

SI Traceability of Calibration Techniques for Online Gas-Phase Mercury Monitors

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Introduction

Mercury is a highly toxic and persistent pollutant found in ambient, indoor and workplace air. Coal-burning power plants are the largest anthropogenic source of mercury emissions to the air, whilst the chlor-alkali industry, crematoria, breaking mercury products, and the burning and improper disposal of products or wastes containing mercury, can also release mercury into the environment. Human exposure to mercury can also be via dental amalgam and the ingestion of crops, animal products or water contaminated by mercury following deposition processes.

Accurate measurement of the concentration of mercury vapour in ambient air is essential in order to meet European legislation [1] established to protect the health of the public. In the UK, NPL operates the UK heavy metals monitoring network [2] on behalf of the Government's Department for Environment, Food and Rural Affairs. This network requires the measurement of the mercury vapour concentration at 15 monitoring sites across the UK. (The concentration of twelve particulate-bound metals the same sites is also determined at by ICP-MS analysis.)

The vast majority of mercury vapour measurements currently undertaken around the world are ultimately traceable to the vapour pressure of mercury. This is given in the scientific literature by several different empirical equations [3], but the agreement between these is not good, with data from different equations sometimes differing by up to 10 % (see Figure 1). There is no current international agreement on which is the best equation to use, meaning that results obtained from methods using different equations may not be able to be compared directly.

The mercury vapour equation is used to calculate the mass of mercury withdrawn from a 'bell-jar' calibration device (see Figure 2) containing a small amount of elemental mercury. A saturated vapour of mercury develops within the bell-jar, and a known volume of this vapour is sampled with a gas-tight syringe via a septum. The temperature of the vapour is recorded, thus allowing the mass of mercury removed to be calculated.

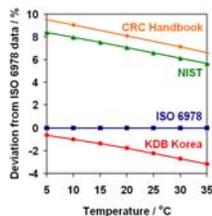


Figure 1 Graph showing the relative difference between four commonly used empirical equations for the vapour pressure of mercury. The data is plotted relative to the vapour pressure calculated by the most commonly used equation, that in ISO 6978-2 [4].



Figure 2 The 'bell-jar' calibration apparatus used to provide a known volume of mercury-saturated air for calibration of the mercury vapour analyser.

For automatic measurements, calibration may also take place by means of a dynamic mercury vapour generator, which produces mercury-saturated air by flowing a constant stream of clean air through a chamber containing a heated mercury reservoir. This dynamic mercury vapour generator is therefore in turn ultimately traceable to the vapour pressure of mercury and the bell-jar. The full traceability chain for these measurements is shown in Figure 3a.

This article provides an overview of recent work at undertaken at NPL [5], which has for the first time linked directly mercury vapour measurements to standards of mass - thus establishing traceability for these measurements to the SI system of units. The work was carried out in collaboration with P S Analytical.

SI traceability has been achieved by collecting the output from a dynamic mercury generator over a period of time long enough such that the amount of mercury accumulated on a desorption tube could be determined gravimetrically. The mass output rate of mercury calculated from this procedure was then used to dose other adsorption tubes with much smaller masses of mercury, similar to the masses removed from the bell-jar during calibration. Using this approach, the saturated mercury vapour concentration in the bell-jar could be linked to the SI by the novel traceability chain shown in Figure 3b. Note that the order of the traceability hierarchy in Figure 3b is different to that shown in Figure 3a as the bell-jar is now positioned below the mercury vapour generator - this difference arises as the dynamic mercury vapour generator is now directly traceable to standards of mass.

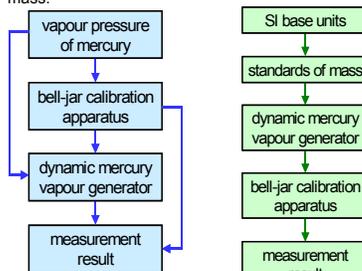


Figure 3 Traceability chains for mercury vapour measurements: traditional (Figure 3a), and novel (as demonstrated in this work) (Figure 3b). The arrows represent the direction in which the traceability hierarchy descends.

Experimental challenges

A number of experimental challenges were overcome during the course of the work. Firstly, in order to weigh the small amount of mercury collected on the tube (a mass of only approximately 140 µg on a tube weighing 8 g, i.e. less than 2 parts in 10⁵), a high accuracy (1 µg resolution) balance with a custom-built pan was used, with precautions taken to eliminate the effects of static charges. A buoyancy correction was also applied to all measurements - this is crucial for a weighing of such accuracy, as a change in air pressure of only 20 mbar between the weighings before and after sampling (a realistic scenario in the United Kingdom) would change the true mass of the tube by over 70 µg - equivalent to half the mass of mercury collected.

Also, as adsorption tubes were dosed for approximately 24 hours to enable a sufficient mass of mercury to be collected, the output of the dynamic mercury generator had to be demonstrated to be stable over long periods of time. This was achieved by calculating the Allan deviation from the response of the mercury generator over an extended period of time, which was shown to generate no significant drift.

Finally, the accuracy of the atomic fluorescence analysis of the adsorption tubes dosed with smaller masses of mercury was improved by using a drift correction procedure, where the response of the instrument to a known mass of mercury was measured regularly during the course of the analysis. A polynomial function was fitted to these data, and subsequently applied to the instrument responses obtained from all calibration injections and analyses of the dosed tubes.

Results

The results from the study are summarised in Figure 4, which shows the relationship between the drift-corrected instrumental response and the mass of mercury for three sets of data:

- (1) 'Bell-jar': Mass of mercury determined from the volume of saturated mercury vapour injected from a syringe and the saturated mercury vapour equation.
- (2) 'Sampled tubes - gravimetric': Mass of mercury determined from the mass output rate determined by gravimetry, multiplied by the sampling time
- (3) 'Sampled tubes - generator': Mass of mercury determined from the mass output rate determined from the instrument settings, multiplied by the sampling time.

In order to enable each set of data to be seen clearly, x-axis offsets of 100 ng and 250 ng have been applied to the second and third data sets respectively.

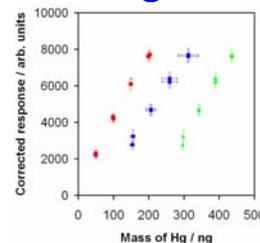


Figure 4 Plot of corrected instrumental response against mass of mercury for three sets of data: (1) 'bell-jar' [•], (2) 'sampled tubes - gravimetric' [■, x-axis offset by 100 ng], (3) 'sampled tubes - generator' [▲, x-axis offset by 250 ng].

To investigate the agreement of the three data sets, generalised least-squares (GLS) fits were performed to the data (thus taking into account the uncertainties inherent in both the x-axis and y-axis data). The GLS output quantity compared is the gradient of the calibration curve, which is effectively the drift corrected sensitivity of the instrument. Variations in the masses of mercury determined for the three sets of data mean that individual points from different data sets cannot be compared directly, but they can be compared as part of a set of points (the calibration relationship) that define the sensitivity of the instrumental response.

Dataset	Gradient
(1) Bell-jar	35.9 ± 1.6
(2) Sampled tubes - gravimetric	30.9 ± 3.7
(3) Sampled tubes - generator	34.4 ± 2.2

Table 1 Gradient and expanded uncertainty of the linear best fit obtained by GLS analysis of the three data sets in Figure 4.

The calculated gradients of each line are shown in Table 1 where it can be seen that all three values agree with each other within their expanded uncertainties. The agreement between the first two sets of data ('bell-jar' and 'sampled tubes - gravimetric') shows that when using the most common equation relating saturated mercury in air concentrations with respect to temperature. [6]:

$$Y_{Hg} = \delta \cdot \frac{D}{T} \cdot 10^{-4} \left(\frac{A}{T} \right)^B$$

The predicted mercury masses are compatible with those determined using a method traceable to the SI system of units through the unbroken chain of traceability shown in Figure 3b.

(In the above equation, Y_{Hg} is the saturated mass concentration of mercury vapour in air; T is the temperature of saturated vapour inside the bell-jar; A , B and D are empirically-determined constants equal to -8.1344, 3,240.9 K and 3,216,522 K.ng.ml⁻¹ respectively; and δ is the deviation of the theoretical saturated vapour mass concentration of mercury in the bell-jar from reality, which was assigned a value of unity for this study.)

Conclusions

The agreement between the data in Table 1 shows that this work has confirmed that a direct traceability link may be made between measurements of mercury vapour in ambient air and the SI. Thus in theory, SI traceable measurements can either be made directly, using the mass output of the mercury vapour generator, or indirectly, using this mass output to provide a calibration of the expected mass concentration of mercury saturated air within the bell jar apparatus. Importantly, this method does not need any knowledge of the predicted output of the mercury vapour generator, or even how it operates; it only requires that its mass output rate, and the rate at which the output is sampled, has a variability or drift over time which is minor in comparison to the ability to perform an analysis of the mercury collected on an adsorption tube.

References

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