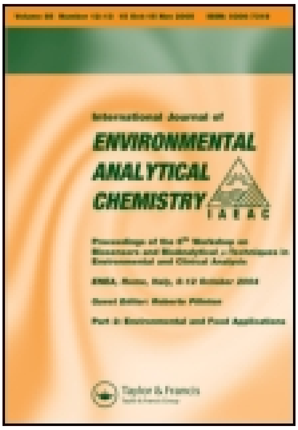

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Mercury determination in sediments by CVAAS after on line preconcentration by solid phase extraction with a sol-gel sorbent containing CYANEX 471X®

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The development of a preconcentration method for the measurement of trace levels of mercury in digested sediments is described. Solid phase extraction (SPE) was used for the preconcentration of mercury coupled on-line by means of a flow injection (FI) system followed by cold vapour atomic absorption spectrometry (CVAAS) detection. The SPE was carried out through a column packed with a sorbent material containing triisobutylphosphine sulfide (CYANEX 471X®) as mercury extractant and prepared by the sol-gel process. The effects of FI variables (argon, eluent, and reductant flow rates, loading and elution times) as well as the eluent concentration on the analytical performance of the method were evaluated. The proposed method was validated under the optimum conditions. The calibration graph was linear from $0.05\,\mu g\,L^{-1}$ to $3.0\,\mu g\,L^{-1}$ of Hg. The detection limit (DL), based on three times the standard deviation of the blank measurement criterion, was $24\,ng\,L^{-1}$. The repeatability was 1.5% and 1.8% RSD ($n = 10$) at concentrations of 0.5 and $1\,\mu g\,L^{-1}$ of Hg, respectively. Method enrichment factors of 16 with a productivity of 30 samples h^{-1} or 32 with a productivity of 17 samples h^{-1} were achieved under selected conditions. Certified reference materials, inductively coupled plasma mass spectroscopy (ICP-MS) and cold vapour atomic fluorescence spectrometry (CVAFS), were used to evaluate the accuracy of the proposed method.

Keywords: mercury; preconcentration; sol-gel; sediments; cold vapour atomic absorption spectrometry

1. Introduction

Cold vapour atomic absorption spectrometry (CVAAS) remains as the most used analytical technique in laboratories that perform routine mercury analyses in diverse types of samples, despite the continuous developments carried out in ICP-MS [1] and CVAFS [2] with the aim of exhibiting higher sensitivities and lower limits of detection. However, in order for CVAAS to be competitive with these novel techniques, it has been necessary to develop preconcentration methods that allow mercury determination at ultra-trace levels [3,4].

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Solid phase extraction (SPE) is one of the most commonly employed methods to achieve the separation and preconcentration of metal ions due to the ease with which it is coupled on-line, particularly when packed columns are used [5]. This possibility allows automated determinations to be carried out, thus introducing further advantages such as increased sample through output and sample contamination reduction. SPE methods using supports containing mercury extractants in the form of ion exchange resins [6,7], chelating resins [8], synthetic fibres [9], and polymeric micro-grains [10], among others [11], have been reported. New types of sorbent materials that have recently been used for metal ion extraction are the sol-gels. The sol-gel procedure allows preparing inorganic materials containing within their matrix organic molecules with high selective and extracting capabilities towards different metals. Their synthesis, at low temperatures under very mild reactions conditions, makes them suitable for routine analysis [12,13]. CYANEX 471X® is an excellent mercury extractant because it contains a sulphur atom in its molecule that behaves as a soft base with high affinity for soft acids. Additionally, it is commercially available. For these reasons several authors have studied its extraction behaviour as well as its selectivity and applications [14–16].

In this work, a material containing CYANEX 471X® immobilised within its matrix, obtained by the sol-gel process, was synthesised, characterised and its performance for total mercury determination in sediment samples evaluated in an on-line preconcentration procedure prior to CVAAS measurement. The results here obtained are compared with those reported for several sulphur containing solid-phase devices coupled to the CVAAS technique [4,17–20]. The developed method was applied for mercury determination in a real sediment sample with naturally occurring levels of the ion ($<0.1\,\mathrm{mg\,kg^{-1}}$ of total Hg). The method was in-house validated evaluating the following parameters: robustness, linear range, detection limit, quantification limit, accuracy under repeatability conditions. An estimation of the different sources of uncertainty of the method and their relative magnitudes was also performed.

2. Experimental

2.1 *Reagents and reference materials*

Tetraethoxysilane (TEOS, Aldrich), ethanol (Aldrich) and CYANEX 471X® (triisobutylphosphine sulfide, kindly supplied by Cytec Canada Inc.) were used in the sol-gel sorbent preparation. Trace metal certified reagents were purchased for the preparation of solutions: HCl (Aldrich, 37%), HNO_3 (Aldrich 65%), and $NaBH_4$ (Aldrich, 98%). The latter solution was daily prepared by dissolving the appropriate amount of the salt in 0.05% w/v NaOH. All of the standards and sample solutions were diluted with high quality water obtained with a Milli-Q purification system (Millipore). The certified reference solution DMR-110b of $1010.5\,\mathrm{mg\,L^{-1}} \pm 8.0\,\mathrm{mg\,L^{-1}}$ of Hg, supplied by CENAM (Centro Nacional de Metrología, Mexico), was used as calibration solution. Working standard solutions were freshly prepared by dilution of the spectrometric solution with 5% (v/v) HNO_3. The following reference materials were measured to evaluate the accuracy: SRM 2709 'San Joaquin Soil' from the National Institute of Standards and Technology (NIST), USA; GSD-9 and GSD-11 'Sewage Sediment' from the Institute of Geophysical and Geochemical Prospecting, China.

2.2 *Instrumentation*

A Perkin Elmer 5100 zl atomic absorption spectrometer coupled to a FIAS 400 flow injection analysis system equipped with an AS90 autosampler was used for CVAAS determinations. A schematic diagram of the five-port FIAS valve modified for automatic on-line preconcentration is shown in Figure 1. An MDS-2100 microwave sample preparation system from CEM Corporation was used for sediment sample digestions. A High Resolution Element I ICP-MS instrument from Finnigan Mat was used for method comparison. Conditions under which these analyses were performed are given in Table 1. Mercury measurements by CVAFS were performed in a PS Analytical instrument Millennium Merlin System. The experimental conditions are also included in Table 1.

2.3 *Sol-gel sorbent preparation*

The sol-gel sorbent was prepared by mixing tetraethoxysilane with an excess of deionised water and 25 mL of an 0.1 mmol L^{-1} CYANEX 471X® ethanolic solution in the presence of HF as catalyser. The mixture was agitated during 30 minutes in an ultrasonic bath and allowed to gel. The gel was dried at room temperature until constant weight, ground and sieved to a 100–250 µm particle size. Material containing no CYANEX 471X® was also prepared for use in background experiments. A quantity of 0.1 g of the sol-gel sorbent was weighted and packed in a column made of silicon tube (4 cm length × 5 mm i.d.), and a disk of filter paper and glass fibre were placed at both ends of the column to prevent sorbent losses. Once in the column, the sol-gel sorbent was washed alternatively with 2 mol L^{-1} HCl and water during 5 operating cycles, before mercury preconcentration analyses.

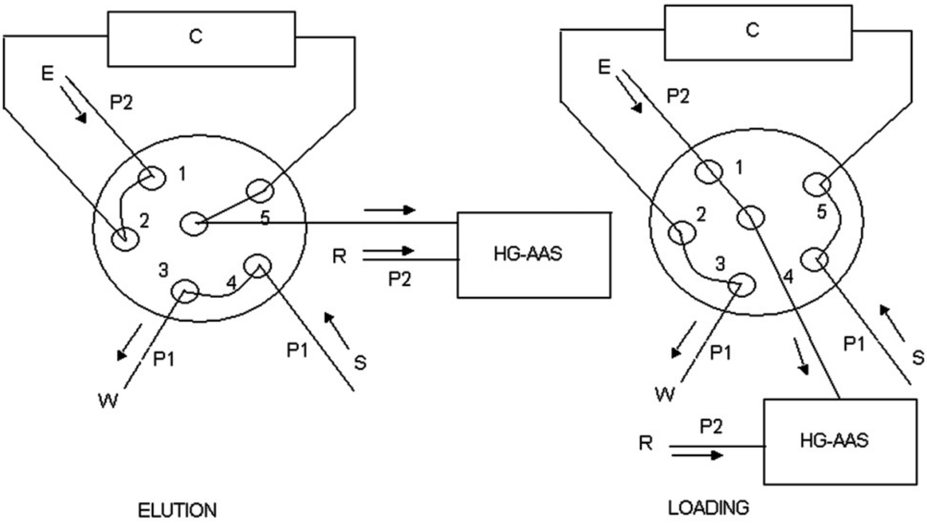

Figure 1. Diagram showing the experimental set-up used to adjust the preconcentration column to the 5-ports valve. C: Column, E: Eluent, R: Reductant, S: Sample, W: Waste, P1: Pump 1, P2: Pump 2.

Table 1. ICP-MS and CVAFS experimental conditions for mercury measurements.

ICP-MS			
ICP-MS conditions		Data acquisition	
Rf power	1200 W	Scan mode	EScan
Resolution	Low	Sweeps per reading	5
Auxiliary gas flow rate	1 L min^{-1}	Samples per peak	30
Nebuliser gas flow rate	0.984 L min^{-1}	Number of replicates	5
Sampler and skimmer cones	Nickel	Sample time	0.01 s
		Isotope measured	^{202}Hg, ^{200}Hg
CVAFS			
Gas	Argon	Delay time	10 s
Shield gas flow rate	300 mL min^{-1}	Analysis time	40 s
Carrier gas flow rate	300 mL min^{-1}	Memory time	60 s
Reductant flow rate	4–5 mL min^{-1}	Dryer gas flow rate	2.5 mL min^{-1}
Reductant solution	2% (m/v) $SnCl_2$ in 10% (v/v) HCl		

2.4 *Off-line batch and column experiments*

All experiments, except the extraction isotherm, were performed using a 50 μg L^{-1} of Hg(II) in 5% (v/v) nitric acid aqueous solution. As for solid-liquid batch extraction experiments, the time necessary to achieve equilibrium was initially determined. It was observed that after contacting 0.005 g of a solid phase with 75 mmol kg^{-1} of CYANEX 471X® with 10 mL of Hg(II) solution, equilibrium was attained after 20 min. Thus, in further experiments 30 min of shaking time were employed. Gel homogeneity was studied by contacting different amounts (0.005–0.020 g) of the adsorbing phase with 10 mL of Hg(II) solution. For the determination of the complex stoichiometry in the sol-gel phase and its corresponding extraction equilibrium constant, nitric acid concentration in the aqueous phase was 1 mol L^{-1}, while the concentration of CYANEX 471X® in the gel was varied from 3.2×10^{-4} to 0.075 mmol g^{-1}. The effect of the concentration of Hg(II) in the aqueous phase on the loading capacity of the sol-gel sorbent was evaluated in the interval from 75 to 600 μg L^{-1} of Hg(II) in 5% (v/v) HNO_3 using 0.005 g of sol–gel phase with 75 mmol kg^{-1} of CYANEX 471X®. The studies of the effect of the eluent in mercury absorption were performed packing a column with 0.1 g of sol–gel phase with 75.76 mmol kg^{-1} of CYANEX 471X®, passing through it 5 mL of mercury solution and eluting the retained metal with 5 mL of the selected phases at 1 mL min^{-1}. To study the effect of extractant concentration the same set up was employed but elution was done with a 6 mol L^{-1} HCl solution and CYANEX 471X® concentration was varied from 0.3 to 75.76 mmol kg^{-1}.

2.5 *Operation of the flow injection system*

The AAS experimental conditions, the optimised values of the studied parameters and the FIAS program for preconcentration and determination of mercury are presented in Table 2. In the prefill step of the FIAS program, the 5-ports valve is in the elute position and Pump 2 (P2) is pumping HCl carrier solution, flowing through the column for rinsing

Table 2. Optimized experimental conditions for FIAS-CVAAS determination of mercury.

AAS. Instrumental parameters	
Wavelength	253.7 nm
Slit	0.7 nm
Lamp	EDL

FIAS parameters	
Carrier	2 mol L^{-1} HCl
Reductant	0.2% (w/v) $NaBH_4$/0.05% (w/v) NaOH
Argon flow rate	50–100 mL min^{-1}
Carrier flow rate	8.5 mL min^{-1}
Reductant flow rate	4.6 mL min^{-1}
Sample flow rate	6.4 mL min^{-1}

FIAS program				
Step	Time (s)	P1 (rpm)	P2 (rpm)	Valve position
Prefill	20	100	120	E
P	80	100	0	L
P	10	100	100	L
E	5	0	100	E-R

P1: Peristaltic pump 1.
P2: Peristaltic pump 2.
P: Pre-concentration.
E: Elution.
L: Loading.
R: Reading.

and conditioning. Meanwhile, Pump 1 (P1) is filling the sample tubing to waste. This step lasts 20 seconds ensuring that all the tubes are filled with the correct solutions. The preconcentration is carried out in two steps: in the first one, the 5-ports valve is in the load position. P1 feeds the sample stream through the preconcentration column between Ports 2 and 5 during 80 seconds to preconcentrate the sample; P2 is turned off to save carrier and reductant solutions. In the second preconcentration step, P1 is still feeding the sample and P2 is turned on to feed the carrier and reductant solutions for 10 seconds to stabilise the streams. In the elution step, the FIAS valve turns to the elute position and the preconcentration column is flushed with the eluent. The preconcentrated sample is then transported to the mixing blocks where it is combined with the reductant stream ($NaBH_4$ solution) to produce the mercury vapour. Finally the mercury vapour is transported by argon to the quartz cell in the spectrometer to read the absorbance signal.

2.6 *Sample preparation*

The sediment analysed as real sample was collected from ‘El Centenario’ basin, located in the Tequisquiapan Municipality of the State of Querétaro in Mexico. The sampled sediment was transported under refrigeration to the Centro Nacional de Metrología (CENAM) located at 25 km from Querétaro City, where it was processed. The wet sediment was dried at room temperature (25°C ± 2°C) until constant weight was achieved. Once dried, the material was ground in a mill using a tungsten carbide vial and sieved through a stainless steel screen in order to have particle size $<63\,\mu m$. The material was then homogenised in a rotating powder homogeniser with the aid of a vibrator and powder splitter. Finally the material was stored in dark glass bottles to protect the content from light (approx. 50 g in each bottle). Measurements of humidity in the material were made using the ASTM D 3976-88 'Standard Practice for Preparation of Sediment Samples for Chemical Analysis' procedure based on measuring the difference in mass of the wet and dry sample weight at 105 ± 2°C. The humidity in the material was determined to be 5.92% ± 0.13%. All reference materials and dry basin samples were digested in a microwave oven, using HNO_3 according to 3051 EPA method. For the microwave digestion, 0.250 g of the sample was weighed and 5 mL of concentrated HNO_3 added. Finally, the samples were filtered and diluted to 100 mL with deionised water.

3. Results and discussion

3.1 *Off-line optimisation and characterisation*

Solid-liquid batch extraction experiments were performed to determine the homogeneity of extractant, distribution constant, loading capacity, and extraction equilibrium of the gel. Gel homogeneity was studied evaluating the dependence of the distribution coefficient, D, defined as:

$$D = \frac{\overline{[\mathrm{Hg(II)}]}}{[\mathrm{Hg(II)}]} = \frac{(C_0 - C_\mathrm{f})}{C_\mathrm{f}}\frac{V_\mathrm{aq}}{M}, \tag{1}$$

as a function of the amount of gel using a sorbent with optimised CYANEX $471\mathrm{X}^{®}$ content. In Equation (1) Hg(II) stands for the sum of all chemical species of mercury present in each phase (total mercury concentration), the bar denotes species in the solid phase, C_0 stands for the initial mercury molar concentration in the aqueous phase, C_f for its equilibrium molar concentration in the same phase, V_aq for the volume of the aqueous phase (mL), and M for the sol-gel mass (g). It was observed that the value of D remained constant at 9200 for a mass above 0.005 g indicating that an adequate reproducibility in the experiments is achieved using at least this amount of gel.

Further characterisation of the gel was performed by solid–liquid phase extraction. The distribution coefficient denoted as:

$$D = \frac{\overline{[\mathrm{Hg(NO_3)_2} \cdot qR]}}{[\mathrm{Hg(II)}]}, \tag{2}$$

was combined with the extraction equilibrium constant (K) for the extraction reaction of mercury with CYANEX $471\mathrm{X}^{®}$ (where R represents the extractant molecules and Hg^{2+} stands for free mercury):

$$\mathrm{Hg}^{2+} + 2\mathrm{NO_3}^{-} + q\overline{R} \Leftrightarrow \overline{\mathrm{Hg(NO_3)_2} \cdot qR} \tag{3}$$

expressed as:

$$K = \frac{\overline{[\mathrm{Hg(NO_3)_2} \cdot qR]}}{[\mathrm{Hg}^{2+}][\mathrm{NO_3^-}]^2\overline{[R]}^q} \tag{4}$$

to obtain the following equation:

$$\frac{1}{D} = \frac{[\mathrm{Hg(II)}]}{K[\mathrm{Hg}^{2+}][\mathrm{NO_3^-}]^2\overline{[R]}^q} \tag{5}$$

Considering the mass balance for mercury species in the aqueous phase:

$$[\mathrm{Hg(II)}] = \left[\mathrm{Hg}^{2+}\right] + \sum_{i=1}^{2} \mathrm{Hg(NO_3)}_i^{2-i} + \sum_{i=1}^{2} \mathrm{Hg(OH)}_i^{2-i}, \tag{6}$$

the ratio $[\mathrm{Hg(II)}]/[\mathrm{Hg}^{2+}]$ may be expressed as:

$$\frac{[\mathrm{Hg(II)}]}{[\mathrm{Hg}^{2+}]} = \left\{1 + \sum_{i=1}^{2} \beta_i^{\mathrm{Hg}^{2+}/\mathrm{NO_3}^-}\left[\mathrm{NO_3^-}\right]^i + \sum_{j=1}^{2} \beta_j^{\mathrm{Hg}^{2+}/\mathrm{OH}^-}[\mathrm{OH}^-]^j\right\} = \alpha_{\mathrm{Hg}^{2+}}, \tag{7}$$

where $\alpha_{\mathrm{Hg}^{2+}}$ is the side-reaction coefficient accounting for collateral reactions in the aqueous phase [21], $\beta_i^{\mathrm{Hg}^{2+}/\mathrm{NO_3^-}}$ are the global formation constants of the nitrate-mercury species in the aqueous phase ($\log\beta_1 = 0.11$, $\log\beta_2 = 0$ [22]) and $\beta_j^{\mathrm{Hg}^{2+}/\mathrm{OH}^-}$ are those of the hydroxyl-mercury species in the same phase ($\log\beta_1 = 10$, $\log\beta_2 = 21$ [22]). The substitution of Equations (7) into (5) leads to Equation (8) once logarithms are taken:

$$\log D = \log K + 2\log\left[\mathrm{NO_3^-}\right] - \log\alpha_{\mathrm{Hg}^{2+}} + q\log\overline{[R]}. \tag{8}$$

Thus, by plotting log D versus $\log\overline{[R]}$ at constant nitrate concentration and pH, a straight line is obtained. From the values of slope and intercept the calculation of the extraction stoichiometry coefficient, q, and the extraction equilibrium constant, K, is then allowed. After performing such analysis, it was observed that the value of q was 1.1, indicating that the extracted species is $\mathrm{Hg(NO_3)_2}R$, in good agreement with liquid-liquid extraction [16] and extraction chromatography [14] data from nitrate media. The calculated value of K is $10^{5.7}$, which compares favourably with that determined in reference 14 (3.8×10^5).

A study of the concentration of Hg(II) in the aqueous phase versus the concentration of Hg(II) in the gel at equilibrium was then done, obtaining the isotherm represented in Figure 2. At the beginning (below $1 \times 10^{-7}\,\mathrm{mmol\,mL^{-1}}$ of Hg(II) at equilibrium in the aqueous phase) a linear increase in Hg(II) concentration extracted by the gel with the increase in Hg(II) concentration in the aqueous phase is observed. This fact is indicative of a constant value of the distribution constant (K_d) of the metallic species in this interval of concentrations. Its value estimated from the slope of the line is $10^{4.6}$. It is also observed from Figure 2 that as the functional sites in the gel become saturated, the steepness of the plot diminishes although mercury concentration in the gel does not reach a constant value within the range of concentrations used. From the figure it can be concluded that the maximum loading capacity attained by the material (C_i) under these conditions is $0.005\,\mathrm{mmol\,g^{-1}}$, indicating that only a fraction of about 6.8% of the extractant is available to participate in the extraction reaction, considering the mass of sorbent used and the content of extractant according to the conditions of synthesis. This fraction is easily understood taking into account that only the extractant present at the surface of the adsorbent is able to participate in the extraction equilibrium. Comparing the K_d and C_i values obtained with those reported for synthesised solid phase extractors via silica gel matrix-immobilised-iminodithiocarbamate derivatives ($C_i = 0.600 - 0.983\,\mathrm{mmol\,g^{-1}}$) [17], and silica gel phases loaded with dithizone based on chemical binding and physical adsorption approaches ($C_i = 15 - 300\,\mathrm{\mu mol\,g^{-1}}$) [18], a lower value for C_i is observed, although, as mentioned before, saturation of the material was not reached indicating that this value could further increase. As for K_d its value is in the order of that found

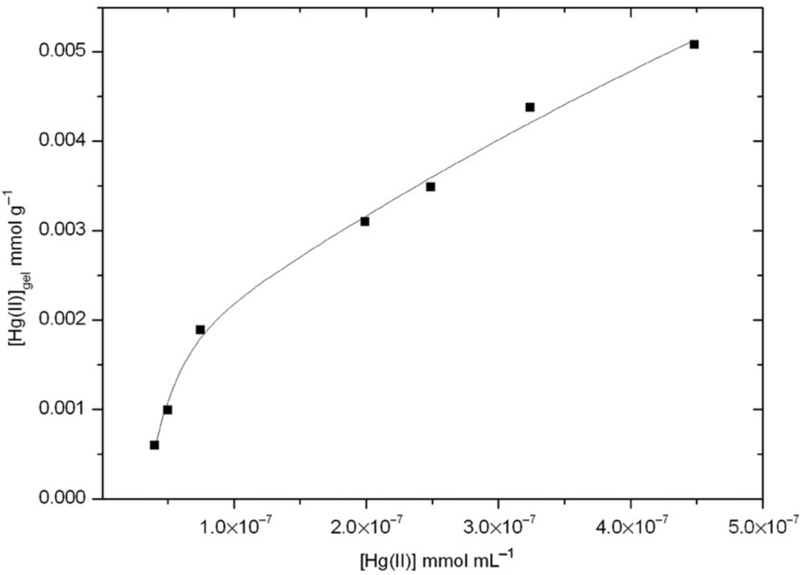

Figure 2. Solid-phase extraction isotherm from which the K_d and C_i values were determined.

Table 3. Influence of extractant concentration on the extraction (E%) and recovery (R%) percentages.

CYANEX 471X® mmol kg^{-1}	E%	R%
0	<5	<5
0.30	9.2	95.0
0.75	9.9	97.8
7.6	90.9	62.8
75.8	97.8	74.8

in sorbents with dithizone ($K_d = 12{,}000 - 50{,}000$) [18], denoting the high affinity of sulphur-containing materials for the adsorption of mercury.

After batch experiments the influence of extractant concentration on the extraction (E%) and recovery (R%) percentages in the column set-up was studied. Table 3 shows that increasing CYANEX 471X® content higher E% values are obtained. The best trade-off between E% and R% is achieved at 75.76 mmol kg^{-1}, and for this reason this content was selected for further optimisation. Also, the selection of an appropriate solution to elute the loaded mercury in column experiments was performed. Under the selected conditions, the amount of metal extracted by this phase was 97.8% ± 0.9% ($n = 3$). Different eluent solutions containing ligands able to form strong complexes with mercury were used, as described in Table 4. The percentages of mercury recovery, referred to the initial mercury content, after elution are also reported. As observed higher values were obtained with HCl solutions. Based on these results, a 2 mol L^{-1} concentration was selected for performing further experiments.

Table 4. Percentage of mercury(II) recovery with different eluents, and values of the global formation constants for ammonia, thiosulfate, iodide, and chloride anions with mercury(II) [22].

Eluent	R%	$\log \beta_1$	$\log \beta_2$	$\log \beta_3$	$\log \beta_4$	Ionic force
$0.01\,mol\,L^{-1}$ NH_4Cl	8.2	8.8	17.4	18.4	19.1	0.5
$0.01\,mol\,L^{-1}$ $Na_2S_2O_3$	28.1	29.2	30.6			0
$0.02\,mol\,L^{-1}$ KI	52.5	12.9	23.8	27.6	29.4	0.5
$2\,mol\,L^{-1}$ HCl	88.9	6.7	13.2	14.1	15.1	0.5
$6\,mol\,L^{-1}$ HCl	74.8					
$12\,mol\,L^{-1}$ HCl	72.4					

3.2 *On-line development and validation of the method for Hg determination*

3.2.1 *Optimisation of flow injection parameters*

The robustness of the method was evaluated during the method development based on the optimisation results. The experimental design applied was varying one factor at a time. An exception of this condition was the study of the eluent and reductant solution flow rates because they were introduced in the system by the same peristaltic pump. The highest peak height absorbance was considered as a sensitivity parameter for the optimisation of the flow injection system. The effects of argon flow rate, eluent concentration, eluent and reductant flow rate, were studied to obtain the best loading and eluting conditions for mercury analysis with the proposed preconcentration system. All these studies were done with a solution containing $0.8\,\mu g\,L^{-1}$ of Hg in 5% (v/v) HNO_3, with a preconcentration and elution time of 60 s and 10 s, respectively. Figure 3(a)–(d) shows the results obtained, where the plotted points (media ± standard deviation) represent the average of 3 replicates. In Figure 3(a) argon flow rate influence on the response is presented. As expected, sharper peak shapes were observed with the increment in flow rates up to values above $100\,mL\,min^{-1}$ at which the absorbance signal decreased due to the short residence times in the detection system. As a consequence, a flow rate between 50 and $100\,mL\,min^{-1}$ is recommended. For the following experiments $100\,mL\,min^{-1}$ was chosen. The effect of HCl concentration within the range $0.4–9\,mol\,L^{-1}$ was studied to assure quantitative elution of the retained mercury in the column, avoiding memory effects. According to Figure 3(b) the peak height absorbance remains almost constant using HCl concentrations within the $2–9\,mol\,L^{-1}$ interval with no memory effects in the blank measurements. Based on this results and the previous described in Table 4, for further experiments $2\,mol\,L^{-1}$ HCl was used as eluent. The effect of the flow rates of the eluent and reductant solutions were evaluated and the results are shown in Figure 3(c) and 3(d), respectively. As both solutions are introduced to the system by the same peristaltic pump, the observed effect is not a result of an independent variable. From the figures it can be seen that the signal decreases as the flow rates of both components decrease. It was also observed that the maximum peak height of the absorbance transient signal was displaced to higher time values as the flow rates decrease. Then, flow rates of $8.4\,mL\,min^{-1}$ for HCl and $4.6\,mL\,min^{-1}$ for $NaBH_4$ were selected.

The effects of loading and elution times were also analysed. Sample loading time (preconcentration time) was studied from 30 to 180 s at a sample flow rate of $6.4\,mL\,min^{-1}$ with $0.8\,\mu g\,L^{-1}$ of Hg(II) in 5% (w/v) HNO_3. The signal increased linearly with time in the

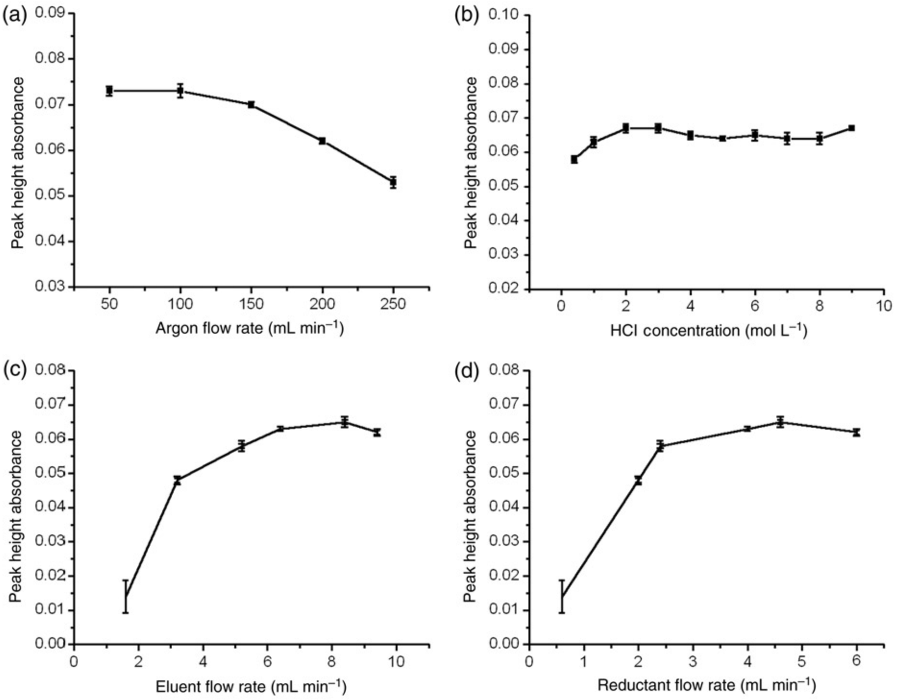

Figure 3. Optimisation of the flow injection parameters in the system.

studied interval, increasing the preconcentration factor; however, system's productivity, measured by the rate at which samples can be analysed, decreases (Figure 4). A time of 90 s was selected for preconcentration time in order to achieve an analysis frequency of 30 samples h^{-1} with enough sensitivity. If necessary, the preconcentration time can be increased to achieve better sensitivity for samples with lower mercury concentrations. The effect of elution time was studied in an interval from 5 to 30 s. Since no significant effect was observed in the intensity and precision of the signal, 5 s were selected in order to have the lowest measuring times.

3.2.2 *Column stability*

Column stability was tested for several mercury preconcentration cycles. This test was carried out using a solution containing 0.5 μg L^{-1} of Hg in 5% (v/v) HNO_3 under the optimised conditions previously established (Table 2). It was observed that after 100 cycles, the column rested in adequate conditions for further use. A 2.5% RSD for 100 measurements was determined. During the analysis of real samples (Section 3.2.5) the column was used at least 20 times without any sign of deterioration.

3.2.3 *Analytical figures of merit*

The performance of the proposed mercury preconcentration method was evaluated using the optimised conditions given in Table 2. A linear range from 0.05 to 3 μg L^{-1} of aqueous

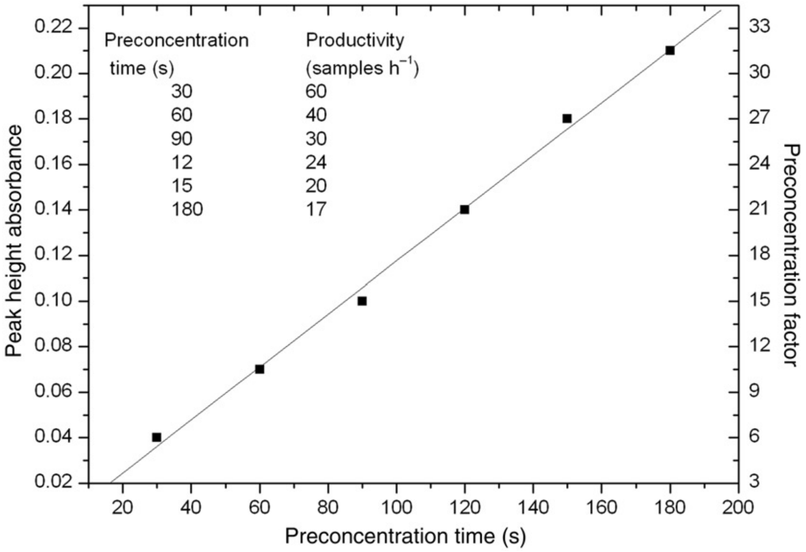

Figure 4. Preconcentration factor as a function of time during column operation and productivity of the system.

mercury standards was obtained. The upper working interval was limited to 3 µg L^{-1} since for higher concentration measurements good sensitivity can be obtained by CVAAS without the need of a preconcentration method. The equation of the straight line was $A = 0.1124\ (\pm 0.0003) \times [\mathrm{Hg}] - 0.0005\ (\pm 0.0004)$ with $r = 0.9997$ for $n = 11$. A detection limit of 24 ng L^{-1} of Hg was calculated, as the analyte concentration giving an absorbance signal equivalent to 3 times the standard deviation of the blank signal plus the net blank intensity.

This value compares very well with those reported for octadecyl silica membrane disks modified with 5,5′-dithiobis(2-nitrobenzoic acid) (0.013 µg L^{-1} [4]), and a silica gel-loaded (E)-N-(1-Thien-2-ylethylidene)-1,2-phenylenediamine phase (30 pg mL^{-1} [19]). Tracing back to the quantity of sample used (250 mg) and considering the final sample dilution volume of 100 mL, this value corresponds to a detection limit of 9.6 ng g^{-1}, which compares with those reported for the solid phase extraction of mercury on sulphur loaded with N-(2-chlorobenzoyl)-N-phenylthiourea (0.012 and 0.003 µg g^{-1}) [20] and a bis(2,4,4-trimethylpentyl)-dithiophosphinic acid-loaded sol-gel sorbent (13.2 ng g^{-1}) [23]. The net signal of the blank was obtained from a 5% (v/v) HNO_3 solution. Repeatability expressed as RSD (%) of 1.5% and 1.8% were determined in terms of repeatability for 10 measurements of 0.5 and 1 µg L^{-1} Hg solutions, respectively. The enrichment factor (EF) calculated from the ratio of the slopes of the calibration lines before and after preconcentration was found to be 16 under the studied conditions. Although this value may seem low in comparison with the values reported for other sulphur-containing materials used for the same purpose [4,18–20], it compares favourably with a recently published dispersive liquid-liquid microextraction method based on an ionic liquid and spectrophotometric determination that uses only 10 mL of sample loading [24]. Additionally as discussed above, the EF value can be increased by increasing the preconcentration time (e.g. using 180 s for sample loading, the preconcentration factor

Table 5. Determination of mercury concentration in real samples.

Sample	Certified (mg kg^{-1})	Found/mg kg^{-1} (proposed method)**	Found/mg kg^{-1} (ICP-MS)**	Found/mg kg^{-1} (CVAFS)**
SRM 2709	1.4 ± 0.08	1.4 ± 0.028	1.36 ± 0.050	1.44 ± 0.020
GSD-9	0.083*	0.079 ± 0.0016	0.082 ± 0.011	–
GSD-11	0.072*	0.075 ± 0.0007	0.075 ± 0.010	–
Basin sediment	–	0.049 ± 0.003	0.049 ± 0.006	0.051 ± 0.003

Notes: *Reference values.
**Mean ± SD.

increases at 32 although system's productivity decreases at 17 samples h^{-1}). However, the upper limit of the preconcentration factor is limited by the absorbance value at which the linearity of the calibration graph decays, making necessary sample dilution, i.e. the preconcentration method needless. The advantages of the selected conditions are the possibility of achieving an analysis frequency of 30 samples h^{-1} in routine analysis without the need for employing high volumes of aqueous phases [11,20] which extend the time of analysis to several hours per sample [17,18].

3.2.4 *Interference behavior and matrix effects*

One main advantage in using CYANEX 471X® over other sulphur-containing extractants, as CYANEX 301 [23], is its well established selectivity over many interfering ions as Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Pb(II) [14,16,25]. Additionally it has been reported that the extraction behaviour of CYANEX 471X® for mercury remains practically the same on changing the aqueous phase from nitric acid to hydrochloric or sulphuric acid [16], allowing the use of the cartridge in different media. Experiments performed with a 100-fold excess of As(V), 600 of Pb(II), 800 of Ni(II), and 1500 of Co(II) showed no change in mercury response using the developed preconcentration system. However, when high concentrations of Zn(II) (2500-fold excess) and Cu(II) (6000-fold excess) were used, a 25% increase in the signal was noticed, probably due to the formation of volatile metallic species additional to mercury in the presence of $NaBH_4$ as indicated by Wickstrom *et al*. [26]. In this form, in order to evaluate the possible presence of matrix effects in the complexity of a sediment sample, the results of mercury determination by direct calibration with aqueous standard solutions were compared with those for standard additions in a basin sediment sample. A difference between the slopes of both calibration curves was detected within the 95% confidence indicating a possible matrix effect (slope of external calibration line = 0.117 Abs L μg^{-1}, slope of standard addition line = 0.142 Abs L μg^{-1}). In order to avoid the interference the standard addition method was applied as the calibration method to determine the concentration of mercury in real sediment and soil samples.

3.2.5 *Analysis of real samples*

One soil and two sediment reference materials as well as the basin sediment real sample were analysed in order to evaluate the accuracy of the proposed method and its possible application for mercury determination in real samples. Table 5 shows the results obtained

Table 6. Relative contributions of different factors in the uncertainty of the developed preconcentration method.

Symbol	Source of uncertainty	Value ($\mathrm{mg\,kg^{-1}}$)	$u(x_i)$ ($\mathrm{mg\,kg^{-1}}$)	$u(x_i)/x_i$	C_i
w_x	Mass fraction of Hg in the sample	0.00011	0.000010	0.091	857.4
w_B	Mass fraction of Hg in the blank	0.000052	0.00000045	0.0087	857.4
fc_d	Instrumental drift correction factor	1.00	0.024	0.024	0.049
f_d	Dilution factor	850	6.08	0.0072	0.000059
f_r	Repeatability factor	1	0.037	0.037	0.050
f_b	Method bias factor	1	0.020	0.0202	0.050
w_{Hg}	0.049	$\mathrm{mg\,kg^{-1}}$	Mass fraction of Hg in the assay material		
u_c	0.0088	$\mathrm{mg\,kg^{-1}}$	Combined uncertainty		
$U(w_{\mathrm{Hg}})$	0.018	$\mathrm{mg\,kg^{-1}}$	Expanded uncertainty ($k = 2$)		

as the mean of 3 independent measurements. It was found that mercury concentration values obtained with the proposed preconcentration method agree well with the certified values. Furthermore, the performance of the proposed preconcentration method was compared with ICP-MS and CVAFS measurements. The values obtained are also given in Table 5. A comparison of the three methods used for mercury measurements in the basin sediment showed no significant differences in their mean values at a 95% significance level.

3.3 *Evaluation of the global uncertainty of the method*

The evaluation of uncertainty was performed according to the EURACHEM/CITAC guide *Quantifying Uncertainty in Analytical Measurements* [27]. The following mathematical model was considered:

$$w_{Hg} = (w_x - w_B) \cdot fc_d \cdot f_d \cdot f_r \cdot f_b.$$

In Table 6 the symbols for the different factors in this equation are clarified. Additionally, the values of the contribution of each factor in mercury determination content in the basin sediment real sample are given. The standard uncertainty, $u(x_i)$, the relative standard uncertainty, $u(x_i)/x_i$, and the sensitivity coefficients, estimated from the partial derivative of the mathematical model, C_i, are included. It is observed from these results that the main contribution to the total uncertainty in the determination corresponds to the evaluation of the mass fraction of mercury in the sample through the standard addition method (w_x). The value of w_{Hg} and its expanded uncertainty in the determination of the basin sediment was $0.049 \pm 0.018\ \mathrm{mg\,kg^{-1}}$ ($k = 2$).

4. Conclusions

The proposed mercury on-line preconcentration method proved to be suitable for mercury determination in sediments with naturally occurring mercury content as well as in contaminated soil samples. The method is based on the use of a CYANEX 471X®-doped sorbent prepared by the sol-gel procedure and coupled by FIAS to CVAAS, and in comparison with other solid sulphur-containing phases used with this detector, it has the advantages of an easy procedure of synthesis, highly sample through-output (30 samples h^{-1} under selected conditions), and competitive limit of detection with small sample volumes (24 ng L^{-1}, obtained after 90 s of preconcentration time for 9.6 mL of analyte solution), together with adequate accuracy. Chemical characterisation of the sorbent indicated that mercury is extracted in the form of $\overline{Hg(NO_3)_2 \cdot R}$ species (where R stands for CYANEX 471X®) with an extraction equilibrium constant of $10^{5.7}$, a K_d of $10^{4.6}$ and a loading capacity of 0.005 mmol g^{-1} when 0.005 g of the solid-phase are used. It was also confirmed gel homogeneity when amounts higher than 5 mg are used. The calibration graph was linear from 0.05 μg L^{-1} to 3.0 μg L^{-1} of Hg. The repeatability was 1.5% and 1.8% RSD ($n = 10$) at concentrations of 0.5 and 1 μg L^{-1} of Hg, respectively. The method enrichment factor varied from 6 to 32 depending on preconcentration time, and the cartridge could be satisfactorily reused over 100 cycles without any sign of deterioration. From uncertainty analysis it was observed that the main contribution to the total uncertainty in the determination corresponds to the evaluation of the mass fraction of mercury in the sample through the standard addition method. Due to its automatisation possibilities, the commercial accessibility of the reagents and excellent performance (in terms of accuracy and stability), the proposed method represents a good alternative for laboratories that employ atomic absorption spectrometers for routine analysis.

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