

Establishing SI traceability for measurements of mercury vapour

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Received 4th March 2008, Accepted 1st April 2008

First published as an Advance Article on the web 30th April 2008

DOI: 10.1039/b803724h

The majority of measurements of mercury vapour, for example those to determine mass concentration in air, are currently ultimately traceable to the vapour pressure of mercury, usually *via* a bell-jar calibration apparatus. This allows a saturated concentration of mercury vapour in air to develop in a confined space in equilibrium with ambient conditions, from which a known mass of mercury can be removed for calibration purposes. Several empirical equations are available to describe the vapour pressure of mercury at a given temperature, but the agreement between them is not good, with data from different equations sometimes differing by 5% or more. In order to remove the dependence of mercury vapour measurement on these empirical equations, and to provide stability, comparability and coherence for mercury vapour measurements, this paper describes work undertaken to link directly mercury vapour measurements to standards of mass, and therefore to establish traceability for these measurements to the SI system of units. This has been achieved by measuring the mass output rate of a dynamic mercury vapour generator gravimetrically, and linking this to the expected mass concentration in the bell-jar apparatus. The SI traceable mercury vapour measurements have been shown to agree with the predicted output from the bell-jar, as defined by the most commonly used empirical mercury vapour pressure equation, within the uncertainty of the measurement.

Introduction

The toxicity, environmental persistence, and potential for bioaccumulation of mercury mean that it is a particularly insidious, and therefore highly important environmental pollutant to monitor and manage. Many national and international authorities are currently acting to reduce human and environmental exposure to mercury.¹ Coal-burning power plants are the largest anthropogenic source of mercury emissions to the air. The chlor-alkali industry, crematoria, breaking mercury products, and the burning and improper treatments of waste containing mercury can also release mercury into the environment. An example of this is the contamination of water through the inappropriate disposal of mercury compounds. The population is exposed to mercury in air (ambient, workplace and indoor) mainly *via* mercury vapour, and the vast majority of this vapour is elemental mercury (except at some industrial and coastal locations).² Human exposure to mercury can also be *via* dental amalgam, the ingestion of crops, animal products or water contaminated by mercury following deposition processes. Exposure in these cases is usually *via* organic mercury compounds, such as methyl mercury, but also *via* some inorganic mercury compounds. Moreover, the health effects of mercury are cumulative.

The measurement of mercury vapour in air is typically carried out using a pump to sample air at a monitoring location at a

known rate for a known time onto an adsorption tube (usually comprising gold-coated silica). The mercury on this adsorption tube is then thermally desorbed, and measured by atomic fluorescence spectrometry or atomic absorption spectrometry (AAS). (Other analysis systems measuring mercury in air directly by Zeeman-AAS without adsorption tubes are available, but are ultimately traceable to the same source as described below.) The analytical instrument is calibrated by use of a gas-tight syringe, making multiple injections of known volumes of mercury vapour at known temperature into the analyser. These known amounts of mercury vapour are generated using a glass bell-jar apparatus (shown diagrammatically in Fig. 1) containing a small amount of elemental mercury. This allows a saturated vapour of mercury to develop within the air in the bell-jar, which is in equilibrium with the atmosphere *via* a capillary tube.³ The temperature of the vapour inside the bell-jar is monitored with a calibrated platinum resistance thermometer, and samples of the

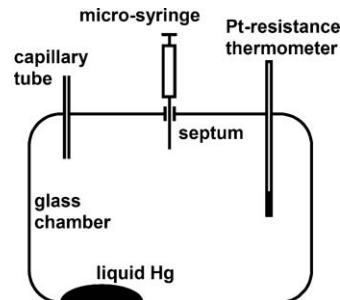


Fig. 1 Diagrammatic representation of the bell-jar calibration apparatus.

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vapour are taken with the gas-tight syringe through a septum in the top of the bell-jar.

Alternatively, especially for automatic measurements, the analytical instruments may be calibrated by means of a dynamic mercury vapour generator that produces mercury-saturated air by flowing a constant stream of air through a chamber containing a heated mercury reservoir. This dynamic mercury vapour generator is then in turn ultimately traceable to the vapour pressure of mercury and the bell-jar. (Note that the measurements of gas flow rate and temperature in this study are traceable to national standards.)

The mass of mercury contained per unit volume of mercury-saturated air in the bell-jar at a given temperature is calculated through the use of an empirical equation [eqn (1) below], and the uncertainty of this method is detailed elsewhere.⁴ The traceability chain for the method described in the previous paragraph is displayed diagrammatically in Fig. 2a, which shows that these measurements are ultimately traceable to the vapour pressure of mercury. Note that both the bell-jar and the mercury vapour generator are shown to be directly traceable to the vapour pressure of mercury as both devices rely upon this parameter to calculate the output mercury concentration. The mercury vapour generator is positioned below the bell-jar in the hierarchy of traceability as measurements from the former can also be traceable to the latter.

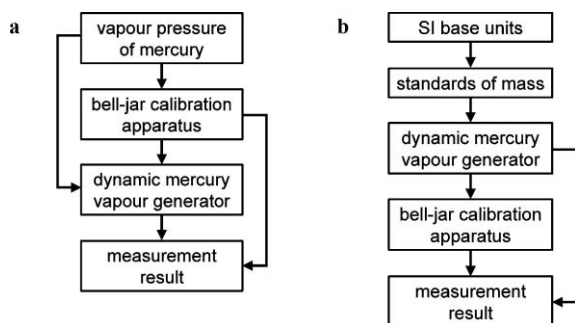


Fig. 2 Traceability chains for mercury vapour measurements: traditional (Fig. 2a), and novel (as demonstrated in this paper) (Fig. 2b). The arrows represent the direction in which the traceability hierarchy descends.

There has been much work to determine the vapour pressure of mercury, dating back to 1801, and almost 70 different data sets are available.⁵ However, a number of these data sets either do not have an uncertainty statement associated with them, or do not agree within the stated uncertainty. In such a situation, data sets that are in common usage, such as the Dumarey³/ISO 6978⁶ data set, will tend to prevail. This relationship describes how the saturated vapour concentration of mercury changes with temperature thus:

$$\gamma_{\text{Hg}} = \delta \frac{D}{T} 10^{\left\{A + \frac{B}{T}\right\}} \quad (1)$$

where γ_{Hg} is the saturated mass concentration of mercury vapour in air (in ng ml⁻¹); T is the temperature of saturated vapour inside the bell-jar (in K); A , B and D are constants equal to -8.1344 , 3240.9 K and 3216522 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. The δ parameter was first introduced in ref. 4 and the uncertainty in δ is often the dominant contributory factor to the overall uncertainty in mercury vapour measurements. However, for the purpose of this study, which attempts to investigate the validity of this equation, δ is assigned a value of unity. A full discussion on this topic is available in ref. 4.

As discussed above, measurements of mercury vapour are not currently directly traceable to the SI system of units, but instead to empirical relationships describing the vapour pressure of mercury at any given temperature. The result of a measurement will therefore depend on which equation is chosen to represent the vapour pressure of mercury, and its accuracy. Implementing a measurement method with direct traceability to the SI system of units for these measurements would provide stability, comparability and coherence,⁷ and would render any argument about the most appropriate vapour pressure equation redundant.

This paper demonstrates a novel procedure to provide SI traceability for mercury vapour measurements by calibrating the saturated vapour concentration of the bell-jar apparatus with respect to the mass output of a dynamic mercury vapour generator, which in turn is measured traceable to standards of mass. Very few other studies aimed at providing traceability for mercury vapour measurements exist in the literature.^{8,9}

In this study, traceability has been achieved by collecting the output from the dynamic mercury generator over a period of time long enough such that the accumulated mercury could be weighed using a high accuracy balance. (It was also important to ensure the temporal stability of the dynamic mercury generator over long periods.) The mass output rate calculated from this procedure was then used to dose adsorption tubes with much smaller masses of mercury, similar to the masses drawn from the bell-jar during calibration. Using this approach, the saturated mercury vapour concentration in the bell-jar could be linked to the SI system of units. This methodology aims to confer a novel traceability chain on these mercury vapour measurements as displayed in Fig. 2b. The order of the traceability hierarchy in Fig. 2b is different to that shown in Fig. 2a as the bell-jar is now positioned below the mercury vapour generator. This difference arises from the direct traceability of the mercury vapour generator to standards of mass, demonstrated through this study.

Experimental

Overview

In order to assist the reader, an overview of the experimental work undertaken to provide SI traceability for measurements of mercury vapour is given here. This is discussed in more detail in subsequent sections:

- The output mass flow rate of mercury from the mercury vapour generator was determined gravimetrically by sampling onto an adsorption tube for an extended period of time and weighing the mass of mercury collected.
- A number of other adsorption tubes were then dosed using the mercury vapour generator for a range of (much shorter) time periods.

(iii) The analytical responses for the measurement of mercury on the tubes dosed in (ii) were compared to the responses from injections of mercury vapour from the bell-jar [using the mass flow rate of mercury determined in (i)].

Bell-jar calibration apparatus

The bell-jar (Fig. 1) contained approximately 1 ml of elemental mercury (99.9995% purity, Aldrich, UK) and was housed in a water bath to ensure that it remained at a constant temperature near to the ambient temperature. The temperature inside the bell-jar was measured using a calibrated platinum resistance thermometer (model 2024T, Digitron, UK) and samples of the vapour were taken using a calibrated gas-tight syringe (Vici, USA). The mass of mercury contained per unit volume of mercury-saturated air at a given temperature was calculated using eqn (1).

Dynamic mercury vapour generator

Mercury was automatically sampled on 'Amasil' (gold-coated silica) adsorption tubes (PS Analytical, UK) using a mercury vapour generator (Cavkit model 10.534, PS Analytical). The set-up of the mercury vapour generator is shown schematically in Fig. 3. Air, at a flow rate of 19 ml min⁻¹, was passed across a heated mercury reservoir within the generator to produce a mercury-saturated gas flow. This was then diluted by a further stream of air at a flow rate of 3 l min⁻¹ to produce an output mass concentration of mercury of 286 ng l⁻¹ [calculated from knowledge of the flow rates and eqn (1)]. A portion of the output from the mercury generator was sampled using a flow rate of 330 ml min⁻¹ regulated by a mass flow-controller (model 5850S, Brooks, USA), whilst the remainder was vented to waste. If the mass of mercury on the tube was to be determined gravimetrically, sampling times were very long (*ca.* 24 h) to enable a weighable mass of mercury to be collected on the tube. Much shorter sampling times (between 30 and 120 s – giving theoretical sampled masses of mercury between approximately 50 and 200 ng) were used to dose tubes for analysis by atomic fluorescence. These shorter sampling times were necessary so that the amount of dosed mercury would not saturate the detector of the atomic fluorescence instrument.

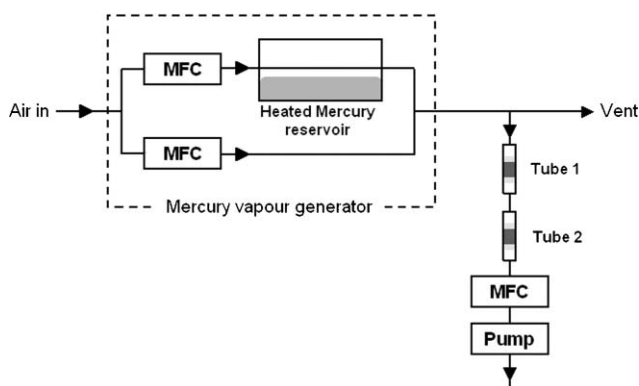


Fig. 3 Schematic representation of the set-up of the mercury vapour generator showing two adsorption tubes positioned in series. 'MFC' represents a mass flow-controller.

Gravimetry

Adsorption tubes were weighed before and after sampling with mercury vapour using a balance (model CC50, Sartorius, Germany) with a sensitivity of 1 µg and a custom-built weighing pan. The balance was calibrated with high accuracy mass pieces traceable to national standards. In order to reduce static effects to a minimum, the tubes were wrapped in aluminium foil, with extreme care being taken not to damage the foil or the tubes between weighings. Prior to weighing the tubes, a series of calibrated mass pieces with a total mass similar to the mass of the adsorption tube (approximately 8 g) were weighed repeatedly in order to allow a correction to be applied for any change in sensitivity of the balance between sets of weighings at the beginning and the end of the experiment. Each adsorption tube was then weighed repeatedly (approximately ten times). The ambient temperature, pressure and relative humidity were recorded before and after the weighing of each artefact in order that a buoyancy correction could be applied. (See the section dealing with gravimetric determination in the Results and discussion section for a full discussion of the application of a buoyancy correction.)

Atomic fluorescence analyser

All samples were analysed using a dual amalgamation atomic fluorescence detection instrument ('Sir Galahad II' model 10.525, PS Analytical) consisting of a permanent trap and a remote trap. Calibration injections were performed by using a gas-tight syringe (previously calibrated as described in ref. 4) to inject a known volume of saturated mercury vapour onto the permanent trap – the trap was then heated to desorb the mercury into a carrier stream of argon, which delivered the mercury to the detector. The sampled tubes were analysed by placing them into the remote trap of the instrument and heating to 900 °C to desorb the mercury onto the permanent trap, which was in turn heated to desorb the mercury onto the detector.

Analytical protocol

The linearity of the detector was first checked by injecting a range of known volumes of saturated mercury vapour onto the permanent trap – these were selected to cover the expected range of the samples to be analysed. The 'recovery' of mercury from the remote trap was then checked by directly spiking an adsorption tube with a known mass of mercury from the bell-jar.

Analysis was carried out in the following order; the three steps below were repeated for each adsorption tube analysed:

(a) 'Quality Assurance' ('QA') sample: a known, constant volume of saturated mercury vapour from the bell-jar (approximately 7.6 ml at 20 °C, thus giving a mid-range mass of mercury of 100 ng for all QA samples) was injected onto the permanent trap of the instrument for analysis. The responses from these injections were used to correct for the drift of the detector.

(b) Bell-jar sample: a known volume of saturated mercury vapour from the bell-jar (chosen to replicate the expected mass of mercury on the subsequent adsorption tube) was injected onto the permanent trap for analysis.

(c) Sampled adsorption tube: an adsorption tube was placed in the remote trap of the instrument and analysed three times in succession. The final analysis was treated as measurement of the tube 'blank' response, and thus the total response for the tube, R_{tot} , was determined by:

$$R_{\text{tot}} = R_1 + R_2 - 2R_3 \quad (2)$$

where R_1 , R_2 and R_3 are the instrumental responses from the first, second and third analyses respectively.

For all the above analyses, the detector response was recorded in terms of peak area. The generalised least squares calculations were carried out using XLGENLINE (National Physical Laboratory, UK).¹⁰

Results and discussion

In this section, we describe the experimental work undertaken to provide SI traceability for measurements of mercury vapour from the bell-jar apparatus. As outlined in the Experimental overview section, the output mass flow rate of mercury from the mercury vapour generator was first determined gravimetrically by sampling onto an adsorption tube for an extended period of time and using gravimetry to establish the mass of mercury collected. Further adsorption tubes were then dosed for much shorter periods of time, and the analytical responses for the measurement of mercury on the tubes compared to the responses from injections of mercury vapour from the bell-jar (using the mass flow rate of mercury determined as described in the previous paragraph).

Operation of the dynamic mercury vapour generator

Dynamic mercury vapour generators typically consist of a heated mercury reservoir above which a saturated mercury vapour concentration is generated. As described earlier, air is passed through this reservoir chamber at a low flow rate (such that equilibrium is not significantly perturbed). This mercury-containing air is then subsequently diluted by a secondary gas flow, usually at a much higher flow rate, and the resulting mixture is the output from the device. Mass flow-controllers regulate the gas flow in each channel. In order to obtain the required mass concentration from the dynamic mercury vapour generators, the reservoir temperature, reservoir flow gas flow rate, and diluent gas flow rate may all be varied – the settings used in this study are described in the Experimental section.

The calculation of measurement uncertainty has been based on the following measurement equation describing the output of the dynamic mercury vapour generator:

$$\gamma_{\text{gen}} = \frac{\gamma_{\text{Hg}} V_{\text{res}}}{V_{\text{res}} + V_{\text{dil}}} \quad (3)$$

where γ_{gen} is the mass concentration of mercury from the dynamic mercury vapour generator, γ_{Hg} is the saturated mass concentration of mercury vapour in air at the temperature of the reservoir, v_{dil} is the actual dilution volume flow rate, and v_{res} is the actual reservoir volume flow rate. The actual flow rate is

related to the flow rate at which the mass flow-controller is set to regulate by:

$$v_i = v_{i,\text{MFC}} \frac{p^\circ T}{p T^\circ} \quad (4)$$

where v_i and $v_{i,\text{MFC}}$ are the actual volume flow rate, and the flow rate at which the mass flow-controller is set to regulate, respectively, on channel i ; T° and T are the standard temperature at which the mass flow-controller is set to operate, and the actual temperature of the gas being regulated, respectively; p° and p are the standard pressure at which the mass flow-controller is set to operate, and the actual pressure of the gas being regulated, respectively. This correction is most significant for the flow rate over the reservoir where the temperature is likely to be elevated.

A portion of this output from the mercury vapour generator is sampled through an adsorption tube at a lower flow rate, v_{sam} , while the remainder of the output is vented to waste. Therefore the theoretical mass collected by sampling in this manner, m , for a time t is given by:

$$m = \gamma_{\text{gen}} v_{\text{sam}} t \quad (5)$$

The mass output rate of the mercury vapour generator is given by $\gamma_{\text{gen}} v_{\text{sam}}$. The standard uncertainty of the mass concentration of mercury from the dynamic mercury vapour generator has been calculated to be 1.0% (with a normal probability distribution) and the relative standard uncertainty in the sampling flow rate is also 1.0% (with a rectangular probability distribution). The standard uncertainty in the sampling time comes not from the accuracy of the timing device used, but from the uncertainty in drop-on and drop-off times at the end of each sampling period. At a conservative estimate, this uncertainty is 1 s (with a rectangular probability distribution).

The mercury vapour generator was used to dose a series of eight adsorption tubes for periods of 30, 60, 90 and 120 s (two tubes for each time period); this gives a relative standard uncertainty (with rectangular distributions) in t of 3.3% for the shortest sampling time and 0.8% for the longest sampling time, and therefore relative standard uncertainties in m of between 2.2% for the shortest sampling time and 1.2% for the longest sampling time.

The experimental methodology used in this paper attempts to relate very small masses of mercury obtained from the bell-jar apparatus (of the order of 10^{-9} g) to much larger masses collected over an extended period of time from the dynamic mercury generator, which are weighable (of the order of 10^{-4} g). This relationship is established *via* a time-independent quantity, the mass output rate of the dynamic mercury generator, which is calculated over an extended time period but applied over a shorter time period in order to deliver masses of mercury similar to those extracted from the bell-jar. The validity of this relationship therefore relies on the stability of the mass output rate of the dynamic mercury vapour generator. The drift in the mass output rate of the dynamic mercury generator over both short and long timescales must be very low in comparison to the stated uncertainty of its mass concentration output, such that the gravimetrically determined mass output rate is still valid when applied to short sampling periods.

The characteristics of the noise processes associated with the mercury vapour generator used in this study were therefore investigated using data covering a time period of approximately one month. These data comprised the dilution volume flow rate, the reservoir volume flow rate and the temperature of the reservoir, all of which were recorded every three minutes over this period. In order to examine the drift characteristics of the device over this extended period of time a quantity called the Allan deviation was calculated. The Allan deviation of the response of the mercury vapour generator, $\hat{\sigma}_{id}(\tau)$, is given practically by eqn (6):¹¹

$$\hat{\sigma}_{id}(\tau) = \sqrt{\frac{1}{2p} \sum_{m=1}^p [\bar{i}_{d(m+1)}(\tau) - \bar{i}_{d(m)}(\tau)]^2} \quad (6)$$

where $\bar{i}_{d(m)}(\tau)$ is the average mercury vapour generator output over a sampling period τ , and $\bar{i}_{d(m+1)}(\tau)$ is the average mercury vapour generator output over the following sampling period τ . The Allan deviation will vary with sampling time – this not only allows classification of any noise processes, but also indicates the optimum sampling time required to provide the most precise measurement. (The advantage of Allan deviation over the classical standard deviation is that it converges for most of the commonly encountered kinds of noise, whereas the classical standard deviation does not always converge to a finite value – this makes it a better tool to identify noise and drift characteristics.) The results of this calculation are shown in Fig. 4. This plot is typical of a system exhibiting only white noise and no significant drift or ‘random walk’ noise and tends towards a minimum over very long sampling times.¹¹ This indicates the absence of significant drift with respect to the mass concentration output of the device on the timescale of the experiment.

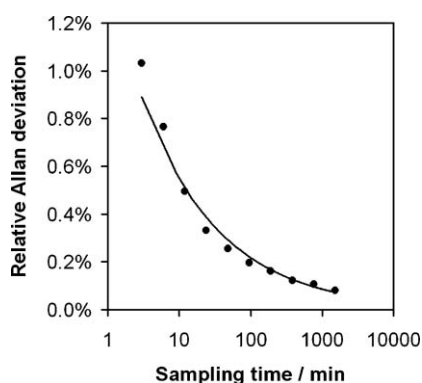


Fig. 4 Relative Allan deviation of the Cavkit output as a function of sampling time.

Gravimetric determination of the flow rate of mercury produced by the dynamic mercury vapour generator

In order to determine the output flow rate of mercury from the mercury vapour generator, an adsorption tube containing 60 mg of the Amasil sorbent material was sampled for a period of 1388 min (just over 23 h) using the mercury vapour generator with settings as described in the Experimental section – this was expected to produce a mass of mercury of approximately 129 μg . It had previously been determined that a 60 mg

adsorption tube was able to hold a mass of mercury greater than 160 μg ,¹² but in case any breakthrough of mercury occurred from the tube, a second adsorption tube was placed in series behind the first tube. The mass of mercury sampled was then determined gravimetrically by weighing both tubes before and after sampling.

The expected change of mass of the tube due to adsorption of mercury is very small – approximately 16 parts-per-million – in relation to the mass of the tube (8 g) and determination of such a change in mass is therefore highly challenging and requires an accurate balance and the application of best gravimetric practice. One key aspect of this is the application of a buoyancy correction to the artefact being weighed in order to determine its true mass. [Commercial balances usually provide a buoyancy-corrected measurement of mass by assuming that the density of the artefact is equivalent to that of stainless steel (8000 kg m^{-3}) and the density of air is 1.2 kg m^{-3} .] This is particularly important because the change in the mass of the tube caused by the adsorption of mercury is very small compared to its overall mass. If the two weighings were carried out in quick succession, then the buoyancy correction in each case would be very similar. However, in this case the two weighings are carried out a day apart, during which time one or more of the ambient temperature, humidity and pressure may change to an extent that is significant – an example of this is described below.

The true mass of an artefact is calculated by use of eqn (7):

$$m_{\text{true}} = \frac{m_{\text{bal}}}{\left(1 + \frac{1.2}{8000} - \frac{\rho_{\text{air}}}{\rho}\right)} \quad (7)$$

where m_{true} is the true mass of the artefact, m_{bal} is the mass of the artefact displayed by the balance, ρ_{air} is the density of air and ρ is the density of the artefact. In this study, the density of the tube (constructed of quartz with a relatively small mass of sorbent material and glass-wool packing) was assumed to be the same as quartz and therefore given a value of $2660 \pm 6 \text{ kg m}^{-3}$.¹³ [Although the tube was wrapped in a small amount (approximately 0.4 g) of aluminium foil in order to reduce static effects, the density of aluminium is very similar to that of quartz and so has little effect on the overall density of the artefact.] The value of ρ_{air} (in kg m^{-3}) is calculated from eqn (8):¹⁴

$$\rho_{\text{air}} = \frac{pM_a}{ZRT} \left[1 - x_v \left(1 - \frac{M_v}{M_a} \right) \right] \quad (8)$$

where p is the air pressure, T is the air temperature, x_v is the mole fraction of water vapour in the air (which is directly related to the relative humidity), M_a is the molar mass of air, M_v is the molar mass of water, R is the molar gas constant, and Z is the compressibility factor.

Returning to the discussion of the significance of a buoyancy correction, consider an adsorption tube of mass 8 g (as displayed on the balance) weighed in a laboratory where $T = 20^\circ\text{C}$ and the relative humidity is 60%. If the air pressure changes from 1.00×10^5 to 1.02×10^5 Pa between the first and second weighings (an entirely realistic scenario in the United Kingdom over a period of 24 h), the true mass of the artefact changes from 8.002 357 g to 8.002 429 g, *i.e.* a change of 72 μg – more than half the

mass of mercury expected to have been adsorbed onto the tube in this study. This example therefore demonstrates how essential accurate buoyancy correction is to the success of the experiment.

The gravimetric results from this study are shown in Table 1. The total mass of mercury produced by the mercury vapour generator was taken as the sum of values of m_{true} for the two tubes as shown in Table 1, *i.e.* $141.8 \pm 18.4 \mu\text{g}$. Combination of this result with the sampling time (1338 min, negligible uncertainty), gave a calculated mass output rate of mercury from the mercury vapour generator of $106.0 \pm 13.8 \text{ ng min}^{-1}$, a value which agrees with the $94.4 \pm 2.4 \text{ ng min}^{-1}$ calculated from the settings of the device within the stated expanded uncertainties (quoted at the 95% confidence level).

Drift correction

In order to correct for the drift of the atomic fluorescence detector, so as to make the analytical determination as accurate as possible, the response from a QA injection of the same known mass (approximately 100 ng) of mercury was measured regularly during the course of the analysis procedure, and these responses were used, after correction for the mass of mercury injected, to apply the multiplicative drift correction based on the procedure described in ref. 15. To summarise the correction method, \hat{R}_{QA} (the mean of the i measured responses from the QA injections, $R_{\text{QA},i}$), is used as an estimate of the 'true' response from a QA injection. The mean scaled deviations, $R_{\text{QA},i}/\hat{R}_{\text{QA}}$, are fitted to a smooth polynomial function, $\varepsilon_{\text{drift}}(t)$ in the time domain and this polynomial function is then used to correct a series of non-QA responses (*i.e.* those from injections from the bell-jar or tube analyses) over time, $R(t)$, by use of eqn (9). This gives a series of corrected responses, $R^{\circ}(t)$.

$$R^{\circ}(t) = \frac{R(t)}{\varepsilon_{\text{drift}}(t)} \quad (9)$$

A practical example of the application of this drift correction procedure is shown in Fig. 5 where the responses of the QA injections (circles) are fitted with a third-order polynomial function. The corrected responses (triangles) are also shown for comparison. The improvement in the data as a consequence of the drift correction is clear to see: before correction, the responses vary significantly from the mean response (by as much

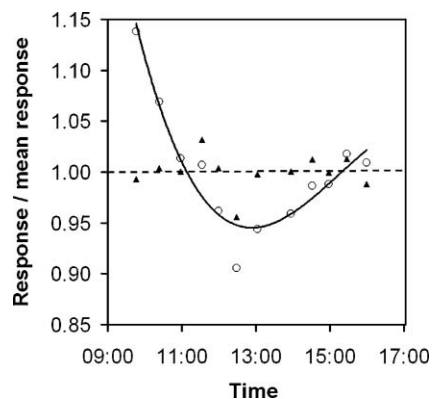


Fig. 5 Data before (○) and after (▲) drift correction. The line is the third-order polynomial best-fit line through the uncorrected data, which have been corrected for the mass of mercury injected. The dashed line indicates the mean response and is a guide to the eye only.

as 14%), whereas after correction the majority of points have a deviation from the mean of less than 1%. This correction is then applied to all other (non-QA) measurements and it is these drift-corrected responses that are used in subsequent calculations.

Comparison of results

The results from the study are presented in Fig. 6, 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.

To enable each set of data to be seen clearly, x -axis offsets of 100 and 250 ng have been applied to the second and third data sets respectively. Note that the plots, if extrapolated, would not necessarily pass through the origin. This is a function of the drift-correction procedure, but is not of concern as we are

Table 1 Summary of gravimetric results [m_{bal} and m_{true} are as defined in eqn (7); $m_{\text{true,corr}}$ is the value of m_{true} corrected for the change in balance sensitivity (marked *), which was applied multiplicatively]. All stated uncertainties in m_{bal} are expanded ($k = 2$) uncertainties, quoted at the 95% confidence interval, calculated from the standard error of the mean taken from a number of (typically ten) repeat measurements. Tube 1 and Tube 2 were positioned in series

	Mass before sampling/ μg	Mass after sampling/ μg	Change in mass/ μg
Mass pieces (sensitivity check): m_{bal}	$7\,700\,366.8 \pm 2.6$	$7\,700\,358.3 \pm 3.2$	N/A
Mass pieces (sensitivity check): m_{true}	$7\,700\,366.0 \pm 3.5$	$7\,700\,367.5 \pm 3.9$	$1.5 \pm 5.3^*$
Tube 1: m_{bal}	$7\,933\,404.4 \pm 6.1$	$7\,933\,516.3 \pm 2.4$	N/A
Tube 1: m_{true}	$7\,935\,811.6 \pm 9.4$	$7\,935\,952.7 \pm 7.6$	141.1 ± 12.0
Tube 1: $m_{\text{true,corr}}$	$7\,935\,813.1 \pm 10.8$	$7\,935\,952.7 \pm 7.6$	139.6 ± 13.2
Tube 2: m_{bal}	$8\,026\,328.3 \pm 4.9$	$8\,026\,301.8 \pm 2.7$	N/A
Tube 2: m_{true}	$8\,028\,763.0 \pm 8.7$	$8\,028\,766.7 \pm 7.7$	3.7 ± 11.6
Tube 2: $m_{\text{true,corr}}$	$8\,028\,764.5 \pm 10.3$	$8\,028\,766.7 \pm 7.7$	2.2 ± 12.9
Total $m_{\text{true,corr}}$	—	—	141.8 ± 18.4

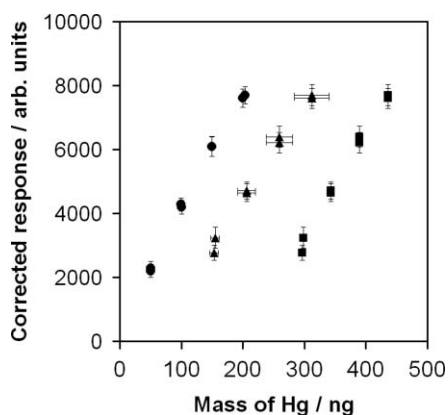


Fig. 6 Plot of corrected instrumental response against mass of mercury for three sets of data: (1) ‘bell-jar’ (●); (2) ‘sampled tubes – gravimetric’ (▲; *x*-axis offset by 100 ng); (3) ‘sampled tubes – generator’ (■; *x*-axis offset by 250 ng) (see the main text for full details). The error bars indicate expanded ($k = 2$) uncertainties, quoted at the 95% confidence interval – where not visible, the error bars are within the points.

comparing the sensitivity of the instrumental response, which is represented by the gradient of the curve.

The error bars shown in Fig. 6 represent expanded uncertainties. The main contributory factor to the uncertainty on the *y*-axis is the repeatability of the atomic fluorescence instrument, which has been determined from prior experience of the performance of the instrument and is discussed elsewhere.⁴ An uncertainty contribution from the drift correction is not included as this is minor compared to the repeatability of the instrumental response.

The uncertainties on the *x*-axis of the ‘bell-jar’ data set are a combination of the uncertainty in the volume of saturated mercury vapour withdrawn from the bell-jar and the uncertainty in the measured temperature of the vapour. These uncertainties are therefore very small, typically 0.5% relative, and are within the points in Fig. 6. It should be noted that the uncertainty of the equation used to calculate the mass of mercury has not been included since testing this is the aim of this study.

For the ‘sampled tubes – gravimetric’ data set, the *x*-axis uncertainty is dominated by the gravimetric determination of the collected mercury (as discussed above, the expanded uncertainty of the mass of mercury determined by gravimetry is 13.0% relative), but also includes a contribution from the flow rate of the mass flow-controllers. Finally, for the third data set (‘sampled tubes – generator’), the expanded uncertainty in the *x*-axis data is 2.5% relative, as calculated from eqns (4) and (5)

To investigate the equivalence of the three data sets, generalised least-squares (GLS)¹⁶ fits were performed on the data. (GLS is a fitting procedure that takes account of the uncertainties inherent in both the *x*- and *y*-axis data and performs a fit weighted to these uncertainties.) 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.

Table 2 Gradient and expanded uncertainty of the linear best fit obtained by GLS analysis of the three data sets in Fig. 6. All stated uncertainties are expanded ($k = 2$) uncertainties, quoted at the 95% confidence interval

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

The calculated gradients of each line are shown in Table 2 where it can be seen that all three values agree with each other within their expanded uncertainties. The agreement between the first two results (‘bell-jar’ and ‘sampled tubes – gravimetric’) demonstrates that the mercury masses predicted using mass concentration values in air given by eqn (1) are compatible with mercury masses traceable to the SI system of units through the unbroken chain of traceability shown in Fig. 2b. The success of this experiment also confirms that a direct traceability link may be made between measurements of mercury vapour in ambient air and the SI system of units. 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 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. This has been shown to be a valid assumption for the work in this study.

In addition to the above discussion on SI traceability, the agreement between the second and third results in Table 2 (‘sampled tubes – gravimetric’ and ‘sampled tubes – generator’) is also of note as this demonstrates that the operation of the mercury vapour generator can be described successfully by eqns (3) and (4).

Conclusion

This paper presents the results of a novel study to provide a direct traceability link between measurements of mercury vapour and the SI system of units, as shown in Fig. 2b. In addition, indirect traceability of the vapour pressure equation used to describe the bell-jar calibration apparatus, for performing routine analytical measurement of mercury vapour, to the SI system of units has been demonstrated.

We have determined, through the application of an accurate gravimetric process, the mass output rate from a dynamic mercury vapour generator, and demonstrated the stability of this flow rate. This has shown that the mercury vapour generator may be used to provide a stable and accurate output of mercury suitable for calibration of mercury analysers.

Comparison of measurements of mercury mass from a series of dosed adsorption tubes with those from samples withdrawn from a calibration bell-jar have shown the two data sets to agree within the uncertainty of the measurement when

using the common expression [eqn (1)] for the saturated mass concentration of mercury in air. (A detailed uncertainty budget for eqn (1) is presented in ref. 4.) This has therefore demonstrated a route to provide SI traceability for measurements of mercury vapour.

Whilst the traceability route requires no knowledge of the equations governing the output of the mercury vapour generator, it has also been shown that the theoretical mass output of the generator agrees with the SI traceable results within the experimental uncertainty.

The complex technical nature of these experiments, especially the extremely delicate gravimetric process has meant that the uncertainties of these results are relatively large. In the future it is hoped that this method can be developed further in order to yield results with smaller uncertainties.

Acknowledgements

The funding of this work by NPL's Strategic Research Programme is gratefully acknowledged. The authors would like to thank Michael de Podesta, Hugh Davies and Alan Dinsdale at NPL for valuable discussions during the preparation of this manuscript.

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