

**Pollutant Type:** Gaseous Pollutants

**Pollutant Name:** Total gaseous mercury

**Measurement Technology:** Direct Cold Vapour Atomic Absorption  
Trap and Desorb Cold Vapour Atomic Absorption  
Trap and Desorb Cold Vapour Atomic Fluorescence

The legislative requirement in Directive 2004/107/EC for mercury measurement in the vapour phase in Europe is for 'total gaseous mercury' (TGM) at background sites. TGM is described as "elemental mercury vapour ( $\text{Hg}^0$ ) and reactive gaseous mercury, i.e. water-soluble mercury species with sufficiently high vapour pressure to exist in the gas phase." Measurements of reactive gaseous mercury (RGM) and mercury in  $\text{PM}_{10}$  are recommended at background sites.

The reference method for the measurement of total TGM in Europe, EN 15852, allows automatic measurement by either cold vapour atomic absorption spectroscopy (AAS) or cold vapour atomic fluorescence spectroscopy (AFS) [Brown, *et al*, 2010]. Cold vapour refers to the fact that measurements of mercury vapour may be made at room temperature. Generally a pre-concentration step is required prior to analysis. This usually involves the collection of total gaseous mercury from the air onto an adsorption tube (usually called a 'trap') containing gold in some form, which strongly binds any mercury. The mercury is then liberated from the traps using thermal desorption, prior to analysis. This pre-concentration process is usually referred to as 'trap-and-desorb'. It is generally accepted that the 'trap-and-desorb' method, which is normally operated with a pre-filter to prevent any particulate matter reaching the trap, collects both gaseous elemental and reactive gaseous mercury, therefore making it suitable for the measurement of TGM. During thermal desorption it is assumed that both the adsorbed elemental and reactive gaseous mercury are liberated as gaseous elemental mercury. In addition to the 'trap-and-desorb' method, EN 15852 allows direct measurement using AAS – providing suitable compensation for cross-interferences is made. In this case only gaseous elemental mercury is measured. However, given that the maximum allowable expanded uncertainty quoted by Directive 2004/107/EC for TGM measurement is 50 % and that the vast majority of gaseous mercury is gaseous elemental mercury (>95%, except at some exceptional polar and industrial locations) it is considered that Zeeman correction-AAS (see below) is fit-for-purpose for TGM measurement in ambient air.

Trap-and-desorb instruments tend to sample at flow rate of 0.5 l/min and below in order to avoid breakthrough on the gold absorption tubes. Direct measurement instruments usually sample at much faster flow rates of 20 l/min to ensure a homogeneous sample when producing high resolution data. Measured concentrations at background sites are usually 1-3 ng/m<sup>3</sup>.

All measurements of mercury vapour in air are currently traceable to the saturated mass concentration of mercury in air [Dumarey, *et al*, 2010].

## **A. Atomic absorbance spectrometers**

### *Direct atomic absorbance spectrometers*

These analyzers directly measure the absorbance of light at 253.7 nm through a sample stream. The difficulty with these analyzers is that there are significant cross interferences from other gaseous compounds, such as ozone, sulfur dioxide and hydrocarbons that absorb at this wavelength. In many cases these interfering compounds will be present at concentrations significantly in excess of that of mercury in ambient air. For this reason these direct analyzers find most uses in stack applications where mercury concentrations are often of the order of  $\text{mg/m}^3$ . Without any background correction mechanism these instruments are likely to be limited to detection limits of a few  $\mu\text{g/m}^3$ . Two mechanisms exist for compensating for cross interferences.

The first of these is to use a dual path instrument, where the second sampling path involves a mercury scrubber prior to the measurement cell and thus the absorbance owing to mercury in the gas stream is given by the difference in these two readings. However, the poor signal-to-noise levels achieved impose a high detection limit.

The second compensation method, Zeeman correction, is more successful. This technique uses magnetic fields to induce frequency splitting in the absorption bands allowing the absorbance owing to mercury to be measured in the absence of interferences. The detection limit achievable using this technique is around  $2 \text{ ng/m}^3$  and it is the only form of direct AAS instrument suitable for ambient air monitoring. Despite the relatively poor detection limit when compared with trap-and-desorb instruments these instruments produce the highest time resolution data – as high as a measurement every second. Usually these instruments are provided with a ‘factory calibration’ where the absorbance of a known mass concentration of mercury has been measured. This measurement is used to calculate the absorption cross section of mercury vapour in the measurement cell, which is then used to calculate unknown concentrations which the instrument is exposed to.

### *Trap-and-desorb atomic absorbance spectrometers*

These instruments work on the same detection principle as the direct AAS instrument, except that they involve an initial pre-concentration step during which mercury vapour is adsorbed onto a gold trap in the gas stream, prior to subsequent thermal desorption and detection. Whilst many potential interferences will be eliminated by this two stage process, some may co-absorb with the mercury vapour onto the gold and will therefore be measured at the same time as the mercury vapour, possibly causing an unknown bias on the measurement result. Usually these instruments heat the mercury absorption tubes in air, resulting in pyrolysis of any other absorbed compounds which can also limit the lifetime of the absorption tubes. The instruments currently on the market have only one trap, so that whilst this trap is being analyzed, no air is being sampled, resulting in a loss of data capture. However there is no reason why these instruments could not be manufactured with dual traps (see later). The sampling period for these instruments could be anywhere between 10 minutes and 1 day depending on the ambient concentration and the particular design of the sampling trap.

These analyzers are calibrated by injection of known volumes of saturated mercury vapour directly onto the sampling trap of the instrument [Brown and Brown, 2008].

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## **B. Atomic fluorescence spectrometers**

All atomic fluorescence spectrometers operate with pre-concentration using gold traps. Some of the traps used in conjunction with AFS instrument have very large capacities, allowing sampling periods to range from 10 minutes to one month. Two types of instrument are available: a single trap instrument which suffers from loss of data capture during thermal desorption (although for longer sampling periods this is negligible), and dual trap instrument which samples onto one tube whilst the other is being heated and analyzed thereby not losing any data capture. The disadvantage of the dual trap system can be that slightly different readings are given by each channel especially if tube degradation is a serious problem. The sample traps are thermally desorbed under an argon atmosphere since any molecular species present in the carrier gas could quench the fluorescence. Hence AFS is not suitable for direct measurement in air.

Free mercury atoms in the carrier gas are excited by a collimated ultraviolet light source at a wavelength of 253.7 nm. The excited atoms re-radiate their absorbed energy via fluorescence at this same wavelength. Unlike the directional excitation source, the fluorescence is omnidirectional and may thus be detected using a photomultiplier tube or UV photodiode. The technique is generally more sensitive, more selective, and is linear over a wider range of concentrations than atomic absorption, and it usually does not suffer from cross-interferences because other species do not both absorb and fluoresce at this frequency. For this reason AFS instruments are more expensive than AAS instruments. Any co-eluting species, such as hydrocarbons which may absorb the fluoresced light may cause a slight cross interference, but a more serious problem is particulate matter, often liberated from the gold traps themselves, which can act to scatter the incident radiation at 253.7 nm and impose a small positive bias on the measurements. Detection limits for trap and desorb methods depend additionally on sample volume, however, conservatively, these methods can achieve  $0.1 \text{ ng/m}^3$  – this is generally limited by the repeatability of the gold traps.

These analyzers are calibrated by injection of known volumes of saturated mercury vapour directly onto the sampling trap of the instrument.

## **C. Reactive gaseous mercury and particulate mercury**

Only one system currently on the market is able to perform automatic measurement of reactive gaseous mercury and/or particulate phase mercury – making these in the  $\text{PM}_{2.5}$  fraction. This system first traps any RGM using an annular denuder (often coated with materials such as KCl) and then downstream the particulate phase mercury is trapped on a quartz particulate filter. The particulate trap is then heated which desorbs any particulate mercury collected and regenerates the trap. Similarly the annular denuder is subsequently heated to allow determination of the RGM. A downstream pyrolyser ensures all mercury species are converted to elemental mercury. In both cases analytical measurement is performed using the trap-and-desorb AFS technology described above. Sampling times are generally at least 30 minutes with high flow rates of 10 l/min to ensure there is enough material to detect, since both RGM and particulate mercury are usually only present at low  $\text{pg/m}^3$  levels in ambient air.

## References

- Brown, RJC, Brown, AS (2008) "Accurate calibration of mercury vapour measurements." *Analyst*, 133: 1611-1618.
- Brown, RJC, Pirrone, N, van Hoek, C, Sprovieri, F, Fernandez, R, Toté, K (2010) "Standardisation of a European measurement method for the determination of total gaseous mercury: results of the field trial campaign and determination of a measurement uncertainty and working range." *Journal of Environmental Monitoring* 12: 689-695.
- Dumarey, R, Brown, RJC, Corns, WT, Brown, A S, Stockwell, PB (2010) "Elemental mercury vapour in air: the origins and validation of the 'Dumarey equation' describing the mass concentration at saturation." *Accreditation and Quality Assurance* 15: 409-414.

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