing contact time between the analyte and the adsorbent material. Thus, the buffer flow rate was 2.5 mL min^{-1} .

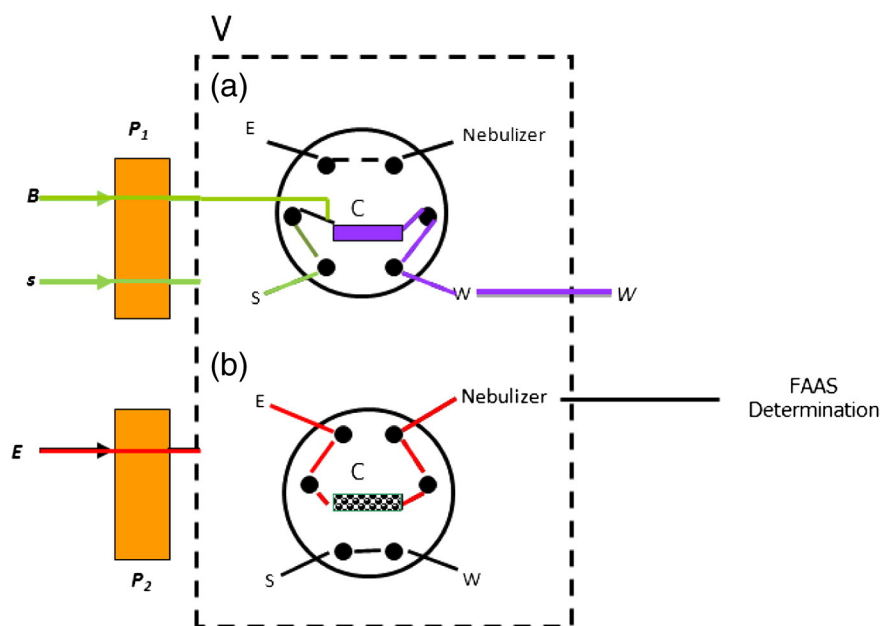


Fig. 1. Schematic diagram of the instrumental setup. S: sample solution (flow rate: 5.0 mL min^{-1}); B: buffer solution (flow rate 2.5 mL min^{-1}); E: eluent (flow rate 4.5 mL min^{-1}); W: waste; P_1 , P_2 : peristaltic pump; C: minicolumn; V: injection valve. Valve positions: (a) sample loading; (b) injection.

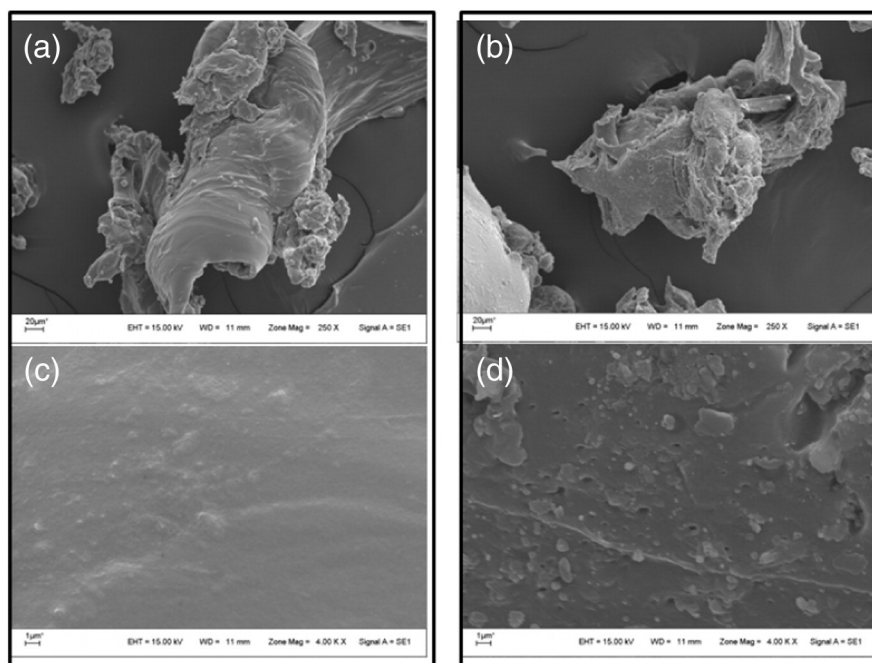


Fig. 2. SEM image of the EVA turnings (a and b) original EVA turnings (c and d) the EVA turnings after coated with buffer and sample solutions. The length depicted corresponds to 20 μm (a and c) and 1 μm (b and d).

3.5. Sample flow rate

The sample flow rate through the minicolumn is a very important parameter in SPE, because this is one of the steps that controls the analysis time, the retention efficiency and the preconcentration. The influence of the sample loading rate on the analytical response was investigated between 1.5 and 12.0 mL min^{-1} . The results showed that at the flow rates greater than 6 mL min^{-1} , the analytical signal of Ni decreased because the retention is not satisfactory. The flow rate of 5 mL min^{-1} presented the optimal response (Fig. 4) and was selected for further studies.

3.6. Effect of eluent

A satisfactory eluent should effectively elute the analyte in a discrete volume in order to obtain the best analyte recovery. Different types of eluents were tested. Organic solvents like methanol and ethanol have been

proposed as effective eluents in solid phase extraction systems. We tested these solvents and the results were not satisfactory. Based on our previous work [30], solutions of nitric and hydrochloric acid were studied at different concentrations in order to evaluate and compare the analytes' recovery. The analyte was completely eluted with 20% (v/v) hydrochloric acid and this one was applied in further experiments.

On the other hand, the effect of the eluent flow rate was studied within the range 1.0–12 mL min^{-1} . The optimum eluent flow rate was 4.5 mL min^{-1} . Above that flow rate, the nickel signal decreased mainly due to the decreasing of the nebulization efficiency or incomplete elution of the retained analyte. Thus the flow rate of 4.5 mL min^{-1} was selected and applied in the determination.

3.7. Interference studies

The effects of potentially interfering species according to the environmental samples, on the on-line solid phase extraction and FAAS

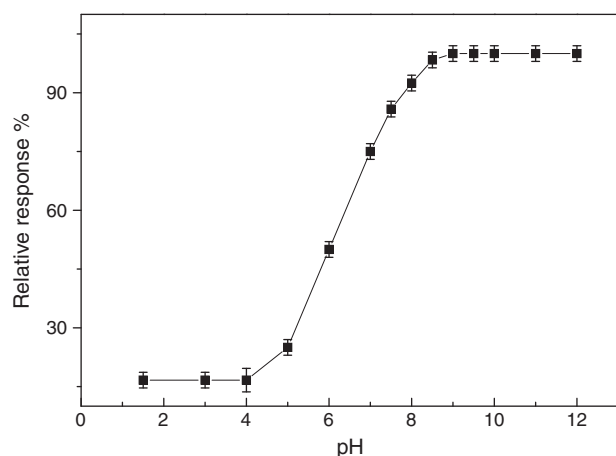


Fig. 3. Relative response % as (expressed in arbitrary units) as a function of the sample solution pH. Ni concentration: 20 mg L^{-1} ; buffer solution concentration: 0.1 mol L^{-1} , flow rate: 2.5 mL min^{-1} ; HCl concentration: 20% (v/v).

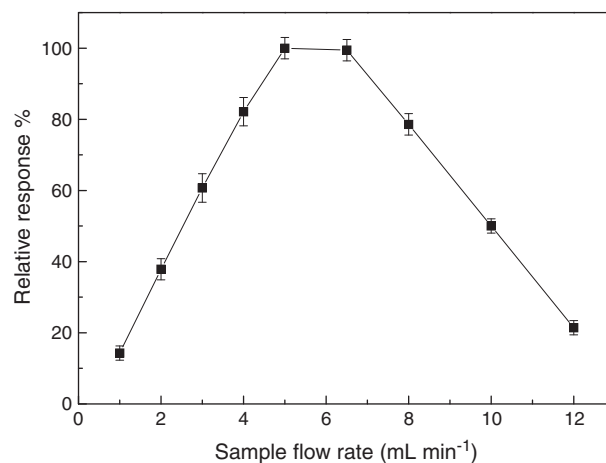


Fig. 4. Relative response % (expressed in arbitrary units) as a function of the sample load flow rate. Ni concentration: 20 mg L^{-1} ; buffer solution concentration: 0.1 mol L^{-1} , pH: 9.0; HCl concentration: 20% (v/v).

Table 2
Effect of interference on preconcentration and determination of Ni(II) on EVA column.

Interference	Added as	Recovery (%)
Na ⁺	NaCl	103
K ⁺	KNO ₃	102
Mg ²⁺	Mg(NO ₃)·6H ₂ O	98
Ca ²⁺	CaCl ₂	93
Cu ²⁺	CuSO ₄	99
Cd ²⁺	Cd(NO ₃)·4H ₂ O	101
Zn ²⁺	ZnNO ₃	96
Co ²⁺	CoCl ₂ ·6H ₂ O	102
Cr ³⁺	Cr(NO ₃)·6H ₂ O	103
Mn ²⁺	Mn(NO ₃)·4H ₂ O	98
Al ³⁺	AlCl ₃	95
Fe ³⁺	Fe(NO ₃)·9H ₂ O	91

Table 3
Comparison of two methods of simple extraction and digestion by microwave for samples of sediments from the rivers sampled.

Sample	Simple extraction (1.0 M HCl)	Digestion method
Sediment of river Trapiche (A)	7.06 mg kg ⁻¹	36.36 mg kg ⁻¹
Sediments of river Grande (B)	9.05 mg kg ⁻¹	46.87 mg kg ⁻¹

determination were investigated. Solutions containing 20 µg L⁻¹ Ni(II) and different concentrations of the potential interfering were treated according to the proposed method. Thus, the tolerance limits of the coexisting ions defined as the largest amount of ion that produces a recovery of Ni less than 90% were evaluated (Table 2). Most of the cations and anions evaluated did not interfere with the SPE of Ni(II). The results showed that Cu(II), Cd(II), Zn(II), Co(II), Cr(III), Mn(II), Al(III), and Fe(III) could be tolerated up to at least 2500 µg L⁻¹. Other common matrix components such as alkaline and alkaline earth elements are not retained on the column under the working conditions.

3.8. Analytical performance

The calibration curves used to determine Ni(II) were made by measuring the absorbance of the working calibration solution at optimal instrumental parameters (viz. wavelength, slit width, lamp current, etc.) and the solution conditions. The calibration graph was linear from levels near to the limit of the quantification (LOQ) and up to at least 300 µg L⁻¹ with a determination coefficient (R²) of 0.9997 and the linearity was verified with corresponding test F. The value of the LOD, calculated as the amount of Ni required to obtain a net peak equal to three times the standard deviation of the blank signal (3σ), was 0.76 µg L⁻¹.

The precision for six replicate determinations (repeatability conditions) at 20 µg L⁻¹ Ni concentration was 4.38% relative

standard deviation. A total enrichment factor (EF) was 46-fold for a preconcentration for 2 min, with respect to the Ni determination by FAAS without preconcentration. The time required for the preconcentration/determination was about 3 min. Hence, the throughput was of 20 samples/h.

A lake sediment reference material TRAP-LRM from IJS was used for the method validation, as seen in Table 4, the results were compared with the certified values using a *t*-test at 95% confidence limits (n = 6). Good agreement was obtained between the estimated content by the proposed method and the certified values for four metal ions. These results also indicate that the proposed preconcentration method for Ni(II) is not affected by potential interferences from the major matrix composition of the analyzed river sediment.

3.9. Application

Determining the total element contents of solid environmental media provides little insight into their bioavailability. Sequential or partial extraction approaches are commonly used to define environmentally relevant phase-associations of elements in atmospheric particulate matter, sediments and soils. Extraction of labile metals from solid media is environmentally more meaningful than a total digestion, since this point of view, HCl has received the greatest attention. In this work we compare Ni concentrations liberated by dilute HCl leach employed and EPA method 3151(A) (Table 3). For the latter, the samples were placed in a fluorocarbon polymer (TFM) microwave vessel and heated in the microwave unit for a specified period of time. After cooling, the vessel contents were filtered, diluted to volume and analyzed by the proposed determinative method. The preconcentration method was applied to Ni determination in river water samples and lake sediments (TRAP-LRM from IJS). Samples treated by EPA method 3051(A) procedures were analyzed by flame atomic absorption spectrometry. These ones are given in Table 4.

4. Conclusions

The developed procedure, using an on-line preconcentration system with FI-FAAS method has shown adequate sensitivity, besides being simple and easily available, inexpensive, safe as only EVA is used for solid phase extraction of Ni without complexation. Compared with other materials used for preconcentration, this sorbent is very cheap and it can be easily packed into the column.

The method was successfully applied to determine Ni in the water and sediment samples and the recovery was more than 90%.

The results showed that the Ni concentrations using EPA method 3151(A) were statistically greater than the dilute HCl leach. Besides the application of the dilute HCl as extraction to solid media provides

Table 4
Concentration of Ni in tap water, river water samples and certified reference material, (95% confidence interval; n = 3).

Sample	Ni(II) conc. Base (µg L ⁻¹)	Ni(II) conc. Added (µg L ⁻¹)	Ni(II) conc. Found (µg L ⁻¹)	Recovery (%)
Tap water	6.00	0.00	6.00	–
		10	15.75	97.50
		20	26.52	102.60
		40	45.17	97.92
Rio Trapiche	4.10	0	5.44	–
		5	9.20	102.00
		10	13.9	98.00
		15	18.75	97.66
Rio Grande	5.82	0	5.82	–
		5	10.90	101.16
		10	15.65	98.30
		15	20.90	100.53
VKI QC METAL LL1	20.6 ± 0.9 µg L ⁻¹	0	20 ± 1.7	–
TRAP-LRM from IJS	39.8 ± 1.3 mg kg ⁻¹	–	38.7 ± 1.4 mg kg ⁻¹	–

a rapid, cost-effective, and environmentally meaningful approach for contaminant monitoring.

As a general conclusion, the results of this work showed that partial extraction provides an acceptable estimation of the bioavailability Ni concentrations in sediments.

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