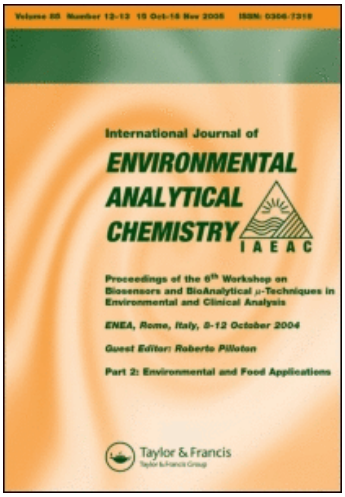

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DETERMINATION OF TRACE ELEMENTS IN ENVIRONMENTAL AND BIOLOGICAL SAMPLES USING IMPROVED SAMPLE INTRODUCTION IN FLAME ATOMIC ABSORPTION SPECTROMETRY (HHPN-AAS; HHPN-FF-AAS)

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Two high performance flow atomic absorption (HPF-AAS) related techniques were chosen to assess their suitability for the determination of several trace elements in complex environmental and biological samples. The technique selected were the Hydraulic High Pressure Nebulization Atomic Absorption Spectrometry (HHPN-AAS), and the Hydraulic High Pressure Nebulization Flame Furnace Atomic Absorption Spectrometry (HHPN-FF-AAS), which were applied directly, or after using off line liquid–liquid separation–preconcentration–back extraction procedures.

Analytical methodologies were developed for Be, Sr, Ba, V, Cr, Mn, Fe, Co, Ni, Cu, Mo, Cd, Ag, Al, Tl, Pb, and Bi, for a variety of samples such as river and seawater, river and marine sediments, soft tissue of mussels, tunicate siphons, aquatic plants, and human samples of clinical interest such as placentas, umbilical cords, and cardiovascular tissues from surgical procedures. The analytical efficiency of the techniques was also proved in a proposed trace metal fractionation approach for river and seawater samples. All samples collected in this work were obtained from the North of Chile, where the most important economic activity is the mining industry.

Keywords: Heavy metals; HHPN-AAS; HHPN-FF-AAS; Sediments; Biota; Clinical samples; Trace metal fractionation; Antofagasta

INTRODUCTION

Heavy metals are recognised worldwide as one of the principal sources of environmental pollution due to their serious impact on ecosystems and damage to the health of human beings [1]. The acceptance of the existence of a relationship between environmental preservation and standard of living has led to the need for an increasing environmental awareness resulting in ever tightening pollution control. Heavy metals are of

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special relevance for countries with an important mining activity [2–5]. Stringent national and international standards have been drawn up to control levels of heavy metals in a variety of complex samples with complex matrices [6], which demand the use of very sensitive, selective and accurate analytical techniques for the determination of trace elements.

Atomic absorption spectrometry (AAS) and inductively coupled plasma atomic emission spectrometry (ICP-AES) are two of the most commonly used analytical techniques employed for measuring trace elements, but samples with high dissolved solid contents, or complex matrices, cause interferences to the analytical signal, and cannot be reliably measured using these techniques. The use of ultrasonic nebulizers has removed some of these problems for some types of materials, but an efficient method is still not available for the analysis of samples with complex matrices, such as saline solutions [7–12].

Various new techniques have been developed to try and overcome the matrix problem, including Flow Analysis (FA) techniques, which are essentially micro-techniques for solution handling, performed under non-equilibrium but reproducible conditions ideally suited for combination with atomic spectrometric detectors. Flow Injection Atomic Spectrometry (FIAS) couples a low-pressure flow system with the nebulizer and atomizer of the atom detection system [13,14]. The latter system has attracted considerable attention due to its high tolerance to the dissolved solids, and its use of on line analyte preconcentration, but its inability to cope with highly polluted samples, and samples with high concentrations of alkaline elements, which overload the chromatographic columns and drastically affect the up take and/or subsequent liberation of analyte, makes it unsuitable for use in the analysis of trace elements in complex matrices. The use of other micro sampling techniques, such as Electrothermal Atomic Absorption Spectrometry (ETAAS), has also been unsuccessful with materials with complex matrices, as the severe interferences encountered could not be eliminated even with the use of matrix modifiers, or background correction devices [14]. The combination of Flow Injection (FI) on line separation and preconcentration with ETAAS has also been proposed, due to its high potential for enhancing the relative sensitivity and selectivity of ETAAS [15], but this is a costly technology, and a more low cost analytical technique is required. Over time FIA and related techniques have been transformed into a flow injection process, which has much wider applications, including the study of chemical interactions and process control, and as a valuable tool in environmental research and the study of life chemistry [16,17].

Although Hydraulic High Pressure Nebulization (HHPN) has been used for more than ten years, little work has been done on its application for producing aerosol, suitable for use in Atomic Spectrometry. This technique would seem to be appropriate for use in the determination of trace elements in environmental, clinical, and biological samples with complex matrices [9,18–20], but as yet, little investigative work has been done. The principles and advantages of the technique have been studied and developed by Berndt *et al.* [21–30]. High performance flow coupled with atomic absorption spectrometry (HPF-FAAS) is used in the generation of aerosols by high-pressure injection using the same methodology used in High Pressure Liquid Chromatography (HPLC). So, an HPLC pump is used to force the liquid for nebulization through a fine Pt/Ir nozzle with an internal diameter of 10–30 μm to produce an aerosol jet, which is converted into a fine aerosol cloud on making contact with a converter ball. In this way, the HPLC bomb produces a high-pressure flow system, in which all the components of the HPLC system, become functional parts of the atomic spectrometer.

Now, if a chromatographic column is inserted between the sampling valve and nebulizer nozzle, an interface is obtained which will allow on line separation and elimination of interfering elements, and the analyte can be measured. However, the process still does not completely remove all interferences, and some of the problems found in FIAS techniques may still be present, and off line separation and preconcentration procedures may be necessary for samples with highly complex matrices [9].

Other nebulization methods which have been developed for the introduction of samples into the atomic absorption spectrometer, using an HPLC pumps, are High Temperature Hydraulic High Pressure Nebulization (HT-HHPN) [31,32], and Thermospray nebulization (TS), which can be interfaced with emission and absorption, atomic spectrometers, to create other similar hyphenated techniques [33–36]. Another related technique available is beam injection flame furnace atomic absorption spectrometry (BIFF-AAS), in which the sample to be analyzed is introduced as a horizontal liquid beam into a heated tube positioned inside the flame of the spectrometer [37].

In this work, two techniques were chosen to assess their suitability for the determination of several trace elements in complex environmental and biological samples, with emphasis on contaminated river, and seawater. The techniques selected were Hydraulic High Pressure Nebulization Atomic Absorption Spectrometry (HHPN-AAS), and Hydraulic High Pressure Nebulization Flame Furnace Atomic Absorption Spectrometry (HHPN-FF-AAS). Off line separation and/or preconcentration of analyte were done without interphasing with the atomic absorption spectrometer. Typical classical separation–preconcentration techniques such as liquid–liquid extraction, and the addition of ion suppressors were used.

Analytical methodologies were developed for the determination of Be, Sr, Ba, V, Cr, Mn, Fe, Co, Ni, Cu, Mo, Cd, Ag, Al, Tl, Pb, and Bi in river and seawater samples, which were also used to develop an operational elemental fractionation approach [38]. Besides, the following samples were also analysed: river and marine sediments, soft tissues of mussels, siphons of tunicates, muscle fish, aquatic plants and human samples of clinical interest such as placentas, umbilical cords and cardiovascular tissues from surgical procedures. All samples used in the study were principally taken from the II Region of Antofagasta in the North of Chile, which has a heavy concentration of mining activity, related to the production of copper and non-metallic salts, producing more than two million tons of copper annually [39]. Presently, Chile contributes 40% of the world production of copper, of which 22% takes place in the II Region of Antofagasta.

EXPERIMENTAL

Instrumentation

Atomic absorption measurements were performed on a GBC 909 PBT atomic absorption spectrometer coupled with a dedicated Knauer HHPN system (A0292) manufactured to our requirements, with a HPLC pump with analytical pump head, solvent filter (5 μm), inert injection valve with Reed contact, a Titanium HHPN nebulizer, a 20 μm Pt/Ir nozzle plate, and PEEK capillary inert injection sample loops. PEEK sample injecting loops with a capacity of no more than 200 μL were used to measure the analytical signal in the high peak mode, and injection loops of the same material

of 200, 500 and 1000 μL capacity were used when the measuring mode was in the peak area. Measurements were made with nitrous oxide–acetylene or air–acetylene flames, according to the trace element being analyzed. In the last case, a quartz collector tube, or atom trap (GBC) was positioned inside the flame to enhance the analytical signal. This configuration combines the hydraulic high-pressure nebulization with flame furnace atomic absorption spectrometry, giving origin to the HHPN-FF-AAS.

Normal hollow cathode lamps (HCL) from Photron were used to measure Ba, Sr, V and Al, and Buck Scientific HCL was employed for Be. Boosted discharge lamps (BDL) from Photron were preferred for Cr, Mn, Fe, Co, Ni, Cu, Mo, Cd, Ag, Tl, Pb, and Bi. Photron manufactured some of the BDL lamps for this work.

Reagents

All acids used were of trace element analysis grade, including Suprapur (Merck), Omni Trace (EM Science) and INSTRA (J.T. Baker). Ultra Resi – Analized (Baker 9077-02) and OmniSolv (EM Science MX0488-1) were used for carrier solutions. Stock solutions of the elements were prepared from Merck Titrisols ampoules. Potassium nitrate was used as an ion suppressor, and all other reagents used were at least of analytical grade.

Certified reference material used for the validation of the techniques and for quality control of the analytical determinations was obtained from the Canadian National Research Council (NRC-CNRC). The reference standard materials (SRMs) used was CASS-3 (coastal sea water), SLRS-4 (river water), DORM-1 (dogfish muscle), TORT-1 (lobster hepatopancreas), LUTS-1 (non-defatted lobster hepatopancreas), MESS-1 (marine sediment). The reference material NASS-4 (open ocean sea water) was used as matrix for all blanks in trace metal analysis of saline water samples. Purified coastal seawater (PCSW) was prepared [40] with an additional solid phase extraction step using C_{18} 3M Empore Bakerbond (J.T. Baker) extraction discs to improve the uptake of trace metals. This matrix was then used to prepare blanks for heavy metal analysis of contaminated saline water samples, and for the preparation of trace element secondary reference material.

Sampling, Samples and Sample Pre-treatment

All samples used in the work were obtained from the North of Chile, where the most important economic activities are the mining industry related with the production of copper and non-metallic salts. The river water samples were taken from the Loa River, which is an aquatic desert ecosystem, and the source of drinking water for the cities in the II Region of Antofagasta in Chile. The seawater samples were collected with inert sampling bottles Niskin Go-Flow (General Oceanic) from marine environments, impacted and not impacted by industrial activities. Vegetable samples were collected by hand and sediments by a pre-treated home made PVC corer from the Loa River ecosystem. The samples of marine invertebrates were collected, from the rocky coast of St. George Bay in Antofagasta, and the samples of marine sediments were collected with the home made PVC corer by means of autonomous diving in Algodonales Bay in Tocopilla in the II Region of Antofagasta, and from Caldera Bay in the III Region of Atacama. The coastal zone of Algodonales Bay has been significantly impacted by the discharge of tailings from copper mining activities, and from the loading of minerals on the ships in the bay. Emissions from power plants

located in the area, which use coal and Pet Coke for fuel, have also added to the contamination.

The samples of human tissues, such as placentas, and umbilical cords from new born babies of mothers who have lived for at least five years in the II Region of Antofagasta; right auricles, mammary artery, and saphenous veins were obtained from a population under study, made up of patients who have also lived at least five years in the II Region of Chile, and population control samples were obtained from the VIII and IX Regions in the South of Chile.

According to the field conditions and the categorized concentration of the fractionation trace metal approach, the acid fixations of the water samples were made in the sampling sites, and in the bench of the "clean laboratory". All procedures for standard additions to SRM's and actual samples, and pre-treatments of biological and sediment samples were made in the "clean laboratory" inside a laminar flow hood (Labconco, Purifier Class II) using inert devices such as plastic and titanium knives, agate grinding mortar, and scalpels, scissors and forceps of surgical stainless steel.

Procedures

The sample is inserted into the high-pressure carrier stream via the sample injection valve, and transported by the corresponding sample loop to the nozzle of the hydraulic high-pressure nebulizer. The fine liquid spray is forced under pressure into the nebulizing chamber, from where it is directed to the burner, which may, or may not be fitted with a quartz atomic collection tube.

The sub-sample which contains the analyte may be injected into the system in several different forms according to the pre-treatment of the sample, as an aqueous acidified solution, as an acid solution produced by a digestion or acid dissolution of the sample, or the analyte may be under the form of an organic derived species produced by means a liquid–liquid extraction step or as a weakly acid aqueous solution coming from a back extraction procedure. The analysis involves two steps: (i) introduction of 200–1000 μL of the sample solution, which contains the analyte into the injection loops, using a glass syringe with the injection valve set in the "load" position. The flow rate of the carrier solution is 2.5–3.0 mL/min. The carrier solution used is a mixture of water and methanol, either 20/80 and 40/60 percent v/v, acidified with 100 μL HNO_3/L of solvent mixture; (ii) changing valve to "inject" position, to introduce the sample into the high pressure carrier stream, which is then directed to the nozzle, to produce a high pressure nebulization, and from there into the spectrometer mixing chamber.

An integration time of 10 s was used in the high peak mode, and 10–30 s in the peak area mode.

Direct Determination of Dissolved and Total Dissolved Concentrations of Trace Metals in River and Seawater [41]

Sample Pre-treatment

For dissolved concentration the samples were filtered through 0.45 μm membranes, and then an addition of HNO_3 was made to give pH 2. For total dissolved concentration the samples were acidified to pH 2, and then filtered.

Determination of the Total Recoverable Concentration of Trace Metals in River Water and Seawater [42]

Sample Pre-treatment

10 mL sample aliquots in a homemade Teflon bombs with 10 mL of nitric acid were digested for 1 h to $140 \pm 5^{\circ}C$ in a ceramic oven.

Determinations of Trace Metals in River and Seawater Using Off Line Matrix Separation–Preconcentration Methodology

Dithiocarbamates [ammonium pyrrolidine dithiocarbamate (APDC), diethylammonium diethyldithiocarbamate (DDTC)] are a well-known group of reagents used for extraction of V, Fe, Pb and other trace metals using methyl isobutyl ketone (MIBK), $CHCl_3$ or 1,1,2-trichlorotrifluoroethane. The selectivity and the efficiency of the extraction can be maximized by careful control of the pH [43–45].

Before being measured, aluminium was chelated with 8-hydroxyquinoline at pH 8.3, in a solution of hydroxylamine–1,10-phenanthroline which masks any Fe present, and then extracted with MIBK, using a strictly controlled agitation time [44]. Then the water sample was made 7 M in HCl [43]. Molybdenum was determined by direct extraction with MIBK. Thallium was chelated with a purified mixed extraction reagent (APDC–DDTC) [45] at pH 4, and then was measured before being re-extracted with nitric acid from the $CHCl_3$ extracts.

Determinations of Cr, Cd and Pb in River and Marine Sediments [46]

Sample Pre-treatment

Screen sizing of dried sediments through Nylon sieves was carried out, and the 120 or 230 mesh fractions were selected for analysis. A sample between 400 and 600 mg was accurately weighed and placed inside the homemade Teflon bomb. A sample between 100–1000 mg of certified reference material was then accurately weight and placed in a second Teflon bomb. 1 mL of deionised water and 12 mL of *aqua regia* reagent were then pipetted into each bomb, and the reaction was allowed to proceed for at least 5 min, until the evolution of gases had stopped. 4 mL of perchloric acid and 2 mL of 30% hydrogen peroxide were then pipetted into each bomb, and the digestion bombs were then sealed and placed into the ceramic oven for 2 h at $150 \pm 5^{\circ}C$.

Determination of Total Concentration of Cr, Mn, Co, Ni, Cu and Cd in Biological Samples (Biota: Plants, Mussels, Tunicate Siphons, and in Human Tissue (Placenta, Umbilical Cord and Cardiovascular Tissue)

Sample Pre-treatment [47,48]

600–1000 mg of homogenized wet biological samples, that is to say, plants, mussel's soft tissues, and tunicate siphons were accurately weighed and placed in Teflon digestion bombs. 50–500 mg of human tissue were accurately weighed and placed in another series of Teflon bombs, and finally 500–1000 mg of certified reference materials were accurately weighted, and placed in a third series of digestion bombs. According to the strength of the sample two digestion techniques were employed. The first procedure

involves the addition of 1 mL of deionised water, and 10 mL of nitric acid to each bomb containing the sample, and allowing at least 5 min for the evolution of gases. In the second one, the samples were treated in the same way, but in an additional stage 3 mL of perchloric acid and 3 mL of 2% $K_2S_2O_8$ solution were also added. The digestion bombs were sealed and placed in the ceramic oven for 2 h at $150 \pm 5^{\circ}C$.

RESULTS AND DISCUSSION

Table I shows the merit figures of the analytic validation data to prove the suitability and efficiency of the HHPN-AAS, and HHPN-FF-AAS techniques for the determination of trace metals in contaminated river and coastal seawater samples. Blank measurements were done with the secondary seawater standard PCSW or using standard reference material NASS-4 and SLRS-4 (NRC-CNRC). For the quality control analyses the SRMs CASS-3, CASS-4, and SLRS-4 were used, when it was necessary the addition of known quantities of trace elements from Titrisol Merck ampoules was made to the samples. Detection limits were calculated in accordance with the IUPAC criteria [49,50]. Multiple standard addition methodology was applied to actual and SRM samples, for which trace element additions were made into samples either with or without additions of an internal standard of the analyte being analysed. The relative standard deviation (RSD) and relative errors (RE) data for SRM samples are reported in Table I.

Table II shows all the relevant validation data, to prove the suitability and efficiency of the HHPN-AAS, and HHPN-FF-AAS techniques for the determination of trace metals in river and marine sediments, biological materials such as river plants, soft

TABLE I Analytic validation of the HHPN-AAS and HHPN-FF-AAS techniques for the determination of heavy metals in river water, and coastal seawaters

Element	*Technique*	*Linear range* (a) (ng/mL)	*Signal*	*RSD* (±%)	*RE* (%)	C_L (ng/mL)
Be	HHPN (b, c)	10–40	A	2.0 ($n=11$)	+1.5 (spiked river water)	1.5
Sr	HHPN (b, c)	1000–4000	A	1.9 ($n=14$)	+3.9 (spiked SLRS-4)	45
Ba	HHPN (b, c)	300–1200	A	0.2 ($n=11$)	−0.4 (spiked SLRS-4)	0.2
V	HHPN (d)	5–20	A	3.0 ($n=5$)	+3.1 (spiked PCSW and CASS-4)	1.1
Mn	HHPN-FF (c)	50–200	A	1.5 ($n=5$)	−0.7 (spiked SLRS-4)	1.0
Fe	HHPN-FF (d)	10–40	HP	5.4 ($n=11$)	+8.3 (spiked CASS-3)	1.4
	HHPN-FF(b, c)	100–400	A	11.5 ($n=9$)	+8.8 (SLRS-4)	2.5
Co	HHPN-FF (b, c)	60–240	A, HP	0.9 ($n=5$)	+1.5 (spiked river water)	4.0
Ni	HHPN-FF (b, c)	30–120	A	3.2 ($n=5$)	+1.7 (spiked SLRS-4)	3.7
Cu	HHPN-FF (b, c)	25–100	A	1.3 ($n=5$)	−0.4 (spiked SLRS-4)	0.2
Mo	HHPN (d)	10–40	A	0.4 ($n=11$)	+0.7 (CASS-3)	0.5
Cd	HHPN-FF (b, c)	2.0–8.0	A	8.9 ($n=5$)	+6.6 (spiked CASS-3)	0.2
Ag	HHPN-FF (b)	1.0–2.5	A	0.5 ($n=5$)	−0.2 (spiked river water)	0.2
	HHPN-FF (c)	0.5–2.0	A	1.0 ($n=9$)	−0.2 (spiked river water)	0.1
Al	HHPN (d)	100–400	A	0.8 ($n=5$)	+0.2 (spiked SLRS-4)	12
Tl	HHPN-FF (e)	15–60	A	3.1 ($n=5$)	+3.0 (spiked river water)	0.3
Pb	HHPN-FF (c)	30–120	A	1.6 ($n=5$)	+2.2 (spiked SLRS-4)	2.4
	HHPN (d)	15–60	A	0.2 ($n=5$)	+2.5 (spiked SLRS-4)	0.4
Bi	HHPN-FF(b, c)	25–100	A	1.6 ($n=11$)	+1.0 (spiked river water)	0.9

(a) Standard additions methodology; (b) direct; (c) then digestion step; (d) MIBK extract; (e) liquid–liquid extraction and acid back-extraction.

TABLE II Analytic validation of the HHPN-AAS and HHPN-FF-AAS techniques for the determination of heavy metals in biological tissues (BT), river and marine sediments (S)

Element	*Matrix*	*Technique*	*Linear range for standard additions* (ng/mL)	*Signal*	*RSD* (±%)	*RE* (%)	C_L (ng/mL)
Cr	BT	HHPN	150–600	HP	1.1 ($n=5$)	−0.4 (DORM-1)	20.7
	S	HHPN	2000–8000	HP	2.8 ($n=12$)	+2.9 (MESS-1)	28.3
Mn	BT	HHPN-FF	10–40	A	2.2 ($n=9$)	–1.3 (LUTS-1)	1.3
	BT	HHPN-FF	30–120	A	0.2 ($n=11$)	+0.9 (LUTS-1)	0.7
Co	BT	HHPN-FF	30–120	A	6.4 ($n=12$)	–2.0 (TORT-1)	7.0
Ni	BT	HHPN-FF	30–120	A	3.0 ($n=5$)	+1.7 (TORT-1)	6.0
Cu	BT	HHPN-FF	10–40	A	2.5 ($n=15$)	+0.3 (LUTS-1)	0.4
Cd	BT	HHPN-FF	6.0–24	HP	1.3 ($n=11$)	+1.5 (DORM-1)	0.5
	S	HHPN-FF	12–48	A	2.7 ($n=9$)	−3.3 (MESS-1)	0.7
Pb	S	HHPN-FF	60–240	A	2.5 ($n=13$)	−1.1 (MESS-1)	1.0

tissue from mussels, tunicate siphons, and human clinical tissue such as placentas, umbilical cords, and cardiovascular tissue recovered from surgical procedures. SRM's MESS-1, MESS-2, DORM-1, and LUTS-1 (NRC-CNRC) were used for quality control measurements and detection limits were calculated according IUPAC criteria [40,50].

Tables IIIa,b, and IV show the results of the analysis of trace metals by HHPN-AAS, and HHPN-FF-AAS techniques on a variety of samples obtained from a desert ecosystem impacted by mining activity, marine environments impacted by industrial activities, and marine environments, unaffected by industrial activity.

The speciation of trace elements has also been proposed as a valuable tool for studying the environmental impact of mining tailings [38, 51–53]. In this work, the HHPN-AAS, and HHPN-FF-AAS were shown to be valuable techniques for obtaining information relating to the chemical fractionation of heavy metal in saline waters which receive discharges or leakage of mine waste materials. To prove the efficacy of the techniques, an operational procedure was developed, which was based on a variation of the pre-treatment of samples [38,41,42,51–53], followed by subsequent measurement using the HHPN-AAS, and HHPN-FF-AAS techniques validated in this study. The metal fractionation approach proposes the following categorized concentrations.

Dissolved Metal Concentration

Corresponds to the fraction which contains all the soluble forms considered thermodynamically reactive, that is environmentally labile chemical species of the element. This fraction is obtained by the micro filtration of the aqueous sample through a 0.45 μm membrane, and subsequent acidification of the filtrate with nitric acid to give a solution with a pH of approximately 2.

Dissolved Total Metal Concentration

This fraction contains all thermodynamically reactive and non-reactive chemical species, which from an environmental chemical point of view means all labile and non-labile chemical species of the elements in question. To obtain this fraction, the previous procedure for dissolved concentration was used, followed by a digestion

TABLE IIIa Application of the HHPN-AAS and HHPN-FF-AAS techniques for the trace elements determinations in river water and seawater samples

Metal	*Technique*	*Sample and metal fractionation*		*Environmental scenario*	*Mean*
Be(μg/L)	HHPN	River water	Dissolved	Base line	12.3
				Post-industrial	8.6
			Total	Base line	37.4
				Post-industrial	37.5
Sr (mg/L)	HHPN	River water	Dissolved	Base line	3.01
				Post-industrial	10.4
			Total	Base line	6.30
				Post-industrial	15.8
Ba (mg/L)	HHPN	River water	Dissolved	Base line	0.20
				Post-industrial	0.18
			Total	Base line	0.67
				Post-industrial	0.68
V (μg/L)	HHPN	Seawater	Total reactive	Base line surface	0.61
				Base line bottom	0.92
Mn (μg/L)	HHPN-FF	River water	Dissolved	Base line	23.2
				Post-industrial	107.1
			Dissolved total	Base line	35.3
				Post-industrial	132.4
			Total reactive	Base line	37.7
				Post-industrial	147.1
			Total	Base line	47.5
				Post-industrial	286.6
Fe (μg/L)	HHPN-FF		Dissolved	Base line	3.7
				Post-industrial	13.3
	HHPN-FF	River water	Dissolved total	Base line	55.5
				Post-industrial	207.0
	HHPN-FF		Total reactive	Base line	10.8
				Post-industrial	251.3
	HHPN-FF		Total	Base line	350.8
				Post-industrial	4043.8
	HHPN-FF	Seawater	Total reactive	Monitoring	1.02–2.95 ($n=32$)
		CASS-3	Dissolved	QC	
				Certified = 1.26 μg/L	1.25 ($n=3$)
Co (μg/L)	HHPN-FF	River water	Dissolved	Base line	2.9
				Post-industrial	8.0
			Dissolved total	Base line	58.4
				Post-industrial	66.9
			Total reactive	Base line	5.0
				Post-industrial	21.1
				Base line	89.6
			Total	Post-industrial	261.3
Ni (μg/L)	HHPN-FF	River water	Dissolved	Base line	4.8
				Post-industrial	7.9
			Dissolved total	Base line	47.2
				Post-industrial	148.7
			Total reactive	Base line	7.5
				Post-industrial	9.8
			Total	Base line	65.6
				Post-industrial	181.5

TABLE IIIb Application of the HHPN-AAS and HHPN-FF-AAS techniques for the trace elements determinations in river water and seawater samples

Metal	*Technique*	*Sample and Metal fractionation*		*Environmental scenario*	*Mean or Range*
Cu (μg/L)	HHPN-FF	River water	Dissolved	Base line	9.0
				Post-industrial	15.7
			Dissolved total	Base line	34.3
				Post-industrial	43.7
			Total reactive	Base line	10.8
				Post-industrial	36.5
			Total	Base line	43.7
				Post-industrial	109.7
Mo (μg/L)	HHPN-FF	River water	Dissolved	Base line	24.9
				Post-industrial	58.4
			Dissolved Total	Base line	283.9
				Post-industrial	352.1
			Total reactive	Base line	57.5
				Post-industrial	105.5
			Total	Base line	410.8
				Post-industrial	551.6
	HHPN	Seawater	Dissolved	Base line	9.65–18.5 ($n=12$)
				Post-industrial	6.62–14.8 ($n=39$)
			Total reactive	Base line	16.3–23.5 ($n=12$)
				Post-industrial	9.24–23.6 ($n=39$)
		CASS-3	Dissolved	QC	
				Certified = 8.95 μg / L	9.08 ($n=5$)
Ag	HHPN-FF	River water	Dissolved	Monitoring	2.41–11.0 ($n=12$)
			Total	Monitoring	6.64–14.5 ($n=12$)
Cd (μg/L	HHPN-FF	River water	Dissolved	Base line	0.39
				Post-industrial	0.34
			Dissolved total	Base line	12.1
				Post-industrial	11.9
			Total reactive	Base line	0.62
				Post-industrial	0.61
			Total	Base line	30.7
				Post-industrial	24.9
	HHPN-FF	Mining waste	Dissolved	Monitoring	1.46 – 45.0 ($n=36$)
Al (mg/L)	HHPN	River water	Dissolved	Base line	0.13
				Post-industrial	0.60
			Total	Base line	4.32
				Post-industrial	469.5
Tl (μg/L)	HHPN-FF	River water	Dissolved	Monitoring	5.74 – 10.5 ($n=13$)
			Total	Monitoring	6.82 – 11.3 ($n=13$)
Pb (μg/L)	HHPN-FF	River water	Dissolved	Base line	10.1
				Post-industrial	9.2
			Dissolved total	Base line	36.8
				Post-industrial	142.8
			Total reactive	Base line	12.5
				Post-industrial	14.5
			Total	Base line	56.2
				Post-industrial	271.8
Bi (μg/L)	HHPN-FF	River water	Dissolved	Base line	15.9
				Post-industrial	17.3
			Total	Base line	39.4
				Post-industrial	39.8

TABLE IV Application of the HHPN-AAS and HHPN-FF-AAS techniques for the heavy metal determinations in sediments and biological tissues

Metal and technique	*Sample*	*Environmental scenario and/or sample description*	*Mean or range* (μg/g)
Cr	*Juncus sp.*	Base line	0.36 (a)
	(River plant)	Post-industrial	1.25 (a)
HHPN	Placenta	Human	0.45–9.51 ($n=116$, b)
	Umbilical cord	Human	0.86–29.6 ($n=66$, b)
	River sediment	Base line	68.3 (b)
	(0.063 mm)	Post-industrial	89.5 (b)
Mn	*Chara sp.*	Base line	41.9 (a)
	(River algae)	Post-industrial	210.7 (a)
	Placenta	Human	0.30–16.0 ($n=116$, b)
	Umbilical cord	Human	0.03–1.80 ($n=66$, b)
	Auricle (right)	Human (studied population)	0.16–42.5 ($n=197$, b)
HHPN-FF		Human (control population)	0.39–13.8 ($n=20$, b)
	Mammary artery	Human (studied population)	0.12–36.5 ($n=188$, b)
		Human (control population)	0.04–10.4 ($n=25$, b)
	Saphenous vein	Human (studied population)	0.06–43.6 ($n=185$, b)
		Human (control population)	0.30–12.5 ($n=21$, b)
Co	Placenta	Human	0.06–1.89 ($n=116$, b)
	Umbilical cord	Human	0.07–17.2 ($n=66$, b)
HHPN-FF	*Juncus sp.*	Base line	0.10 (a)
	(River plant)	Post-industrial	0.29 (a)
Ni	*Juncus sp.*	Base line	1.08 (a)
	(River plant)	Post-industrial	0.79 (a)
HHPN-FF	Placenta	Human	0.20–2.00 ($n=116$, b)
	Umbilical cord	Human	0.14–23.4 ($n=66$, b)
Cu	Auricle (right)	Human (studied population)	0.27–49.3 ($n=208$, b)
		Human (control population)	0.76–12.7 ($n=21$, b)
	Mammary artery	Human (studied population)	0.35–45.0 ($n=188$, b)
HHPN-FF		Human (control population)	0.52–27.5 ($n=25$, b)
	Saphenous vein	Human (studied population)	0.73–59.1 ($n=185$, b)
		Human (control population)	1.54–41.0 ($n=21$, b)
Cd	*Juncus sp.* (river plant)	Base line	0.18 (a)
		Post-industrial	1.39 (a)
	River sediment (0.063 mm)	Base line	2.26 (b)
		Post-industrial	3.19 (b)
	Marine sediment (≤ 2 mm)	Monitoring	0.20–0.48 ($n=32$, b)
	MESS-2	QC	
HHPN-FF		Certified = 0.24 μg / g (b)	0.25 ($n=4$)
	Perumytilus purpuratus	Monitoring; soft tissue	0.55–1.05 ($n=12$, a)
	Pyura praeputialis	Monitoring; siphons	0.008–0.033 ($n=12$, a)
	DORM-1	QC	
		Certified = 0.086 μg / g (b)	0.087 ($n=4$)
	Placenta	Human	0.016–0.446 ($n=116$, b)
	Umbilical cord	Human	0.008–3.554 ($n=66$, b)
Pb	River sediment	Base line	24.9 (b)
	(0.063 mm)	Post-industrial	25.8 (b)
HHPN and	Marine sediment (Tocopilla)	Base line	3.21 (b)
HHPN-FF	(0.063 mm)	Impacted area	41.9 (b)
	Marine sediment (Caldera)	Non-impacted area	1.59 (b)
	(0.125 mm)		

(a) Wet weight normalized results; (b) dry weight normalized results.

stage of the micro filtered sub-sample to break down the elements bound up in inorganic and organic ligands, which are designated as non-labile chemical species, thus producing a solution which contains all the labile and non-labile chemical species in a form which can be measured by the applied instrumental analytical technique.

Total Dissolved or Total Reactive Metal Concentration

This fraction is obtained by acidifying an unfiltered aqueous sample with nitric acid to obtain a solution with a pH about 2. The fraction contains all the soluble, colloidal, and particulate metallic forms, considered thermodynamically reactive, that is all the environmentally labile chemical species of the elements.

Total Concentration or Total Recoverable Metal Concentration

This categorized concentration is obtained by subjecting the unfiltered sample to an acid digestion procedure, similar to that done for the *dissolved total metal concentration* fraction.

In this way the major part of all chemical forms of the metal are liberated in a form, which is suitable for be measured by the applied instrumental technique. This category of concentration includes all the dissolved and particulate chemical species of the metals, which move between thermodynamically reactive (labile), and thermodynamically unreactive or inert forms (non-labile) of the trace metals. *Particulate metal concentration* is defined as the difference between the *total recoverable concentration* and the *dissolved concentration* of the metal in the sample [42]. For the purposes of this work the *particulate metal concentration* was included, because water samples containing particulate matter were also analyzed. The Loa River water samples are enriched in finely particulate matter due to the flow of water through the geological strata of the aquatic desert ecosystem, and by leakage of mining wastes and settleable particulate matter. Seawater samples contaminated with mines tailings and mineral shipping activities were also considered.

The characteristics of the system produced by combining hydraulic high pressure nebulization with atomic absorption spectrometry (HHPN-AAS) has many benefits including high aerosol yield, small diameter droplets, negligible effect from sample viscosity, low interferences from sample matrix and a considerable increase in detection levels due to the more efficient sample delivery system. The increment of the detection levels is increased even more in the case of the HHPN-FF-AAS due to the longer residence time of the gaseous atoms in the radiation absorption zone inside the atom trap cell. These features should make the HHPN-AAS and HHPN-FF-AAS suitable for application to the determination of some trace elements in environmental and biological samples with complex matrices. However, the HHPN does not eliminate the chemical interferences [29], and some separation technique is necessary to eliminate the matrix and at the same time preconcentrate the analyte, which can be made on-line or in an independent way off-line.

The liquid–liquid extraction technique is the most commonly used separation procedure used in analytical laboratories due to its high efficiency in removing unwanted interfering constituents from a sample matrix, and its ability to easily preconcentrate the analyte. It also provides an additional benefit, as the presence of the organic solvent produces an increase in the analytical signal of the flame atomic

absorption spectrometry. However, the procedure can be laborious, and introduces contamination risks from the materials and atmosphere of the laboratory, which may introduce unwanted complications in trace analysis. To minimize these effects extractions were carried out, recovering the MIBK phase in the necks of 100 mL volumetric flasks.

The use of atom collection tubes for increasing detection levels [54,55] has two drawbacks, the short useful life of the quartz tubes used in the atom traps, and the increment of the background absorption, caused jointly by the adsorption of salts and carbon from the matrix of the saline samples and the incomplete combustion of the solvent. These negative effects must be taken into account in the analysis of large batches of samples. In this work, the use of micro samples in the HHPN-FF-AAS technique ensures that these negative effects are minimized.

Another aspect, which can improve the analytical signal, is the selection of the type of hollow cathode lamp to be used. The advantage of BDL lamps for some elements is that it makes it possible to work with a greater band pass, with subsequent increase in sensitivity [56]. However, spectrometers with background absorption correction system based on deuterium lamps can be an inefficient way of carrying out the correction because the analytical signal can be masked by the instrumental noise. However, in some cases, accurate measurements can still be made using a higher band pass, after disconnecting the deuterium background correction system, always ensuring that the matrix of the ''blank'' is matched with the sample matrix, and the multiple standard additions procedure is applied.

The Coastal–Andean Mountain–Upper Highlands Ecosystem of the II Region of Chile is an important area of the Atacama Desert, of which the River Loa basin is a part. This particular ecosystem suffers from the chronic impact of endogenous arsenic due to volcanism in the area, and anthropogenic delivery of arsenic and other heavy metal due to mining activity, which transports trace elements more rapidly into the ecosystem in comparison to the normal geological process, thus spreading the heavy metals to human beings, through the biogeochemical cycles [57–60]. The waters of hyporheic subsystem and surface streams have very high hardness and salinity contents, with enrichment in boron, and arsenic and others heavy metals [59,61]. The ecosystem has also been subjected to the environmental impact from the presence of the world's biggest open cast copper mine, and other mining operations. Most of the mining operations of extraction, processing, and disposition of wastes, take place near the water resources [59], which is dangerous for a desert stream ecosystem with an important hiporheic subsystem [62], as is the case with the Loa River. The infiltration from tailings dams [63] becomes an invisible source of contamination of certain tracts of the river, altering even more the heterogeneous dynamic of nutrients of the desert ecosystem streams.

CONCLUSIONS

The results of this work show that HHPN-AAS and HHPN-FF-AAS can be applied successfully to the determination of trace metals in environmental and biological samples. The techniques can be used directly, or after applying off line analyte separation–preconcentration for samples with complex matrices. To illustrate the application of the techniques, the results of the levels of concentration of a group of trace elements

are presented in a variety of samples coming from the II Region of Chile. Several of these heavy metals are considered pollutants of high-priority importance [60].

The HHPN-AAS, and HHPN-FF-AAS were also shown to be valuable techniques for obtaining information relating to the chemical fractionation of heavy metal in river saline waters.

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