JAAS

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/jaas

Simultaneous multi-element determination of chemical vapour generation forming elements (As, Bi, Sb, Se, Sn, Cd, Pt, Pd, Hg) and non chemical vapour forming (Cu, Cr, Mn, Zn, Co) by inductively coupled plasma-optical emission spectrometry.

M. M. López Guerrero, E. Vereda Alonso,* J. M. Cano Pavón, M. T. Siles Cordero and A. García de Torres

Abstract

Silica-coated magnetic nanoparticles (MNPs) modified with [1,5-bis (2-pyridyl)-3-sulphophenyl methylene] thiocarbonohydrazide (PSTH-MNPs) were synthesized and characterized. These magnetic nanoparticles (PSTH-MNPs) were employed as a solid phase extraction (SPE) adsorbent for separating and concentrating trace amounts of 14 elements (Pd, Cr, Mn, Zn, Cd, Hg, As, Sb, Bi, Cu, Pt, Sn, Se, Co) from environmental water samples. The main aim of this work was to develop a precise and accurate method for the simultaneous determination of maximum possible number of elements by using this new absorbent and a multimode sample introduction system (MSIS) which not only acts as a system for generation, separation and introduction of chemical vapours (CVG) but also as the introduction system of a sample aerosol, in a simultaneous form, into an inductively coupled plasma-optical emission spectrometer.

The on-line SPE-CVG-ICP-OES developed system was applied to the determination of the aforementioned metals from natural water samples (sea water, estuarine, lake and river water), with the least demanding and simple sample preparation procedure. The developed method was validated by analysing natural water certified reference materials (SLRS-4, TMDA 54.4, SW2 Batch 125, SRM 1643e). Sea water and water well samples collected from Malaga (Spain) were analysed too. The procedure has demonstrated to be fast, easy, automatic, selective, low cost and with good sensitivity. The main advantage of PSTH-MNPs is its very good stability and resistance because chemisorption of chelating molecules on the surface of solid supports provides immobility, mechanical stability and insolubility. Precision (RSD), accuracy (by

---

[*] *Department of Analytical Chemistry, Faculty of Sciences, University of Málaga*

Campus of Teatinos, 29071 Málaga, Spain. E-mail: eivereda@uma.es;
Fax: +34952132000; Tel: +34 952131883

† *Electronic supplementary information (ESI) available: Synthesis of chelating reagent and tables of its characterization*

standard addition or recovery) and limit of detection (LOD) were used to evaluate characteristics of the procedure. The detection limits obtained are adequate for the analyzed samples, within 0.01 and 11.30 µg L^{-1}, RSDs from 1% to 7% and enrichment factor between 1 and 385.5. Furthermore, the method proposed has permitted the simultaneous determination of the 14 elements, saving time of analysis, reagents, and sample volume, and achieving a sample throughput of about 13 h^{-1}.

1 Introduction

Environmental problems are becoming one of the most human concerns all over the world. The many industrial waste water streams contain heavy metals, which can discharge to water and waste water or into surface waters[1] due to this fact, the number of ecological and health problems associated with environmental contamination continues to rise. Thus, the extraction and determination processes of trace metal ions or species from different matrices especially aqueous samples have become paramount importance and received more and more attention.[2,3] Environmental pollution monitoring requires determination of toxic heavy elements at trace levels.

Generally, As, Bi, Sb, Se, Sn, Cd, Pt, Pd, Hg, Cu, Cr, Mn, Zn and Co are found in low concentrations and their determinations require the use of sensitive techniques. Inductively coupled plasma optical emission spectrometry (ICP-OES) is widely used in chemical analysis because of its multi-elemental character, high throughput, and capability for simultaneous determination. However, ICP-OES may present limitations for determining trace elements when conventional liquid sample introduction systems are used.[4,5]

All inductively coupled plasma optical emission and mass instruments are designed for liquid sample introduction, as the vast majority of samples in daily routine are in the liquid form.[6,7] In contrast, the ideal sample for an ICP would be in gaseous phase. Due to this fact, sample introduction has been one of the key factors in the successful development of atomic spectrometry.[8-10] Introducing the analytes as a gaseous hydride (more of the sample can be introduced into the plasma), and these drawbacks can be avoided, and even this increases the sensitivity. Chemical vapour generation (CVG) atomic spectrometry is currently the most popular technique for routine determination of trace amounts of elements which generate volatile species, because of the enhanced detection limits attained in comparison with conventional nebulization of a sample[11]. However, these devices are not always ideal for use with plasma instrumentation because of the required carrier gas flow rates and back pressure in the gas–liquid separator, degrading plasma stability. Besides, CVG technique is only applicable to a limited number of elements and hence cannot be regarded as a universal solution to improve sensitivity.

In response to many of the problems associated with the CVG technique, McLaughlin and Brindle described the Multimode Sample Introduction System (MSIS) designed for ICP that allows smooth reaction of BH_4^- with the acidic sample over the surface of a ground glass cone, rapidly stripping the resulting volatile species from the solution.[12] This novel design, combining both nebulization and CVG, provided lower detection limits for a number of elements that form volatile species through the reaction with $NaBH_4$. The MSIS has also been shown to improve relative standard deviations and lower amount of condensation and liquid entering to the excitation source, without sacrificing sensitivity. [12] Furthermore, a minor memory effect, shorter contact time of the hydride formed with the first solution, which helps to diminish the level of interferences are some of the advantages presented by these novel generators when compared with other hydride generation systems.

Three years later, Asfaw and Wibetoe[13] developed a procedure for the simultaneous determination of hydride and non-hydride forming species using the commercial MSIS by ICP-OES. Wiltsche et al. [14] used the same MSIS for multi-elemental analysis of high alloy steels using masking agents by ICP-OES. Also Matusiewicz[15,16] used the MSIS for the determination of hydride forming, cold vapour and non-hydride forming elements by microwave induced plasma spectrometry (MIP-OES). The historical development of dual-mode sample introduction systems used ICP-OES for the simultaneous determination of hydride-and-non-hydride-forming elements by means HG and pneumatic nebulization have been revisited by Pohl and Sturgeon.[17]

On the other hand, solid phase extraction (SPE), is a very important enrichment technique due to its simplicity, high pre-concentration factors, environmental friendly, low costs and time for sample preparation. The choice of a selective adsorbent is a critical factor in SPE. Recently, nanometer-sized materials have attracted substantial interest in the scientific community because of their special properties.[18] The size range of nanoparticles is from 1 to almost 100 nm, which falls between the classical fields of chemistry and solid state physics. The relatively large surface area and highly active surface sites of nanoparticles enables them to have a wide range of potential applications. Magnetic nanoparticles (MNPs), a new kind of nanometer-sized material, are widely used in the fields of biotechnology and biomedicine.[19,20] These particles are superparamagnetic, which means that they are attracted to a magnetic field, but retain no residual magnetism after the field is removed. Therefore, suspended superparamagnetic particles adhered to the target can be removed very quickly from a matrix using a magnetic field, but they do not agglomerate after removal of the field.[21-25] The modification with organic chains has become a larger focus of interest in the employment of MNPs as adsorbent in SPE. Schiff bases, an important class of ligand obtained by condensation of aldehyde with amines, play a significant role in such applications. Our research group has synthesized and studied a resin based on aminopropyl-controlled pore glass (cpg) with [1,5-bis (2-pyridyl)-3-sulphophenyl methylene] thiocarbonohydrazide (PSTH) chemically bonded to the surface.[26] The resin PSTH-cpg was applied with very good results on the determination of some metal ions. For this reason in the present work, this adsorbent material silica-coated MNPs modified with PSTH (PSTH-MNPs) were synthesized, characterized and employed as a SPE adsorbent for separating and concentrating trace amounts of 14 elements from environmental water samples. The main aim of this work was to develop a precise and accurate method for the simultaneous determination of the maximum possible number of elements, CVG and non-CVG forming elements from natural water samples (sea water, estuarine, lake and river water) by the on line pre-concentration SPE-CVG-ICP-OES system using PSTH-MNPs and a commercial MSIS, with the least demanding and simple sample preparation procedure. The developed method was validated by analysing natural water certified reference materials (SLRS-4, TMDA 54.4, SW2 Batch 125, SRM 1643e). Sea water and water well samples collected from Malaga (Spain) were analysed too. These samples contain high concentrations of dissolved salts (up to 3.5% wt) and low concentrations of analytes.

2 Experimental.

2.1 Instrumentation

A Perkin Elmer Optima 7300 DV inductively coupled plasma optical emission spectrometer (Perkin Elmer SCIEX Instruments, Concord, Canada) equipped with a Multimode Sample Introduction System cyclonic spray chamber (MSIS) (Marathon Scientific, Niagara Falls, Canada), a concentric nebulizer and an AS-91 autosampler was used throughout. The optimum operation conditions are summarized in Table 1. A Perkin Elmer FIAS 400 AS system, which consists of two peristaltic pumps with PVC tubings of various diameters and a five way rotatory valve, was used as the flow injection accessory controlled by the Optima software. The FIAS 400 AS system was connected directly to the Optima by means of 14 cm length of PVC tubing (1.75 mm i.d.), the less possible distance to avoid sample dispersion. Analytical lines of Pt 214.423 nm, Pd 340.458nm, Cr 267.716 nm, Mn 257.610 nm, Zn 206.200 nm, Cd 228.802nm, Hg 253.652 nm, As 188.979 nm, Sb 206.836 nm, Bi 223.061nm, Cu 324.752nm, Sn 283.998 nm and Co 231.160 nm were measured.

The reactor containing PSTH- MNPs was a PTFE tube (150 mm x 0.5 mm i.d.) packed with 50 mg of PSTH-MNPs and knotted round a Nd/Fe/B powerful magnet (2 Teslas) and sandwiched between two circular Nd/Fe/B magnets with a holding strength of 81.4 N. This reactor was placed in the sample loop of a five-port rotatory valve. At both ends of the knotted reactor, polyethylene frits (Omnifit, Cambridge, UK) were fixed to prevent material losses. The knotted reactor was initially flushed with 2 M nitric acid; subsequent use of the eluent in each operating cycle was sufficient to make it ready for re-use. Tygon pump tubings were used to deliver sample, reagents and withdraw waste. The FI system and the ICP-OES instrument were coupled and operated completely synchronously.

2.2 Reagents and samples

High purity reagents were used in all experiments. All plastic and glassware were cleaned with hot concentrated nitric acid and stored soaked in 10% (wt/wt) nitric acid, they were rinsed several times with water immediately before use. Doubly de-ionized water (18 MΩ cm) obtained from a Milli-Q water system (Millipore, Bedford, MA, USA) was used throughout.

The knotted reactor was packed with PSTH-MNPs. This adsorbent was synthesized and characterized by first time in this work (ESI†).

As, Bi, Sb, Se, Sn, Cd, Pt, Pd, Hg Cu, Cr, Mn, Zn and Co, stock standard solutions 1000 mg L^{-1} (Merck, Darmstadt, Germany) and (Perkin Elmer pure, Atomic Absorption Standard, Darmstadt, Germany) were used. Hydrochloric acid 0.2 M (Merck, Darmstadt, Germany) was used to adjust the optimum pH (pH=1). A 2.5% (wt/vol) sodium tetrahydroborate (III) ($NaBH_4$) (Merck, Darmstadt, Germany) solution prepared in 0.5% (wt/vol) NaOH (Merck, Darmstadt, Germany) was used as reductant and a 3.5% (wt/vol) thiourea (Merck, Darmstadt, Germany) in 8.0% (wt/wt) hydrochloric acid was used as eluent, for the simultaneous elution and determination of As, Bi, Sb, Se, Sn, Cd, Pt, Pd, Hg Cu, Cr, Mn, Zn and Co.

The certified reference materials (CRMs) analyzed to determine the accuracy of the proposed procedure were from National Research Council of Canada (NRCC): TMDA 54.4 Fortified Lake Waters, SLRS-4 River water, and from National Institute of Standards and Technology of USA, (NIST): SPS-SW2 Batch 125, Surface Water and SRM 1643e, trace elements in water. In order to study the applicability of the method, sea and water well samples were collected in polypropylene bottles (previously cleaned by soaking for 24 h in 10 % (wt/wt) nitric acid and finally rinsed thoroughly with ultrapure water before use). Samples were immediately filtered by using a membrane of 0.45 µm pore size cellulose nitrate filters from Millipore (Bedford, MA, USA). After that, the samples were acidified to 0.1% (vol/vol) by the addition of concentrated HNO_3 and were stored in low density polypropylene bottles at 4º C as recommended by Method 3010B from the Environmental Protection Agency (USA), for less than 3 days until analysis. For the analysis of these samples, aliquots of them were placed in volumetric flasks of 50 mL, then the pH was fixed to 1 with HCl and finally, de-ionized water was added up to the mark.

2.3. Chemical vapor generation and liquid nebulization dual mode system.

Chemical vapor generation and liquid nebulization was accomplished in the continuous mode using a commercial MSIS.[27] The MSIS served as the reaction chamber/gas–liquid separator. In dual-mode the environmental water sample passes through both, the nebulizer sample line and the hydride generator sample line. The hydrides formed are introduced to the ICP-OES instrument simultaneously with the sample aerosol by a stream of the nebulizer argon. The waste solution was rapidly removed from the chamber to drains by peristaltic pump (17.0 mL min^{-1}). The MSIS system, has been described in detail in previous paper.[12]

2.4. Pre-concentration and elution procedure

A schematic diagram of the FI-SPE-MSIS-ICP-OES system is shown in Fig. 1. The experimental conditions are given in Table 1. The FI system was operated as follows: during the 240 s sample loading period, valve in the "fill" position, a 2.6 mL min^{-1} flow of sample (standard or blank) at pH 1.0 was pumped (via pump P1) through the knotted reactor (located in the loop of the valve). The As, Bi, Sb, Se, Sn, Cd, Pt, Pd, Hg Cu, Cr, Mn, Zn and Co, analytes were retained on the functionalized MNPs while the sample matrix components were directed to waste.

At the beginning of the 40 s elution stage, the valve position was changed to the inject position and the sample pump P1 was stopped. The eluent passes through the knotted reactor. Thus, the accumulated target analytes were eluted at an elution rate of 3.6 mL min^{-1} and merged with 2.0 mL min^{-1} flow of reductant flow in the mixing coil, where direct generation of As, Bi, Sb, Se, Sn, Cd, Pt, Pd, Hg Cu, Cr, Mn, Zn and Co, vapour and aerosol take place. The gas generated and the liquid are swept into the plasma by a stream of argon (0.7 L min^{-1}) during 40 s. With this procedure, the FI system and the ICP-OES instrument were coupled and operated completely synchronously. Peak areas were used for analytical measurements.

2.5 Optimization strategy

The configuration of the FI-system, and the effect of different parameters on the accumulation and recovery of As, Bi, Sb, Se, Sn, Cd, Pt, Pd, Hg Cu, Cr, Mn, Zn and Co were studied in order to optimize conditions for achieving the best results. Two different strategies were used: one-at-a-time method (changing one parameter each time while keeping the others constant) and surface designs with multiple response.

Due to the large number of parameters that are relevant to the optimization, which might be classified as parameters relating to: (1) elution of As, Bi, Sb, Se, Sn, Cd, Pt, Pd, Hg Cu, Cr, Mn, Zn and Co in the manifold and reaction conditions for CVG and non-CVG (reagent concentrations); and (2) FI parameters of the 14 elements, two surface designs [28,29] were performed. In design (1) the variables to be optimized were concentrations of $NaBH_4$, thiourea and HCl. The lower and upper values given to each factor were 0.5% and 2.0% for $NaBH_4$ concentration, 0.5% and 3.0% for thiourea and 3.0% and 9.0% for HCl concentration. In design (2) all variables commented above were kept constant at the optima values found previously (2.5% $NaBH_4$, 0.5% NaOH, 3.5% thiourea and 8% HCl) and the sample, elution and reductant flow rates were varied by changing the speed of the peristaltic pumps (P1, P2 and P3) and the inner diameter of the pump tubes. The lower and upper values given to the factors were 0.6 and 4.0 mL min^{-1} for elution and sample flow rates and 0.6 and 2 mL min^{-1} for reductant flow rate. The response surface designs used were, a central composite design (CCD) for (1) and a Box-Behnken design for (2). The 16 and 15, respectively, experiments required for these designs were randomly performed.

The experimental data were processed by using the STATGRAPHICS centurion program (version 16.1.11 for Windows).[30] For both designs, the significance of the effects was checked by analysis of the variance (ANOVA) and using *p*-value significance levels. This value represents the probability of the effect of a factor being due solely to random error. Thus, if the *p*-value is less than 5% the effect of the corresponding factor is significant.

2 3. Results and discussion

The determination of trace elements in aqueous environmental samples is difficult not only due to the low analyte concentrations present but also due to the complexity of the samples. Thus, the proposed on line column pre-concentration, CVG and non-CVG, procedure allows the simultaneous separation and pre-concentration of the target analytes from the matrix before quantification by ICP-OES. Therefore, several problems related to interfering species were decreased or eliminated. For this purpose, a new chelating resin, PSTH-MNPs, was used. This chelating resin has good chemical properties as a general chelating reagent, with good adsorption capacities, is stable over a wide pH range (1.0-10.0), besides being stable for a very long time. From this study can be deduced that the ferromagnetic resin is stable over a wide range of time and the knotted reactor packed with this resin was used for more than 600 loads and elutions without the necessity of regeneration, hence, the material can be stored and applied conveniently.

In view of the simultaneous multi-element capability of ICP-OES, optima parameters for single determination of all analytes were compared and, indeed, compromise conditions were selected for a simultaneous determination, provided that the selected values were not totally unsuitable for a particular element.

3.1.Characterization of the functionalized MNPs.

The detailed characterization of AP-MNPs and PSTH-MNPs was carried out using XPS, FTIR, MS Spectrometry, SEM and TEM measurements.

The contents of iron, oxygen, silicon and sulfur in the PSTH-MNPs and AP-MNPs measured with SEM were 62.2% O; 1.0% Si; 35.9% Fe and 0.9 % S for PSTH-MNPs and 65.2% O; 3.4% Si; 31.4% Fe for AP-MNPs. The presence of sulfur only in PSTH-MNPs confirmed that the synthesis would be able to have been effective.

The infrared spectrum (KBr pellets) is complicated because the large mass of silica and the aromatic portion of the molecule produced numerous bands, the overlap of which makes detailed assignments difficult. The band at 3416 cm^{-1} was attributed to O-H stretching and the band at 1744 cm^{-1} was assigned to C=N stretching, the band at 1384 cm^{-1} was assigned to C=S and that at 1096 cm^{-1} was attributed to SO_3. These bands were assigned on comparison with the spectrum of pure PSTH as reference material. The spectrum exhibits several other bands, which are weak and difficult to assign, but those discussed above appeared to be the most useful.

The mass spectrum has been recorded by evaporation until 250 ºC from PSTH-MNPs and the attribution of some peaks was made (ESI† Table 1).

XPS has been used for the study of the surface composition (major and minor) of the samples. The atomic concentration calculation is expressed as a percentage in a tabular form based on the area under the peak, multiplied by the sensitivity factor for each element, and provides a ratio of a single element to the sum of the other elements presents. [31] The error of the method is approximately of 10%. The percentage (in % of total area) approximately for both samples was calculated (ESI† Table 2). It is observed that the concentration of N was increased in PSTH-MNPs and S was appeared, this fact confirmed that the synthesis had been effective.

TEM analysis gives the actual individual particle size.[32] (ESI† Fig 2) The average particle size of AP-MNPs is found around 8 nm, and the size of PSTH-MNPs is a little bit bigger than AP-MNPs, which can be indicated that the functionalization of AP-MNPs took place properly.

3.2. Optimization of the experimental variables.

The configuration of the FI-system and the effect of different parameters on the accumulation and recovery of the 14 target elements were studied in order to optimize conditions for achieving the best results. Consequently, most efforts were focused on the conditions for sample loading and elution from the column, as well as the flow system which was coupled on line with the pre-concentration and separation unit in order to obtain high sensitive, accurate and reproducible results. For measurements to be useful, it was considered that a relative standard deviation (RSD) of about 5% was acceptable. The best signal to noise (S/N) ratios between a blank and a standard solution of 100 μg L^{-1} of the analytes were used as optimization criteria. Peak areas were used for analytical measurements. The scanning of each sample was repeated four times. Two experimental surface designs were used for most of the variables optimization, although, several one-at-a-time methods were also used for optimization of some variables.

3.2.1. Selection of eluent.

To minimize the needed time for quantitative elution and to facilitate eluate delivery, dispersion during elution and elute introduction must be reduced, while a highly efficient eluent should be used. It is well known that strong acids are effective in dissociating complexes and releasing free metal ions, thus, HCl, HNO_3, thiourea, and their mixtures were investigated. 2.6 mL of solution containing 200 μg L^{-1} of 14 elements at pH 1.0 passed through the resin during 60 s and then, eluted with 2.4 mL with different percentage of these eluents. In all the experiments, the eluent was passed through the knotted reactor in a reverse flow relative to the pre-concentration step. The results obtained showed that the mixture HCl-thiourea provided the highest S/N ratios and recoveries. Thus, this eluent was selected for further experiments.

3.2.2. Effect of the pH

The pH value plays an important role in complexation of different ions with the PSTH-MNPs resin, which in turn determines the percentage of the 14 target elements retained. In order to evaluate the effect of pH, the pH value of sample solutions were adjusted to a range of 1.0-10.0. The pH 1 was adjusted with HCl, the pH from 2.0 to 5.0 was adjusted using glycine-HCl or sodium acetate-acetic acid buffer and from 5.0 to 9.0 using borax-boric acid buffer, and pH 10 using NaOH. In order to accomplish the determination of the target elements, a pH value of 1.0 was chosen as overall optimum due to the fact that the vast majority of the studied elements present an increase in the signal to noise ratio.

3.2.3. Effect of $NaBH_4$, HCl and thiourea.

The concentrations of $NaBH_4$, HCl and thiourea were considered to be dependent variables and the effects of these were studied by applying a CCD involving 16 runs in order to obtain the optima conditions. The estimated surface response for the multiple response of all elements is shown in Fig. 2. The data indicate that the interaction usually occur between principal factors. This means that the response surface in the factorial space is curved in the domain of the experimental design. The experiments were carried out randomly to avoid bias. As result of these observations, the optima conditions for the multiple response of the 14 target analytes obtained were 11.0% HCl (wt/vol), 3.0% thiourea (wt/vol) and 2.2% $NaBH_4$ (wt/vol). However, due to the fact that As S/N signals were the lowest, and in order to improve the sensitivity of this element because is one of the most toxic elements in this study, the relative importance assigned to this element to the response was increased. The relative importance is a comparative scale for weighting each of the analyte resulting in the overall desirability product and it varies from the least important 1 to the most important 10. It is noteworthy that the outcome of the overall desirability depends on the relative importance value. A relative importance of 10 was assigned to As. Thus, the new optima conditions obtained were: 8.0% HCl (wt/vol), 3.5% thiourea (wt/vol) and 2.5% $NaBH_4$(wt/vol).

At a fixed $NaBH_4$ (2.5% (wt/vol)) and due to the fact that the reduction by $NaBH_4$ is preferentially performed in acidic medium, it was studied the influence of NaOH between 0% and 2.5% (wt/vol). The employment of NaOH solution is simply to stabilize $NaBH_4$ by avoiding its adverse reaction with water during the storage. The excessive increase of NaOH concentration will definitely decrease the acidity of the reaction mixture and hence, the reaction rate of CVG. The best S/N signals were obtained at 0.5% NaOH. For further experiments, a NaOH of 0.5% (wt/vol) was adopted throughout.

3.2.4. Selection of FI variables.

A Box Behnken desing involving 15 runs was used in the optimization of the FI parameters for the 14 target elements. The flow rate of the sample, eluent and reductant were varied by changing the speed of the peristaltic pumps (P1 and P2) and the peristaltic pump of the ICP-OES, P3, and using different id Tygon peristaltic pump tubing in order to obtain the adequate flow rate. The three dimensional representation for the multiple response of all elements is shown in Fig. 3. In this case, the elements which had lowest S/N ratios were As, Pt, Sn and Zn and in order to improve the sensitivity of these, the relative importance to the response assigned to these elements were 10 for As, Pt, and Sn and 9 for Zn. Thus, the optima conditions obtained were: sample flow rate 2.6 mL min^{-1}, eluent flow rate 3.6 mL min^{-1} and reductant flow rate 2 mL min^{-1}.

On the other hand, the flow rate of the waste from the MSIS spray chamber was studied using one-at-a-time method from 8.9 to 20 mL min^{-1}. The best S/N signals of the vast majority of the elements studied were obtained at a flow rate of 17 mL min^{-1}.

3.2.5. Optimization of the operating parameters

In order to optimize the plasma conditions to minimum interferences, the effect of the nebulizer gas flow rate were studied. The nebulizer gas affects transport and extraction from the gas-liquid separator in the MSIS system. To optimize the nebulizer Argon gas flow for multi-element determination, the optimum flow rate of all elements was estimated in the total range of 0.2 to 1.2 L min^{-1}. It was observed that the nebulizer gas flow rate had a significant effect on emission intensities and thus proved to be a critical parameter. In general, it was observed that when the flow rate was 0.7 L min^{-1}

the signal to noise ratio reached the maximum. Above or below this value, the vast majority of 14 target element signal decreased.

3.2.6. Pre-concentration time.

Furthermore, in time-based pre-concentration systems the loading time indicates the pre-concentration time and affects directly the enrichment factor. Thus, the loading time was investigated in the range between 1 min and 7 min for each analyte, using the optima conditions described above. The peak areas were linear practically up to 7 min for all the analytes. Although sensitivity increases on increasing the sample loading time, the loading time was set to 4 min in order to achieve a high sample frequency with a reasonable sensitivity. Longer loading times can be used for samples with low concentrations of the elements.

3.3. Performance of the method.

Under the optima conditions described above, performance data of the on line SPE-CVG-ICP-OES system for simultaneous determination of the 14 elements were obtained. For 4 min pre-concentation time and a sample flow rate of 2.6 mL min^{-1}, the linear calibration graph from 0.5 – 200 µg L^{-1} for each element are shown in Table 2. A complete cycle of the FI-operation is 4,7 min per all analytes. The 14 target elements in a sample can be determined with a throughput of about 13 h^{-1}.

The detection (LOD) and quantification limits (LOQ) were calculated as the concentration of analyte giving signals equivalent to three and ten times, respectively, the standard deviation of the blank plus the net blank intensity (n=11). The precision for aqueous standards was evaluated as the relative standard deviation obtained after analyzing standards of 5 µg L^{-1} of Hg, Cd, Se, Sb, As, Bi, Co and 25 µg L^{-1} of Pt, Pd, Cu, Mn, Zn, Sn and Cr (11 replicates); and 20 µg L^{-1} of Hg, Cd, Se, Sb, As, Bi, Co and 100 µg L^{-1} of Pt, Pd, Cu, Mn, Zn, Sn and Cr (11 replicates). The enrichment factors (EF) were calculated as the ratio of the slopes of the linear sections of the calibration graphs with and without pre-concentration (changing the knotted reactor by another unfilled). All these parameters were shown in Table 2. The EF, LOD and LOQ can be improved by increasing the pre-concetration time which can be increased at least up to 7 min.

Although is difficult to compare figures of merit for the developed method directly with results from other workers, because of different experimental conditions such as column dimensions, sample flow rate, techniques, *etc.*, some estimations can be made. A comparison of the precisions, detection limits and enrichment factor of the PSTH- MNPs procedure with some of the reported ones with detection by various spectrometric techniques are summarized in Table 3. In this table it can be compared the results obtained in this work with other works of literature. This work is one of the works that more analytes determined simultaneously, it is also one that has a higher enrichment factor and lower LOD even using a technique such as ICP OES less sensitive than ICP MS.

3.4. Analytical applications.

In order to test the accuracy and applicability of the proposed method to the analysis of natural water samples, four reference materials were analyzed, SLRS-4 river water, TMDA 54.4 fortified lake water, SPS-SW2 Batch 125 Surface Water and SRM 1643e, besides, two sea water samples collected from two different villages of Malaga beach and an underground water well. All determinations were performed by using standard addition for calibration. Correlation coefficients of 0.99 or better were obtained for all graphs, indicating good linearity for the working ranges employed. The results are the average of three separate determinations and they are given in Table 4. In general, there is good agreement between certified and found values.

For the sea water and underground water well collected locally, the method of standard addition was used to the verification, and also, a recovery study was developed on spiked samples containing known additions for the 14 target elements. From the results in Table 5 was found that recovery values from 111.3 to 84% of the metals added to water samples were obtained. The accuracy achieved for the spiked samples demonstrated that the method is not affected by high salinity (35 g L^{-1} in sea water). In addition, no significant interferences were observed in the analysis of these samples form the transition metal or CVG forming elements and consequently, offer accurate simultaneous determination of analytes in sea water and underground water samples.

3 4 Conclusion

The FI on line pre-concentration and separation system using PSTH-MNPs as a sorbent material has been evaluated, and demonstrated to be promising for routine determination of the trace amount of As, Bi, Sb, Se, Sn, Cd, Pt, Pd, Hg Cu, Cr, Mn, Zn, Ni and Co in environmental waters by ICP-OES. The procedure has demonstrated to be fast, easy, automatic, selective, low cost and with good sensitivity. The main advantage of PSTH-MNPs is its very good stability and resistance because chemisorption of chelating molecules on the surface of solid supports provides immobility, mechanical stability and insolubility. It costs is low compared with other commercial chelating sorbents. The detection limits obtained are adequate for the analyzed samples. Furthermore, the method proposed has permitted the simultaneous determination of the 14 elements, saving time of analysis and achieving a sample throughput of about 13 h^{-1}.

4 5Acknowledgements

The authors thank the Spanish Ministerio de Ciencia y Tecnología (MCyT project no. CTQ2013-44791-P) for supporting this study and also FEDER funds.

References.

1 M.H. Karbasi, B. Jahanparast, M. Shamsipur , J. Hassan, *J. Hazard. Mater.*, 2009, **170**, 151.

2 Y.W. Liu, X.J. Chang, Y. Guo, S.M. Meng, J. Hazard. Mater. B, 2006, **135**, 389.

3 X. Chang, H. Luo, Y. Cui, X. g Zhu, Y. Zhai, Z. Hu, Q. He, *J. Mol. Struct.*, 2008, **891**, 45.

4 A. Montaser, D.W.X. Golightly, Wiley-VCH, New York City, New York, 1992.

5 J.A. McLean, M.G. Minnich, L.A. Iacone, H. Liu, A. Montaser, *J. Anal. At. Spectrom.*, 1998, **13**, 829.

6 A. Montaser, M.G. Minnich, H. Liu, A.G.T. Gustavsson, R.F. Browner, in: A. Montaser (Ed.), Inductively Coupled Plasma Mass Spectrometry, VCH, New York, 1998, pp. 335–420.

7 A. Montaser, J.A. McLean, H. Liu, J.M. Mermet, in: A. Montaser (Ed.), Inductively Coupled Plasma Mass Spectrometry, VCH, New York, 1998, pp. 1–31.

8 J. Mora, S. Maestre, V. Hernandis, J.L. Todoli, *Trends Anal. Chem.*, 2003, **22**, 123.

9 J.L. Todoli, J.M. Mermet, *Trends Anal. Chem.*, 2005, **24**, 107.

10 J.L. Todoli, J.M. Mermet, *Spectrochim. Acta Part B,* 2006, **61**, 239.

11 P. Wu, L. He, Ch. Zheng, X. Hou, R.E. Sturgeon, *J. Anal. At. Spectrom.,* 2010, **25**, 1217.

12 R.L.J. McLaughlin, I.D. Brindle, *J. Anal.At. Spectrom.*, 2002, **17**, 1540.

13 A. Asfaw, G. Wibetoe, *Anal. Bioanal. Chem.*, 2005, **382**, 173.

14 H. Wiltsche, I.B. Brenner, K. Prattes, G. Knapp, *J. Anal. At. Spectrom.*, 2008, **23**, 1253.

15 H. Matusiewicz, M. Slachcinski, *Microchem. J.,* 2007, **86**, 102.

16 H. Matusiewicz, M. Slachcinski, *Spectrosc. Lett.,* 2014, **47**, 415.

17 P. Pohl, R.E. Sturgeon, *Trends Anal. Chem.,* 2010, **29**, 1376.

18 A. Henglein, *Chem. Rev.*, 1989, **89**, 1861.

19 G. Giakisikli, A.N. Anthermidis, *Anal. Chim. Acta*, 2013, **789**, 1.

20 M. Wierucka, M. Biziuk, *Trend Anal. Chem.,* 2014, **59**, 50.

21 R.S. Faye, S. Aamdal, H.K. Hoifodt, *Clin. Cancer Res.*, 2004, **10**, 4134.

22 J.C. Frias, Y.Q. Ma, K.J. Williams, *Nano. Lett.,* 2006, **6**,2220.

23 H.H. Yang, S.Q. Zhang, X.L. Chen, Z.X. Zhuang, J.G. Xu, X.R. Wang, *Anal. Chem.*, 2004, **76**, 1316.

24 F. Wiekhorst, C. Seliger, R. Jurgons*, J. Nanosci. Nanotechnol.*, 2006, **6**, 3222.

25 R. Hergt, R. Hiergeist, I. Hilger, *J. Magn. Magn. Mater.*, 2004, **270**, 345.

26 E. Vereda Alonso, M.T. Siles Cordero, A. García de Torres, J.M. Cano Pavón, *Anal. Bioanal. Chem.,* 2006, **385**, 1178.

27 A.R. Khorrami, T. Hashempur, A.Mahmoudi, A.R. Karimi, *Microchem. J.*, 2006, **84**, 75.

28 G. Sado and M. C. Sado, Les plans d'experiences: de l'expérimentation `a l'assurance qualite, Afnor Techniques, París, 1991, p.100.

29 J. Gouply, Plans d´Experiences Pour Surfaces de Response, Dunod, 1991, p253.

30 Statgraphics Plus Version 6.0, Reference Manual, Manugistics, Rockwille, MD, 1992.

31 E. Ermer and W.S. Ptak, Physical Electronics, Multitechnique ESCA, Reference manual for the PC-ACCES Software Version 6.0, Physical Electronics, Minneapolis, USA, 1995.

32 D. Kin, D.T. Nikles and C.S. Brazel, Materials, 2010, **3**, 4051.

33 L.B. Xia, B. Hu, Z.C. Jiang, Y.L.Wu, Y.Liang. *Anal. Chem.,* 2004, **76**, 2910.

34 S. Fragueiro, I. Lavilla and C. Bendicho, *Spectrochim. Acta B*, 2004, **59**, 851.

35 S. Gil, M.T.C. De Loos-Vollebregt and C. Bendicho, *Spectrochim. Acta B*, 2009, **64**, 208.

36 L. Xia, Y. Wu and B. Hu, *J. Mass Spectrom*., 2007, **42**, 803.

37 H. Sereshti, V. Khojeh and S. Samadi, *Talanta.* 2011, 83, 885.

38 X. Q. Guo, M. He, B.b. Chen and B. Hu, *Talanta*, 2012, **94**, 70.

39 M. Mirzaei, M. Behzadi, N.M. Abadi*, J. Hazard. Mater.* , 2011, **186**, 1739.

40 Y. Yamini, M. Rezaee, A. Khanchi, M. Faraji and A. Saleh, *J. Chromatogr. A*, 2010, **1217,** 2358.

Figure 1. Component diagram of the SPE-FI-MSIS-ICP-OES system for the pre-concentration, separation and determination of the 14 target analytes; P1, P2 and P3, peristaltic pump.

Figure 2. (a) Response surface of the 14 target elements.

Figure 3. Response surface obtained from Box Behnken pumps design for 14 target analytes.

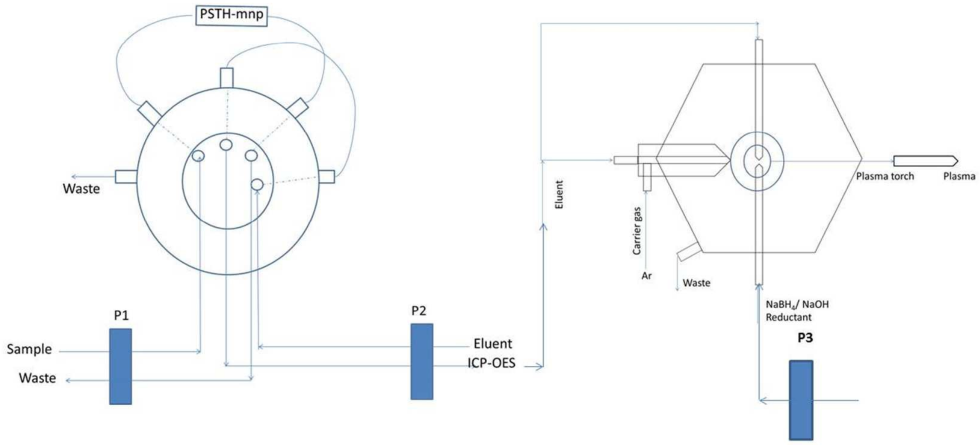
PSTH-mnp
Waste
P1
Sample
Waste
P2
Eluent
ICP-OES
Eluent
Carrier gas
Ar
Waste
Plasma torch
Plasma
$NaBH_4$/ NaOH
Reductant
P3

Figure 1.

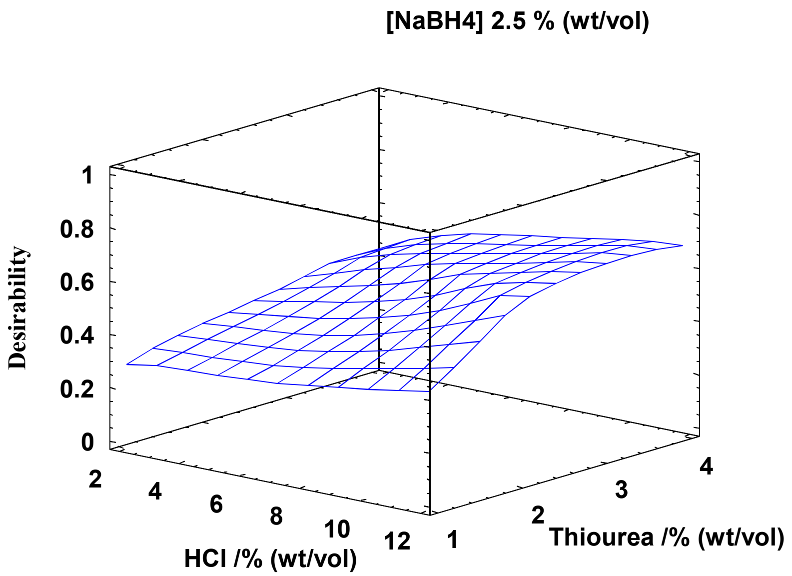
[NaBH4] 2.5 % (wt/vol)
Desirability
1
0.8
0.6
0.4
0.2
0
2
4
6
8
10
12
HCl /% (wt/vol)
1
2
3
4
Thiourea /% (wt/vol)

Figure 2

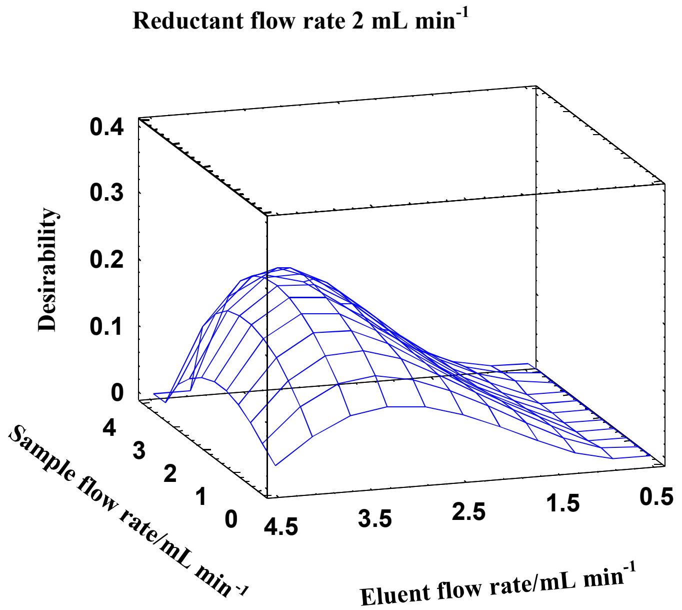
Reductant flow rate 2 mL min^{-1}
Desirability
0.4
0.3
0.2
0.1
0
Sample flow rate/mL min^{-1}
4
3
2
1
0
4.5
3.5
2.5
1.5
0.5
Eluent flow rate/mL min^{-1}

Figure 3.

Table 1. Operating parameters for FI-SPE-CVG-ICP-OES.

ICP-OES Instrument	Perkin-Elmer Optima 730 DV
Solution flow mode	Continuous
Transducer Frequency (MHz)	1400
Spray chamber	Multimode Sample Introduction System (MSIS)
Carrier/nebulizer Ar flow rate/L min^{-1}	0.7
Reductant:	
$NaBH_4$/NaOH solution concentration/ % (wt/vol)	2.5/0.5
Flow rate / mL min^{-1}	2
Eluent:	
HCl/Thiourea solution / % (wt/vol)	8 / 3.5
Flow rate / mL min^{-1}	3.6
Sample:	
Flow rate / mL min^{-1}	2.6

Table 2. Analytical performance

Element	Calibration functions	Correlation coefficients	LOD/µg L^{-1}	LOQ/µg L^{-1}	Enrichment factor	$^{(a)}$ RSD/%	$^{(b)}$ RSD/%
Pd	y=846.3x+1659.7	0.991	3.67	17.23	6.5	1.74	2.13
Cr	y=382.5x-30071.0	0.991	7.16	25.26	1.0	6.83	10.99
Mn	y=179.1x+1044.0	0.992	3.16	22.92	1.5	2.11	2.09
Zn	y=359.6x+5914.3	0.991	11.30	51.70	2.1	3.72	2.86
Cd	y=7992.3x+14453.0	0.997	0.59	4.02	46.9	4.38	4.39
Hg	y=5981.2x+58171.0	0.991	0.02	0.75	1.8	1.07	1.29
As	y=11770.0x+13909.0	0.993	0.01	2.32	113.4	3.48	3.48
Sb	y=33721.0x+13913.0	0.999	0.04	0.96	32.3	2.33	2.62
Bi	y=24166.0x+84961.0	0.999	0.02	0.23	31.3	2.95	2.97
Cu	y=972.1x+15920.0	0.992	7.07	28.42	1.0	1.52	1.34
Pt	y=828.8x+17992.0	0.990	0.02	8.81	2.7	4.46	5.93
Sn	y=2562.7x+1968.1	1.000	5.11	17.10	3.3	4.53	5.80
Se	y=12391x+18220.0	0.992	0.03	2.85	83.6	4.79	4.79
Co	y=43611x+43644.0	0.990	0.05	0.49	385.5	2.69	3.26

(a) 5 µg L^{-1} of Hg, Cd, Se, Sb, As, Bi, Co and 25 µg L^{-1} of Pt, Pd, Cu, Mn, Zn, Sn and Cr.

(b) 20 µg L^{-1} of Hg, Cd, Se, Sb, As, Bi, Co and 100 µg L^{-1} of Pt, Pd, Cu, Mn, Zn, Sn and Cr

Table 3. Comparison of analytical performance data with other data reported in the literature

Sample	Analyte	Extraction solvent	Extraction time /min	Enrichment factor	LOD /ng L^{-1}	RSD /%	Detection technique	Ref.
Human hair, human urine (CRM) synthetic water samples	Be, Co, Pd, Cd	BZA-benzene	10	70-300, 40-180	0.072-0.83, 0.12-1.5	12-16, 11-16	ETV-ICP-MS	33
Seawater	As, Se and Sb	Pd(II)-containing aqueous drop	2	70	100- 200	3.5-2.5	ETAAS	34
NWRI TM-28.3 (trace element fortified water from Lake Ontorio)	As, Sb, Bi, Pb, Sn and Hg	Pd(II)-containing aqueous drop	3.5	9-138	10-800	4-8	ETV-ICP-MS	35
Peach leaves, sea water(CRM), human serum, lae and river water	Cu, Zn, Pd, Hg, Pb, and Bi	DDTC-CCl_4	15	20-305	1.6-28.7	6.1-10.8	ETV-ICP-MS	36
Natural water	Cr, Cu, Ni, Zn	CCl_4	--	8-9	230-550	2.1-3.8	ICP OES	37
Lake and river water	Co, Pd, Cd, Hg, Pb and Bi	1-dodecanol and p-xylene	--	20-324	2-17	2.8-10	ETV-ICP-MS	38
Well, river and waste water	Ni, Co, Pb, Cr	1-undecanol	--	800	0.2-1.3	6.2-7.2	ETAAS	39
Tap, sea and mineral water	Mn, Cr, Co, Cu	1-undecanol	--	57-96	100-300	3.4-7.5	ICP OES	40
Environmental water samples	Pt, Pd, Cr, Mn, Cu, Zn, Cd, Hg, As, Sb, Bi, Sn, Co and Se	HCl and Thiourea	0.66	1-385.5	10-11300	1.0-6.8	FIA ICP OES	This work

Table 3. Continue

Sample	Analyte	Extraction solvent	Extraction time /min	Enrichment factor	LOD /ng L^{-1}	RSD /%	Detection technique	Ref.

Table 4. Analytical applications, certified reference material.

	Element	Certificate Concentration /μg L^{-1}	Found Concentration /μg L^{-1}	Recovery /%		Element	Certificate Concentration /μg L^{-1}	Found Concentration /μg L^{-1}	Recovery / %
SPS-SW2	Pt	--	256±20	--	SLRS-4	Pt	--	0.56*	--
	Pd	--	20±5	--		Pd	--	--	--
	Cr	10.0±0.05	9.6*	96.0		Cr	0.33±0.02	<LOD	--
	Mn	50.0±0.3	51.6±0.3	103.2		Mn	3.37±0.18	3.16*	93.8
	Cu	100.0±1	100±7	100.0		Cu	1.81±0.08	<LOD	--
	Zn	100±2	100±8	100.0		Zn	0.93±0.10	<LOD	--
	Cd	2.50±0.02	2.68*	107.2		Cd	0.012±0.002	<LOD	--
	Hg	--	6.7±0.2	--		Hg	--	0.21*	--
	As	50.0±0.3	50±2	100.0		As	0.68±0.06	0.60*	88.2
	Sb		0.29*	--		Sb	0.23±0.04	0.24*	104.3
	Bi		1.01±0.05	--		Bi	--	--	--
	Sn		8.57*	--		Sn	--	--	--
	Se	10.00±0.05	10.4±0.3	104.0		Se	--	0.14*	--
	Co	10.00±0.05	10.1±0.8	101.0		Co	0.033±0.006	<LOD	--
TMDA 54.4	Pt	--	43.0±2.3	--	1643e	Pt	--	3.67*	--
	Pd	--	--	--		Pd	--	--	--
	Cr	438±40	421±3	96.1		Cr	20.40±0.24	23.7±0.9	116.2
	Mn	275±21	260±3	94.5		Mn	38.97±0.45	38.7±0.6	99.3
	Cu	443±37	445±5	100.5		Cu	22.76±0.31	25.4±0.9	111.6
	Zn	537±58	523±9	97.4		Zn	78.5±2.2	75±2	95.5
	Cd	158±17	157±2	99.4		Cd	6.568±0.073	6.7±0.7	102.0
	Hg	--	8.01±0.08	--		Hg	--	0.26*	--
	As	43.6	42±1	96.3		As	60.45±0.72	66.82±0.02	110.5
	Sb	25.7	24.6±0.6	95.7		Sb	58.30±0.61	55±2	94.3
	Bi	17^{+}	15.04±0.06	88.5		Bi	14.09±0.15	16.2±0.6	115.0
	Sn	48.2	48±2	100.7		Sn	--	5.78*	--
	Se	33	31.8±0.8	96.4		Se	11.97±0.14	11.92±0.14	99.6
	Co	309±27	281±5	90.9		Co	27.06±0.32	23.5±0.7	86.8

$^{+}$ No certified value

*Indicative value (< LOQ)

Table 5. Analytical applications, natural water samples.

Well water Element	Spiked/ µg L^{-1}	Found/µg L^{-1}	Recovery /%	Seawater Zone 1 Element	Spiked/ µg L^{-1}	Found/ µg L^{-1}	Recovery /%	Seawater Zone 2 Element	Spiked/ µg L^{-1}	Found / µg L^{-1}	Recovery / %
Pt	--	--	--	Pt	--	4.48	--	Pt	--	2.99	--
	20	19±1	95.0		40	45.7±0.5	103.0		20	23±1	100.0
	40	42±2	105.0		80	82.5±2	97.5		40	44±1	102.5
Pd	--	--	--	Pd	--	--	--	Pd	--	--	--
	20	18.6±0.8	93.0		40	40.7±0.2	101.8		40	41.2±0.9	103.2
	40	41±2	102.5		80	81.11±0.13	101.4		80	81.8±0.9	102.2
Cr	--	--	--	Cr	--	--	--	Cr	--	--	--
	20	16.8±0.6	84.0		40	41±6	102.5		40	39.5±0.3	98.8
	40	42.5±0.3	106.3		80	79±6	98.7		80	80±2	100.0
Mn	--	--	--	Mn	--	15.17*	--	Mn	--	--	--
	20	20.3±0.5	101.5		40	55±2	99.6		40	42±2	105.0
	40	42±2	105.0		80	94.4±0.8	99.0		80	79.3±0.7	99.1
Cu	--	--	--	Cu	--	--	--	Cu	--	7.68*	--
	40	36±1	90.0		40	44.3±1	110.7		40	49.7±2	105.0
	60	62±2	103.3		80	74.6±0.7	93.3		80	88.7±1	101.3
Zn	--	--	--	Zn	--	--	--	Zn	--	--	--
	40	39±1	97.5		40	41±9	102.5		80	85±1	106.3
	80	85±7	106.3		80	79±2	98.8		120	118.6±0.3	98.8
Cd	--	--	--	Cd	--	1.76*	--	Cd	--	7±2	--
	20	18.4±0.6	92.0		20	22.6±0.9	104.2		20	26±3	95.0
	40	42.25±0.11	105.6		40	46±1	110.6		40	49±6	105.0

Table 5. Continue

Well water Element	Spiked/ µg L^{-1}	Found/µg L^{-1}	Recovery /%	Seawater Zone 1 Element	Spiked/ µg L^{-1}	Found/ µg L^{-1}	Recovery /%	Seawater Zone 2 Element	Spiked/ µg L^{-1}	Found / µg L^{-1}	Recovery / %
Hg	--	1.5±0.2	--	Hg	--	0.33*	--	Hg	--	12±1	--
	10	11.2±0.4	97.0		20	18.3±0.2	90.0		20	34±1	110.0
	20	21.1±0.5	98.0		40	43±1	106.7		40	55±1	107.5
As	--	--	--	As	--	0.37*	--	As	--	--	--
	10	10.3±2	103.0		20	20±4	98.2		20	20±2	100.0
	20	21±1	105.0		40	43.3±0.1	107.3		40	37±3	92.5
Sb	--	--	--	Sb	--	--	--	Sb	--	0.98±0.17	--
	20	20.5±0.3	102.5		20	21.44±0.16	107.2		20	19.1±0.6	90.6
	40	40±2	100.0		40	37.8±0.31	94.5		40	45.5±0.6	111.3
Bi	--	--	--	Bi	--	22±3	--	Bi	--	0.51±0.16	--
	20	21.4±0.6	107.0		20	43.2±0.8	106.0		20	22.5±0.6	109.9
	40	39.5±0.8	98.8		40	63.9±0.8	104.8		40	39.9±0.56	98.5
Sn	--	--	--	Sn	--	--	--	Sn	--	--	--
	20	19±2	95.0		40	43.9±0.7	109.7		40	43.5±0.3	108.7
	40	40±4	100.0		80	79±4	98.8		80	82.1±0.3	102.6
Co	--	--	--	Co	--	--	--	Co	--	--	--
	10	9±3	90.0		20	17.8±0.8	89.0		20	19.4±0.8	97.0
	20	20.32±0.04	101.6		40	43±2	107.5		40	41.9±0.2	104.7
Se	--	0.193*	--	Se	--	0.04*	--	Se	--	0.75*	--
	20	20.7±0.5	102.0		20	18±1	90.0		20	19.3±0.3	92.8
	40	39.77±0.12	98.9		40	43±2	107.5		40	45±2	110.6