

On-line Adsorption/Preconcentration Using a Knotted Reactor for Total Hg Determination in Drinking Water by Flow Injection CV-AAS

J.C.A. de Wuilloud^a, R.G. Wuilloud^a, J.A. Gásquez^a, R.A. Olsina^{a, b}, and *L.D. Martínez^{a, b}
^aDepartment of Analytical Chemistry, Faculty of Chemistry, Biochemistry and Pharmacy,
National University of San Luis, Chacabuco y Pedernera, P.O. Box 375, 5700 San Luis, Argentina
^bConsejo Nacional de Investigaciones Científicas y Técnicas (CONICET)

INTRODUCTION

Mercury is considered a highly dangerous element because of its accumulative character in the environment and in biota (1). Mercury is present in all parts of the environment and both inorganic and organic mercury compounds are generated in industrial processes and agriculture (2-4). Therefore, the determination of mercury is very important in environmental and toxicological studies. Mercury enters the human body in drinking water (1-4); hence, its determination in these types of samples is very important. Recent reports (5) estimate a total mercury concentration in natural waters ranging from 0.2 to 100 ng/L; the upper limit for total mercury concentration in drinking water recommended by the European Community being 1 µg/L (4). The lower limit for mercury is not stated in the regulations; however, due to its elevated toxicity, it is convenient to determine it accurately even for concentrations below the recommended upper limit. Since mercury concentrations in non-polluted waters are very low, powerful techniques are required and only few show sufficient sensitivity.

Different analytical methods have been developed for the determination of mercury at low concentrations, and the most commonly used ones are cold vapor atomic absorption spectrometry (CV-AAS), cold vapor atomic fluorescence spectrometry (CV-AFS), inductively coupled plasma atomic optical emission spectrometry (ICP-OES), and inductively coupled plasma mass spectrometry (ICP-MS) (6-12).

*Corresponding author.
e-mail: ldm@usnl.edu.ar

ABSTRACT

An on-line mercury preconcentration and analysis system using atomic absorption spectrometry (AAS) and flow injection (FI) with cold vapor (CV) generation was studied. The mercury was retained as a mercury-2-(5-bromo-2-pyridylazo)-5-diethylaminophenol [Hg(II)-(5-Br-PADAP)] complex, at pH 9.2. The mercury complex was removed from the knotted reactor (KR) with 3 mol/L hydrochloric acid. An enrichment factor of 25 was obtained with respect to CV-AAS. The detection limit for the preconcentration of 25 mL aqueous solution was 5 ng/L. The precision, calculated at peak height for 10 replicate determinations at the 1 µg/L-Hg level, was 2.8% relative standard deviation (RSD). The calibration curve using the preconcentration system for mercury was linear with a correlation coefficient of 0.9995 at levels near the detection limits up to at least 100 µg/L. The method was successfully applied to the determination of mercury in drinking water samples.

Although CV-AAS is the most common technique for trace level determination of mercury, the low-level mercury concentrations in drinking water are not compatible with the detection limits of this technique (13,14). Therefore, almost all applied procedures with CV-AAS are based on the separation and preconcentration of mercury from an initially large water sample, followed by its determination. The preconcentration methods usually used are sorption (15,16), amalgamation on silver or gold (17-19), or extraction (20,21).

Flow injection on-line preconcentration based on the sorption of metallic complexes on the inner

walls of a PTFE knotted reactor (KR) has been successfully applied. Most studies using KRs have coupled the KR to flame atomic absorption spectrometry (FAAS) (22,23) or to electrothermal atomic absorption spectrometry (ETAAS) (24-28). Otherwise, the most widely used reagents for metal preconcentration in KR have been diethyldithiocarbamate (DDTC) (24,28) and ammonium pyrrolidine dithiocarbamate (APDC) (25,28). Pyridylazo reagents form insoluble chelates with numerous metallic ions. 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP) has been used as a reagent in the spectrophotometric determination of numerous metallic ions (29-31), including mercury (29,32). However, precautions had to be taken in order to avoid the precipitation of the corresponding chelate, such as addition of a surfactant agent. This fact suggested to us that, in the absence of a surfactant, 5-Br-PADAP could be a suitable reagent for preconcentration of mercury on the KR. In fact, we have reported (33) its application in preconcentration systems with the KR coupled to ICP-OES. Knotted reactors have been used for the preconcentration of many elements, but no references in the literature have been found to its application on mercury preconcentration coupled with hydride generation and cold vapor systems.

In the present work, a method for the preconcentration and determination of mercury using a KR is proposed. Mercury was retained in the form of a Hg(II)-(5-Br-PADAP) complex. The determination was performed using CV-AAS coupled with FI methodology. All variables related to cold vapor generation from the particular eluent solution

in the presence of the complexing reagent were studied.

EXPERIMENTAL

Instrumentation

The measurements were performed with a Shimadzu AA-6800 atomic absorption spectrometer equipped with a 15-cm long (0.8-cm i.d.) absorption cell. The AAS and cold vapor generator operating conditions are listed in Table I. A Gilson® Minipuls 3 peristaltic pump (Villiers-Le-Bell, France) was used. Sample injection was achieved using a Rheodyne® (Cotati, CA, USA) Model 50, four-way rotary valve. For sorption of the complex, a KR was made from a 2-m long PTFE tubing (0.5-mm i.d.) by tying interlaced knots of approximately 5-mm diameter loops. Tygon™-type pump tubing (Ismatec, Cole-Parmer, Vernon Hills, IL, USA) was employed to carry the sample, reagent, and eluent.

A home-made gas-liquid separator was used (Figure 1) for the separation of mercury vapor. The dimensions were as follows: 95-mm long, 15-mm i.d.. Two inlets were present: one for the gas-liquid mixture and another for nitrogen. Continuous waste extraction was accomplished with a peristaltic pump and the whole device was connected to the quartz cell.

Reagents

A 10^{-2} mol/L solution of 5-Br-PADAP (Aldrich, Milwaukee, WI, USA) was prepared by dissolution in ethanol. Lower concentrations were prepared by serial dilution.

A stock mercury standard (1000 µg/mL) was prepared from Hg(II) chloride (Merck, Darmstadt, Germany) in nitric acid and made to 1000-mL volume with ultrapure water.

The buffer solution (0.05 mol/L) was prepared dissolving sodium tetraborate calcined and brought to 1000-mL volume with ultrapure water.

AAS Conditions	
Lamp	Mercury hollow cathode lamp
Lamp current	6 mA
Slit width	0.7 nm
Quartz cell dimensions	150 mm x 8.0 mm (i.d.)
Analytical line: Hg	253.7 nm
Cold Vapor Generator Conditions	
NaBH ₄ concentration	1.0% (m/v)
HCl concentration	3 mol/L
HCl solution flow rate	5 mL/min
NaBH ₄ solution flow rate	3 mL/min
Carrier gas flow rate	0.5 L/min

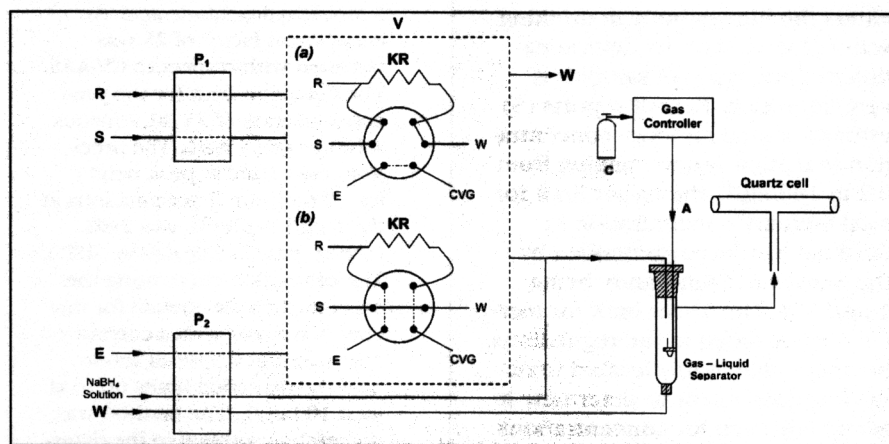


Fig. 1. Schematic diagram of instrumental setup. R: 5×10^{-5} mol/L 5-Br-PADAP solution (3.0 mL/min) S: sample (flow rate: 5.0 mL/min), E: eluent (flow rate: 5.0 mL/min), C: N₂ (flow rate: 0.5 L/min), CV: cold vapor generation, W: waste, P₁, P₂: peristaltic pumps, V: injection valve, KR: Knotted Reactor. Valve positions: (a) sample loading; (b) injection.

Sodium tetrahydroborate reagent was freshly prepared daily by dissolving the appropriate amount of NaBH₄ (Merck, Darmstadt, Germany) in 0.5% (m/v) sodium hydroxide solution (Merck, Darmstadt, Germany). After dissolution of the reagents, the solution was filtered through a 0.45-mm pore size membrane filter (Millipore Corporation, Bedford, MA, USA).

Hydrochloric acid (Merck, Darmstadt, Germany) was of ultrapure reagent grade.

Ultrapure water (18 MΩ/cm) was obtained from EASYpure RF (Barnstedt, Iowa, USA).

All reagents were of analytical reagent grade and the presence of mercury was not detected in the working range.

Sample Collection and Preparation

To obtain the samples, tap water was allowed to run for 20 minutes before approximately 1000 mL was collected. The water samples were previously acidified with nitric acid to pH = 2 and then filtered through

0.45- μm pore size membrane filters immediately after sampling. All glass instruments used were previously washed with a 10% (v/v) HNO_3 water solution and ultrapure water.

Preconcentration and Determination Procedure

The aqueous sample solution (0.01 mol/L hydrochloric acid) containing mercury (at a flow rate of 5.0 mL/min), and 5-Br-PADAP 5×10^{-5} mol/L (at a flow rate of 3.0 mL/min) buffered to pH 9.2 with sodium tetraborate (final concentration 5×10^{-3} mol/L), was mixed on-line to form the metal complex. This mixture was then loaded on the KR for 5 minutes with valve V in load position (Figure 1a). Finally, peristaltic pump P_1 was stopped, and the injection valve V was switched on to the injection position (Figure 1b). The retained metal complex was then eluted with 3 mol/L hydrochloric acid at a flow rate of 5.0 mL/min. This solution was mixed with 1.0% (m/v) NaBH_4 (at a flow rate of 3.0 mL/min) in 0.5% (m/v) NaOH , and carried directly to the gas-liquid separator and AAS. The operating conditions were established and the determination was carried out. FI system measurements were expressed as peak height absorption, which was corrected against the reagent blank. The measurements were expressed as peak height since the software used could not express them as peak areas. The obtained peaks were sharp, which permitted us to determine their maximum height with precision. This can be observed from the linear calibration curve which has a correlation coefficient of 0.9995.

Method Validation

In order to demonstrate the validity of this method, 1 L drinking water was collected and divided into 10 portions of 100 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 of sample and mercury was determined by the same method (Table II). Additionally, the proposed method was applied to National Institute of Standards and Technology standard reference material, NIST SRM 1641d Mercury in Water, with a mercury content of 1.590 ± 0.018 mg/kg; the density of SRM 1641d at 22°C is 1.007 g/mL. Using the proposed method, the content of mercury determined in this SRM was 1.572 ± 0.000025 mg/kg.

RESULTS AND DISCUSSION

Effect of pH on Preconcentration Performance

The study of the preconcentration variables was performed by modifying one variable at a time,

while keeping the others constant. The influence of the pH on the degree of preconcentration was studied in the pH interval between 5 and 12. The mercury signal was monitored by measuring it with CV-AAS at various pHs of the solution that passes through the KR. It can be seen from Figure 2 that the optimum pH range to achieve best performance of the preconcentration system is 8 to 10.3. According to these results, pH 9.2 was selected.

Sample Solution Flow Rate

The sample flow rate through the KR is an important parameter since it is related to the magnitude of the centrifugal force generated by the knots. Therefore, the sample flow rate determines the possibility that the precipitate particles impinge against the KR walls (34). Furthermore, this is one of the steps that controls the time of

TABLE II
Method Validation

Aliquots	Base Value ($\mu\text{g/L}$)	Quantity of Hg added ($\mu\text{g/L}$)	Quantity of Hg found ($\mu\text{g/L}$)	Recovery (%) ^a
1	—	0.000	0.352 ± 0.020	—
2	0.352	1.000	1.327	97.5
3	0.352	3.000	3.310	98.6
4	0.352	5.000	5.352	100.0
5	0.352	10.000	10.332	99.8

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

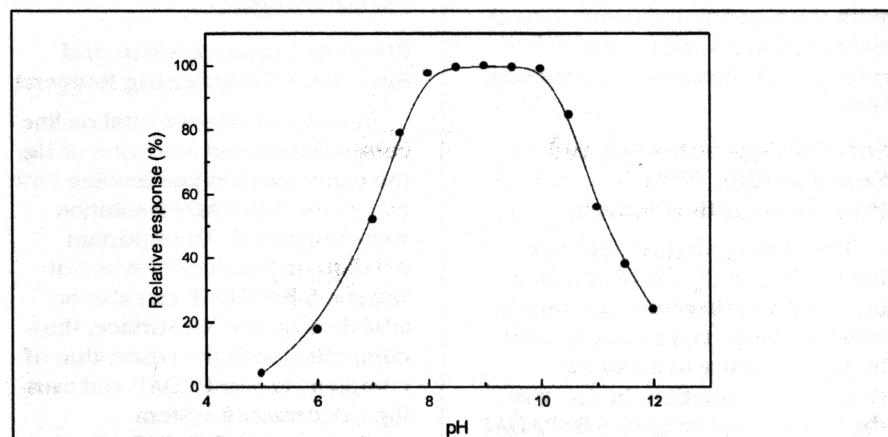


Fig. 2. Dependence of Hg preconcentration on pH of loading solutions. Preconcentration time was 5 min and the loading flow rate was 5 mL/min. Hg concentration was $20 \mu\text{g l}^{-1}$; 5-Br-PADAP concentration was 5×10^{-5} mol/L.

analysis. The optimum sample loading flow rate was achieved at 5 mL/min, which enables an enrichment factor (EF) value of 25.

Evaluation of Optimum KR Length

An important parameter to be optimized was KR length. Good results were obtained for a length of 200 cm; further increases in length did not show any improvement in the enhancement factors. No significant increase of the signal dispersion was detected when increasing the reactor length.

Influence of Preconcentration Time Hg Retention

An important variable in the study of preconcentration with a KR is the preconcentration time, since it indicates the retention capacity of the KR. The preconcentration time also influences the degree of surface saturation, which affects the retention capacity. The dependence of the percent of recovery of mercury on sample loading time is shown in Figure 3. The highest enrichment factor (EF) variation was obtained up to a preconcentration time of 5 minutes. Longer times did not substantially modify the EF value, which could indicate a saturation of the KR retention capacity. Therefore, in order to obtain a high enhancement factor compatible with the mercury concentrations in the samples, a loading time of 5 minutes was used for preconcentration.

Solvent Concentration and Compatibility With Preconcentration System

The complexing reagent 5-Br-PADAP is slightly soluble in aqueous medium; therefore, an organic solvent or a surfactant agent must be used in order to avoid the reagent precipitation. In this way, the solutions of reagent 5-Br-PADAP were prepared with ethanol as the organic solvent. It was observed that with 10% (v/v) of ethanol, 5-Br-

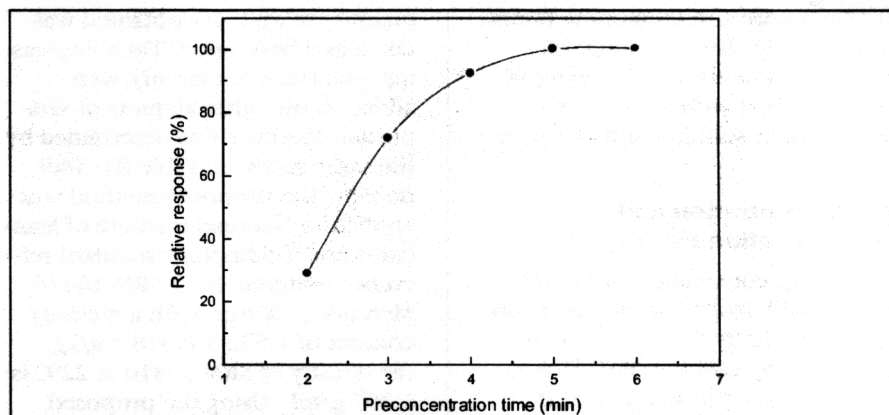


Fig. 3. Influence of preconcentration time on response obtained. Loaded flow rate was 5 mL/min; the elution flow rate was 5.0 mL/min; Hg concentration was $20 \mu\text{g L}^{-1}$; 5-Br-PADAP concentration was $5 \times 10^{-5} \text{ mol/L}$.

PADAP remained in solution up to concentrations on the order of 10^4 mol/L . The influence of ethanol concentration on the preconcentration of complex Hg-5-Br-PADAP was assessed. The preconcentration decreased when ethanol concentrations above 20% (v/v) were used in the 5-Br-PADAP solution. This can be accounted for by considering the higher solubility of the Hg-5-Br-PADAP complex when increasing the solvent concentration, which hinders its precipitation and adsorption on the KR walls. The ethanol concentration was set at 5% (v/v), which enabled to achieve stability of the complexation reagent solution and efficiency of the system for preconcentration of the Hg-5-Br-PADAP complex.

Effect of Concentration and Flow Rate Complexing Reagent

In order to achieve total on-line complexation and retention of Hg, the concentration and loading flow rate of the 5-Br-PADAP solution were optimized. An important detail to be considered was that reagent 5-Br-PADAP can also be adsorbed on the KR surface, thus competing with the adsorption of complex Hg-5-Br-PADAP and causing a decrease in system performance. A 5-Br-PADAP concentration of $5 \times 10^{-5} \text{ mol/L}$ was found to be compatible with the

performance of preconcentration. The optimum load rate of the 5-Br-PADAP solution, which produced best results with regard to efficiency of the on-line preconcentration process, was 3.0 mL/min.

Study of Hg Vapor Generation From the Eluent Solution

Cold vapor generation from the eluent solution of the retained complex was carefully studied in order to reach the conditions of maximum sensitivity. The NaBH_4 concentration was an important parameter to be optimized so that it permitted cold vapor generation even in the presence of the complexing reagent. It was verified that the best signal-to-noise ratio was obtained with a concentration of 1.0% (m/v). It can be seen in Figure 4a that higher concentrations of the reducing agent did not lead to important signal changes. Hence, the above-mentioned NaBH_4 concentration was adopted as the working concentration. The HCl concentration most suitable and compatible with the preconcentration and cold vapor generation systems was also studied. The results obtained show (Figure 4b) that maximum response for both systems was obtained at concentrations above 2.5 mol/L HCl. Hence, 3 mol/L HCl was adopted as the working concentration.

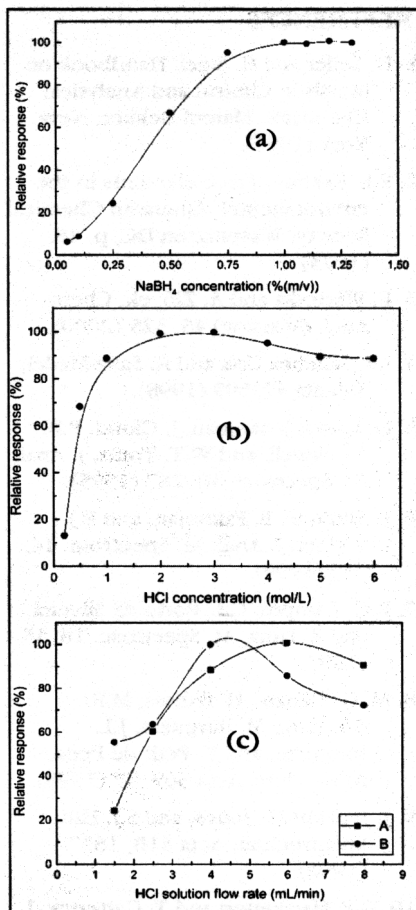


Fig. 4. (a): Effect of NaBH₄ concentration. (b): Effect of HCl concentration. (c): Effect of HCl solution flow rate on cold vapor generation (A) and preconcentration (B) responses. Sample loading period was 5 min; loading flow rate 5 mL/min; elution flow rate 5.0 mL/min, 5-Br-PADAP concentration 5×10^{-5} mol/L; and Hg concentration $20 \mu\text{g L}^{-1}$.

The elution rate of the retained complex was studied in order to match the optimum elution complex from the KR with the optimum cold vapor generation conditions. To do this, the behavior of the preconcentration system at different eluent solution flow rates was analyzed and compared with the effect of the carrier (eluent) solution rate on the response of the cold vapor generation system. As can be observed from Figure 4c, the optimum flow rates in each

case do not match. Therefore, in order to obtain working conditions compatible with both systems, a HCl solution flow rate of 5 mL/min was adopted. Improvements in sensitivity and a lower memory effect were obtained with the homemade gas-liquid separator used for separation of the mercury vapor in comparison to the classical commercial model. These results could be ascribed to the lower dead volume of the proposed model.

Complex Removal Conditions From KR and Elution Profiles

Selection of the eluent for the complex was critical, since it had to allow both easy removal of the Hg-5-Br-PADAP complex and be compatible with a suitable generation of cold vapor. Hydrochloric acid turned out to be a good eluent for the Hg-5-Br-PADAP complex with 3 mol/L as the minimum concentration necessary to obtain the best response. Besides, this acid concentration matches the mercury vapor generation process in the subsequent cold vapor system. The effect of the eluent flow rate was studied, and the best CV-AAS signal was achieved at 5 mL/min. Under these conditions, the Hg-5-Br-PADAP complex retained was rapidly eluted from the KR, which can be verified by observation of the corresponding elution profile in Figure 5.

Interferences

The effects of potentially interfering species were tested at levels found in the sample. Thus, Cu²⁺, Zn²⁺, Cd²⁺, Ni²⁺, Co²⁺, Mn²⁺, and Fe³⁺ could be tolerated up to at least 2000 $\mu\text{g/L}$. Commonly encountered matrix components such as alkali and alkaline earth elements generally do not form stable complexes and are not retained on the KR. The value of the reagent blank signal was not modified in the presence of the potentially interfering ions assayed.

Performance of Preconcentration System

The overall time required for preconcentration of 25 mL of sample (5 minutes at flow rate of 5 mL/min), elution (approx. 0.2 minutes at flow rate of 5.0 mL/min) and washing (0.2 minutes at flow rate of 5.0 mL/min) was about 5.4 minutes. Thus, sample throughput was about 11 samples per hour. An enrichment factor of 25 was obtained with respect to CV-AAS.

Determination of Hg in Drinking Water Samples

The relative standard deviation (RSD) for 10 replicates containing 1 $\mu\text{g/L}$ of Hg was 2.8%. The calibration curve was linear with a correlation coefficient of 0.9995 at levels near the detection limits up to at least 100 $\mu\text{g/L}$. The detection limit (DL), calculated as the amount of mercury required to yield a net peak that was equal to three times the standard deviation of the background signal (3σ), was 5 ng/L. Finally, the results of the method applied to mercury determination in drinking water samples are shown in Table III. The Hg concen-

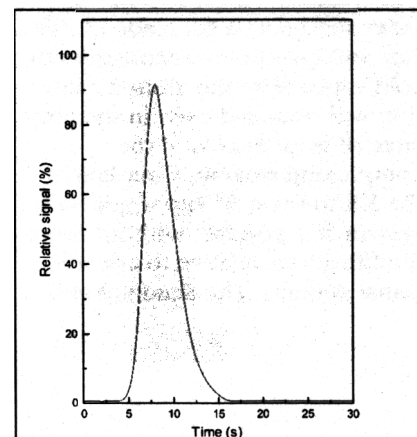


Fig. 5. Peak profile obtained by preconcentration of 25 mL of sample using the system depicted in Figure 1. Loading flow rate 5 mL/min; elution flow rate 5.0 mL/min; Hg concentration $10 \mu\text{g L}^{-1}$; and 5-Br-PADAP concentration was 5×10^{-5} mol/L.

TABLE III
Concentrations of Hg in Drinking Water Samples
(95% confidence interval; n=6)

Sample	Hg concentration ($\mu\text{g/L}$)
1	0.352 ± 0.020
2	0.325 ± 0.019
3	0.290 ± 0.018
4	0.122 ± 0.024
5	0.091 ± 0.030

trations were in the 0.091 - 0.352 $\mu\text{g/L}$ range. The results obtained are in good agreement with those of Navarro et al. (35); the mean values of mercury concentration reported in waters by these authors are 0.30 $\mu\text{g/L}$.

CONCLUSION

The on-line coupling of a FI sorption preconcentration system with a knotted reactor to FI-CV-AAS increases the speed of the preconcentration and analysis processes as well as reducing sample consumption and contamination risks. The results of this work demonstrate the possibility of using 5-Br-PADAP for preconcentration of mercury, since the Hg-5-Br-PADAP complex was effectively adsorbed on the inner surface of a KR made of PTFE. Fast and quantitative generation of cold vapor from the elution solution was obtained even in the presence of great excess of the complexing reagent. Coupling of the KR to the cold vapor generation system was possible without major modifications relative to conventional systems. The dead volume in

the proposed separator was kept constant and to minimum value, which allowed increased reproducibility of the FI system and decreased the dispersion of the transient signals generated. The proposed system of preconcentration associated with mercury cold vapor generation allows mercury determinations in drinking water samples at levels as low as $\mu\text{g L}^{-1}$ or less. The quantification of Hg in other samples such as river and seawater is a possibility provided the experimental conditions are adequately adjusted. The determination procedure shows good reproducibility and accuracy.

ACKNOWLEDGMENTS

This work was supported by Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET); Agencia Nacional de Promoción Científica y Tecnológica (FONCYT) (PICT-BID); FOMEC program and Universidad Nacional de San Luis (Argentina).

Received June 15, 2001.

REFERENCES

1. H. Seiler and H. Sigel, *Handbook on Metals in Clinical and Analytical Chemistry*, Marcel Dekker, New York (1994).
2. E.L. Kothny, *Trace elements in the environmental*, American Chemical Society, Washington DC, p. 48, (1973).
3. E. Wieteska and A. Zió_ek, *Chem. Anal. (Warsaw)* 45, 325 (2000).
4. J.E. Sánchez Uría and A. Sanz-Medel, *Talanta* 47, 509 (1998).
5. D. Cossa, J. Sanjuan, J. Cloud, P.B. Stockwell, and W.T. Toms, *J. Anal. At. Spectrom.* 10, 287 (1995).
6. J. Allibone, E. Fatemian, and P.J. Walker, *J. Anal. At. Spectrom.* 14, 235 (1999).
7. R.C. Campos, C.L. Porto da Silveira, and R. Lima, *At. Spectrosc.* 18, 55 (1997).
8. M. Gallignani, H. Bahsas, M.R. Brunetto, M. Burguera, J.L. Burguera, and Y. Petit de Peña, *Anal. Chim. Acta* 369, 57 (1998).
9. J. Murphy, P. Jones, and S.J. Hill, *Spectrochim. Acta* 51B, 1867 (1996).
10. C.F. Harrington and T. Catterick, *J. Anal. At. Spectrom.* 12, 1053 (1997).
11. K.C. Bowles and S.C. Apte, *Anal. Chem.* 70, 395 (1998).
12. Y. Cai, R. Jaffé, A. Alli, and R.D. Jones, *Anal. Chim. Acta* 334, 251 (1996).
13. S. McIntosh, *At. Spectrosc.* 14, 47 (1993).
14. S. McIntosh, J. Baasner, Z. Grosser, and C. Hanna, *At. Spectrosc.* 15, 161 (1994).
15. H. Emteborg, D.C. Baxter, and W. Frech, *Analyst* 118, 1007 (1993).
16. M.F. García, R.P. García, N.B. García, and A. Sanz-Medel, *Talanta* 41, 1833 (1994).
17. R.J. Watling, *Anal. Chim. Acta* 75, 281 (1975).
18. Y. Nojiri, A. Otsuki, and K. Fuwa, *Anal. Chem.* 53, 544 (1986).
19. E. Saouter, *Anal. Chem.* 66, 2031 (1994).

20. K. Chiba, K. Yoshida, K. Tanabe, H. Haraguchi, and K. Fuwa, *Anal. Chem.* 54, 450 (1983).
21. J. Yamamoto, Y. Kaneda, and Y. Hikasa, *Int. J. Environ. Anal. Chem.* 16, 1 (1983).
22. Z. Fang, M. Sperling, and B. Welz, *J. Anal. At. Spectrom.* 6, 301 (1991).
23. H. Chen, S. Xu, and Z. Fang, *Anal. Chim. Acta* 298, 167 (1994).
24. M. Sperling, X. Yan, and B. Welz, *Spectrochim. Acta* 51B, 1891 (1996).
25. S. Nielsen and E. Hansen, *Anal. Chim. Acta* 366, 163 (1998).
26. E. Ivanova and F. Adams, *Fresenius J. Anal. Chem.* 361, 445 (1998).
27. E. Ivanova, X.-P. Yan, W. van Mol, and F. Adams, *Analyst* 122, 667 (1997).
28. E. Ivanova, K. Benkhedda, and F. Adams, *J. Anal. At. Spectrom.* 13, 527 (1998).
29. D.A. Johnson and T.M. Florence, *Anal. Chim. Acta* 53, 73 (1971).
30. L. Martinez, J. Gasquez, R. Olsina, and E. Marchevsky, *Chem. Anal. (Warsaw)* 41, 275 (1996).
31. L. Martinez, E. Perino, E. Marchevsky, and R. Olsina, *Talanta* 40, 385 (1993).
32. W. Fu-Sheng, Z. Yu-Rui, and Y. Fang, *Anal. Letters* 13, 1533 (1980).
33. R.G. Wuilloud, J.A. Salonia, R.A. Olsina, and L.D. Martinez, *Spectrochim. Acta* 55B, 671 (2000).
34. Z.-L. Fang, *Flow Injection Separation and Preconcentration*, VCH, Weinheim (1993).
35. M. Navarro, H. Lopez, M. Sánchez, and M. C. López, *Arch. Environ. Contam. Toxicol.* 24, 11 (1993).