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ON-LINE PRECONCENTRATION OF INORGANIC MERCURY AND METHYLMERCURY IN SEA-WATER BY SORBENT-EXTRACTION AND TOTAL MERCURY DETERMINATION BY COLD VAPOUR ATOMIC ABSORPTION SPECTROMETRY

Matilde Fernández García,[1] Rosario Pereiro García,[1] Nerea Bordel García[2] and Alfredo Sanz-Medel[1]*

[1]Department of Physical and Analytical Chemistry, Faculty of Chemistry, C/ Julian Claveria, 8, University of Oviedo, 33006 Oviedo, Spain

[2]Department of Physics, Faculty of Physics, University of Oviedo, Spain

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Summary—A comparative study of three mercury chelate forming reagents [diethyldithiocarbamate, pyrrolidin-1-yldithioformate and diphenylthiocarbazone (dithizone)] has been carried out for the preconcentration of ultratrace amounts of inorganic mercury and methylmercury in silica C_{18} minicolumns as the solid sorbent. Sample flow injection in-line sorbent extraction was coupled with continuous cold vapour atomic absorption spectrometry (CVAAS) for detection. Results showed the superiority of the carbamate type reagents over the dithizone for the on-line formation and preconcentration of the corresponding mercury chelates. Using diethyldithiocarbamate (DDC) as reagent, aqueous sample volumes of 100 ml can be preconcentrated with 100% efficiency for both inorganic mercury and methylmercury. Quantitative release of the retained DDC chelates was obtained for volumes of eluent (ethanol) of 50 μl. Following the proposed procedure, detection limits of 16 ng/l. of mercury were achieved for sample volumes of 25 ml. The relative standard deviation was $\pm 3.4\%$ at 0.5 μg/l. Hg(II) levels. The method has been successfully applied to the determination of low levels of mercury in sea-water.

During recent years particular concern has been devoted to the presence of mercury species in aquatic food chains, which was recognized long ago[1] as a major environmental pollution issue and health hazard for humans. It is well known today that inorganic mercury is converted into the more toxic methylmercury by aquatic organisms and thus speciation of the Hg chemical forms is often required in environmental samples.[2]

The determination of total mercury in solution is usually done by cold vapour atomic absorption spectrometry (CVAAS).[3–5] Due to the low levels of mercury species to be analysed in most cases in environmental and biological samples, the use of a preconcentration step is usually mandatory, particularly if speciation (*i.e.* fractionation) is to be carried out.

Several mercury preconcentration methods have been proposed in atomic spectroscopy including amalgamation on Au,[6] Ag[7] or alloys,[8] liquid–liquid extraction[9,10] and solid phase extraction.[11–17] It seems that solid phase extraction has some advantages over liquid–liquid procedures, such as higher preconcentration factors, better efficiency, greater reproducibility and greater simplicity in sample handling and transfer.[18]

Using such solid–liquid systems, preconcentration of mercury has been described in off-line procedures with immobilized reagents (such as picolinic acid amide,[11] dithiocarbamates[12,13] or hystidine[14]) in adequate solid supports. On-line procedures[18,19] have also been proposed for mercury preconcentration using chelating columns with cysteine,[15] dithiocarbamates[16] or quinolin-8-ol.[17] The release of the analyte from these columns involves the breaking of the covalent reagent–Hg bonds formed during retention of the metal.

Ruzicka and Arndal first demonstrated the possibility of trace metal preconcentration with 'sorbent extraction' columns using flow injection techniques.[20] Sorbent extraction based

*Author to whom correspondence should be addressed.

on the reversed-phase absorption, on a hydrophobic polymeric phase, of hydrophobic complexes of metals offers interesting advantages,[21–24] *e.g.* the possibility of using selective reagents with high binding constants with the metal, allowing for high flow rates for the preconcentration step to be used; possible losses of complexed metals on container walls is mitigated by the on-line formation of the complex. Moreover, complete and rapid elution can be expected because the complexes are not bound chemically to the sorbent. On the other hand, and because organic solvents are normally used for elution, preconcentration systems based upon this methodology could be easily coupled on-line to gas or liquid chromatographic systems.

In this paper, a comparative study of several organic reagents is carried out for the preconcentration of inorganic mercury and methylmercury in sea-water. Taking into account the high affinity of both Hg species to organic reagents with sulfur donor atoms, the reagents selected for comparison were sodium diethyldithiocarbamate (DDC), ammonium pyrrolidin-1-yldithioformate [pyrrolidine dithiocarbamate (APDC)] and diphenylthiocarbazone [dithizone (DZ)]. Solid extraction on different hydrophobic solid sorbents with on-line analyte determination by continuous CVAAS was investigated in detail.

EXPERIMENTAL

Reagents

Unless stated otherwise, all chemicals used were of analytical-reagent grade. A standard stock solution of 1000 μg/ml of Hg(II) was prepared by dissolving mercury(II) chloride in 0.1*M* HCl. The standard stock methylmercury solution was prepared by dissolving 250 mg of CH_3HgCl (from ICN Biomedicals Ltd) in 200 ml of acetone to give 1000 μg/ml of mercury. All methylmercury solutions were protected against light and heat. Standard solutions were prepared daily by appropriate dilution of these stock solutions with the chosen buffer solution. Buffer solutions of 0.01*M* sodium acetate–acetic acid (Merck) of different pHs were prepared.

APDC, DDC and DZ were obtained from Merck. Solutions of these reagents were prepared by dissolution of the adequate amounts in a pH 9.2 solution made of 0.02*M* ammonium hydroxide + 0.01*M* acetic acid (Merck). The solid sorbents investigated were silica C_{18} (100–200 mesh, Merck), Amberlite XAD 2 (20–50 mesh, Sigma) and Amberlite XAD 7 (20–50 mesh, Sigma). Other particle sizes for solid sorbents were prepared in the laboratory by crushing and sieving procedures of the commercial resins.

Sodium tetrahydroborate (III) solution (1% m/v) was prepared by dissolving tetrahydroborate (III)) powder (Probus) in water stabilized by 0.1% m/v sodium hydroxide (final concentration). The solution was prepared every day and filtered before use.

Ultrapure water (Milli Q, Millipore) was used for the preparation of all the above solutions.

Flow system and procedure

The manifold used in this study is shown in Fig. 1. The set-up consisted of a four channel Gilson Minipuls peristaltic pump, three rotary valves, connecting PTFE tubing (0.8 mm i.d.) and fittings, a minicolumn, a gas–liquid separator, a quartz cell and a detector. The preparation of the minicolumn has been described previously.[25]

Ultrapure water was pumped continuously (at a selected flow rate of 4.5 ml/min) through

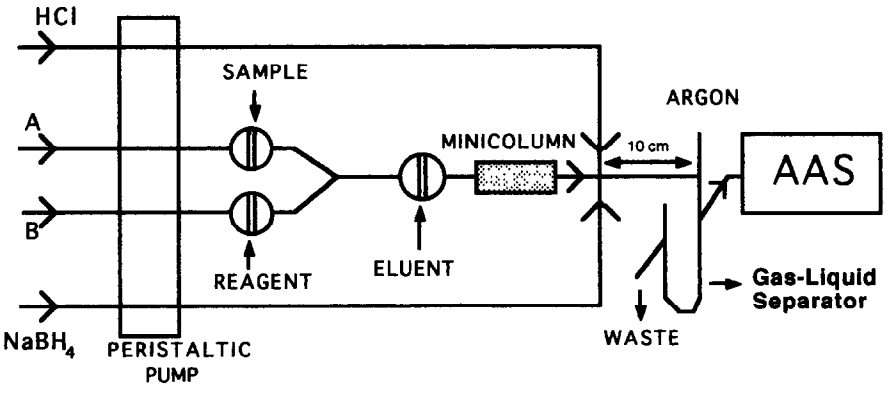

Fig. 1. Schematic flow diagram of the system used for the preconcentration and determination of mercury.

channels A and B. Samples and reagents were injected simultaneously into the corresponding channel. Both solutions merged at a T-piece where the neutral chelates were formed. After passing through a 15 cm reaction coil, the chelates were retained on the hydrophobic minicolumn (silica C_{18} was employed during the optimization steps). Optimization studies were carried out for 1 ml sample [20 ng/ml of mercury (as Hg^{2+} or as CH_3Hg^+)] and 1.1 ml reagent injections to ensure complete mixing of the sample with the reagent in the flow system. After the preconcentration step was completed, the chelate was released by an ethanol solution.

The plug with the eluent and the preconcentrated chelates were mixed in the continuous flow system with $NaBH_4$ and HCl solutions using a triple merging point. Optimized cold-vapour reagent concentrations and flow rates for our system (using ethanol as eluent) were: 1% $NaBH_4$ (1.8 ml/min) and 15% HCl (4.5 ml/min). The generated cold vapour along with the liquid passed through a gas–liquid separator (GLS) similar in design to that described previously.[26] Our GLS consisted of a glass cylindrical chamber (10 cm long and 1 cm I.D.) filled with 3 mm diameter glass beads and with a U-tube drain attached at the bottom.[27] In the GLS the liquid was drained by gravity and the gaseous products swept by an Ar stream (200 ml/min) to the detector. Connection tubing between the GLS and the detector was kept as short as possible (25 cm).

Apparatus

A Perkin Elmer 2280 atomic absorption spectrometer equipped with a 16.5 cm T-shaped quartz absorption cell (I.D. = 1.2 cm, no windows) was used throughout this work. The quartz absorption cell was heated by an air–acetylene flame. A mercury electrodeless discharge lamp (operated from an external power supply) from Perkin Elmer was used as the line source at 253.7 nm.

RESULTS AND DISCUSSION

Optimization of analytical parameters

The effect of sample pH on the preconcentration step was evaluated for each reagent. For this purpose Hg^{2+} standard solutions were prepared in the pH range 3–9 and the absorbance of the cold vapour generated after the elution of the preconcentrated chelate was measured. No change was observed for DDC and APDC in the pH range studied. However, as can be seen in Fig. 2, when DZ was used a clear dependence between the pH of reaction (that is, the pH after the mixing of sample and reagent) and the analytical signals was observed. For further experiments with DZ it was ensured that the reaction pH was kept at 8.

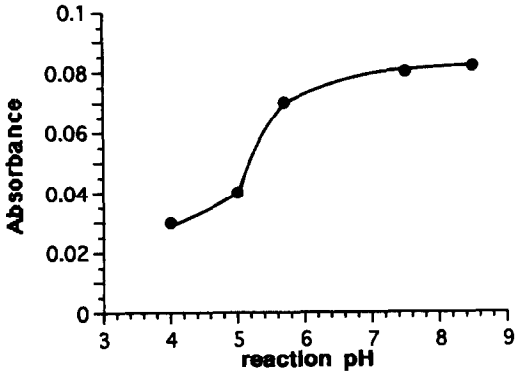

Fig. 2. Influence of the pH on the formation/retention of the dithizonate mercury chelate.

The effect of the concentration of the chelating agent solution on the on-line sorbent extraction of Hg(II) was also investigated. For DDC and APDC the studied reagent concentration range (0.01–0.1%) had no effect on the analytical signals. A concentration of 0.05% was chosen for subsequent experiments. However, there was a tendency for DZ to be retained on the column. To avoid solid support overloading by an excess of reagent which could hinder the full retention of the formed chelate, a DZ concentration of 0.01% was chosen. This 0.01% still represents more than 1000 times excess over the mercury concentration.

Using a 15 cm reaction coil, no influence of the flow rate used on the chelate formation/retention was observed, working with APDC and DDC. A high flow rate (4.5 ml/min for each of the channels) was selected in order to increase the sampling frequency. This flow rate was close to the maximum allowed by the peristaltic pump. For DZ a clear influence of the preconcentration flow rate on the efficiency of the reaction/retention step was found. For this reagent it was observed that the lower the flow rate the higher the amount of chelate formed and retained (the elution was performed at a total flow rate of 6 ml/min in all cases). As a compromise between efficiency of DZ chelate formation and sampling frequency, a flow rate of 0.5 ml/min was chosen for each channel. Moreover, in order to increase the reaction time

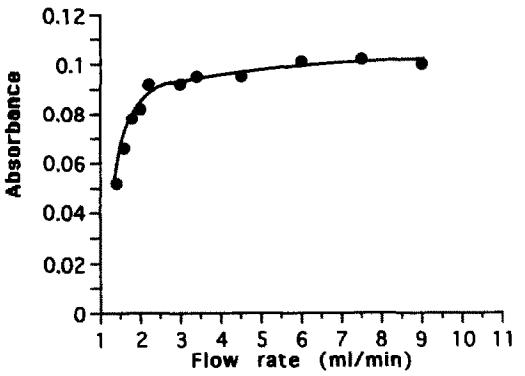

Fig. 3. Influence of the chelate elution flow rate on the CVAAS signals obtained for mercury determination. The plot was obtained when using DDC as reagent.

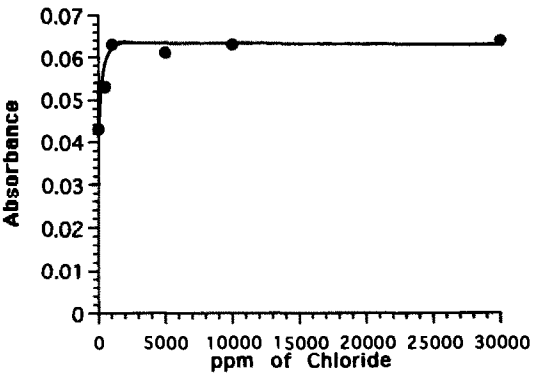

Fig. 4. Effect of NaCl, incorporated into the Hg(II) standards, on Hg(II) preconcentration when using DDC as chelate forming reagent. Similar plots were observed when using APDC and DZ as reagents.

when using DZ as reagent, the mixing coil was lengthened to 2 m.

The optimum elution flow rate was also investigated. Results when using DDC as chelating reagent are shown in Fig. 3. Similar elution plots were obtained for all the reagents. In order to keep a simple operation procedure the same flow rate for elution as those chosen for the preconcentration steps was selected.

Three different hydrophobic solid substrates were investigated: silica C_{18}, Amberlite XAD 2 (a styrene-*p*-divinilbenzene resin) and Amberlite XAD 7 (cross-linked polymer of methyl methacrylate). To evaluate the performance of each column, the effluent from the column was collected during the preconcentration step in a calibrated flask. Eluates of ethanol containing the Hg complex were also collected in separated calibration flasks. Both types of solutions were analysed for Hg by CVAAS. As can be seen in Table 1, the most critical factor of the solid support influencing the efficacy of the chelate retention proved to be the particle size. In all cases the overall Hg recoveries (Hg not retained + Hg eluted) were $100 \pm 5\%$. Complete retention was observed for DDC and APDC complexes when using Amberlite XAD 2 (100–200 mesh) or silica C_{18}.

Incomplete chelation reaction was demonstrated under the conditions of the experiment, and was responsible for the low values observed in Table 1 for DZ.

Methanol, acetonitrile and ethanol were evaluated as eluents. Ethanol was the solvent which offered the best Hg signals. The Hg analytical signals observed with methanol and acetonitrile were slightly smaller (96% for methanol and 94% for acetonitrile). The minimum volume of ethanol necessary to ensure complete chelates elution was 50 μl for DDC and APDC complexes, and 100 μl for the DZ chelate.

Effect of salt matrix and foreign ions

The effect of adding increasing amounts of NaCl to the inorganic Hg(II) standard was investigated. It was observed with the three reagents (Fig. 4) that in the proposed systems the Hg signals increased with increasing NaCl concentrations up to approximately 1000 μg/ml of Cl, and then remained constant up to the maximum concentration assayed (30,000 μg/ml Cl). The addition of sodium sulphate (up to 10,000 μg/ml sulphate) did not disturb the expected mercury signal.

The effect of different cations present in sea-water was also investigated in detail. Results showed that for the proposed procedures neither Ca^{2+} nor Mg^{2+} or K^+ interfered, at the high concentration levels present in sea-water (it

Table 1. Mercury retained on different solid sorbents (as % of initial amount injected)

	XAD 7 (20–50 mesh)	XAD 2 (20–50 mesh)	XAD 2 (100–200 mesh)	C_{18} (100–200 mesh)
DDC	74.7 ± 2	77.7 ± 2	100.6 ± 5	100.3 ± 3
APDC	74.6 ± 3	77.9 ± 3	101.2 ± 2	100.2 ± 2
DZ	52.4 ± 2	58.2 ± 3	64.3 ± 4	68.7 ± 2

Table 2. Effect of foreign transition metal cations on the recovery of 20 ng of Hg(II)

Cation	Concentration (mg/l)	DDC	APDC	DZ
0	0	100	100	100
Fe(III)	10	99	102	103
Cr(III)	10	102	103	101
Zn(II)	10	101	82	102
	5	—	98	102
Cu(II)	10	58	70	104
	5	70	—	102
	1	90	70	101
	0.5	—	98	105

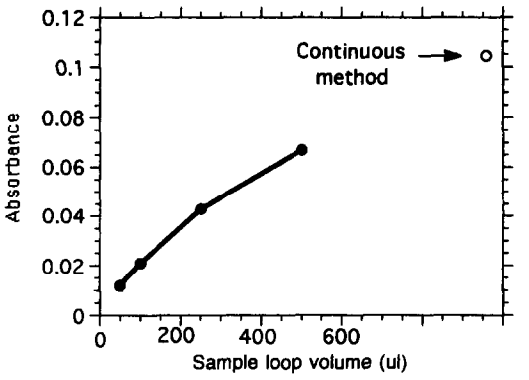

Fig. 5. Effect of sample loop volume when using a Hg–FIA–CVAAS system without any preconcentration step.

was assayed at a maximum concentration of 3000 μg/ml of each), with the CVAAS subsequent determination of Hg. The influence of adding other cations such as Fe(III), Cr(III), Zn(II) and Cu(II), was also tested. As shown in Table 2, it was found that when using DDC or APDC reagents, the presence of Cu(II) in the mercury standard causes interference at concentrations of Cu(II) higher than 500 ng/ml. This concentration is much higher than those expected in sea-water (<1 ng/ml) and so no interference in the real sample analyses could be expected. It is interesting to note that, in the proposed flow system, when using DZ no interference of Cu(II) at the concentrations assayed (Table 2) was observed. This could be explained in terms of the kinetics of the dithizonates formation in the flow manifold; the rate of formation of the copper dithizonate complex is smaller than that of the chelate of mercury.[28]

Analytical performance characteristics

Analytical performance characteristics of the proposed on-line preconcentration and CVAAS methods were evaluated under selected conditions for each reagent. Detection limits for Hg^{2+} were calculated as three times the standard deviation of the blank signal and the relative standard deviations ($n = 5$) were calculated at the 500 ng/l level of Hg(II), using sample volumes of 25 ml for preconcentration. Results are summarized in Table 3. The Hg detection limit (D.L.) obtained with the continuous system, without any preconcentration step, was 0.7 μg/l. A worsening of this directly obtained D.L. was noted when using Flow Injection Analysis (FIA) techniques (Fig. 5), and a strong dependence between the sample volume and the D.L. obtained was observed. For our GLS this worsening was quantified as about one order of magnitude when comparing the continuous Hg CVAAS generation system to the FIA-CVAAS for 50 μl sample volume.

Table 3. Analytical performance characteristics achieved with each reagent

	D.L. (ng/l)	RSD* (%)	Linear range (μg/l)
DDC (25 ml)†	16	±3.4	Up to 40
APDC (25 ml)	18	±3.3	Up to 40
DZ (10 ml)	67	±4.5	Up to 200

*Relative standard deviation.

†The volumes used for the preconcentration are given in parentheses.

The final Hg CVAAS signal should depend on the total Hg retained rather than on its concentration in the preconcentrated solution. In fact, it has been confirmed that the sensitivity and useful range of the method can be easily extended by changing the preconcentrated volume of sample (preconcentration ratio): the same calibration curve slopes were obtained when preconcentrating sample volumes from 1 to 100 ml (maximum volume assayed) provided that the total Hg amount was kept constant (50 ng in our experiments).

The analytical potential of these systems to preconcentrate/analyse methylmercury was also evaluated. Experiments showed that using the recommended flow procedures the three organic reagents under investigation behaved in a similar manner for preconcentrating inorganic mercury or for methylmercury. Table 4 shows, for the DDC system, that for preconcentrated sample volumes from 1 to 100 ml the CVAAS analytical signals are independent of the Hg chemical form in the sample [inorganic Hg(II) or methylmercury] and of the preconcentrated sample volume whenever the total mass of Hg is constant.

Table 4. Comparison of CVAAS analytical signals obtained with the DDC preconcentration system for different preconcentrated volumes of inorganic mercury and methylmercury

	Relative absorbance
500 ng/l Hg^{2+} (1 ml)*	100 ± 1.8%
500 ng/l Hg (as CH_3Hg^+) (1 ml)	101 ± 1.6%
50 ng/l Hg^{2+} (10 ml)	102 ± 2.1%
50 ng/l Hg (as CH_3Hg^+) (10 ml)	99 ± 2.5%
5 ng/l Hg^{2+} (100 ml)	98 ± 2.9%
5 ng/l Hg (as CH_3Hg^+) (100 ml)	97 ± 3.2%

*The volumes used for the preconcentration steps are given in parentheses.

Table 5. Determination of Hg (as inorganic mercury and methylmercury) in sea-water

(Hg^{2+} + CH_3Hg^+) spiked	Total Hg found ± RSD
0.2 μg/l Hg^{2+} (25 ml)*	0.17 μg/l ± 5.8%†
0.2 μg/l Hg (as CH_3Hg^+) + 0.2 μg/l Hg^{2+} (25 ml)	0.43 μg/l ± 2.3%†
0.1 μg/l Hg^{2+} (50 ml)	0.094 μg/l ± 6.4%†
0.1 μg/l Hg (as CH_3Hg^+) (50 ml)	0.103 μg/l ± 5.2%†

*The sea-water volumes used in each case for the preconcentration are given in parentheses.
†Five replicates were carried out for each sample.

Analysis of sea-water

In order to validate the methology, the method proposed using DDC as organic reagent for complexation was selected and applied to the determination of mercury in sea-water samples. The analyses were performed on synthetic 'reference' samples prepared from Cantabric Sea water that did not originally give Hg signals by our method. They were then adequately 'spiked' with inorganic Hg(II) and MeHgCl. To compensate for the observed effect of chloride (see Fig. 4), 10,000 μg/ml of Cl (as NaCl) was added to all the mercury standards used for calibration. In order to shorten the general analytical procedure, calibration graphs were prepared with injections of 1 ml of the appropriate Hg(II) standards (as stated above, the CVAAS signals depend on the total analyte amount retained on the minicolumn rather than upon the preconcentrated volume). The results obtained in these analyses are given in Table 5, which shows that the values found agree well with the expected values for the four samples evaluated.

CONCLUSIONS

The experiments reported in this study reveal the feasibility of preconcentration of mercury species by sorbent extraction in a flow system and the continuous determination by CVAAS. The comparative study of three reagents showed the superiority of the carbamate groups containing reagents over dithizone for the on-line formation of the respective mercury chelates. In the preconcentration experiments performed, similar behaviour of inorganic mercury and methylmercury was observed in all instances. The proposed methodology offers a rapid and efficient way for the preconcentration of these mercury species, and the optimized procedure was successfully applied to the determination of ultratraces of mercury in sea-water by CVAAS.

It is well known that Hg(II) forms strong bonds with reagents containing thiol groups. Solid-phase preconcentration techniques which require the breakage of these bondings to release the preconcentrated mercury usually require strong conditions and/or large volumes of eluent, and the recoveries of the preconcentrated analyte are lower than 100% in most

Table 6. Comparison of enrichment factors obtained for different on-line mercury preconcentration procedures

	Solid–liquid procedures Maximum sample volume preconcentrated/eluent volume
(Immobilized DDC)[16]	500 ml sample/0.9 ml eluent = 555.6
(Immobilized Cysteine)[15]	5 ml sample/0.06 ml eluent = 83.3
(Immobilized Quinolin-8-ol.)[17]	14.25 ml sample/0.3 ml eluent = 47.5
Our method	100 ml sample/0.05 ml eluent = 2000
	Liquid–liquid procedures Enrichment factor
[10] f.r.* = 4.1	1.52 sample f.r.*/0.37 organic phase

*f.r. = flow rate (*ml/min*).

cases. A major advantage of the preconcentration systems described in this paper is the low eluent volumes (50 μl of ethanol) necessary to obtain the release with 100% efficiency of the preconcentrated species. This low volume of eluent implies the obtention of preconcentration factors higher than 1000 times for sample volumes of 100 ml (Table 6).

The overall improvement of D.Ls. when compared to continuous Hg cold vapour generation was about 45 times (for 25 ml samples). This relatively low improvement (compared with the enrichment factor obtained in the preconcentration step) can be attributed to the dead volume of the cold vapour system used, which gives rise to a high dilution in the gas phase of the transient plug containing the eluent, as was observed when comparing a continuous Hg CVAAS system with a FIA-CVAAS manifold. This dead volume may also explain the poorer detection limits obtained when comparing our results to other solid-phase Hg preconcentration procedures.[17]

The flow injection solid–sorbent extraction methods proposed here could easily be on-line coupled to gas or liquid chromatographic separation systems in order to investigate the speciation of the preconcentrated mercury species.

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