

The use of sorbent tubes and a semi- continuous emissions monitor for the determination of atmospheric total gaseous mercury in Pretoria, South Africa

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Summary

Semi-continuous emissions monitors (SCEM) are widely used for the determination of atmospheric mercury. These sophisticated instruments perform nearly real-time measurements of atmospheric mercury. However, their high cost and limited mobility do not make them suitable tools for field measurements. On the other hand actively pumped Hopcalite-type sorbent tubes, connected to a vacuum pump, can be deployed to sample air even at remote locations without the need for an instrument shelter. This is particularly important for developing countries where the cost of a dedicated mercury analyser may be prohibitive to its widespread use. Analysis of the mercury content of exposed sorbent tubes may be performed by cold vapour atomic absorption spectroscopy (CVAAS). The necessary instrumentation is versatile, not limited to the determination of mercury and is used in many laboratories.

During a five month monitoring campaign in Pretoria, South Africa, weekly average atmospheric mercury concentration data were generated using an Ophis HG 200 SCEM. They were compared to results obtained by exposing Carulite C300 sorbent tubes to ambient air, followed by CVAAS analysis of the absorbed mercury. The average mercury concentration during four months of measurements with the Ophis analyser was $1.7 \pm 1.9 \text{ ng m}^{-3}$ mercury, while $1.6 \pm 0.4 \text{ ng m}^{-3}$ were determined by sorbent tube / CVAAS analysis.

Keywords: Mercury, Hopcalite, SCEM, atmosphere, developing countries, CVAAS

Introduction

Atmospheric mercury pollution is a global problem, particularly with respect to the deposition of atmospheric mercury in waterways and its subsequent concentration along the marine food chain [1]. While volcanic and other geothermal activities are natural sources of atmospheric mercury [2], anthropogenic sources include coal fired power plants, incinerators, chloralkali plants, battery production and others [3]. Atmospheric mercury mainly consists of elemental mercury which, due to its volatile and inert properties, may remain in the atmosphere for up to two years after emission. This leads to a global distribution of the element, with a background atmospheric concentration of 1.3 ng m^{-3} being reported even in remote, non-exposed areas, [4]. In urban areas, average values of 4.5 ng m^{-3} total gaseous mercury (TGM) have been measured in the city of Toronto, Canada [5] and values exceeding 30 ng m^{-3} have been reported for suburbs of the highly polluted city of Beijing during adverse weather conditions [6].

Semi-continuous emissions monitors (SCEM), based on the amalgamation principle, are well established for the determination of atmospheric mercury. Mercury is captured as amalgam on a gold wire mesh through which a defined volume of air is drawn. Periodic heating of the gold releases the mercury as elemental mercury vapour into a small volume of air, which can be quantified by atomic absorption spectroscopy or atomic fluorescence spectroscopy [7]. Such instruments are capable of almost real time measurements and their high sensitivity allows for the detection of atmospheric mercury even in remote, non-exposed areas. However, due to sensitive optical alignment, the need for power supply and the size of the system, such analysers may have to be kept in shelters or inside buildings. This necessitates the use of a long, heated transfer line between the outside air inlet and the analyser.

Hopcalite-type sorbent tubes have long been used for monitoring of mercury vapours in the workplace where mercury concentrations in air far exceed environmental levels [8]. Sorbent tubes contain granular Hopcalite, a mix of copper and manganese oxide, which binds elemental mercury as well as oxidised mercury irreversibly. Particulate-bound mercury may be caught in a glass wool plug contained in the sorbent tube which is analysed together with the Hopcalite granules [9]. This method can therefore not distinguish between any mercury species but determines the total concentration of mercury. After exposure, the mixed oxide is dissolved in acid and the absorbed mercury can be analysed by cold vapour atomic absorption spectroscopy (CVAAS) [10]. Actively pumped sorbent tubes are commonly used for personal monitoring during a typical working shift and their performance has successfully been compared to mercury vapour determination by the double amalgam method in a workplace environment [11].

The usefulness of a combination of sorbent tube and vacuum pump was investigated as an economical alternative to established methods for atmospheric mercury determination. The equipment is easily set up at a sampling location and, in the case of battery powered pumps, is even independent from an external power supply. The relatively low cost, compared to SCEM's, allows for multiple, simultaneous measurements to be performed in the area of interest. The sorbent tube method provides time integrated results, usually over a period of one week. The mercury measurements, in conjunction with meteorological data, could be used for pinpointing an emission source. Furthermore, the analytical equipment needed for the analysis of exposed tubes is present in most analytical laboratories and would not have to be acquired solely for the purpose of atmospheric mercury monitoring.

Materials and Methods

Measurement site

The Council for Scientific and Industrial Research (CSIR) is located in Pretoria's eastern suburb of Brummeria (S 25°44'58" E 28°16'51") at an elevation of 1396 m above sea level. All measurements were performed by sampling air from a partially opened window approximately 10 m above ground, with both the Anasorb C300 sorbent tubes (SKC Inc. Eighty Four, PA, USA) and the HG 200 semi-continuous mercury analyser (Opsis AB, Furulund, Sweden) inlet tubing protected from rain by a roof overhang. The mercury analyser and the vacuum pumps were installed in an office, air-conditioned at 20 °C.

The CSIR premises are in an area with little vehicle traffic but highways are located 500 m to the west and 1 km to the north and east of the sampling site. Potential point sources of atmospheric mercury are a cement factory and a coal-fired power station, located approximately 20 km to the west.

Atmospheric mercury sampling using sorbent tubes

Originally intended for industrial occupational monitoring, Anasorb C300 tubes are used to detect mercury in the $\mu\text{g m}^{-3}$ range, according to NIOSH method 6009 (1994), while an environmental application would demand a detection limit near 1 ng m^{-3} . As the flow through an Anasorb C300 tube should not exceed 12 l h^{-1} according to a published method [10], the exposure time was extended from eight hours to seven days. Breakthrough effects when sampling large volumes of air were not expected to occur due to the irreversible bond between mercury and the sorbent material [9].

For atmospheric monitoring, an Anasorb C300 tube, containing 200 mg of a Hopcalite-type sorbent, was opened at the ends and connected to a vacuum pump by silicone tubing. Sampling was conducted in parallel from a CSIR office, with the sorbent tubes hanging out of a slightly opened window. The pumps were operated at approximately 12 l h^{-1} for seven days, as determined by a flow meter, resulting in a sample volume of approximately 2 m^3 . To eliminate possible errors caused by pump fluctuations, a gas meter was placed between sorbent tube and pump. Gas meter readings were recorded before starting a pump and after completion of a seven day sampling period.

After exposure, tubes were broken and the sorbent was poured into a plastic screw-cap vial and 1 mL each of nitric acid (65%, mercury analysis grade, Sigma-Aldrich, Steinheim, Germany) and hydrochloric acid (37%, mercury analysis grade, Sigma-Aldrich, Steinheim, Germany) were added. The vial was slightly warmed until a

strong formation of bubbles was visible. After dissolution of the sorbent granules, the volume was made up to 10 mL with water (ultrapure, 18 MΩ resistance) and the solution was sonicated for 30 min. At least four non-exposed tubes were opened and processed in the same way as exposed tubes to serve as blanks.

To improve the limit of detection, none of the dilution steps after dissolution of the Hopcalite granules, as stipulated in the published method [10], were performed. The total volume of the solution was thus limited to 10 mL, instead of 250 mL after aliquot dilution. The extended exposure time and reduced liquid volumes were expected to lower the detection limit of the NIOSH 6009 method from 300 ng m⁻³ to approximately 0.6 ng m⁻³.

As the tube content was dissolved in a mixture of concentrated nitric acid and hydrochloric acid, elemental chlorine was produced during dissolution and was present in the solution to be analysed by CVAAS. Since elemental chlorine absorbs light at the absorption wavelength of mercury of 253.7 nm [12], it was therefore removed from solution by sonicating all samples for 30 min.

Mercury analysis by CVAAS

Analysis of dissolved Hopcalite granules plus glass wool plugs by cold vapour atomic absorption spectrometry (CVAAS) was performed using a Perkin Elmer Analyst 700 atomic absorption spectrometer with a FIAS 100 cold vapour generation unit. The carrier solution was 3.7% hydrochloric acid, prepared from the 37% hydrochloric acid used for sorbent dissolution, and the reduction solution contained 5% w/v tin (II) chloride (analytical grade, Sigma-Aldrich, Steinheim, Germany), dissolved in the carrier solution.

Mercury calibration solutions with concentrations between 0.1 and 50 µg ℓ⁻¹ were prepared from a 1000 mg ℓ⁻¹ NIST traceable standard solution (Tecnolab AB, Kungälv, Sweden). An ultra-pure water sample was added as a solution blank. To match the standards to the sample matrix, each 10 mL of calibration standard solution contained 1 mL of nitric acid and hydrochloric acid, respectively. The atmospheric mercury concentration was calculated by multiplying the result of the mercury analysis of dissolved granules by a factor of ten to transform the µg ℓ⁻¹ result to ng / 10 mL, or ng / sorbent tube content. The result was further divided by the volume of air that had passed through the sorbent tube to obtain the atmospheric mercury concentration in ng m⁻³.

Method Evaluation

To assess possible breakthrough of mercury through a sorbent tube, two tubes were connected with a short piece of tubing and operated in series for seven days. Subsequently, the amount of mercury absorbed onto each tube was analysed by CVAAS.

The maximum possible load of mercury onto Anasorb C300 tubes was established by opening four sorbent tubes and pouring the sorbent material onto separate watch glasses. These were placed in a sealed desiccator containing a small beaker of mercury to expose the sorbent granules to a mercury saturated atmosphere for one week. After exposure, granules were acid dissolved and analysed by CVAAS.

The repeatability of sorbent tube exposure and subsequent CVAAS analysis was determined by simultaneously exposing six sorbent tubes to ambient air for seven days at a pump flow rate of 12 ℓ h⁻¹. Tubes were then broken and the granules analysed by CVAAS.

Mercury determination in ambient air by SCM

An Oxis HG 200 analyser was installed at the CSIR and operated continuously. Air was drawn into the instrument through a 0.45 µm membrane filter and a moisture and carbon dioxide trap, containing soda lime pellets. Elemental mercury was kept in an Erlenmeyer flask sealed with a rubber septum and calibration of the instrument was performed by injecting between 20 and 50 µℓ of saturated mercury headspace from this flask into the inlet tubing of the mercury analyser with an airtight syringe. For this purpose, a piece of silicone tubing was added to the inlet and it was removed after calibration to avoid traces of mercury influencing following ambient air measurements. The temperature of the headspace above mercury in the Erlenmeyer flask was monitored with a thermometer and the concentration of mercury in the gas phase calculated according to a table provided by Oxis AB. The zero offset was determined by connecting a mercury trap for the generation of mercury free air to the instrument's air inlet. This trap was constructed by breaking five Anasorb C 300 tubes and pouring their content into a 10 mm diameter glass tube with a glass wool plug at the bottom. An approximately 20 mm thick layer of activated Charcoal (20-80 mesh, Sigma-Aldrich) was added to the Hopcalite.

Instrument parameters were set to 10 min sampling, resulting in approximately 12 ℓ of air being drawn through the internal gold trap. Heating of the trap and simultaneous atomic absorption spectroscopic determination were performed for 1 min, followed by a trap cooling period of 4 min. A measurement cycle was completed every 15 min. Air monitoring with the Opsis HG 200 was conducted in parallel to atmospheric mercury sampling by means of sorbent tubes.

Results and Discussion

Limit of detection of the CVAAS method,

Six mercury standards with concentrations between 0.1 and 20 $\mu\text{g } \ell^{-1}$ as well as a reagent blank were analysed by CVAAS (n = 5) and a limit of detection (LOD) of 0.06 $\mu\text{g } \ell^{-1}$ at 10 x Std Dev_{Blank} was calculated according to published calculations [13]. Given a limit of detection of 0.06 $\mu\text{g } \ell^{-1}$ for the CVAAS method, the theoretical limit of detection for atmospheric TGM would be 0.3 ng m⁻³ for a 2 m³ sampling volume.

Method evaluation

After operating four pairs of sorbent tubes with two tubes in series as shown in Table 1, it could be seen that the concentration of mercury found in the second tube after acid dissolution and CVAAS analysis only exceeded the blank value of non-exposed tubes in one case. Breakthrough was therefore not considered to have a significant impact on air monitoring results.

Table 1 – Breakthrough experiments with two tubes in series

	$\mu\text{g } \ell^{-1} \text{ Hg}$
Blank (n=6)	0.1
Std Dev Blank	0.0
Primary Tube A	0.4
2nd Tube	0.2
Primary Tube B	0.4
2nd Tube	0.1
Primary Tube C	0.4
2nd Tube	0.1
Primary Tube D	0.4
2nd Tube	0.1

The mercury content of four sorbent granule samples, exposed to saturated mercury vapour for one week, was found to be $625 \pm 25 \mu\text{g} / 100 \text{ mg}$ Hopcalite granules after acid dissolution and CVAAS analysis. The mercury absorption capacity of the Hopcalite granules in one tube therefore well exceeded the amount of approximately 4 ng mercury absorbed during seven days of ambient air sampling.

After sampling of ambient air with six sorbent tubes, operated simultaneously for seven days in one location, and analysis by CVAAS, an average concentration of $1.8 \pm 0.2 \text{ ng m}^{-3}$ total gaseous mercury in air was calculated, as shown in Table 2.

Table 2 – Parallel air sampling with six sorbent tubes

Sampler Tube	ng m ⁻³ Hg
A	1.8
B	1.5
C	1.7
D	1.9
E	2.2
F	1.6
Average	1.8
Std Dev	0.2
% RSD	13

The relative standard deviation of $\pm 13 \%$ was deemed acceptable for a newly developed analytical method.

Atmospheric mercury monitoring

Atmospheric elemental mercury was measured by the Opsi HG 200 analyser for 21 weeks at 15 minute intervals, rendering an almost continuous reading as seen in Figure 1. The average elemental mercury concentration recorded was $1.7 \pm 1.9 \text{ ng m}^{-3}$. However, several short spikes with concentrations of up to 64 ng m^{-3} were detected during the monitoring period.

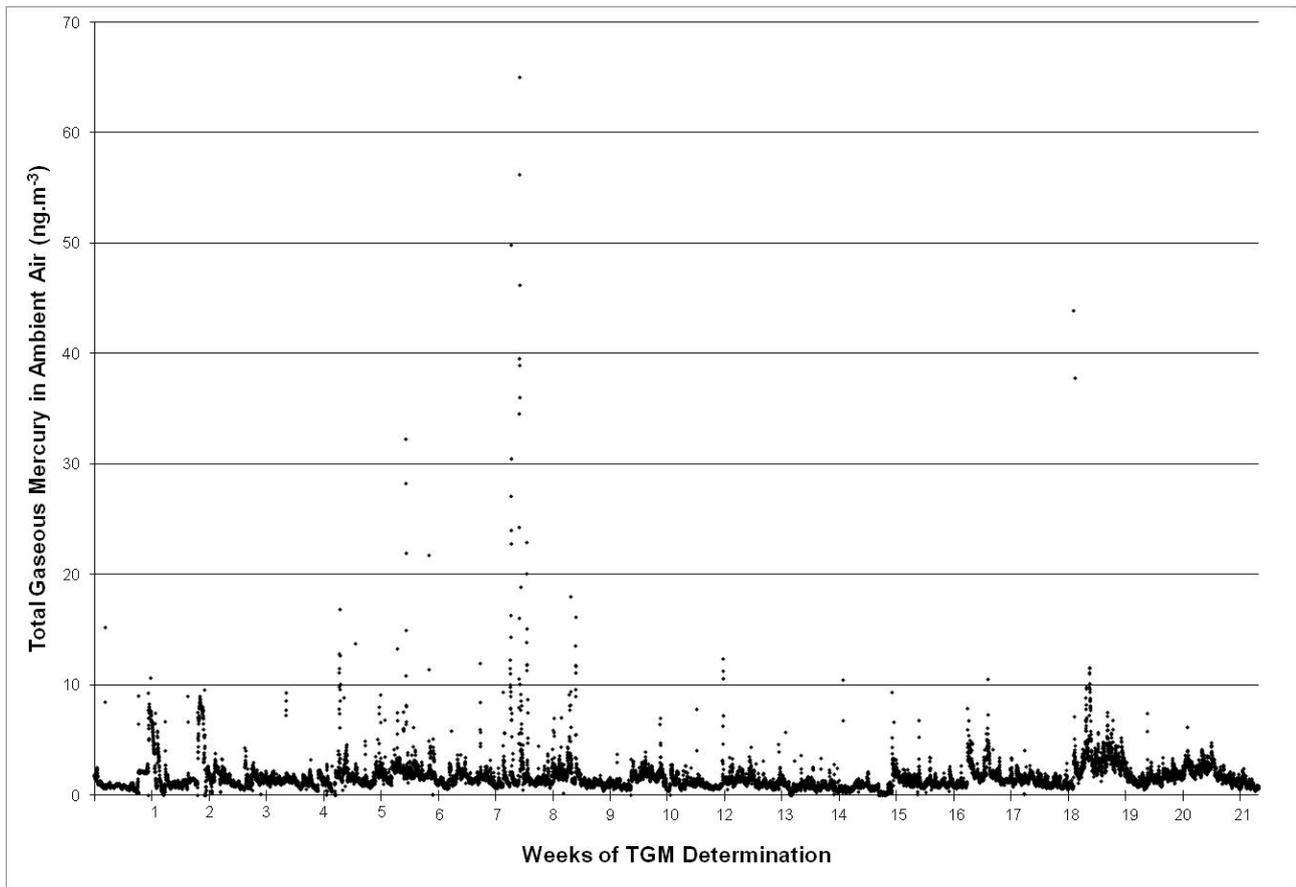


Figure 1 – Continuous atmospheric mercury measurements performed by the Opsis HG 200 SCEM

An average value was calculated from 672 Opsis HG 200 data points, recorded during seven days of operation at 15 minute intervals, to allow a comparison with the weekly TGM results obtained from analysing sorbent tubes after seven days of exposure. Weekly average elemental atmospheric mercury concentrations, determined with the Opsis HG 200, and weekly average TGM results, determined by exposing sorbent tubes in duplicate with subsequent CVAAS analysis, are compared in Figure 2. From the first week to the 11th week, both methods showed good agreement with a correlation of $r^2 = 0.8$. From the 12th week to the 21st week of exposure, a poor correlation of $r^2 = -0.6$ was achieved.

It should be noted that, according to the instrument manufacturer, the Opsis HG 200 only measures elemental atmospheric mercury. Particulate bound mercury is removed by the 0.45 μm filter and oxidised mercury is not amalgamated on the gold trap. The sorbent tubes, on the other hand, bind oxidised and particulate – bound mercury [9]. Elemental mercury is in general the dominating species in the atmosphere with concentrations measured in the ng m^{-3} range, while oxidised mercury and particulate - bound mercury are measured in the pg m^{-3} range [7]. However, in the proximity of an industrial emission source oxidised mercury may be present in much higher proportions [4]. A surge in atmospheric TGM concentrations, as recorded by the sorbent tube method but not by the mercury analyser between the 12th and 15th week, may therefore be indicative of elevated atmospheric levels of oxidised mercury.

Although no lower atmospheric TGM concentration than 1 ng m^{-3} was detected by the sorbent tube method and the theoretical limit of detection was 0.3 ng m^{-3} , it was not attempted to shorten the exposure time as this would have increased the method error. As seen in Figure 2, the RSD within duplicate tubes during the sampling campaign exceeded $\pm 13 \%$, determined in the initial study, in six instances and a shorter exposure time was therefore not desirable.

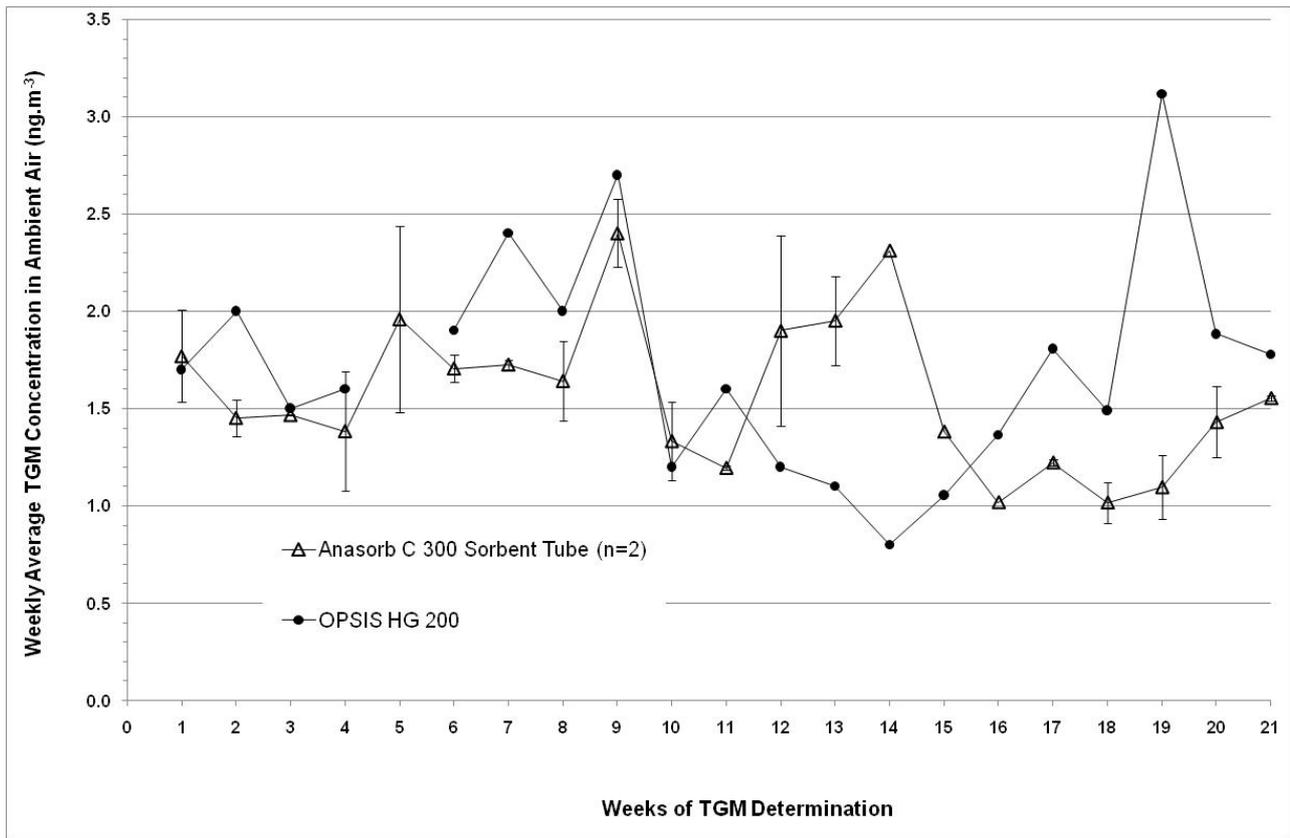


Figure 2 – Comparison of weekly average atmospheric TGM concentrations determined by sorbent tube exposure (n=2) and SCEM measurements

The average TGM concentration recorded with the Opsis HG 200 for 21 weeks was $1.7 \pm 1.9 \text{ ng m}^{-3}$ mercury, while $1.6 \pm 0.4 \text{ ng m}^{-3}$ was determined by sorbent tube / CVAAS analysis. The higher standard deviation of results obtained with the mercury analyser is due to the fact that fast temporal changes in the atmospheric mercury concentration were not recorded when using the sorbent tube method, as it only yielded a weekly average value.

Conclusions

Measurements of atmospheric mercury were performed simultaneously with an Opsis HG200 mercury analyser as well as with a combination of sorbent tube trapping with subsequent CVAAS analysis. Weekly average values during the first half of the sampling campaign as well as overall average atmospheric mercury concentrations were in good agreement, showing the sorbent tube approach to atmospheric mercury monitoring to be potential economical alternative to the use of an SCEM.

The apparent disadvantage of using sorbent tubes is that short spikes would not be recorded due to a minimum of one week exposure time for Anasorb C300. However, a number of actively pumped sorbent tubes, placed around a suspected emission source, will deliver valuable information if wind speed and direction are included in the evaluation of results. In fact, this approach may be more effective in pin-pointing mercury emissions than placing one SCEM at a fixed position for a prolonged period of time.

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