Analytical Methods

PAPER

View Article Online
View Journal | View Issue



Cite this: *Anal. Methods*, 2014, **6**, 4537

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

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

Received 6th March 2014
Accepted 16th April 2014

DOI: 10.1039/c4ay00573b

www.rsc.org/methods

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), the recovery was (97 ± 2)% and (85 ± 9)%, respectively. The accuracy was checked by analyzing paired sampling filters by both methods (DMA and U.S. EPA) and did not show any significant difference ($p > 0.05$).

## 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 methods. 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 under 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. In contrast, 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 to be 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 home-made,[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

*Institute of Chemistry, University of Campinas-Unicamp, P.O. Box 6154, 13083-970, Campinas, SP, Brazil. E-mail: fostier@iqm.unicamp.br*