



## NRC Publications Archive Archives des publications du CNRC

### **A novel approach to cold vapor generation for the determination of mercury in biological samples**

dos Santos, Eder José; Herrmann, Amanda Beatriz; Azzolin Frescura, Vera Lúcia; Sturgeon, Ralph Edward; Curtius, Adilson José

This publication could be one of several versions: author's original, accepted manuscript or the publisher's version. / La version de cette publication peut être l'une des suivantes : la version prépublication de l'auteur, la version acceptée du manuscrit ou la version de l'éditeur.

For the publisher's version, please access the DOI link below. / Pour consulter la version de l'éditeur, utilisez le lien DOI ci-dessous.

#### **Publisher's version / Version de l'éditeur:**

<https://doi.org/10.1590/S0103-50532008000500018>

*Journal of the Brazilian Chemical Society*, 19, 5, 2008

#### **NRC Publications Record / Notice d'Archives des publications de CNRC:**

<https://nrc-publications.canada.ca/eng/view/object/?id=13c5cbda-fa8c-4c39-9380-37dfa3e2239b>

<https://publications-cnrc.canada.ca/fra/voir/objet/?id=13c5cbda-fa8c-4c39-9380-37dfa3e2239b>

Access and use of this website and the material on it are subject to the Terms and Conditions set forth at

<https://nrc-publications.canada.ca/eng/copyright>

READ THESE TERMS AND CONDITIONS CAREFULLY BEFORE USING THIS WEBSITE.

L'accès à ce site Web et l'utilisation de son contenu sont assujettis aux conditions présentées dans le site

<https://publications-cnrc.canada.ca/fra/droits>

LISEZ CES CONDITIONS ATTENTIVEMENT AVANT D'UTILISER CE SITE WEB.

**Questions?** Contact the NRC Publications Archive team at

PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca. If you wish to email the authors directly, please see the first page of the publication for their contact information.

**Vous avez des questions?** Nous pouvons vous aider. Pour communiquer directement avec un auteur, consultez la première page de la revue dans laquelle son article a été publié afin de trouver ses coordonnées. Si vous n'arrivez pas à les repérer, communiquez avec nous à PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca.



## A Novel Approach to Cold Vapor Generation for the Determination of Mercury in Biological Samples

Eder José dos Santos,<sup>\*,a</sup> Amanda Beatriz Herrmann,<sup>a</sup> Vera Lúcia Azzolin Frescura,<sup>b</sup>  
Ralph Edward Sturgeon<sup>c</sup> and Adilson José Curtius<sup>b</sup>

<sup>a</sup>Instituto de Tecnologia do Paraná, TECPAR, 81350-010 Curitiba-PR, Brazil

<sup>b</sup>Departamento de Química, Universidade Federal de Santa Catarina, 88040-900 Florianópolis-SC, Brazil

<sup>c</sup>Institute for National Measurement Standards, National Research Council Canada, ON K1A 0R9, Ottawa, Canada

Propõe-se uma nova maneira de gerar vapor de mercúrio em altos valores de pH pela adição de NaOH ou de outra base a uma solução contendo íons de mercúrio, sem utilizar redutor, como NaBH<sub>4</sub> ou SnCl<sub>2</sub>. Após dissolução total da amostra em sistema de microondas fechado, empregando HNO<sub>3</sub> e H<sub>2</sub>O<sub>2</sub>, o pH da solução da amostra é elevado para 13 com NaOH. Após 90 min de repouso, o vapor frio é transportado até o plasma por um fluxo de gás argônio. O Hg é determinado em 253,652 nm em um espectrômetro de emissão óptica com plasma indutivamente acoplado com configuração axial. O procedimento foi aplicado a cinco amostras biológicas certificadas obtendo-se um limite de detecção (3s, n = 10) de 0,04 µg g<sup>-1</sup> para uma massa da amostra de 0,5 g em um volume final de 50 mL. A calibração foi realizada com soluções padrão aquosas em NaOH 0,1 mol L<sup>-1</sup>. O procedimento foi eficiente, com recuperações dos valores certificados entre 85 e 113%, demonstrando concordância entre o valor encontrado e o certificado para um nível de 95% de confiança (teste-t). A precisão apresentou resultados aceitáveis com desvios padrão relativos de 7 a 9%. Mercúrio a partir de espécies orgânicas em solução, não foi detectado; somente Hg<sup>2+</sup> em solução produz sinal. O procedimento é novo, simples, pode permitir estudos de especiação e serve para demonstrar liberação de vapor de mercúrio de soluções aquosas em altos valores de pH.

A novel approach to the generation of mercury vapor at high pH by the simple addition of NaOH or other base to a solution containing mercury ions is described. Subsequent addition of another reducing agent, such as NaBH<sub>4</sub> or SnCl<sub>2</sub>, is unnecessary. Following total dissolution of sample using HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> in a closed microwave vessel, the pH of the sample solution is increased to 13 by the addition of NaOH. After standing for 90 min in a closed vessel, the Hg<sup>0</sup> is directed to the plasma by a flow of argon. Emission from mercury is measured at 253.652 nm by an axial view inductively coupled plasma optical emission spectrometer (ICP OES). The procedure was applied to five certified biological samples, yielding a detection limit (3s, n = 10) of 0.04 µg g<sup>-1</sup> based on a nominal sample mass of 0.5 g in a final volume of 50 mL. Calibration was achieved using simple aqueous standard solutions containing 0.1 mol L<sup>-1</sup> NaOH. The procedure was efficient, with determined values lying in the range of 85-113 % of the certified values, showing good agreement at the 95% confidence level (t-test). The precision was fit for purpose, with relative standard deviations ranging from 7 to 9%. Organomercury species in solution were not detected; only Hg<sup>2+</sup> in solution produces a signal. This new procedure provides for a simple approach to quantitation (and potentially speciation).

**Keywords:** mercury, alkaline pH, inductively coupled plasma optical emission spectrometry, cold vapor generation, biological samples

### Introduction

The chemical transformation of an analyte species to a volatile form is known as chemical vapor generation

(CVG). The main advantages of CVG are the separation of the analyte from the matrix and high sample introduction efficiency, resulting in enhanced sensitivity, selectivity and detection limits.<sup>1</sup> This is a widely utilized methodology in atomic spectrometry for the determination of trace and ultra-trace concentrations of elements such as As, Sb, Bi,

\*e-mail: eder@tecpa.br

Ge, Pb, Hg, Se, Te and Sn. Currently,  $\text{NaBH}_4$  remains the most popular reagent for CVG, forming volatile species of not only the aforementioned elements, but also of Ag, Au, Cd, Cu, In, Ni, Pt, Rh, Tl, and Zn with important analytical applications.<sup>1-4</sup> Several alternative means of CVG, not using  $\text{NaBH}_4$ , have also been proposed: electrochemical vapor generation;<sup>5</sup> alkylation reactions, such as those using Grignard reagents (e.g., for tributyltin with pentylmagnesium bromide<sup>1</sup>) and, more recently, photochemical vapor generation with UV irradiation. Examples of the latter include generation of volatile species of Se(IV) in formic, acetic and propionic acids (with formation of  $\text{SeH}_2$ , dimethylselenium and diethylselenium respectively<sup>6</sup>) and of Ni by reaction with CO (yielding  $\text{Ni}(\text{CO})_4$ <sup>7</sup>). There is a particular interest in the determination of Hg because of its toxicity, mobility and ability to accumulate in various organisms. Cold vapor (CV) generation coupled to atomic absorption (AAS) or atomic fluorescence spectrometry (AFS) are the techniques most frequently used for detection.<sup>8-10</sup> In addition, photochemical vapor generation<sup>11-13</sup> and ultrasound-assisted vapor generation<sup>14,15</sup> have recently been proposed.

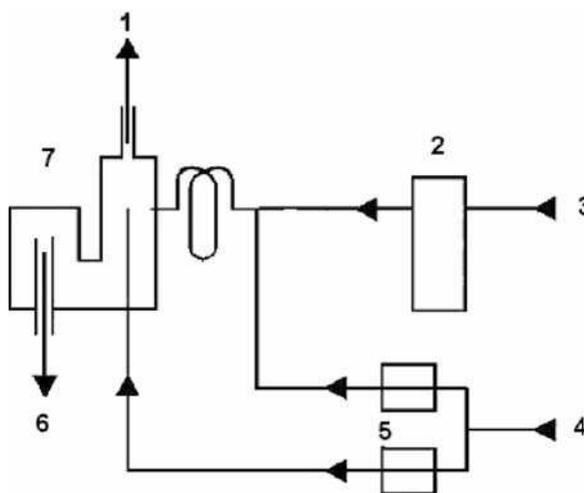
We have found that mercury ions in aqueous solution can be reduced to elemental mercury by simply increasing the pH of the solution through addition of NaOH or other base, without the need for any additional reducing agent. Taking into account this finding, an analytical method for the determination of mercury by CV-ICP OES is presented herein.

## Experimental

### Instrumentation

All measurements were made using a simultaneous axial view ICP OES spectrometer, model VISTA PRO (Varian, Mulgrave, Australia), coupled to an on-line continuous vapor generation system (Varian, model VGA-76P). Within the VGA-76P system, the argon gas supply is divided into two branches by a suitable "T" piece. One branch is controlled by a solenoid stop valve and argon gas to the inlet side of the reaction coil. The other branch supplies argon gas directly through the gas/liquid separator. With this system, only the sample line was employed, using 2.90 mm i.d medical grade PVC purple/black tubing (Kendall No. 1160549160) for the sample treated with NaOH. A scheme illustrating the vapor generation system coupled to the ICP OES spectrometer is shown in Figure 1. The experimental conditions are summarized in Table 1. Peak height emission intensities were measured at 253.652 nm. Argon (99.996% purity, White Martins, São Paulo, Brazil)

was used. Samples were totally digested in a closed CEM microwave system (model MDS 2100, Matthews, NC, USA). A Shimadzu model AA-6601F single beam atomic absorption spectrometer (Nakagyo-Ku, Kyoto, Japan) equipped with deuterium lamp background correction and Hg hollow cathode lamp L233 from Hamamatsu Photonics K.K. (Shizuoka, Japan) was used to verify the generation of  $\text{Hg}^0$ .



**Figure 1.** Scheme of chemical vapor generation system (Varian model VGA-76P): 1. to the ICP OES; 2. peristaltic pump (50 rpm); 3. sample (flow rate of 8 mL min<sup>-1</sup>); 4. carrier gas flow rate (120 mL min<sup>-1</sup>); 5. flow controller; 6. drain (Nalgene tubing); 7. phase separator.

**Table 1.** Instrumental parameters for ICP OES and cold vapor generation

ICP OES	
Radiofrequency	40 MHz
Radiofrequency power	1.2 kW
Plasma gas flow rate	15.0 L min <sup>-1</sup>
Auxiliary gas flow rate	1.5 L min <sup>-1</sup>
Replicate read time	3 s
Stabilization time	35 s
Replicates	4
Torch	Quartz for axial view
Analytical line	253.652 nm
<i>Vapor generator</i>	
Sample flow rate	8 mL min <sup>-1</sup>
Carrier gas flow rate	120 mL min <sup>-1</sup>

### Reagents and materials

All chemicals were of analytical grade, unless otherwise specified. High purity water (resistivity of 18.2 M $\Omega$  cm) was de-ionized in a Milli-Q system (Bedford, MA, USA). The following reagents were used: Suprapur<sup>®</sup> 65% v/v  $\text{HNO}_3$  (Merck, Darmstadt, Germany No. 1.00441.1000), sodium hydroxide (Merck, No. 1.06498.1000), 30% (v/v) hydrogen

peroxide (Merck No. 1.07210.1000), 1000  $\mu\text{g mL}^{-1}$  Hg standard solution (Merck No. 1.19795.0500). A Thimerosal stock solution, containing 100  $\mu\text{g L}^{-1}$  of Hg, was prepared by dissolving the salt ( $\text{C}_9\text{H}_9\text{HgNaO}_2\text{S}$ ) (Merck No. 8.17043.0100) in water. A methylmercury chloride stock solution was prepared by dissolving  $\text{CH}_3\text{HgCl}$  (Fluka, 98% m/m purity) in ethanol (Merck No. 1.00983.1000).

The following certified reference materials were analyzed: DOLT-2 (Dogfish Liver), TORT-2 (Lobster Hepatopancreas) and DORM-1 (Dogfish Muscle) from the National Research Council Canada (NRCC, Ottawa, Ontario, Canada); BCR 186 (Lyophilized Pig Kidney), from the European Community Bureau of Reference (Brussels, Belgium); SRM 1566a (Oyster Tissue) from the National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA).

### Procedures

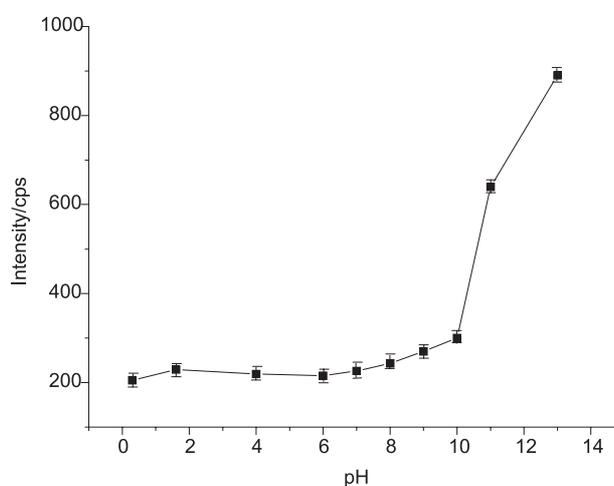
Nominal 0.1-0.5 g samples of biological tissue were weighed into each microwave vessel (Advanced Composite Vessel, from CEM), followed by the addition of 5 mL concentrated  $\text{HNO}_3$  and 2.5 mL of 30% (v/v)  $\text{H}_2\text{O}_2$ . After standing for 1 h, the samples were digested in the microwave system in accordance with EPA method SW 846-3051 (closed vessel). The resultant clear solutions were transferred to 50 mL volumetric flasks. Sufficient NaOH was added to each digested sample solution to achieve pH 13 (reached when the NaOH concentration was typically 0.1 mol  $\text{L}^{-1}$ ); the volume was made up with high purity water and the flask was capped. After standing for 90 min in the closed flask under normal lab conditions, the sample (or standard calibration solutions which had been similarly mixed with the base) was introduced into the on-line generation system and emission from Hg was measured. Quantitation was performed against simple aqueous calibration solutions containing 1.0-20  $\mu\text{g L}^{-1}$   $\text{Hg}^{2+}$ . A reagent blank solution was run parallel to the determination and its result was taken into consideration. To study the effect of temperature, a solution containing 10  $\mu\text{g L}^{-1}$  of  $\text{Hg}^{2+}$  in 0.1 mol  $\text{L}^{-1}$  NaOH was placed in a closed vessel and left to stand for 90 min under normal lab conditions. The solution was then transferred to a beaker, a thermometer inserted, and the solution then placed on a heating plate. When a predetermined temperature was reached, the solution was immediately aspirated into the on-line vapor generator. Experiments were also undertaken in the dark to assess the influence of ambient laboratory lighting. After the addition of the NaOH solution to a 10  $\mu\text{g L}^{-1}$   $\text{Hg}^{2+}$  standard, the container was covered with aluminum foil and left to stand for 90 min in the dark before being introduced into the on-line vapor generator.

## Results and Discussion

This study initially utilized a tetramethylammonium hydroxide (TMAH) medium for vapor generation, resulting in the production of a signal for mercury after adjusting the solution pH to 13 with  $\text{NH}_4\text{OH}$ . Although it was then concluded that this reagent was reducing mercury in solution, it was subsequently determined that it was the pH change and not the TMAH that was responsible for production of mercury vapor. Using only TMAH, without adding another base to change the pH, a small intensity signal is obtained for mercury. However, if TMAH is added until pH = 13, the signal intensity is relatively high.

### Effect of pH

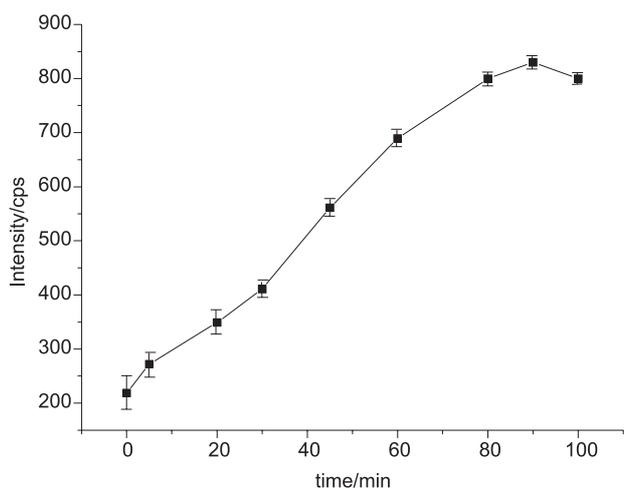
Aqueous solutions containing 10  $\mu\text{g L}^{-1}$  of  $\text{Hg}^{2+}$  were adjusted to different pHs by addition of NaOH or  $\text{HNO}_3$ . As shown in Figure 2, the signal increases with pH, most intensively in the range pH = 11 to 13. We do not yet know the mechanism of reduction arising by the addition of NaOH and therefore currently have no explanation for this observation.



**Figure 2.** Effect of pH on signal intensity from an aqueous standard solution containing 10  $\mu\text{g L}^{-1}$   $\text{Hg}^{2+}$  with pH adjusted with NaOH and/or  $\text{HNO}_3$ . Error bars represent standard deviation of three replicate measurements.

### Effect of time

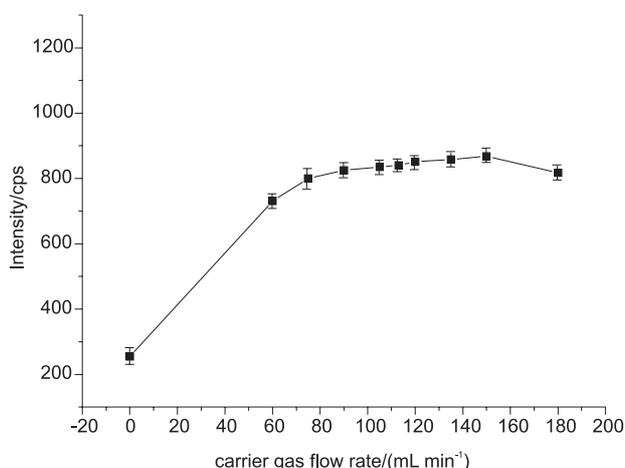
Figure 3 shows the signal intensity arising from a 10  $\mu\text{g L}^{-1}$  solution of  $\text{Hg}^{2+}$  containing 0.1 mol  $\text{L}^{-1}$  NaOH (pH = 13) as a function of the reaction time. It is clear that an incubation period of 90 min is required to obtain a maximum signal. This time was adopted for the standard and for the sample solutions. The vessel was kept capped during the incubation time.



**Figure 3.** Effect of incubation time on signal intensity from an aqueous standard solution containing  $10 \mu\text{g L}^{-1}$  of  $\text{Hg}^{2+}$  in  $0.1 \text{ mol L}^{-1}$  NaOH. Error bars represent the standard deviation of three replicate measurements.

#### Effect of the carrier gas flow rate

Different carrier gas flow rates in the range  $60\text{--}180 \text{ mL min}^{-1}$  were tested, again for a solution containing  $10 \mu\text{g L}^{-1}$   $\text{Hg}^{2+}$  in  $0.1 \text{ mol L}^{-1}$  NaOH. Measurements commenced 90 min after the addition of the NaOH. The results in Figure 4 show that response increases rapidly for flow rates up to  $60 \text{ mL min}^{-1}$  and thereafter less intensively. A flow rate of  $120 \text{ mL min}^{-1}$  was adopted for further study as this was optimal for efficient operation of the phase separator and the transfer of  $\text{Hg}^0$  from the solution. Without a carrier gas, the signal intensity is the same as for the blank, indicating that insufficient  $\text{Hg}^0$  is transferred from the solution to the plasma to produce a signal under this condition.



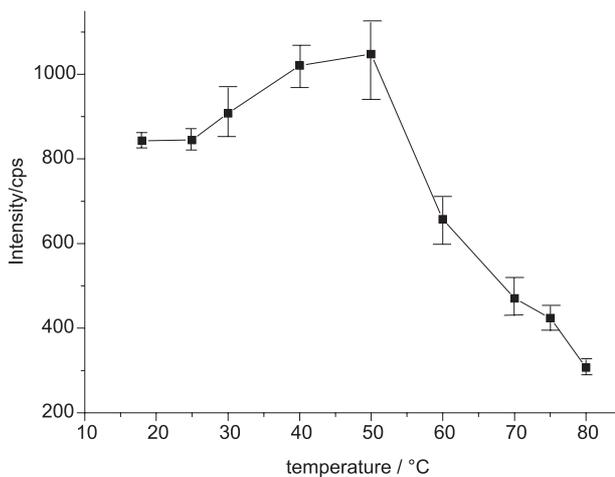
**Figure 4.** Effect of carrier gas flow rate on signal intensity from an aqueous standard solution containing  $10 \mu\text{g L}^{-1}$  of  $\text{Hg}^{2+}$  in  $0.1 \text{ mol L}^{-1}$  NaOH. Error bars represent the standard deviation of three replicate measurements.

#### Effect of visible light

The signal intensity arising from a solution containing  $10 \mu\text{g L}^{-1}$   $\text{Hg}^{2+}$  in  $0.1 \text{ mol L}^{-1}$  NaOH, prepared and measured in the dark (flask covered with aluminum foil in the dark) was identical to that arising from a solution prepared under normal laboratory illumination conditions, demonstrating that the reduction of mercury is not influenced by light.

#### Effect of temperature

Figure 5 shows the signal intensity arising from a solution containing  $10 \mu\text{g L}^{-1}$   $\text{Hg}^{2+}$  in  $0.1 \text{ mol L}^{-1}$  NaOH as a function of the temperature of the reaction vessel. The signal intensity increases up to  $50 \text{ }^\circ\text{C}$ , decreasing for higher temperature. Certainly, mercury is lost from the flask during heating. The loss is especially noticeable for temperatures higher than  $50 \text{ }^\circ\text{C}$ . Increased temperature likely favors liberation of the vapor from the solution due to decreased solubility.<sup>16</sup> Better precision was obtained at room temperature, which was adopted for all further experiments.



**Figure 5.** Effect of temperature on signal intensity from an aqueous standard solution containing  $10 \mu\text{g L}^{-1}$  of  $\text{Hg}^{2+}$  in  $0.1 \text{ mol L}^{-1}$  NaOH. Error bars represent the standard deviation of three replicate measurements.

#### Figures of merit

Calibration curves, using Hg standard solutions spanning the concentration range  $1.0\text{--}20 \mu\text{g L}^{-1}$ , were obtained using the selected conditions. The linear correlation coefficient was 0.997, and the limit of detection (LOD), defined as 3 times the standard deviation of 10 measurements of the blank divided by the slope of the calibration curve, was  $0.04 \mu\text{g g}^{-1}$  for 0.5 g of the solid sample in a final volume of 50 mL. This LOD was adequate for the analysis of the certified biological samples.

**Table 2.** Analytical results for biological samples,  $\mu\text{g g}^{-1}$  ( $n = 3$ )

sample	certified	found	recovery (%)	RSD (%)
DOLT-2	$2.14 \pm 0.28$	$2.35 \pm 0.22$	110	9
TORT-2	$0.27 \pm 0.06$	$0.23 \pm 0.02$	85	9
DORM-1	$0.798 \pm 0.074$	$0.745 \pm 0.05$	93	7
BCR 186	$1.97 \pm 0.04$	$2.24 \pm 0.18$	113	8
SRM 1566a	$0.0642 \pm 0.0067$	$0.069 \pm 0.005$	107	7

### Generation of $\text{Hg}^0$

In order to verify the formation of  $\text{Hg}^0$  by the addition of NaOH, as opposed to other Hg species that would be decomposed in the plasma, measurements were also made based on cold vapor atomic absorption spectrometry using a quartz cell at room temperature and the same VGA-76P vapor generation equipment. A calibration curve was obtained, demonstrating that  $\text{Hg}^0$  is in fact formed.

### Analytical application

The procedure was applied to the analysis of five biological certified reference materials. The results are summarized in Table 2. The recoveries of the certified values, between 85 and 113%, were acceptable and all results were in agreement with the certified values in accordance with a *t*-test at the 95% level of confidence.<sup>17</sup> Precision was acceptable, with relative standard deviations (RSD) in the range 7-9%.

### Additional studies

Possible vapor generation of Ag, Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Ni, P, Pb, Sb, Se, Si, Sn, Tl, U, V, Y and Zn species from aqueous solutions in  $0.1 \text{ mol L}^{-1}$  NaOH was also investigated, but only Hg produced an ICP OES signal. The presence of these elements in solution did not influence the Hg signal, even at added concentrations of  $1000 \mu\text{g L}^{-1}$ .

The procedure was applied to the analysis of other environmental certified samples, including river and marine sediments as well as sewage sludge, but the recovery was too low, between 20% and 70%. This may be explained because the addition of NaOH resulted in the formation of hydrous oxides and hydroxides from concomitants in the sample solution which produced a gelatinous precipitate that occluded  $\text{Hg}^0$  and  $\text{Hg}^{2+}$ .

Several alternative strong bases were also examined for their efficiency of cold vapor generation, including  $0.1 \text{ mol L}^{-1}$  solutions of hydroxides of  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{NH}_4^+$ . Approximately the same signal intensity was obtained for all bases, except for  $\text{NH}_4\text{OH}$ , for which the intensity was about half.

Aqueous solutions of thimerosal ( $\text{C}_9\text{H}_9\text{HgNaO}_2\text{S}$ ) and ethanolic solutions of methylmercury ( $\text{CH}_3\text{HgCl}$ ), containing  $10 \mu\text{g L}^{-1}$  total Hg were mixed with different proportions of an aqueous standard solution of  $\text{Hg}^{2+}$ . The mixtures were (or not) submitted to acid digestion in a microwave oven. The results are shown in Table 3. It was found that, without digestion, only  $\text{Hg}^{2+}$  was detected, while after digestion both were detected. Only  $\text{Hg}^{2+}$  appears to lead to the formation of  $\text{Hg}^0$  by reduction with NaOH, while other Hg species do not respond.

**Table 3.** Analytical results for spiked and digested thimerosal and methylmercury solutions,  $10 \mu\text{g L}^{-1}$  ( $n = 3$ )

Spike $\text{Hg}^{2+}/$ ( $\mu\text{g L}^{-1}$ )	MeHg/ ( $\mu\text{g L}^{-1}$ )	Thimerosal/ ( $\mu\text{g L}^{-1}$ )
0 (with digestion)	$10.3 \pm 0.7$	$9.2 \pm 0.2$
5 (with digestion)	$15.2 \pm 0.2$	$14.5 \pm 0.4$
10 (with digestion)	$20.5 \pm 0.4$	$21.7 \pm 0.4$
0 (without digestion)	ND	ND
5 (without digestion)	$5.2 \pm 0.2$	$4.7 \pm 0.3$
10 (without digestion)	$9.8 \pm 0.3$	$10.5 \pm 0.1$

ND: not detectable at level of  $0.4 \mu\text{g L}^{-1}$ .

The signal intensity arising from vapor generation by the addition of only NaOH to an aqueous standard solution containing  $\text{Hg}^{2+}$  is about five-fold lower than that arising from the addition of  $\text{NaBH}_4$  and HCl in the traditional on-line flow injection manifold using a strong reducing agent. Certainly, the presence of a reducing agent enhances the rate of reduction and its efficiency, providing a much higher intensity signal.

## Conclusions

Aqueous inorganic mercury can be reduced to  $\text{Hg}^0$  by the single addition of NaOH (in the absence of any further reducing agent such as  $\text{NaBH}_4$  or  $\text{SnCl}_2$ ). The mechanism of reduction is not yet known, but requires a high pH, most probably indicating production of the  $\text{Hg}^0$  from  $\text{Hg}(\text{OH})_2$ . This new finding was applied to the determination of total Hg in digested biological samples by simply treating them with NaOH. Only  $\text{Hg}^{2+}$  can be converted to  $\text{Hg}^0$ , any organo-mercury species present must be decomposed

before being treated with NaOH. This observation opens the possibility for development of a rapid and easy speciation methodology for mercury. The procedure can likely be improved by designing a more efficient vapor generation apparatus, by accelerating reduction/phase separation steps by heating or sonication and/or by collecting the vapor before measurement (*i.e.*, trapping on gold).

## Acknowledgments

The authors are thankful to Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq, Brazil) for financial support and for A. J. Curtius scholarship.

## References

1. Takase, I.; Pereira, H. B.; Luna, A. S.; Grinberg, P.; Campos, R. C.; *Quim. Nova* **2002**, *25*, 1132.
2. Pohl, P.; *Trends Anal. Chem.* **2004**, *23*, 21.
3. Pohl, P.; *Trends Anal. Chem.* **2004**, *23*, 87.
4. Hywel, E. H.; Day, J. A.; Fisher, A.; Price, W. J.; Smith, C. M. M.; Tyson, J. F.; *J. Anal. At. Spectrom.* **2004**, *19*, 775.
5. Bolea, E.; Laborda, F.; Castillo, J. R.; Sturgeon, R. E.; *Spectrochim. Acta, Part B* **2004**, *59*, 505.
6. Guo, X.; Sturgeon, R. E.; Mester, Z.; Gardner, G. J.; *Anal. Chem.* **2003**, *75*, 2092.
7. Guo, X.; Sturgeon, R. E.; Mester, Z.; Gardner, G. J.; *Appl. Organomet. Chem.* **2004**, *18*, 205.
8. Capelo, J. L.; Maduro, C.; Mota, A. M.; *J. Anal. At. Spectrom.* **2004**, *19*, 414.
9. Tsalev, D. L.; *J. Anal. At. Spectrom.* **1999**, *14*, 147.
10. Long, Z.; Xin, J.J.; Hou, X. D.; *Spectrosc. Lett.* **2004**, *37*, 263.
11. Han, C.; Zheng, C.; Wang, J.; Cheng, G.; Lv, Y.; Hou, X.; *Anal. Bional. Chem.* **2007**, 388, 825.
12. Yin, Y.; Qiu, J.; Yang, L.; Wang, Q.; *Anal. Bional. Chem.* **2007**, 388, 831.
13. Vieira, M. A.; Ribeiro, A. S.; Curtius, A. J.; Sturgeon, R. E.; *Anal. Bional. Chem.* **2007**, 388, 837.
14. Ribeiro, A. S.; Vieira, M. A.; Willie, S.; Sturgeon, R. E.; *Anal. Bional. Chem.* **2007**, 388, 849.
15. Gil, S.; Lavilla, I.; Bendicho, C.; *Anal. Chem.* **2006**, *78*, 6260.
16. Feng, Y. -L.; Lam, J. W.; Sturgeon, R. E.; *Spectrochim. Acta, Part B* **2004**, *59*, 667.
17. Miller, J. N.; Miller, J. C.; *Statistics and Chemometrics for Analytical Chemistry*, 4<sup>th</sup> ed., Person Education: England, 2000.

Received: October 23, 2007

Web Release Date: April 25, 2008