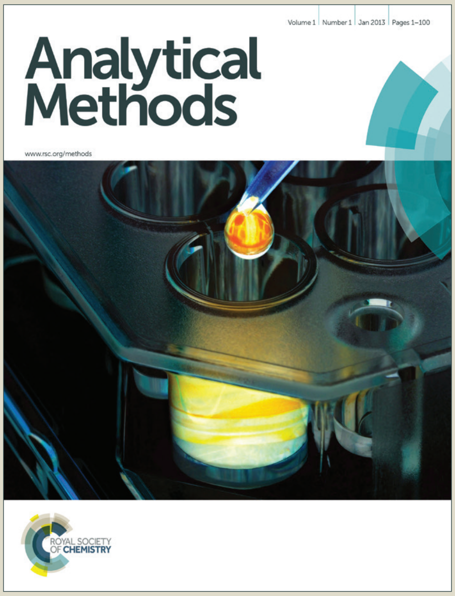
Analytical Methods

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/methods

A very simple and fast analytical method for atmospheric particulate-bound mercury determination

Stacy Ferlin,[a] Anne Hélène Fostier*[a] and Jose Javier Melendez-Perez [a]

[a]Institute of Chemistry, University of Campinas–Unicamp, P.O. Box 6154, 13083-970, Campinas, SP, Brazil

*Corresponding author: fostier@iqm.unicamp.br

Abstract:

In this paper, we present the results obtained for the determination of particulate-bound mercury (PHg) collected on a glass fiber filter by a combustion–AAS technique using a Direct Mercury Analyzer® (DMA-80 TRICELL; Milestone Inc., Italy). The accuracy of the method was demonstrated by comparison with the U.S. EPA IO-5 method. Sampling was always performed in duplicate using two identical sampling devices arranged side by side. The limit of quantitation of the proposed method was 0.22 ng, which was in the same order as that observed for the U.S. EPA method (0.23 ng), and corresponds to 5.0 pg m^{-3} for a sampling flow of 30 L min^{-1} and a 24-h sampling period. For paired sampling filters, the precision was <10% for PHg concentrations in the range of 6.5 to 29.3 pg m^{-3}. For triplicate filters spiked with 0.3000 and 1.000 ng Hg(II), recovery was (97±2)% and (85±9)%, respectively. The accuracy was checked by analyzing paired sampling filters by both methods (DMA or U.S. EPA) and did not show any significant difference (p>0.05).

Keywords: Particulate-bound mercury; direct combustion analysis

1. Introduction

Due to its high toxicity and its capacity for long range transport in the atmosphere, mercury (Hg) is a significant concern as attested by the recently adopted "Minamata convention on mercury".[1,2] Mercury can be emitted to the atmosphere by natural (e.g., volcanoes, geothermal areas) or anthropogenic sources, fossil-fuel burning and incineration of municipal wastes, and it has been estimated that the present atmospheric Hg concentrations are 300 to 500% higher than in preindustrial times.[3] In the atmosphere, mercury is mainly present as gaseous elemental mercury (Hg^0, GEM), gaseous oxidized Hg (Hg(II), GOM) and particulate-bound mercury (PHg).[4] Once emitted, Hg can be transformed from one form to another by chemical and physical processes. Although GEM generally comprises >95% of atmospheric Hg,[5] PHg can account for up to 40% of the total atmospheric mercury in industrial areas,[6] and GOM and PHg are more important than GEM with respect to atmospheric deposition due to their large dry deposition velocities and scavenging coefficients.[7] Speciation of mercury is therefore critical to understand the behavior and cycling of this element in the environment.

Atmospheric Hg concentrations are in the range of ng m^{-3} for GEM and pg m^{-3} for PHg. For this reason, sampling methods generally include a pre-concentration step to accumulate a quantity of Hg that is above the limit of quantitation (LOQ) of the analytical techniques. For PHg, the filtration-based method is still the most widely used for collection. This method relies on pulling a large volume of air through filter media [e.g., quartz-fiber filters, cellulose-acetate filters, glass-fiber filters, and Teflon® filters]. Because the most common detection techniques (cold vapor atomic absorption spectrometry-CVAAS and cold vapor atomic fluorescence spectrometry-CVAFS) require release of elemental mercury from the sample matrix, the more oxidized forms of mercury [Hg(I) or Hg(II)] have to be reduced to complete the Hg(0) detection. For this purpose, wet-acid digestion and thermoreduction are mainly employed.[8] The wet digestion procedure generally involves a number of reagents both for acidic digestion (performed at high temperature and/or high pressure conditions) and mercury reduction and is therefore time-consuming and presents risks of mercury loss due to volatilization and contamination due to the addition of reagents and significant manipulation of the samples. On the contrary, dry pyrolysis at very high temperatures (e.g., 800–900 °C) under a reducing atmosphere (Ar, He and N_2) associated with CVAAS or CVAFS detection has already been proven as an effective method to reduce the uncertainties associated with wet-digestion procedures because it allows for the direct thermoreduction of Hg associated with particulate matter. Nevertheless, pyrolysis systems are generally homemade,[9, 10] except in the fully automated Tekran® 2537-1130-1135 atmospheric mercury speciation system,[11] and always require a reducing gas supply. In addition, Lynam and Keeler[10]compared the thermoreductive method (as an alternative) with the classical acid-extraction method and found that the former tends to yield low values of PHg relative to the latter. Nonetheless, another approach that can measure total mercury directly in many solid and liquid matrices has become available in automated commercial instrumentation. Such systems combine sample combustion (thermal decomposition in the presence of O_2), Hg amalgamation, and atomic absorption spectrometry.[12]

In this paper, we present the results obtained for the determination of PHg collected on a glass fiber filter by the combustion-AAS technique. The accuracy of the method was demonstrated by comparison with the U.S. EPA IO-5 method[13] for determination of atmospheric PHg.

2. Experimental section

2.1. Sampling

Total atmospheric particulate matter was sampled according to the U.S. EPA IO-5 method[13] for the determination of atmospheric PHg. For each sampling, a 47-mm-diameter glass fiber filter (Sartorius Stedim Biotech) was placed on a Teflon® filter holder (Cole Parmer) completely opened on the air entrance side and connected to an air pump (DOA-V191-AA, Gast, USA) by a silicone tube. The pump flow was approximately 30 L min^{-1}, and the sampling time varied between approximately 3 and 52 h. A volume meter (G1, Lao Indústria, Brazil) was placed between the filter holder and the air pump to record the total sampled volume. Sampling was always performed in duplicate using two identical sampling devices arranged side by side, which allows for paired sampling filters (named sampling batch). For preliminary tests (comparison of methods), the sampling devices were placed outdoors, 2 m from the external wall of the laboratory, which is on the first floor ~10 m above the ground. Because this sampling position is not suitable for atmospheric monitoring (very close to a vertical barrier), a final sampling was also performed on the roof of the Institute of Chemistry of the University of Campinas-Unicamp (Brazil) located in a suburban area (22°48´57"S; 47° 03´33"W), between 11/11 and 12/4/2013.

2.2. Analysis

Filters were directly analyzed by a Direct Mercury Analyzer® (DMA-80 TRICELL, Milestone, Italy). This equipment contains an automatic sampler, a quartz furnace, a cobalt-manganese oxide catalyst, a gold-coated sand amalgamator and an atomic absorption detection cell with three different pathlengths. The different steps of the analysis are controlled by software. A detailed description of the DMA-80 was given in Melendez-Perez et al.[14] The equipment was initially designed to work with an automatic sampler where solid or liquid samples are placed in nickel or quartz boats of approximately 360 mm (L), 110 mm (l) and 110 mm (h). For analysis, the sample boat is automatically transferred to a carrier linked to a horizontal pneumatic actuator, which allows for the introduction of the sample boat in the furnace. Because of the small size of the sample boats, the entire filter cannot be put in at once. Therefore, for the filter analysis, the boat was not used, but the boat carrier was used as the filter holder. To introduce the entire filter into the furnace, the actuator was opened by appropriate command from the software, and the filter was directly placed on the boat carrier after the temperature of the furnace decreased to room temperature to avoid Hg volatilization. Then, the actuator was activated to push the filter into the furnace. The instrumental analytical conditions are described in Table 1; air was used as the carrier gas.

Table 1. Analytical conditions for the glass fiber filter in the DMA-80.

Condition	Setting
Drying temperature and time	~25 to 200 ºC for 50 s 200 ºC for 40 s
Ashing temperature and time	200to650 ºC for 90 s 650 ºC for 90 s
Purge time	30 s
Amalgamator heating temperature and time	850 ºC for 12s
Cuvettes temperature	125 ºC
Signal recording time	24 s
Air pressure	3.1 bar
Air flow rate	100 mL min^{-1}

2.3. Validation

The method was *in house* validated by the evaluation of the following performance parameters: linear range, linearity, matrix effects, recovery, precision, limit of detection and limit of quantitation.

The linearity and linear range for 0.1000 to 3.000 ng of Hg were established through a calibration curve obtained by triplicate analyses of aliquots of Hg standard solutions placed in quartz boats. The homoscedasticity of the residuals was verified with the Levene test.[15, 16] The matrix effect was evaluated for glass fiber filters by comparing the calibration curve obtained as described above with the one obtained when analyzing entire glass fiber filters spiked with appropriate volumes of a standard solution; Student´s t-test was applied to compare the angular coefficients of both linear regressions. The limits of detection (LOD) and quantitation (LOQ) were determined as 3 times and 10 times the standard deviation of the residuals from the linear regression, respectively, divided by the angular coefficient value of the linear equation.[17]

Because no standard reference material is available for PHg, the accuracy was calculated as the percentage of recovery by triplicate analyses of filters spiked with Hg standard solutions in two Hg(II) mass levels (0.3000 and 1.000 ng). The proposed method was also compared with the U.S. EPA IO-5 method[13] in which Hg is determined by CVAFS after acidic digestion of the glass fiber filter in a microwave oven. The precision of the sampling plus the analytical method was established for both methods (i.e., DMA and U.S. EPA method) by analyzing paired sampling filters by the same method. Paired sampling filters were also analyzed by both methods (i.e., one for each filter), and the results were compared by applying a paired Student´s t-test.

For the analysis with the U.S. EPA IO-5 method,[13] each filter was digested with 20 mL 10% (v/v) HNO_3 in a closed PTFE flask in an analytical microwave oven

(Provecto Analítica, Brazil) by applying a three-step program (400 W/3 min; 200 W/17 min; 0 W/30 min). After the flask was cooled at room temperature, 1 mL of BrCl 25% (v/v) was added, and after 1 h, 3 mL of hydroxylamine hydrochloride 15% (w/v) was also added. The digested solution was then quantitatively transferred to a 50.0 mL volumetric flask and the volume completed with deionized water. Mercury reduction was performed in a gas-liquid separator flask containing 80 mL of deionized water and 20 mL of $SnCl_2$ 10% (w/v), where 20.0 mL of the sample and 1 mL of $SnCl_2$ (10% w/v) were added. Nitrogen was used as a carrier gas, and Hg^0 was trapped on a quartz column with a 6 mm diameter and 10 cm length, filled with 0.4 g of coated gold sand. The analytical procedure for Hg detection using AFS includes a double stage amalgamation that consists of thermal desorption (450 ºC) of the Hg^0 amalgamated in the sampling column and subsequent amalgamation/desorption in a second column (analytical). Hg^0 is carried by a 45 mL min^{-1} flow of argon directly to the AFS detector (Model-III, Brooks Rand, USA).

2.4. Clean procedure, reagent and solutions

Clean techniques were applied to perform sampling and before the analysis. Filter holders and glassware were adequately decontaminated in a 10% (v/v) HNO_3 bath for 24 h. Filters were previously decontaminated by ashing at 500 °C for 60 min and were stored in individual Petri dishes closed with Teflon® tape. Acid-cleaned Teflon® coated forceps were used to manipulate the filters, and particle-free gloves were used during the sampling and analytical procedures. Just before using, the DMA quartz boats were decontaminated by heating in the DMA furnace. All solutions were prepared with deionized water (18MΩ cm) obtained from a Milli-Q water purification equipment (Direct-Q 5, Millipore, Brazil); HNO_3 (Synth, Brazil) and HCl (Merck, Germany) were purified by distillation (BSB-939-IR subboiling unit, Berghof, Germany). The carrier gases (N_2 and Ar) were also purified by passing through a gold trap before use. Hg(II) standard solutions (10.0 and 100.0 ng mL^{-1}) were prepared from a stock Hg standard solution (1.000 ± 0.003 mg mL^{-1}) (Tec-Lab® Hexis, Brazil) diluted in 10% (v/v) HNO_3. For filter digestion and analysis, BrCl 25% (v/v) was prepared with KBr 99.7% (Mallinckrodt, Brazil) and $KBrO_3$ 100% (J.T. Backer, Brazil) in distilled HCl. The hydroxylamine hydrochloride solution 15% (w/v) was prepared with $NH_2OH{\cdot}HCl$ 69.49% (Nuclear, Brazil). The 10% (w/v) $SnCl_2$ solution was prepared with $SnCl_2{\cdot}2H_2O$ 98.0-103.0% (Synth, Brazil) in HCl 10% (v/v), and the solution was purged with Ar flow for 30 min before using.

3. Results and discussion

The figures of merit for both calibration curves obtained by analyzing standard solutions (S) and spiked filters (F) by DMA are presented in Table 2.

Table 2. Figures of merit of the DMA calibration curves obtained with standard solutions (S) and with filters spiked with standard solution (F).

	S	**F**
Dynamic linear range (ng Hg)	0.1000 – 3.000	0.1000 – 3.000
Linear equation	Abs = a Hg + b	Abs = a Hg + b
a (s_a)*	0.0926 (0.0004)	0.0958 (0.0012)
b (s_b)$	0.0012 (0.0006)	0.0060 (0.0015)
$S_{y/x}$#	0.0020	0.0037

R^2	0.9994	0.9981
LOD (ng)	0.06	0.12
LOQ (ng)	0.22	0.39

*s_a: standard deviation of the slope a; $ s_b: standard deviation of the intercept b; # $s_{y/x}$: standard deviation of the residual from the linear equation.

As shown by the standard deviation values of the linear regressions parameters, precision was slightly better when calibration curve was obtained with standard solutions (S) than with filters spiked with standard solution (F). This results in the apparent difference in the LOD (and LOQ) obtained from both calibration curves. Nevertheless, Student´s t-test showed that the angular coefficients of both linear regressions were not significantly different ($p>0.05$). These data showed that no significant matrix effect should be considered and that calibration curve can be directly obtained from standard solutions, which represents a significant advantage because it is faster than when spiking filters and it also decreases the consumption of filters.

The recovery test resulted in (97±2)% and (85±9)% when analyzing triplicate filters spiked with 0.3000 and 1.000 ng of Hg(II), respectively (data presented as the mean ± 1 standard deviation).

Paired sampling filters were therefore analyzed by DMA, and the results are presented in Table 3.

Table3. Hg mass and corresponding air PHg concentration obtained by analyzing paired sampling filters by DMA-80.

Sampling batch number	**Filter code**	**Mass of Hg (ng)**	**Sampled volume (m^3)**	**Air PHg concentration ($pg \cdot m^{-3}$)**
1	1A	0.9532	22.629	42.1

	1B	1.0372	23.775	43.6
2	2A	0.9554	35.956	26.6
	2B	0.8136	31.783	25.6
3	3A	0.3796	20.004	19.0
	3B	0.4098	22.394	18.3

A paired Student´s t-test, applied to compare the analytical results of samples collected with the two sampling devices, designated as A and B, showed that PHg concentrations were not significantly different ($p>0.05$) when air was sampled with the A or B device. The precision for paired samples was <2.0 % (precision calculated as $\frac{|x_i - \bar{x}|\times 100}{\bar{x}}$, where x_i is the Hg concentration find for one sample and $\bar{x}$ is the mean of the Hg concentrations find for both samples). Because samplings were performed on different days, different PHg concentrations are expected between different sampling batches.

To guarantee the robustness of the sampling method and the precision of the analytical method, three pairs of samples were also analyzed according to the U.S. EPA method. For the CVAFS calibration curve, the linearity ranged between 0.200 and 2.000 ng Hg, and the LOD and LOQ were 0.07 and 0.23 ng Hg, respectively. Sampling filters were therefore analyzed by the U.S. EPA method; the results are presented in Table 4.

Table 4. Hg mass and corresponding air PHg concentration obtained by analyzing paired sampling filters by the U.S. EPA method.

Sampling batch number	Filter code	Mass of Hg (ng)	Sampled volume (m^3)	Air Hg concentration ($pg \cdot m^{-3}$)

4	4A	2.2179	93.273	23.8
	4B	2.1965	92.499	23.7
5	5A	0.7936	22.873	34.7
	5B	0.9978	27.345	36.5
6	6A	0.6689	31.504	21.2
	6B	0.8591	38.204	22.5

As for the DMA analysis, a paired Student´s t-test applied to compare the paired samples did not show any significant difference ($p>0.05$) when the atmospheric particulate matter was collected with the A or B device and the filters analyzed according to the U.S. EPA method; the precision for paired samples was <3.0%.

After the good precision of the sampling and both analytical methods (DMA and U.S. EPA) were proved, paired sampling filters were analyzed by both methods, and the results are presented in Table 5.

Table 5. Hg mass and corresponding air PHg concentration obtained by analyzing paired sampling filters by the DMA and the U.S. EPA method.

Sampling batch number	Filter code	Analytical method	Mass of Hg (ng)	Sampled volume (m^3)	PHg concentration ($pg \cdot m^{-3}$)
7	7A	U.S. EPA	1.5641	68.334	22.9
	7B	DMA	1.5831	74.413	21.3
8	8A	U.S. EPA	0.4861	29.645	16.4
	8B	DMA	0.5542	36.174	15.3
9	9A	U.S. EPA	0.1123	4.921	22.8
	9B	DMA	0.1428	6.029	23.7

A paired Student´s t-test applied to compare samples A and B collected in the same sampling batch but analyzed by different methods (U.S. EPA or DMA) did not show any significant difference ($p>0.05$); the precision for paired samples was <4.0%.

The PHg concentrations obtained for sampling performed on the roof of the Institute of Chemistry are presented in Table 6. A paired Student´s t-test did not show any significant difference ($p>0.05$) between paired samples A and B, and the precision was <10%. The concentrations of PHg measured in this study range from 6.5 to 29.3 pg m^{-3}, which are in the same range as those reported in the literature for total particulate mercury in suburban areas.[9, 18] In Brazil, the only PHg concentrations were reported by Fostier and Michelazzo,[19] who found 465±252 pg m^{-3} at Unicamp. Nevertheless, in this study, air sampling was performed at 2 m, which could have significantly increased the PHg concentration because of the soil dust influence.

Table 6. Hg mass and corresponding air PHg concentration obtained by analyzing paired filters by the DMA method for sampling performed at Unicamp on suitable monitoring conditions.

Sampling batch number	Filter code	PHg (pg m^{-3})	PHg mean concentration (pg m^{-3})	Precision (%)
10	10A	28.8	29.3	1.7
	10B	29.7		
11	11A	19.7	18.5	6.5
	11B	17.3		
12	12A	16.5	18.2	9.3
	12B	19.8		
13	13A	6.8	7.1	4.2

	13B	7.3		
14	14A	6.6	6.5	2.3
	14B	6.3		
15	15A	16.6	16.1	3.1
	15B	15.6		

4. Conclusion

The presented data show that the determination of atmospheric PHg can be accurately performed by analyzing sampling filters by DMA-80®,even if the equipment does not seems to be initially projected for this application.When compared to the U.S. EPA method, the LOQ was on the same order (0.22 and 0.23 ng for DMA and EPA method, respectively), which, for a sampling flow of 30 L min^{-1} and a 24-h sampling period, corresponds to an LOQ of 5.0 pg m^{-3}. On the other hand, the proposed method is much simpler and faster (approximately 6 min for filter analysis in the DMA, whereas filter digestion requires ~60 min plus ~15 min for CVAFS analysis with the U.S. EPA method). In addition, filter analysis is much less susceptible to contamination because no sample preparation is required.

Acknowledgments

The authors would like to acknowledgethe São Paulo Research Fundation (FAPESP project 2010/19040-4) for financial support and the Conselho National de DesenvolvimentoCientífico e Tecnológico (CNPq) for graduate scholarship.

References

1UNEP, 2013a. *Minamata Convention on Mercury*. Website Available <http://www.mercuryconvention.org/> (accessed 18 Dec 2013).

2 UNEP, 2013b. *Global Mercury Assessment 2013: Sources, Emissions, Releases and Environmental Transport*. UNEP Chemicals Branch, Geneva, Switzerland, 2013.

3 R. P. Mason, A. L. Choi, W. F.Fitzgerald, C. R.Hammerschmidt, C. H.Lamborg, A. L.Soerensen and E. M.Sunderland, *Environ. Res.*, 2012, **119**, 101.

4 W. H. Schroeder and J. Munthe, *Atmos. Environ.*, 1998, **32**, 809.

5 J. Munthe, I. Wängberg, N. Pirrone, Å. Iyerfeldt, R. Ferrara, R. Ebinghaus, X. Feng, K. Gårdfeldt, G. Keeler, E. Lanzillotta, S. E. Lindberg, J. Lu, Y. Mamane, E. Prestbo, S. Schmolke, W. H. Schroeder, J. Sommar, F. Sprovieri, R. K. Stevens, W. Stratton, G.Tuncel and A.Urba, *Atmos. Environ.*, 2001, **35**, 3007.

6 C. J. Lin and S. O. Pehkonen, *Atmos. Environ.*, 1999, **33**, 2067.

7 J. D. Shannon and E. C. Voldner, *Atmos. Environ*., 1995, **29**, 1619.

8 S. K. Pandey, K-H. Kim, R. J. C. Brown,*TrAC, Trends Anal.Chem.*, 2011,**30**, 899.

9J. Y. Lu, W. H. Schroeder, T. Berg, J. Munthe, D. Schneeberger, F. Schaedlich, *Anal. Chem.*, 1998,**70**, 2403.

10 M. M. Lynam, G. J. Keeler, *Anal. Bioanal. Chem.*, 2002, **374**, 1009.

11 M. S. Gustin, J. Huang, M. B. Miller, C. Peterson, D. A. Jaffe, J. Ambrose, B. D. Finley, S. N. Lyman, K. Call, R. Talbot, D. Feddersen, H. Mao and S. E. Lindberg, *Environ. Sci. Technol.*, 2013, **47**, 7295.

12 H. M. Boylan and S. Kingston, *Am. Lab.*, 1998, **30**, 25.

13 U.S. EPA, Compendium of Methods for Inorganic Air Pollutants. Chapter IO-5, Sampling and analysis for atmospheric mercury. U.S. Environmental Protection Agency, Cincinnati, 1999.

14 J. J. Melendez-Perez, A. H. Fostier, *J. Braz. Chem. Soc.*, 2013, **24**, 1880.

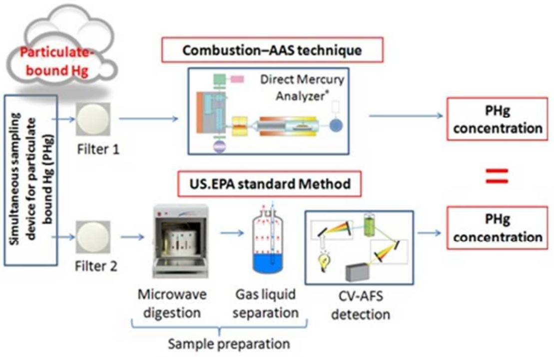
15 H. Levene, *Robust test for equality of variances;* Stanford University Press: Stanford, 1960.

16 M. B. Brown. and A. B. Forsythe, *J. Am. Stat. Assoc.*, 1974, **69**, 364.

17 J. N. Miller and J. C. Miller, *Statistics and chemometrics for analytical chemistry,* ed. 4; Pearson: Edinburgh 2000.

18 P-R.Kim, Y-J. Han, T. M. Holsen and S-M Yi, *Atmos. Environ.*, 2012,**61**, 94.

19 A. H. Fostier and P. A. M. Michelazzo, *J. Braz. Chem. Soc.*, 2006, **17**, 886.



Glass fiber filters analyzed by a combustion–AAS technique: no sample preparation; no contamination risks; method validated with the US.EPA standard method.