Determination of Total Mercury in Ambient Air using Amalgamation with Atomic Fluorescence Spectrometry

Accurate air quality measurements for total gaseous mercury (TGM) are required to monitor the exposure of the general population, assess legislative compliance limits and to provide information to the general public. Mercury is recognised as an important pollutant because of its detrimental effects on human health. Coal-burning power plants are the largest anthropogenic source of mercury emissions to the air.

Burning hazardous wastes, the chlor-alkali industry, crematoria, breaking mercury products, and spilling mercury, as well as the improper treatment and disposal of products or wastes containing mercury, can also release it into the environment. Elemental mercury primarily causes health effects when it is inhaled in the vapour form, where it can be absorbed through the lungs. Symptoms of high exposure can include: tremors; emotional changes; insomnia; neuromuscular changes; headaches; disturbances in sensations; changes in nerve responses; and performance deficits on tests of cognitive function. At extreme exposures there may be kidney effects, respiratory failure and death. The population is exposed to mercury in ambient air mainly via mercury vapour, and the vast majority of this mercury vapour is elemental mercury (except at some industrial and coastal locations). The health effect of mercury is cumulative.

We will describe the instrumentation and methodology for manual and automated TGM measurements using amalgamation – atomic fluorescence spectrometry. Typical results will be presented from various sites around Europe.

Sampling and Instrumentation

The PSA 10.525 Sir Galahad system is shown in Figure 1. Calibration is achieved by injection of saturated Hg vapour at known temperature using a gas tight syringe [1]. The analyser can be configured for manual remote sampling or automated continuous measurements. For manual sampling a pump is used to pull the sample across the gold impregnated silica trap (AmasilTM) at a controlled flow rate. Typically a sample flow rate of 100ml/min is used and traps are exchanged weekly. This equates to a sample volume of 1 m^3. During the development of this method it was established that the no poisoning of the gold trap was found even with such large sample volumes. This is due to the large surface area of the AmasilTM trap and the self cleaning routine during the measurement. It is worth noting that the gold trap amalgamation will collect all forms of mercury so the measurement represents TGM. The sampling arrangement for manual sampling is shown in Figure 2.

Figure 1: The PSA 10.525 Sir Galahad Amalgamation – AFS System

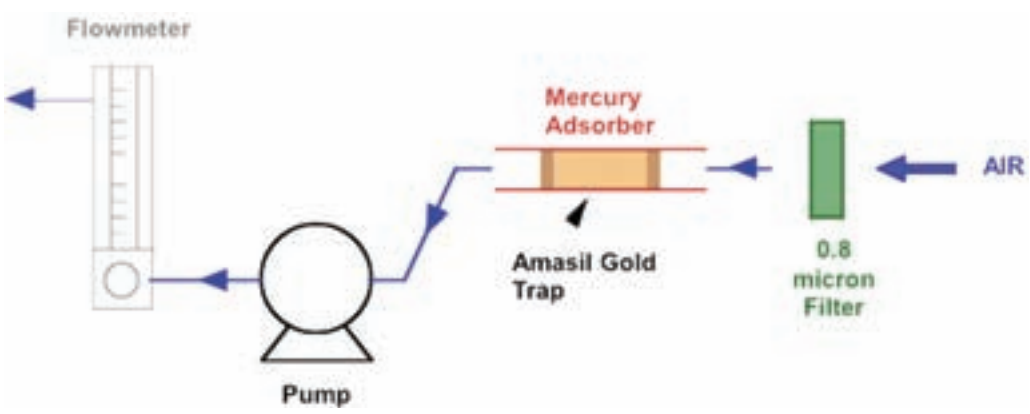

Figure 2: Schematic drawing of Manual Sampling Arrangement

After sampling, the tubes are returned to the laboratory for determination of mercury. This is achieved by thermally desorbing the Hg from the remote trap using a temperature of approximately 800°C. A carrier gas of argon transfers the desorbed Hg from the remote trap to a permanent trap. This Hg is then thermally desorbed and delivered to an atomic florescence spectrometer. The advantage of this approach is that one analyser located in a central laboratory can be used to monitor the mercury at numerous sites. The large sample volume and inherent sensitivity of the instrumentation provide method detection limits below 0.01ng/m^3. The duration for the measurement cycle is less than 5 minutes and once cleaned the traps can be re-used. A schematic drawing showing the analysis of remote traps is shown in Figure 3.

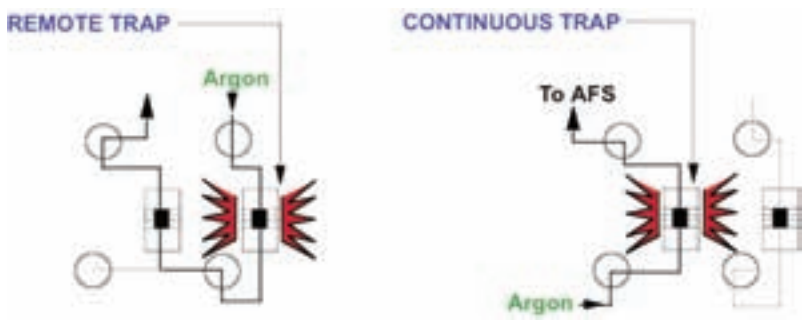

Figure 3: Schematic of Remote tube Analysis using dual amalgamation – AFS

Typical Results

The National Physical Lab (NPL) currently makes measurements of total gaseous mercury at 13 locations around the United Kingdom as part of its operation of the UK Heavy Metals Monitoring Network on behalf of the UK Department for Environment, Food and Rural Affairs (DEFRA). Mercury concentration plots based on weekly averages over a 3 year period at four UK urban/industrial sites are presented in Figures 4-7.

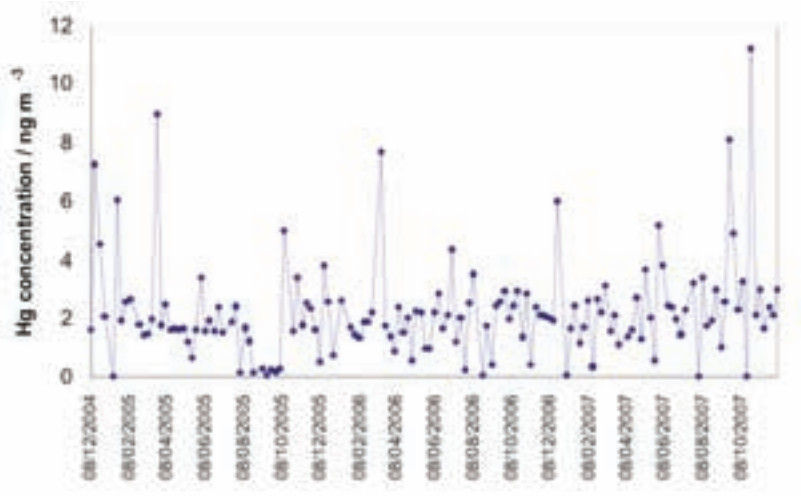

Figure 4: Total Gaseous Mercury in West Midlands, UK at a site close to a company producing copper based alloys

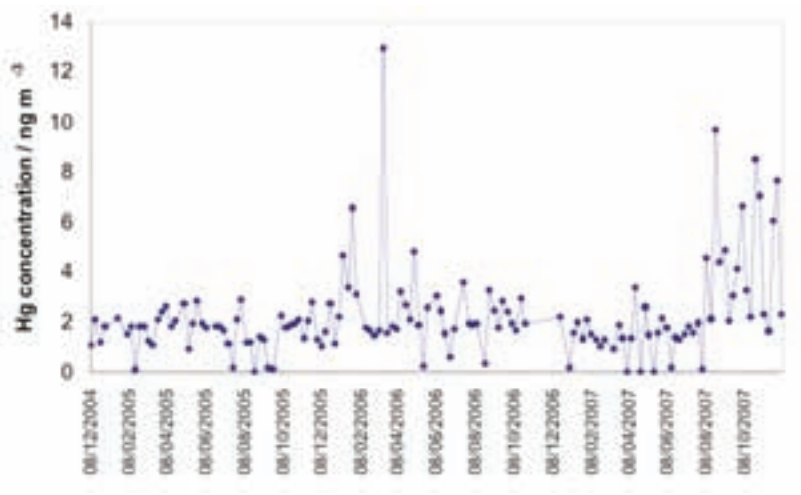

Figure 5: Total Gaseous Mercury in West Midlands, UK at a site close to a copper refinery.

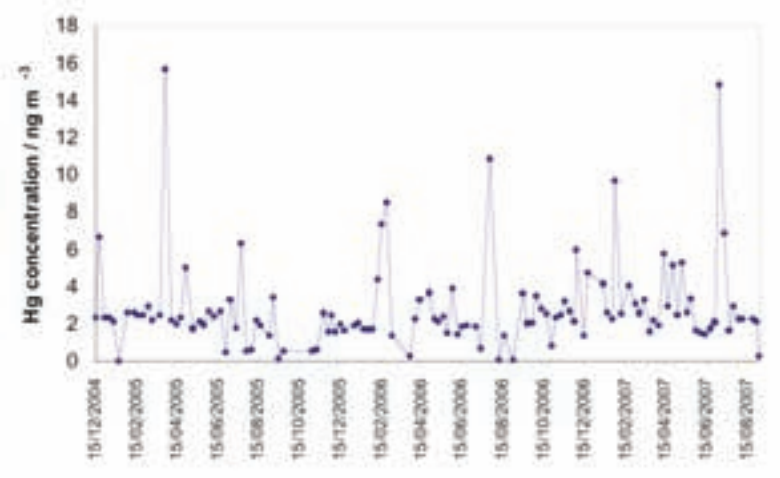

Figure 6: Total Gaseous Mercury at former steel works (Elswick 6) in Newcastle, UK

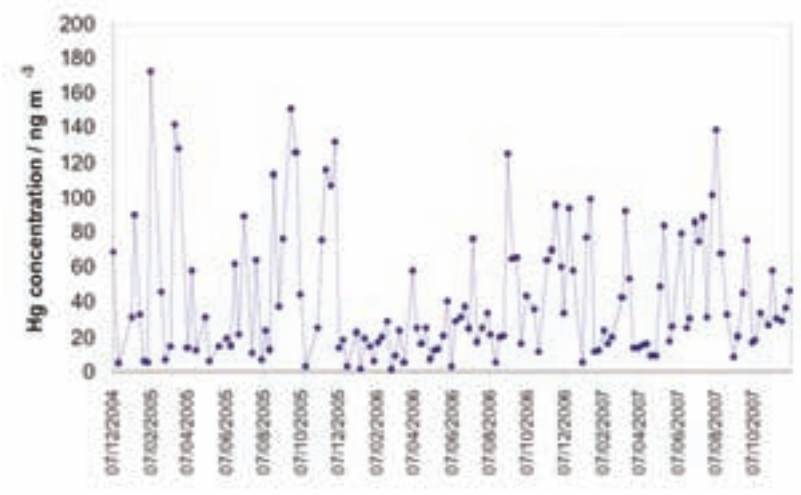

Figure 7; Total Gaseous Mercury in Runcorn, UK at a site close to a chlor-alkali plant

Automated Continuous Measurements

The 10.525 Sir Galahad can be configured for continuous automated measurements of TGM. In this case a pump and mass flow controller arrangement is used to continuously draw sample across the permanent trap. A schematic drawing is shown in Figure 8 illustrating a typical arrangement. The sample flow rate is typically between 800-1000ml/min with a collection times between 5-30 minutes depending in the expected concentration range at the air monitoring site. A TGM concentration plot against time is shown in Figure 9. This study was conducted in a coastal area in Sweden using two parallel PSA analysers. Good agreement was obtained between the two analysers. The average value produced by each analyser agreed within the uncertainty of the measurement. This is particularly impressive since, for automatic measurements, one is measuring only about 5-30 pg of mercury during each sampling period

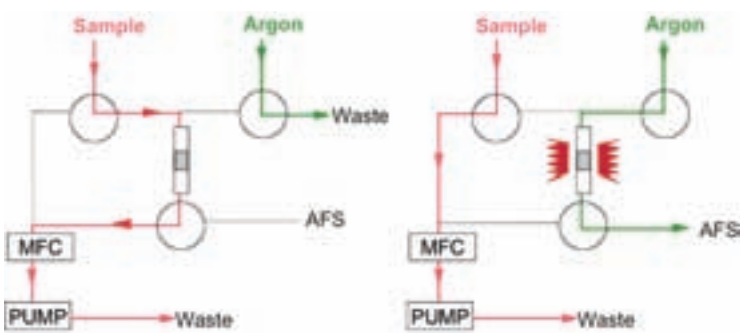

Figure 8: Schematic Drawing of Continuous Automated Measurements

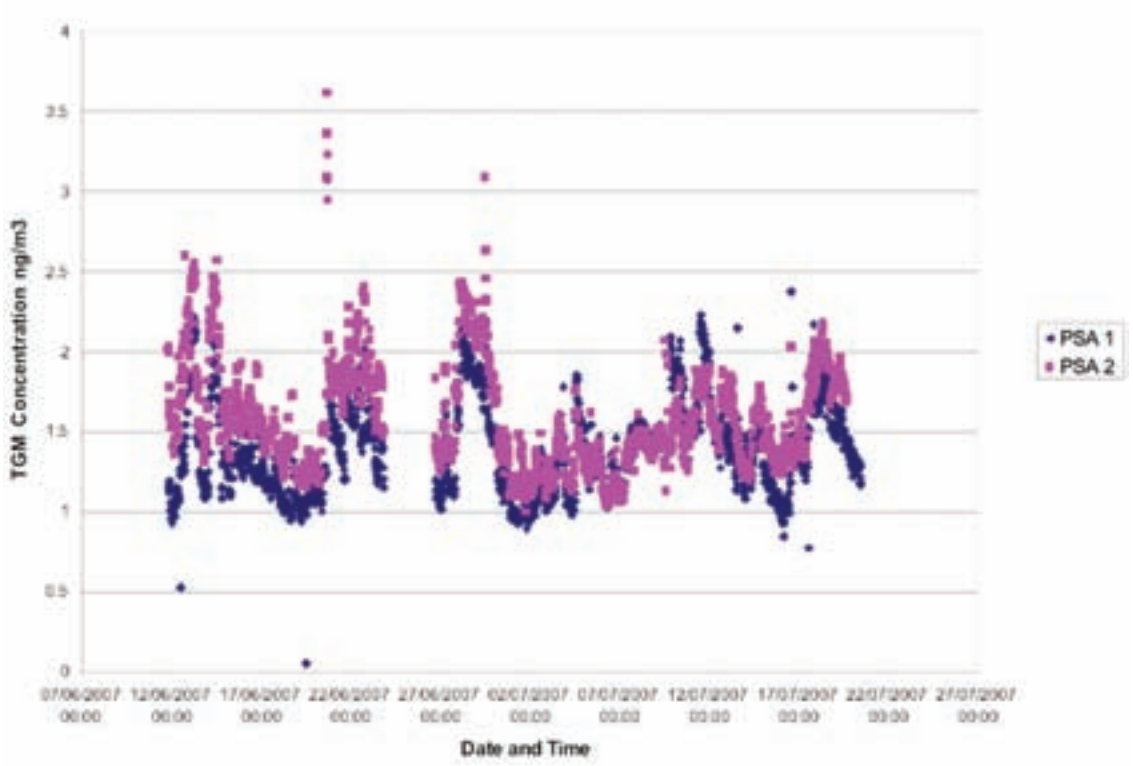

Figure 9: Parallel Measurements of TGM using two PSA online analysers over a 2 month period

Conclusions

In this article we have outlined the importance of conducting TGM measurements so that exposure of Hg to the general population can be monitored and sensible legislations can be developed. We have described the methodology and instrumentation for both manual and automated approaches. The manual approach has been used successfully by the NPL for several years and this approach offers the advantage of running many air monitoring sites with a single analyser located in a central laboratory. The ability to collect large sample volumes without poisoning the gold trap is largely down to high surface area provided by the AmasilTM material. Method detection limits for manual sampling are below 0.01ng/m^3.

For the measurements made by NPL as part of its operation of the UK Heavy Metals Monitoring Network, it has been determined that the expanded uncertainty, at the 95% confidence interval, of the concentration of total gaseous mercury in ambient air is 16.7% [2]. Please note that this is well below the target uncertainty of 50% set by the European Union for these measurements [3]. Automated online measurements offer the advantage of concentration trending which is particularly important when monitoring urban and industrial sites so that the higher levels of exposure due to industrial activity can be observed and controlled. The method detection limit for the automated approach is below 0.05ng/m^3 which is well below the typical concentration of TGM in ambient air.

References

[1]R. Dumarey, E. Temmerman, R. Dams and J. Hoste, The accuracy of the vapour injection calibration method for the determination of Hg by amalgamation CV-AAS. Anal. Chimica Acta., 1985, 170, 337.

[2] R. J. C. Brown, A. S. Brown, R. E Yardley, W. T. Corns, P. B. Stockwell, A practical uncertainty budget for ambient mercury vapour measurement. Atmospheric Environment (2008), doi:10.1016/j.atmosenv.2007.12.012

[3] Council Directive 2004/107/EC of the European Parliament and of the Council of 15 December 2004 relating to arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons in ambient air, Official Journal of the European Union, L023, 2005, 3-16.

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