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Sensitive determination of mercury in tap water by cloud point extraction pre-concentration and flow injection-cold vapor-inductively coupled plasma optical emission spectrometry

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Abstract

A pre-concentration and determination methodology for mercury at trace levels in water samples was developed. Cloud point extraction was successfully employed for the pre-concentration of mercury prior to inductively coupled plasma optical emission spectrometry coupled to a flow injection with cold vapor generation system. The mercury was extracted as mercury-2-(5-bromo-2-pyridylazo)-5-diethylaminophenol [Hg(II)-(5-Br-PADAP)] complex, at pH 9.2 mediated by micelles of the non-ionic surfactant polyethyleneglycolmono-*p*-nonylphenylether (PONPE 5). Cold vapor generation was developed from 100 μ l of the extracted surfactant-rich phase by means of a stannous chloride (SnCl₂) solution as reductant. An exhaustive study of the variables affecting the cloud point extraction with PONPE 5 and cold vapor mercury generation from the surfactant phase was performed. The 50-ml sample solution pre-concentration allowed us to raise an enrichment factor of 200-fold. The lower limit of detection obtained under the optimal conditions was 4 ng l⁻¹. The precision for 10 replicate determinations at the 0.5- μ g l⁻¹ Hg level was 3.4% relative standard deviation (R.S.D.), calculated with the peak heights. The calibration graph using the pre-concentration system for mercury was linear with a correlation coefficient of 0.9998 at levels near the detection limits up to at least 50 μ g l⁻¹. The method was successfully applied to the determination of mercury in tap water samples. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Cloud point extraction; Mercury; ICP-OES; Cold vapor; Flow injection

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1. Introduction

Although mercury is not an abundant chemical element in nature, it has become widespread as a result of many industrial and agricultural applications [1–4]. Therefore, the determination of mercury is very important in environmental and toxicological studies. One of the routes of incorporation of mercury into the human body is drinking water [1–4]. Hence, its determination in this type of sample becomes very important. Recent reports [5] estimate a total mercury concentration in waters ranging from 0.006 to 3 $\mu\text{g l}^{-1}$, the upper limit for total mercury concentration in drinking water recommended by the European Community being 1 $\mu\text{g l}^{-1}$ [3].

Since mercury concentrations in non-polluted waters are very low, powerful techniques are required and only few of them show enough sensitivity. Different analytical methods have been developed for the determination of mercury at low concentrations, but the most commonly used ones are cold vapor atomic absorption spectrometry (CV-AAS), cold vapor atomic fluorescence spectrometry (CV-AFS), flow injection-inductively coupled plasma optical emission spectrometry (FI-ICP-OES), and inductively coupled plasma mass spectrometry (ICP-MS) [6–9]. There are several disadvantages associated with the use of AAS as a detection method. These result from the limited linear calibration range and spectral interference arising from non-specific background absorption of volatile organic species [10]. ICP-MS is used for the determination of mercury due to its high sensitivity, high selectivity, and high sample throughput. However, the cost of instrumentation may be prohibitive to many laboratories. Although ICP-OES and CV-AAS are the most used techniques in the determination of traces of mercury, the low concentration level of mercury in water is not compatible with the detection limit of these techniques. In order to achieve accurate, reliable and sensitive results, pre-concentrations and separations are needed when the concentrations of analytes in the sample are too low to be determined directly by ICP-OES, even with mercury vapor generation.

A scheme of pre-concentration can thus be proposed, mediated by surfactants (CPE, cloud point extraction) instead of organic solvents. CPE is an impressive alternative to conventional solvent extraction because it produces high extraction efficiencies and concentration factors and uses inexpensive, non-toxic reagents. A very interesting feature is that cloud point partition constants of metal chelates depend on the nature of metal ions [11], with consequent potential increase of selectivity. Highly concentrated aqueous solution of some non-ionic and zwitterionic surfactants are homogeneous and isotropic [12–14]. Upon alteration of the conditions such as temperature, pressure or additives, the solution becomes turbid due to the diminished solubility of the surfactant in water [12–14]. Above the cloud point (temperature at which this phase behavior occurs), the solution is separated into two phases: one, the aqueous phase that contains the surfactant at a concentration close to the critical micellar concentration (cmc), and the other, the surfactant-rich phase, whose volume is very small [12–14]. Any species initially present in the solution that interact with the micellar aggregates are thus extracted and may be pre-concentrated in the small volume of the surfactant-rich phase. The use of CPE process for extraction of metal chelates, biological and clinical samples; and environmental clean-up procedure have been reported [11,15–27].

In view of the possibility of mercury chelation with the pyridylazo reagent 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP) [28,29], and from our previous experience [30,31] on CPE using pyridylazo chelating reagents, the aim of the present paper was to develop an extraction–pre-concentration scheme for Hg in tap water mediated by micelles of PONPE 5. It has to be pointed out that, to date, both, the surfactant PONPE 5 and the reagent 5-Br-PADAP have never been used in CPE systems. Indeed, until now this extraction methodology has never been used with mercury.

In the present work, a CPE pre-concentration methodology has been developed and optimized for the determination of mercury in tap water. Mercury was chelated with 5-Br-PADAP, and later pre-concentrated mediated by PONPE-5. Mercury

determination was performed through cold vapor generation from the surfactant-rich phase using a FI system coupled to ICP-OES.

2. Experimental

2.1. Reagents

All the reagents were of analytical–reagent grade and the presence of mercury was not detected within the working range. A stock mercury standard ($1000 \mu\text{g ml}^{-1}$) was prepared from mercury(II) chloride (Merck, Darmstadt, Germany) in nitric acid (Merck, Darmstadt, Germany) and made to 1000 ml with ultrapure water. A $1 \times 10^{-2} \text{ mol l}^{-1}$ solution of 5-Br-PADAP (Aldrich, Milwaukee, WI, USA) was prepared by dissolution in ethanol (Merck, Darmstadt, Germany). Lower concentrations were prepared by serial dilution with ethanol. As it is not possible to obtain a real aqueous solution of the surfactant polyethyleneglycolmono-*p*-nonylphenylether (PONPE-5, Tokyo Kasei Industries, Chuo-Ku, Tokyo, Japan) (cloud point below room temperature) it was experimentally convenient to prepare a stock solution as follows: 20 ml of PONPE-5 and 40 ml of distilled ethanol, were mixed and made up to 100 ml with doubly distilled water. A 2% (m/v) SnCl_2 solution in 5% (v/v) HCl was used as the reductant. The buffer solution ($5 \times 10^{-2} \text{ mol l}^{-1}$) was prepared dissolving sodium tetraborate calcined (Merck, Darmstadt, Germany) and taken to 1000 ml with ultrapure water. A NaClO_4 (Merck, Darmstadt, Germany) solution was used in order to adjust ionic strength. Antifoam 204 and Antifoam A (purchased from Sigma, St. Louis, USA) were tested during the cold vapor generation. Ultrapure water ($18.3 \text{ M}\Omega \text{ cm}^{-1}$) was obtained from Barnstead EASY pure RF water system (Iowa, USA).

2.2. Apparatus

The measurements were performed with a sequential ICP spectrometer [Baird (Bedford, MA, USA) ICP 2070]. The 1-m Czerny–Turner monochromator is based on a holographic grating with 1800 grooves/mm. The ICP and cold vapor gen-

erator operating conditions are listed in Table 1. A Minipuls 3 peristaltic pump [Gilson (Villiers-Le-Bell, France)] was used. A sample loop of 100 μl and a Rheodyne (Cotati, CA, USA) Model 50, four-way rotatory valve were used in the cold vapor generation system. For the mixing of the surfactant-rich phase with the reductant solution, a knotted reactor (KR) was made from a 2-m length of PTFE tubing of 0.5 mm internal diameter by tying interlaced knots of approximately 5 mm diameter loops. Tygon-type pump tubing (Ismatec, Cole-Parmer, Vernon Hills, IL, USA) was employed to propel the sample, reagent and eluent.

A home made gas–liquid separator was used (Fig. 1) for the separation of mercury vapor. The characteristics were as follows: internal diameter = 15 mm, length = 95 mm, an inlet for the gas–liquid mixture and another for Ar, continuous waste extraction by means of a peristaltic pump and connection to the torch. The 194.227-nm spectral line was used.

2.3. General cloud point pre-concentration procedure

Surfactant solution (0.25 ml), 0.2 ml of $1 \times 10^{-2} \text{ mol l}^{-1}$ chelating solution, 0.5 ml of $2.5 \times 10^{-5} \text{ mol l}^{-1}$ metal-ion solution and 5 ml of buffer solution (pH 9.2) were placed in a centrifuge tube. The mixture was diluted to 50 ml with ultrapure water. The resultant solution was equilibrated at 60°C (temperature well above cloud point temperature of the system, which is 15°C) for 5 min. In order to separate the phases, the turbid solution was centrifuged [5 min at 3500 rev./min ($1852.2 \times g$)], and then cooled in an ice- NaCl bath for 5 min. The removal of the aqueous phase was carried out by means of a peristaltic pump.

In the case of pre-concentration of 50 ml of tap water sample, the CPE procedure was performed in the same way.

2.4. FI-CV-ICP-OES measurements

The surfactant-rich phase (250 μl) was acidified with 0.05 ml of HNO_3 ; and 0.1 ml of ethanol was added. A 100- μl aliquot of this solution was

Table 1
CPE-ICP and cold vapor generation system instrumental parameters

<i>ICP parameters</i>	
RF generator power	1.0 kW
Frequency of RF generator	40.68 MHz
Plasma gas flow rate	9 l min ⁻¹
Auxiliary gas flow rate	1 l min ⁻¹
Observation height (above load coil)	15 mm
Analytical line: Hg	194.227 nm
<i>Cold vapor generator parameters</i>	
Sample loop volume	100 μl
SnCl ₂ concentration	2% m/v
HCl concentration	5% (v/v)
SnCl ₂ solutions flow rate	4.5 ml min ⁻¹
HCl solutions flow rate	9 ml min ⁻¹
Carrier gas flow rate	0.5 l min ⁻¹
Temperature of generation	80 °C
<i>Cloud point extraction parameters</i>	
Equilibration temperature	60 °C
Equilibration time (before and after centrifugation)	5 min
Centrifugation time	5 min
Cooling time	5 min
Working pH	9.2
Buffer solution (concentration)	sodium tetraborate (5 × 10 ⁻² mol l ⁻¹) 4 × 10 ⁻⁵ mol l ⁻¹
Chelating reactive	< 0.35 mol l ⁻¹
Ionic strength	% (v/v)
Surfactant	99.9%
%E ^a	

^a Percentage extracted by the successive extraction method (2).

determined by FI-CV-ICP-OES. The optimized conditions for this cold vapor generation system are given in Table 1. A schematic diagram of the cloud-point extraction procedure, the determination step, is shown in Fig. 1.

2.5. Sample collection

Tap water was allowed to run for 20 min and approximately 2000 ml of tap water was collected. The water samples were filtered through 0.45-μm pore-sized membrane filters immediately after sampling. The sample was collected immediately before use. It was irradiated for 3 h with a 150-W UV lamp in order to photooxidize organo-mercury compounds, which could be present in tap water [32]. All the glass instruments used were previously washed with a 10% v/v HNO₃ water solution and then with ultrapure water.

3. Results and discussion

3.1. Study of the CPE system variables

3.1.1. Effect of ethanol

Several trials were carried out in order to study the effect of ethanol concentration prior to CPE. No variation took place on either the enrichment factor or kinetics of phase separation within the ethanol concentration range: 0.6–15% (v/v). Higher ethanol concentrations led to non-reproducible results due to inefficient phase separation. A minimum ethanol concentration [0.6% (v/v)] is needed in order to achieve a convenient cloud point temperature (Fig. 2) and an increase of phase separation rate. Fig. 2 shows the variation on cloud point temperature with ethanol concentration for the system, PONPE-5-ethanol-water.

3.1.2. Effect of reagent excess

In order to determine the optimal reagent–metal-ion relation, an experiment was carried out in which the other experimental variables, except reagent concentration, remained constant. The results are shown in Fig. 3a. Above a reagent to metal-ion excess of 2:1, no variation took place in the analytical signal. The stoichiometry in the Hg(II)-5-Br-PADAP-PONPE 5 system was determined using the molar ratio method. The complex was found to have a stoichiometry of 2:1 [5-Br-PADAP: Hg(II)].

3.1.3. Effect of buffer concentration and ionic strength

Sodium tetraborate buffer agent was chosen as optimal. The system was studied within sodium tetraborate concentration range: 5×10^{-4} – 5×10^{-2} mol l⁻¹ and ionic strength within the range: 0–1 mol l⁻¹, adjusted with NaClO₄. The best performance (higher extraction percentage; optimal stability; lower equilibration time and ease of phase separation) was achieved for a sodium

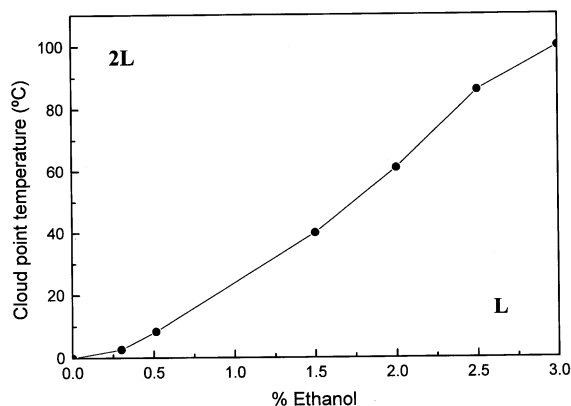


Fig. 2. Effect of the ethanol concentration on cloud point temperature for the system, PONPE 5-ethanol-water. L=one isotropic phase; 2L=two isotropic phases, the cloud point is determined by observing the onset of turbidity upon heating. Condition: [PONPE 5]=0.1% (v/v).

tetraborate concentration of 5×10^{-3} mol l⁻¹ and ionic strength 0–0.35 mol l⁻¹. For ionic strength higher than 0.4 mol l⁻¹, a quantitative phase separation was not possible.

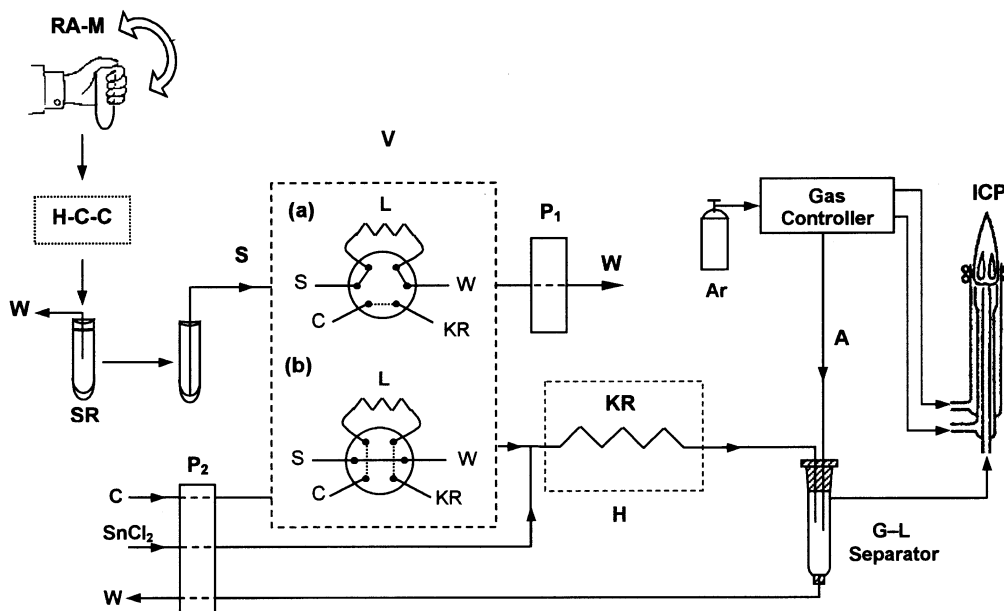


Fig. 1. Schematic diagram of the instrumental setup. RA–M: Reagent adding and mixing, H–C–C: heating, centrifugation and cooling, SE: supernatant removing, S: sample [surfactant-rich phase (250 μ l) + 100 μ l de ethanol + 50 μ l HNO₃], C: carrier solution [HCl: 5% (v/v)], A: Ar (flow rate: 0.5 l min⁻¹), W: waste, P1, P2: peristaltic pumps, V: injection valve, H: heating (80 °C), L: Sample loop (100 μ l). Valve positions: (a) sample loading; (b) injection.

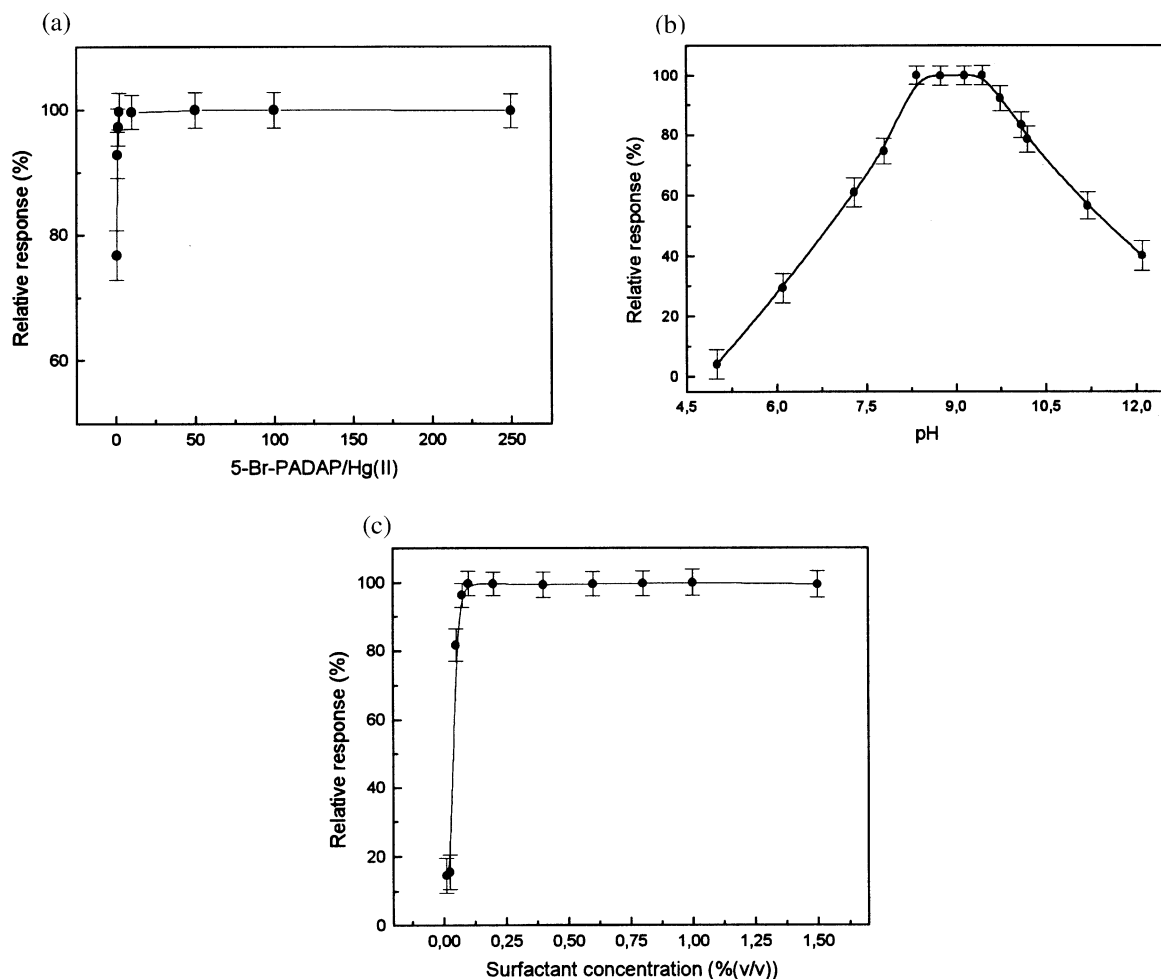


Fig. 3. (a) Effect of chelating reagent excess. (b) Effect of pH. Each desired pH was obtained with additions of suitable amounts of diluted HCl or NaOH. (c) Effect of surfactant concentration. Other conditions are given in Table 1.

3.1.4. Effect of pH

The effect of pH upon the complex formation of Hg-5-Br-PADAP was studied within the range of pH 5–12. The results are shown in Fig. 3b. As can be seen, the complex extraction begins at pH 6 and starts to decrease at pH 9.7, showing a plateau for the range pH 8.3–9.5.

3.1.5. Surfactant concentration

The variation of extraction efficiency upon the surfactant concentration was examined within range: $C_{\text{PONPE 5}} = 0.025\text{--}1.5\%$ (v/v). The results are shown in Fig. 3c. Quantitative extraction was

observed for a surfactant concentration higher than 0.07% (v/v). In order to achieve a good enrichment factor, 0.1% (v/v) was chosen as optimal.

3.1.6. Effects of equilibration temperature and time

The enrichment factor is affected by equilibration time and temperature [28]. Therefore, these parameters were studied within the ranges: 25–70 °C and 2–30 min, respectively. The cloud point temperature of the system under study is 15 °C. A temperature of 60 °C was selected in order to achieve the minimum equilibration time (5 min),

to avoid complex decomposition and to reach the optimal enrichment factor.

3.1.7. Effect of centrifugation time

A centrifugation time of 5 min at 3500 rev./min was selected as optimum, since complete separation occurred for this time and no appreciable improvements were observed for longer times.

3.1.8. Efficiency and enrichment factors for CPE

An extraction percentage higher than 99.9% was achieved when the procedure was carried out under the optimal experimental conditions (Table 1). Consequently, the enrichment factor achieved for this system was 200-fold.

3.2. Study of the FI-CV system variables

3.2.1. Surfactant-rich phase conditioning

Due to the high viscosity of the surfactant-rich phase and the need to decompose the Hg-5-Br-PADAP complex, the micellar phase had to be conditioned before its introduction into the FI-CV system. Hence, 100 μ l of ethanol and 50 μ l of HNO₃ (conc.) were added to 250 μ l of the surfactant-rich phase. The resultant solution and the sample loop were thermostated at 60 °C.

3.2.2. Optimization of the FI-CV-ICP-OES system

The cold vapor generation parameters from the surfactant-rich phase were carefully studied in order to reach the conditions of maximum sensitivity. The optimization of the cold vapor parameters was performed from the surfactant-rich phase obtained after the pre-concentration by CPE of 50 ml of an aqueous solution [$C_{\text{Hg(II)}} = 50 \mu\text{g l}^{-1}$].

The use of NaBH₄ as a reducing agent produced a significant quantity of foam during the cold vapor generation from the surfactant-rich phase, which diminished the reproducibility of the technique. The use of anti-foaming agents was studied in order to avoid this problem, but unsatisfactory results were obtained, so SnCl₂ was chosen as a reductant agent. This reductant showed satisfactory results. The SnCl₂ concentration was an important parameter to be optimized because cold vapor generation should be carried out in the presence of higher concentrations of organic matter. It could

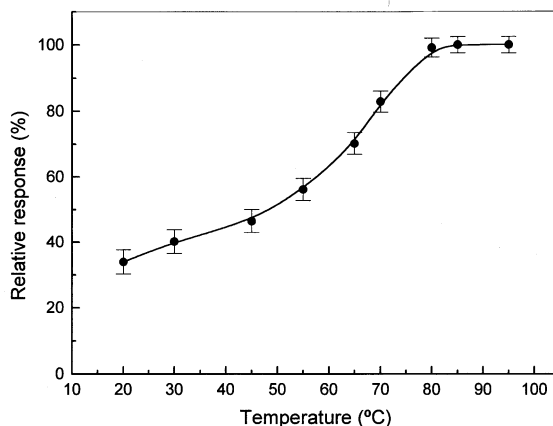


Fig. 4. Effect of temperature on cold vapor generation from surfactant-rich phase.

be verified that the best signal-to-noise ratio was obtained with a concentration of 2% m/v. Higher concentrations of the reductant agent did not lead to important signal changes. Hence, the above mentioned SnCl₂ concentration was adopted as the working concentration.

The carrier solution (HCl) concentration that was most suitable and compatible with the system of cold vapor generation was studied. The results obtained showed that the maximum response for the system was obtained at concentrations above 4.5% (v/v) HCl. Therefore, 5% (v/v) HCl was adopted as the working concentration.

Fig. 4 shows the influence of the temperature on the analytical response. No appreciable changes were observed for temperatures higher than 78 °C. A cold vapor generation temperature of 80 °C was chosen as optimal.

A 200-cm knotted reactor was used in order to reach an efficient mix up of the surfactant-rich phase with the reductant solution as well as the optimal cold vapor generation temperature.

Substantial operative improvements were attained with the home made gas–liquid separator used for the separation of mercury vapor compared to the classical commercial model; including sensitivity and lower memory effects. These could be ascribed to the lower dead volume of proposed model, and the methodology used for waste extraction.

Table 2
Method validation

Aliquots	Base value ($\mu\text{g l}^{-1}$)	Quantity of Hg added ($\mu\text{g l}^{-1}$)	Quantity of Hg found ($\mu\text{g l}^{-1}$)	Recovery (%) ^a
1	–	0.00	0.50 ± 0.02	–
2	0.50	0.50	0.98	96
3	0.50	1.00	1.49	99
4	0.50	3.00	3.54	101
5	0.50	5.00	5.53	100

^a $100 \times [(\text{Found} - \text{base}) / \text{added}]$.

4. Interferences

The effects of representative potential interfering species were tested. Thus, Cu^{2+} , Zn^{2+} , Cd^{2+} , Ni^{2+} , Co^{2+} , Mn^{2+} and Fe^{3+} could be tolerated up to at least $2000 \mu\text{g l}^{-1}$. Commonly encountered matrix components such as alkali and alkaline earth elements generally do not form stable complexes and are not CPE-extracted. The value of the reagent blank signal was not modified by the presence of the potentially interfering ions assayed. A high concentration of 5-Br-PADAP reagent was added in order to guarantee the complete chelation of the analyte even in the presence of interferents.

5. Analytical performance

The relative standard deviation (R.S.D.) resulted from the CPE-FI-CV-ICP-OES analysis of 10 replicates of 50 ml solution containing $0.5 \mu\text{g l}^{-1}$ Hg(II) was 3.4%. The calibration graph was linear with a correlation coefficient of 0.9998 at levels near the detection limits up to at least $50 \mu\text{g l}^{-1}$. The detection limit (DL) was 4 ng l^{-1} , calculated as the amount of mercury required to yield a net peak was calculated considering three times the standard deviation (S.D.) of the background signal (3σ).

The overall time required for loop loading, injection, and FI signal development was approximately 30 s. Thus, the number of determinations per h was approximately 120. By means of CV, an enhancement factor of 100 was achieved respect to ICP-OES using pneumatic nebulization, while the enrichment factor was 200-fold.

6. Method validation

In order to validate this method, 500 ml of tap water were collected and divided into 10 portions of 50 ml each. The proposed method was applied to six portions and the average quantity of mercury obtained was taken as a base value. Then, increasing quantities of mercury were added to the other aliquots, and mercury was determined following the recommended procedure (Table 2). Additionally, the proposed method was applied to a standard reference material, QC METAL LL3 mercury in water, with a mercury content of $6.48 \pm 0.51 \mu\text{g l}^{-1}$. Using the proposed method, the content of mercury determined in this CRM was $6.46 \pm 0.21 \mu\text{g l}^{-1}$ ($\pm 95\%$ confidence interval; $n = 6$).

7. Determination of total mercury in tap water

The method was applied for mercury determination in six different samples of drinking water taken from different points, but all from the same city, San Luis, Argentina. The concentrations were in the range $0.47\text{--}0.53 \mu\text{g l}^{-1}$ of mercury; 95% confidence interval $0.02 \mu\text{g l}^{-1}$. Our obtained results are in good agreement with the mean mercury concentration of $0.30 \mu\text{g l}^{-1}$ reported by Navarro et al. [33].

8. Conclusions

Some of the advantages of the use of micellar systems, comparing their efficiencies with similar extraction systems using conventional procedures with organic solvents [34,35], include experimental convenience, low cost and enhanced analytical

sensitivity due to the fact that the pyridylazo complex can be easily extracted from the bulk aqueous solution into the much smaller volume element of the surfactant-rich phase following phase separation. The results for this work demonstrate the possibility of using the 5-Br-PADAP-PONPE-5 system for the pre-concentration of mercury, since the Hg-5-Br-PADAP complex was quantitatively extracted, and an enrichment factor of 200-fold was obtained. A fast and quantitative generation of cold vapor from the surfactant-rich phase was obtained. The pre-concentration method coupled to mercury cold vapor generation allows mercury determinations in tap water samples at levels of Hg as low as ng l^{-1} with good accuracy and good reproducibility.

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References

- [1] H. Seiler, A. Sigel, H. Sigel, *Handbook on Metals in Clinical and Analytical Chemistry*, Marcel Decker, New York, 1994.
- [2] E.L. Kothny, *Trace Elements in the Environmental*, American Chemical Society, Washington DC, 1973, p. 48.
- [3] J.E. Sánchez Uría, A. Sanz-Medel, Inorganic and methylmercury speciation in environmental samples, *Talanta* 47 (1998) 509–524.
- [4] C.F. Harrington, The speciation of mercury and organomercury compounds by using high-performance liquid chromatography, *Trends Anal. Chem.* 19 (2000) 167–179.
- [5] V. Stresko, J. Polakoviková, J. Kubová, Atomic absorption spectrometric determination of ultra-trace amounts of mercury in waters, *J. Anal. At. Spectrom.* 9 (1994) 1173–1175.
- [6] S. Mc Intosh, The determination of mercury at ultratrace levels using and automated amalgamation technique, *At. Spectrosc.* 14 (2) (1993) 47–49.
- [7] P. Cañada Rudner, J.M. Cano Pavón, F. Sanchez Rojas, A. García de Torres, Use of flow injection cold vapor generation and preconcentration on silica functionalized with methylthiosalicylate for the determination of mercury in biological samples and sea-water by inductively coupled plasma atomic emission spectrometry, *J. Anal. At. Spectrom.* 13 (1998) 1167–1171.
- [8] D.W. Bryce, A. Izquierdo, M.D. Luque de Castro, Continuous microwave assisted pervaporation/atomic fluorescence detection: an approach for speciation in solid samples, *Anal. Chim. Acta* 324 (1996) 69–75.
- [9] L. Jian, W. Goessler, K.J. Irgolic, Mercury determination with ICP-MS: signal suppression by acids, *Fresenius J. Anal. Chem.* 366 (2000) 48–53.
- [10] P. Cañada Rudner, A. García de Torres, M. Cano Pavón, On-line preconcentration and determination of mercury by flow injection inductively coupled plasma atomic emission spectrometry, *J. Anal. At. Spectrom.* 8 (1993) 705–709.
- [11] H. Watanabe, T. Saitoh, T. Kamidate, H. Haraguchi, Distribution of metal chelates between aqueous and surfactant phases separated from a micellar solution of a nonionic surfactant, *Microchim. Acta* 106 (1992) 83.
- [12] E. Pramauro, E. Pelizzetti, *Surfactant in Analytical Chemistry*, Elsevier, New York, 1996.
- [13] E. Pelizzetti, E. Pramauro, Analytical applications of organized molecular assemblies, *Anal. Chim. Acta* 169 (1985) 1–29.
- [14] M.J. Rosen, *Surfactants and interfacial phenomena*, John Wiley and Sons, New York, 1978.
- [15] S.R. Sirimanne, J.R. Barr, D.G. Patterson, Cloud point extraction and capillary electrochromatography: an approach for the analysis of selected environmental toxicants in spiked human serum, *J. Microcolumn Separations* 11 (1999) 109–116.
- [16] N. Maniasso, Ambientes micelares em química analítica, *Quim. Nova* 24 (2001) 87–93.
- [17] M.O. Luconi, M.F. Silva, R.A. Olsina, L.P. Fernández, Cloud point extraction of lead in saliva via use of nonionic PONPE 7.5 without added chelating agents, *Talanta* 51 (2000) 123–129.
- [18] H. Watanabe, H. Tanaka, A non-ionic surfactant as a new solvent for liquid extraction of Zinc(II) with 1-(2-pyridylazo)-2-naphthol, *Talanta* 25 (1978) 585–589.
- [19] P. Frankewich, W.L. Hinze, Evaluation and optimization of the factors affecting nonionic surfactant-mediated phase separations, *Anal. Chem.* 66 (1994) 944–954.
- [20] M.A. Mesquita da Silva, V.L. Azzolin Frescura, A.J. Curtius, Determination of trace elements in water samples by ultrasonic nebulization inductively coupled plasma mass spectrometry after cloud point extraction, *Spectrochim. Acta Part B* 55 (2000) 803–813.
- [21] G. Stangl, R. Niessner, Micellar extraction — a new step for enrichment in the analysis of napropamide, *Intern. J. Environ. Anal. Chem.* 58 (1995) 15–22.
- [22] C. García Pinto, J.L.P. Pavón, B.M. Cordero, E. Romero Beato, S. García Sanchez, Cloud point preconcentration and flame atomic absorption spectrometry: application to the determination of cadmium, *J. Anal. At. Spectrom.* 11 (1996) 37–41.

- [23] A.E. Büyükbayram, M. Volkan, Cloud point preconcentration of germanium and determination by hydride generation atomic absorption spectrometry, *Spectrochim. Acta Part B* 55 (2000) 1073–1080.
- [24] M.A. Mesquita da Silva, V.L. Azzolin Frescura, F.J. Nome Aguilera, A.J. Curtius, Determination of Ag and Au in geological samples by flame atomic absorption spectrometry after cloud point extraction, *J. Anal. At. Spectrom.* 13 (1998) 1369–1373.
- [25] W.L. Hinze, E. Pramauro, A critical review of surfactant-mediated phase separations (cloud point extractions): theory and applications, *Anal. Chem.* 24 (2) (1993) 133–177.
- [26] A. Sanz-Medel, M.R. Fernandez de la Campana, E. Blanco Gonzales, M.L. Fernandez-Sanchez, Organised surfactant assemblies in analytical atomic spectrometry, *Spectrochim. Acta Part B* 54 (1999) 251–287.
- [27] F.H. Quina, W.L. Hinze, Surfactant-mediated cloud point extractions: and environmentally benign alternative separation approach, *Ind. Eng. Chem. Res.* 38 (11) (1999) 4150–4569.
- [28] D.A. Johnson, T.M. Florence, Spectrophotometric determination of uranium(VI) with 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP), *Anal. Chim. Acta* 53 (1971) 73–79.
- [29] W. Fu-Sheng, Z. Yu-Rui, Y. Fang, Spectrophotometric determination of mercury using 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol, *Anal. Lett.* 13 (1980) 1533–1540.
- [30] M.F. Silva, L. Fernandez, R.A. Olsina, D. Stacchiola, Cloud point extraction, preconcentration and spectrophotometric determination of erbium(III)-2-(3,5 dichloro-2-pyridylazo)-5-dimethylaminophenol, *Anal. Chim. Acta* 342 (1997) 229–238.
- [31] M.F. Silva, L. Fernandez, R.A. Olsina, Monitoring the elimination of gadolinium-based pharmaceuticals. Cloud point preconcentration and spectrophotometric determination of Gd(III)-2-(3,5 dichloro-2-pyridylazo)-5-dimethylaminophenol in urine, *Analyst* 123 (1998) 1803–1807.
- [32] P. Freimann, D. Schimidt, Determination of mercury in seawater by cold vapor atomic absorption spectrophotometry, *Fresenius Z. Anal. Chem.* 313 (1982) 200–202.
- [33] M. Navarro, H. Lopez, M. Sánchez, M.C. López, The effect of industrial pollution on mercury levels in water, soil, and sludge in the coastal area of Mortil, Southeast Spain, *Arch. Environ. Contam. Toxicol.* 24 (1993) 11–15.
- [34] K.L. Cheng, K. Ueno, T. Imamura, *Handbook of Organic Analytical Reagents*, Boca Raton, Florida, 1982.
- [35] J. Stary, *The Solvent Extraction of Metal Chelates*, Pergamon Press, New York, 1964.