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ORIGINAL PAPER

Applicability of a liquid membrane in enrichment and determination of nickel traces from natural waters

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Abstract In this work, a bulk liquid membrane method has been applied for Ni enrichment and separation from natural waters. The carrier-mediated transport was accomplished by pyridine-2-acetaldehyde benzoylhydrazone dissolved in toluene as a complexing agent. The preconcentration was achieved through pH control of source and receiving solutions via a counterflow of protons. The main variables were optimized by using a modified simplex technique. High transport efficiencies (101.2±1.8–99.7±4.2%) were provided by the carrier for nickel ions in a receiving phase of 0.31 mol L^{-1} nitric acid after 9–13 h depending on sample salinity. The precision of the method was 2.05% (without a saline matrix) and 4.04% (with 40 g L^{-1} NaCl) at the 95% confidence level and the detection limit of the blank was 0.015 µg L^{-1} Ni for detection by atomic absorption spectroscopy. The applicability of the method was tested on certified reference and real water samples with successful results, even for saline samples. The relative errors were −0.60% for certified reference materials and ranged from −0.39 to 2.90% and from 0.3 to 11.05% for real samples, obtained by comparison of inductively coupled plasma mass spectrometry and adsorptive cathodic stripping voltammetry measurements, respectively.

Keywords Nickel · Natural water · Liquid membrane · Preconcentration · Pyridine-2-acetaldehyde benzoylhydrazone

Introduction

Heavy metals are typically found in natural waters in the low microgram per litre or nanogram per litre range. Determination by atomic absorption or emission spectroscopy has been widely used. Analysis using inductively coupled plasma mass spectrometry ICP-MS offers a wide variety of options for multielement analysis and with use of hyphenated techniques, such as liquid chromatography–ICP-MS), quantification of trace metal compounds can be carried out [1]. Nevertheless, not all laboratories are equipped with high-cost ICP-MS instruments and difficulties in the determination are caused by matrix interferences, principally high salt content and very low concentrations of metal ions. Similar requirements are necessary for total reflection X-ray fluorescence, another well-established multielement analysis technique [2]. It is well suited for direct analysis of water samples, but alkaline and alkaline-earth elements from the saline matrix must be removed in order to eliminate the background level; therefore, chemical separation and preconcentration procedures are required.

Several techniques have been applied to separate trace quantities of metals from the matrix: coprecipitation, solid-phase extraction, ion exchange or liquid–liquid extraction [3–7]. Membrane extraction, an improved version of solvent extraction, has found application in the environmental sciences, in water-pollution control and in hydrometallurgical separation. This technology offers high selectivity, simultaneous separation and preconcentration

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of elements, simplicity and low operational costs. Recently, it has been shown to be an attractive alternative to these sample pretreatment methods for metal ions from complex matrices [8–10]. Also, it is very useful for speciation studies and as a model for studying the cation transport through membranes in biological systems [9, 11–13].

In general, a membrane may be regarded as a semipermeable barrier. When placed between two aqueous phases, chemical species can move through the membrane from a solution of high solute concentration into a solution of low solute concentration by means of a diffusion process. The transport is often facilitated by the presence of carrier compounds in the membrane phase and may be aided by a proton countercation gradient or a coanion gradient, increasing the selectivity and uphill transport of solute. The carrier is essentially a complexing agent, selective toward the target metal ion. Therefore, the overall transport process consists of a mixture of diffusion steps and complexation/decomplexation reactions at two independent and possible interfaces, in a single stage.

Among the several liquid membrane (LM) configurations, bulk LMs are suitable for screening a novel carrier-mediated transport system on the laboratory scale and are appropriate for application as analytical tools, because of the simplicity and easy accessibility of the aqueous phase [14].

Few studies have been made on the application of LMs to trace metal analysis in natural water [11–13, 15, 16] and still fewer for analysis in seawater [17, 18]. Permeation fluxes of the target ion from seawater can be lower because of the cotransport of other ions, principally alkali metal ions from the saline matrix. These interferences decrease the efficacies of the processes, and it is therefore necessary to propose new carriers with higher selectivity.

Different ligands have been used as carriers in LM metal extraction: phosphine oxides [19], diaza crown ethers [13–20], β-diketones [21, 22], hydroxyoximes [23, 24] and other chelate agents [25].

Heterocyclic hydrazones are an important group of complexes which have attracted attention of medicinal chemists owing to their remarkable antiviral and antimalarial effects and iron scavenging and antitubercular activities. These biological activities have been described as being related to their ability to form stable chelates with transition metal ions [26] and the formation of lipid soluble metal chelates which facilitate metal biouptake fluxes [12, 27]. The permeation through a biological membrane can be compared with fluxes across a LM and this analogy of the processes can be used to mimic transport in different conditions: pH, water hardness, dissolved organic matter, salinity, etc. The capability of the LM can be modified to measure concentrations of the free metal ion, labile hydrophilic or lipophilic species, providing useful information for metal bioavailability studies. So, these ligands can be a good proposal for development of appropriate tools to perform chemical speciation measurements in environmental analysis.

Nickel is a ubiquitous trace metal and occurs in soil, water, air and the biosphere. It is commonly used for electroplating, stainless steel manufacture and in nickel–cadmium batteries. Natural waters (pristine streams, rivers and lakes) contain 0.2-10 μg L^{-1} total dissolved nickel and surface water near mines and smelters contain up to 6.4 mg L^{-1}.

Coastal, bay and estuary waters contain nickel concentrations from about 0.20 to 5.3 μg L^{-1} and ocean surface water contains 0.15–0.93 μg L^{-1} [28]. This metal has long been considered to be relatively nontoxic, but different studies have shown chronic effects of nickel exposure, such as the inhibition of growth and reproduction in invertebrates [29]. Therefore, the determination of nickel in waters is being used increasing in contamination monitoring in order to guarantee good water quality, and nickel is included in the EU Water Framework directive as a dangerous chemical substance for chemical pollution of waters.

In this work, we report on the efficient transport of nickel ions through a bulk LM containing pyridine-2-acetaldehyde benzoylhydrazone (2-APBH, $C_{14}H_{13}N_3O$) and the application for metal enrichment and separation from natural waters. 2-APBH was found to react with transition metal ions, forming neutral metal chelates as a tridentate ligand, coordinating through carbonyl oxygen in the enol form, azomethine nitrogen and/or acetylpyridine ring nitrogen. The metal complexes can be extracted into organic solvents [30, 31] and we propose this ligand as carrier agent of the LM.

Experimental

Reagents and solutions

All reagents and solvents were of the highest purity available (pro analysis or Suprapur grade) and aqueous solutions were prepared using Milli-Q deionized water (Millipore, USA).

Nickel standard solutions were prepared by dilution of 1,000 mg L^{-1} atomic spectroscopy standard solutions from Merck (Darmstadt, Germany) in 0.05 mol L^{-1} nitric acid. The 2-APBH ligand was prepared as previously described [30] by reaction of pyridine-2-acetaldehyde with benzoylhydrazide, supplied by Sigma-Aldrich (Steinheim, Germany). Solutions of 0.002–0.011 mol L^{-1} 2-APBH in toluene were used as the LM, and they were stable for 3 days.

The pH of the feed solutions (range 3–6.4) was adjusted using Britton–Robinson buffer (0.21 mol L^{-1}) prepared as previously reported [32] and using *o*-boric acid, *o*-phosphoric acid, acetic acid and sodium hydroxide of Suprapur grade (Merck, Darmstadt, Germany). Aqueous nitric acid (0.06–0.46 mol L^{-1}) was used as the receiving solution for metallic ions.

Real samples were collected from surface water from Martin Pérez River and Havana Bay (Cuba). Conductivity values of 0.6–0.8 mS cm^{-1} were obtained for river water and 39.9 mS cm^{-1} for seawater. The sampling bottles (low-density polyethylene) were previously soaked in 2 M HNO_3 for a few days and were thoroughly rinsed with Milli-Q deionized water. After sampling, real waters were acidified and kept at 4 °C. Before analysis, organic matter in the samples was destroyed by acid digestion using an Ethos 1600 microwave oven (Milestone, Italy), using EPA method 3015 [33]. Aliquots of 45 mL aqueous sample were digested in 5 mL concentrated HNO_3 in a TFM digestion vessel for 20 min at 170 °C. After the digestion process, the samples were cooled, and then filtered. Prior to analysis, they were neutralized with ammonia of Suprapur grade (Merck, Darmstadt, Germany).

ICP-MS multielemental internal standard (^{6}Li, ^{45}Sc, ^{89}Y, ^{115}In, ^{159}Tb, ^{165}Ho, ^{209}Bi, ^{103}Rh) was used for ICP-MS measurements by dilution of 10 g L^{-1} solutions in 2% HNO_3 (AccuStandar, EE.UU).

Apparatus

Metal ion analyses were performed by atomic absorption spectroscopy using a Solaar M series spectrometer (Thermo Elemental, UK). Parameter settings, such as lamp current and wavelength, were those recommended by the manufacturer. The proposed method was validated by comparing the results with those obtained using ICP-MS and adsorptive cathodic stripping voltammetry (AdCSV) techniques. The ICP-MS equipment was an X7 series plasma scan sequential inductively coupled mass spectrometer (Thermo Elemental, UK), operating under recommended conditions for nickel. A Metrohm model 746 VA trace analyzer processor with a Metrohm 747 VA electrode stand (Metrohm, Switzerland) with an automated hanging mercury drop electrode was used for voltammetric measurements of nickel, using the dimethylglyoxime method by AdCSV [34]. pH measurements were made using a model 2001 pH meter with a 52-02 combined glass–Ag/AgCl electrode (Crison, Spain).

LM device and kinetic procedure

LM experiments were performed using a homemade glass device which consisted of two concentric cylindrical cells (12.0-cm internal diameter of the outer cylinder and 3.0-cm internal diameter of the inner cylinder) containing feed and receiving phases, respectively (described elsewhere [17]). The volumes used for these solutions (V_f=288 mL and V_r=16 mL, respectively) produced a preconcentration factor of 18 when total metal transport was accomplished (provided by the ratio of V_f/V_r). A toluene solution containing 2-APBH, as the membrane phase, was located at the top of the cell, above the aqueous solutions. The three phases were gently stirred with two Teflon-coated stirring bars using a model Agimatic-S magnetic stirrer (Selecta, Spain) at 900 rpm. During the experiments, the LM device was covered with a glass plate to minimize evaporation and avoid contamination of solutions and was manipulated into a laminar flow hood. The transport experiments were performed at controlled temperature using a thermostatic bath (TECTRON-100, 3473100, Selecta, Spain).

The amount of metal passing through the LM was measured by flame atomic absorption spectrometry (FAAS). Different aliquots (2 mL) were taken out from receiving solution at scheduled time intervals; the same volume of HNO_3 solution saturated in toluene was added to keep the volume of the receiving solution constant. After FAAS measurements, the concentration values obtained were corrected taking into account the amount of metal in the aliquots of the receiving solution previously removed.

The parameter used to control the flux of Ni through the LM was the overall permeability *P* (centimetre per minute), evaluated from the first-order kinetics of Ni transport:

$$\ln\frac{[\mathrm{Ni}]_{\mathrm{f},0}}{[\mathrm{Ni}]_{\mathrm{f}}}=\frac{PA}{V_{\mathrm{f}}}\,t,$$

where $[\mathrm{Ni}]_{\mathrm{f},0}$ is the initial Ni concentration in the feed solution, $[\mathrm{Ni}]_{\mathrm{f}}$ is the time-dependent concentration of Ni in the receiving solution, *A* (94.39 cm^2 for the membrane device used) is the surface area of the membrane and V_f is the feed solution volume. *P* was evaluated from the slope of the plot of the left-hand term versus time.

Results and discussion

Previous experiments

Initial experiments were performed to determine whether transport of Ni occurs across a LM that contains 2-APBH dissolved in toluene. It is outstanding that in the absence of the carrier, the enrichment of nickel was negligible. The data showed better results for permeability and repeatability when the temperature was maintained at 30 °C. At higher temperature, hydrolysis of the carrier probably occurred and transport decreased. At lower temperature, the complexation/decomplexation reaction of the metal and the diffusion of the transported species (owing to the temperature dependency of the membrane viscosity) could be retarded. Further, the transport of the metal was favoured for moderately acid conditions of the feed solution and stirring rates of the aqueous solutions up to 900 rpm (for higher rates, mixing of different phases occurred). The experimental results showed that the increase of the stirring rate increased the kinetics of the process, producing a good uniform mixing of phases and minimizing the thickness of aqueous boundary layers.

In order to achieve the highest efficiency in the transport of Ni across the membrane system, the influences on the permeability of metal of significant variables such as the pH of the feed phase, the receiving phase composition, the concentration of the carrier in LM and the LM volume were optimized sequentially. A modified simplex method was applied by using the software Multisimplex 2.0 [35].

Optimization of the transport process

In order to accomplish the optimization of the system, a set of preliminary experiments was established and used as the initial conditions of the simplex with four significant variables (five vertices). Table 1 shows the initial simplex, the permeability coefficients obtained for the experiments as the response and the variance of the initial simplex. Sequential vertices were calculated by evaluating the response variable obtained and following the trend that improved the permeability. The simplex was stopped after simplex 20 (35 experiments) using the variance criterion. This criterion compares the variance of each simplex with the variance of the proposed method by calculating the corresponding *F* values [36]. When the first one is statistically lower than the last one, the variation among experiments of the simplex is similar to error of the method and the optimal condition can be selected from the experiments of this simplex. The results of the final simplex are also detailed in Table 1. The variance of the proposed method obtained was 1.23×10^{-6}. It was evaluated from four replicates of experiment 5, with the following values of the variables: pH 4 in the feed solution, 0.2 mol L^{-1} HNO_3 in the receiving solution, 0.007 mol L^{-1} 2-APBH in the LM and 75 mL LM.

Experiment 26 was selected as the optimum conditions obtained from simplex 20: pH 5.3 in the feed solution, 0.31 mol L^{-1} HNO_3 in the receiving solution and 70 mL toluene with 0.004 mol L^{-1} 2-APBH concentration as the LM. The coefficient of permeability obtained in these conditions was 24.14×10^{-3} cm min^{-1}.

Table 1 Simplex optimization of variables (feed solution 400 μg L^{-1} Ni; transport time 5 h)

Number of simplex	Vertex	Organic volume (mL)	pH of feed solution	HNO_3 (mol L^{-1})	2-APBH (mol L^{-1})	Permeability × 10^3 (cm min^{-1})	Variance of simplex
1	1	75	6	0.4	0.004	19.31	2.97×10^{-5}
	2	125	6	0.2	0.007	8.45	
	3	125	4	0.2	0.004	17.30	
	4	125	4	0,4	0.007	17.71	
	5	75	4	0.2	0.007	23.34	
.	.	.	.	.	.	.	.
.	.	.	.	.	.	.	.
.	.	.	.	.	.	.	.
4	1	75	6	0.4	0.004	19.31	4.26×10^{-6}
	4	125	4	0,4	0.007	17.71	
	5	75	4	0.2	0.007	23.34	
	8	69	5.7	0.42	0.008	19.32	
	10	100	5.1	0.3	0.006	19.72	
.	.	.	.	.	.	.	.
.	.	.	.	.	.	.	.
.	.	.	.	.	.	.	.
20	26	70	5.3	0.31	0.004	24.14	1.59×10^{-6}
	16-R1	77	5	0.33	0.008	20.92	
	5-R2	75	4	0.2	0.007	23.39	
	29	85	4.6	0.29	0.007	23.74	
	31	84	4.7	0.28	0.007	23.34	

2-APBH pyridine-2-acetaldehyde benzoylhydrazone, *R1*, *R2*,...: replicates of the vertex

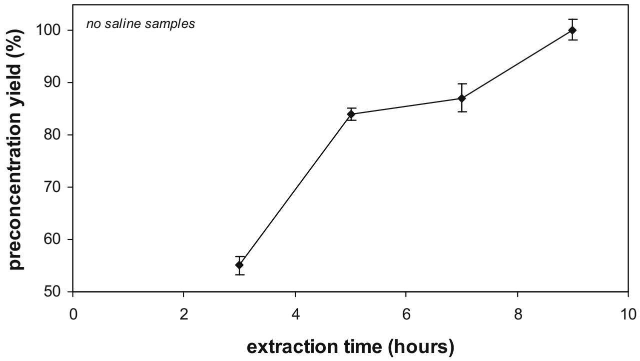

Fig. 1 Temporal variation of preconcentration yield (n=2). Feed solution 400 μg L^{-1} Ni, pH 5.3, 0 g L^{-1} NaCl. Receiving solution 0.31 mol L^{-1} HNO_3. Bulk liquid membrane (BLM) 0.004 mol L^{-1} pyridine-2-acetaldehyde benzoylhydrazone (2-APBH) in 70 mL toluene

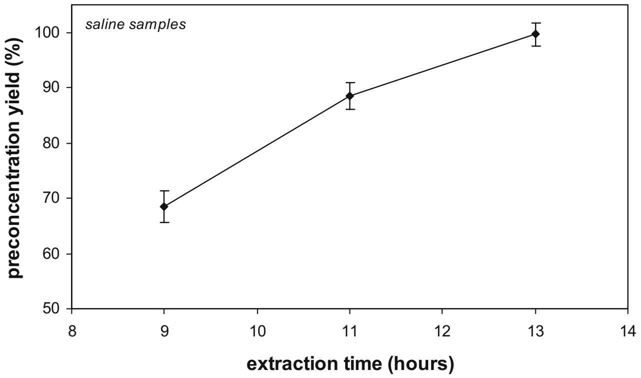

Fig. 3 Temporal variation of preconcentration yield (n=2) for saline samples. Feed solution 400 μg L^{-1} Ni, pH 5.3, 40 g L^{-1} NaCl. Receiving solution 0.31 mol L^{-1} HNO_3. BLM 0.004 mol L^{-1} 2-APBH in 70 mL toluene

Time dependence of nickel transport

The time dependence of nickel transport through the LM was investigated under the optimal experimental conditions. Several experiments with two replicates were carried out over 3, 5, 7 and 9 h. The efficiency–time profile of metal transport is shown in Fig. 1. After 9 h, the concentration of nickel in the receiving solution was independent of the time and the transport was completed with a preconcentration yield of approximately 100%.

Influence of sample salinity on the preconcentration efficiency of nickel

An attempt was made to apply the already described transport study to the preconcentration of nickel from seawater with a high salinity matrix. Hence, we studied the variation of the nickel concentration in the receiving solution for five samples (two replicates) with different salinity values (0, 10, 20, 30 and 40 g L^{-1} NaCl). The samples used contained 0.40 mg L^{-1} Ni and were preconcentrated over 9 h. A plot of percentage nickel recovery against salinity is given in Fig. 2. The diminished efficiency of nickel transport with salinity was probably due to the cotransport of alkali metal ions from the saline matrix. In spite of that, better results could be obtained when the preconcentration time was increased. Figure 3 shows the average preconcentration yield versus preconcentration time for several experiments with 40 g L^{-1} NaCl in the feed phase. In these highly saline conditions, 13 h was necessary for 100% nickel transport. Using kinetic parameters, one can evaluate metal concentrations with shorter times, although lower preconcentration factors are obtained.

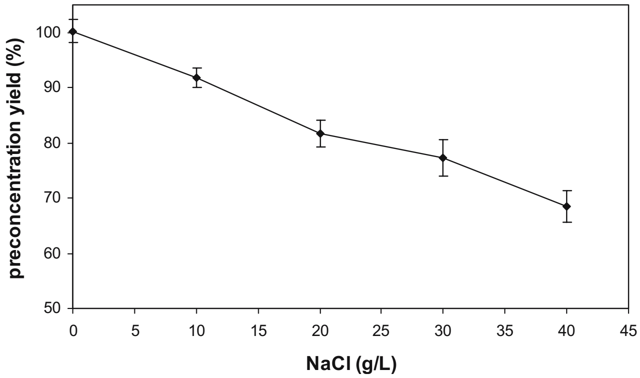

Fig. 2 Effect of salinity of the feed phase on preconcentration yield (n=2). Feed solution 400 μg L^{-1} Ni, pH 5.3. Receiving solution 0.31 mol L^{-1} HNO_3. BLM 0.004 mol L^{-1} 2-APBH in 70 mL toluene. Time of extraction 9 h

Influence of nickel concentration in feed phase

In order to determine the behaviour of the membrane in the transport of variable quantities of nickel, several experiments (two replicates) with different concentrations of metal were performed. The concentration of nickel was different for each sample: 0.025, 0.05, 0.1, 0.2 and 0.4 mg L^{-1}. Efficient preconcentration was achieved after 9 h, with no saline samples, and the average preconcentration yield was 101.7± 1.2%. It was seen that no significant change in recovery was observed with different concentrations of nickel in the samples.

Table 2 Application of the method proposed for nickel determination in certified reference water, TMDA-62

	Ni (μg L^{-1})	
	Determined by LM-FAAS (mean ± SD, n=2)	Certified value
TMDA-62	97.21±0.95	97.8±8.77

LM liquid membrane, *FAAS* flame atomic absorption spectrometry, *SD* standard deviation

Table 3 Analysis of real water samples from Martin Pérez River (*MPR*) and Havana Bay (*HB*) (Cuba) using the proposed liquid membrane method and comparison of results using adsorptive cathodic stripping voltammetry (*AdCSV*) and inductively coupled plasma mass spectrometry (*ICP-MS*) techniques

Sample	Ni (μg L^{-1})			Relative error (%) versus	
	Determined by LM-FAAS (mean ± SD) (n=2)	Determined by AdCSV (mean ± SD) (n=3)	Determined by ICP-MS (mean ± SD) (n=3)	AdCSV	ICP-MS
MPR-1	3.62±0.21	3.37±0.08	3.56±0.82	+7.63	+1.91
MPR-2	3.38±0.24	3.24±0.07	3.35±0.61	+4.33	+0.87
MPR-3	2.80±0.38	2.52±0.12	2.72±0.45	+11.05	+2.90
HB	11.85±0.48	11.82±0.07	11.90±0.71	+0.30	−0.39

Procedure for the new proposed method

An analysis was performed using 288 mL sample, adjusted to pH 5.3 with Britton–Robinson buffer solutions (0.21 mol L^{-1}) or ammonia and placed as the feed phase (V_f) into the cell; 16 mL of 0.31 mol L^{-1} HNO_3 was used as the receiving solution (V_r); and 70 mL of 0.004 mol L^{-1} 2-APBH in toluene was placed over both aqueous solutions. The system was stirred magnetically (900 rpm) for 9–13 h depending on sample salinity and the temperature was maintained at 30 °C. The receiving phase was measured by FAAS.

The blank determination was performed after the proposed enrichment method using Milli-Q deionized water adjusted to pH 5.3 with cleaned Britton–Robinson buffer (by liquid–liquid extraction, employing 2-APBH organic solution) and cleaned LM (by liquid–liquid extraction, employing 0.31 mol L^{-1} aqueous nitric acid). The blank value was 0.022±0.005 μg L^{-1} Ni for four replicates. The limit of detection, calculated as 3 times the standard deviation, was 0.015 μg L^{-1} Ni, and the limit of quantification for the preconcentration, calculated as 10 times the standard deviation, was 0.051 μg L^{-1} Ni. Receiving solutions of blank samples were measured by graphite furnace atomic absorption spectroscopy, because the detection limit of FAAS was not sufficient.

The precision of the proposed method was evaluated for samples containing 400 μg L^{-1} Ni and different salinities: without NaCl after 9 h of preconcentration and 40 g L^{-1} NaCl in the feed phase after 13 h. Nickel recoveries were 101.2±1.8 and 99.7±4.2% and the precision evaluated for the 95% significance level and n=5 was 2.05 and 4.04%, respectively.

Validation and application of LMs in real samples

The LM method for nickel determination was validated using a certified reference material: TMDA-62, fortified water from Lake Ontario. Previously, certified reference water was digested by oxidizing UV photolysis with 1% (v/v) hydrogen peroxide (Suprapur grade, Merck, Darmstadt, Germany) using a low-pressure mercury lamp and adjusted to the optimal pH (5.3) of the preconcentration with ammonia (Suprapur grade, Merck, Darmstadt, Germany). The results of the validation are shown in Table 2. Good agreement was achieved between the certified values and the values obtained using LM-FAAS.

For the application of the proposed method, the determination of nickel in waters from Martin Pérez River and Havana Bay was attempted. The samples were treated by acid digestion using a microwave oven and the pH was adjusted with ammonia before application of the LM method. The results were compared with those obtained by AdCSV [34] and by ICP-MS after the same previous treatment of samples. The results obtained are shown in Table 3. The relative error was −0.39 to 2.90 and 0.30–11.05% for the measurements by ICP-MS and AdCSV, respectively. These results clearly show the effectiveness of the proposed method for enrichment and separation of nickel and removal of the saline matrix before analysis by FAAS, a common and simple technique but with outstanding saline interferences.

Conclusions

We have developed a transport system for nickel through a bulk LM containing 2-APBH, which has been satisfactorily applied to study the separation and preconcentration of this metal from natural water. The method results in a high preconcentration efficiency with a preconcentration factor of 18, which can be easily further improved by modification of the homemade glass cell (increasing the ratio V_f/V_r). After application, the receiving solution obtained permits the precise determination of the concentration of this metal using a simple analytical technique (FAAS). The proposed procedure has important advantages such as simplicity, reproducibility and economy, and it enables matrix interferences to be eliminated, having been successfully applied to certified reference water and real waters from Havana aquatic ecosystems.

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