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Temperature dependence of Hg vapour mass concentration at saturation in air: New SI traceable results between 15 and 30°C

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ABSTRACT

There is a need internationally for an agreement on reference values for the calibration of mercury vapour concentration measurements. These reference values are obtained from the relationship between Hg vapour mass concentrations at saturation in air (γ_{Hg}, in ng cm^{-3}) and temperature (T, in K). This relationship was re-evaluated by fitting replicated ($n = 3,4$) SI traceable measurement results obtained for mL size mercury-saturated air samples at temperatures of around 288.4, 293.3, 298.2 and 303.1 K (2.4%, 0.20%, 0.51% and 1.6% relative standard errors of the means, respectively). It gave $\gamma_{Hg} = C/T^{*}10^{(-B/T)}$ with $B = 3282.92$ K and $C = 6.73257 \times 10^{14}$ K ng cm^{-3}, at an estimated relative expanded (combined) uncertainty of 5.9% ($k = 2$). The measurement procedure was based on temperature controlled automated sampling of the gaseous mercury, isotope dilution of the mercury following trapping into the liquid phase under closed circuit conditions, and inductively coupled plasma mass spectrometry for the signal acquisition.

Contents

1. Introduction

When released into the atmosphere mercury can be transported over long distances. It is persistent in the environment, has the ability to bioaccumulate in ecosystems and is considered a very hazardous substance for human health and the environment. This is why mercury was eventually recognised as a chemical of global concern [1].

In Europe the legislation requires that information on concentrations of mercury in ambient air is obtained through quantitative measurements (Directives 2004/107/EC, 2008/50/EC and 2010/75/EU) but, currently, limit values only exist for emissions to air under 2010/75/EU. This is partly "because there is not yet agreement on a procedure and a set of results allowing SI (international system of units) traceable and sufficiently accurate calibrations of the mercury vapour measurement equipment" [2]. Traceability of these measurement results in air is ultimately to the mass

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concentration of mercury in air at saturation, which is temperature (T) dependent. The relationship most commonly used at present and historically to calculate reference values is known as the "Dumarey equation". It corresponds to the least squares best fit of results obtained for measurements of the mercury mass concentration in air at saturation between 288 and 298 K. These results were never published; only the measurement procedure was reported, by Dumarey et al. [3–5]. This presents a problem since, as emphasised elsewhere [6], the "Dumarey equation" is recommended for use in standard methods, such as ISO 6978-2:2003 [7] and ASTM D6850-03 [8]. Moreover this expression is not in agreement with a second prediction model based on data calculated by Huber et al. [9] from results of mercury vapour pressure measurements in the presence of only liquid mercury, assuming that the ideal gas law applies [9]. The "Dumarey equation" produces data which are approximately 7% lower at room temperature.

A procedure developed recently for the measurement of SI traceable Hg mass concentrations at saturation in air samples [2] was adapted to re-evaluate the relationship to temperature conditions. This procedure is based on isotope dilution (ID) of the natural gaseous mercury trapped in liquid phase by oxidation, and inductively coupled plasma mass spectrometry (ICPMS) for the signal acquisition. The system designed allowed the sampling and the processing of large volumes (several mL) of mercury saturated air under fully closed and automated conditions, thus not requesting manual interventions before the end of the air/liquid mixing sequence for ID purposes. It was originally operated under room temperature conditions, and a first series of five results was obtained over a range of approximately 0.7°C between 20 and 21°C (i.e. around $T = 293.8$ K) [2]. In order to be able to carry out measurements under temperature conditions different than ambient, the experimental setup needed to be transferred to a thermally regulated chamber. This paper describes these new developments, the re-validation of the procedure and the new results obtained between 15 and 30°C. A new model for the prediction of the temperature dependence of the Hg mass concentration at saturation in air from 280 to 305 K (i.e. from 7 to 32°C, approximately) is proposed and discussed.

2. Experimental

Most aspects of the experimental design, of the materials and reagents used and of the sample preparation steps were already described in detail previously [2]. A summary is provided in the Supplementary material. The instrumentation used and its operation were for the most part (including the ICPMS) the same as previously described [2]. The two modifications introduced are illustrated in Fig. 1. First, computer controlled valves 1 and 3 were mounted by screwing these onto syringes 1 and 3, respectively. These were 4-way valves (with 38 μL dead volume) from Norgren Kloehn (Las Vegas, USA), similar to valve 2 on syringe 2. Valve 1 replaced the manual valve in the original setup (and there was no valve originally on syringe 3). Second, the experimental setup was enclosed into an ICP 500 incubator from Memmert (Büchenbach, Germany). This apparatus was operated in a standard way and according to the manufacturer's instructions. Air was supplied to bell-jars from outside the incubator through a capillary tube connected to bell jar 1. A feed-through located on the side was used to pass all the necessary tubing and electrical cables. The temperature inside the inner chamber was regulated to within ± 0.1°C.

Air inside this cabinet was at atmospheric pressure, and had to be purified continuously to remove possible traces of Hg vapours. This was done with a "mercury scrubber" (part 30-25260-00) and

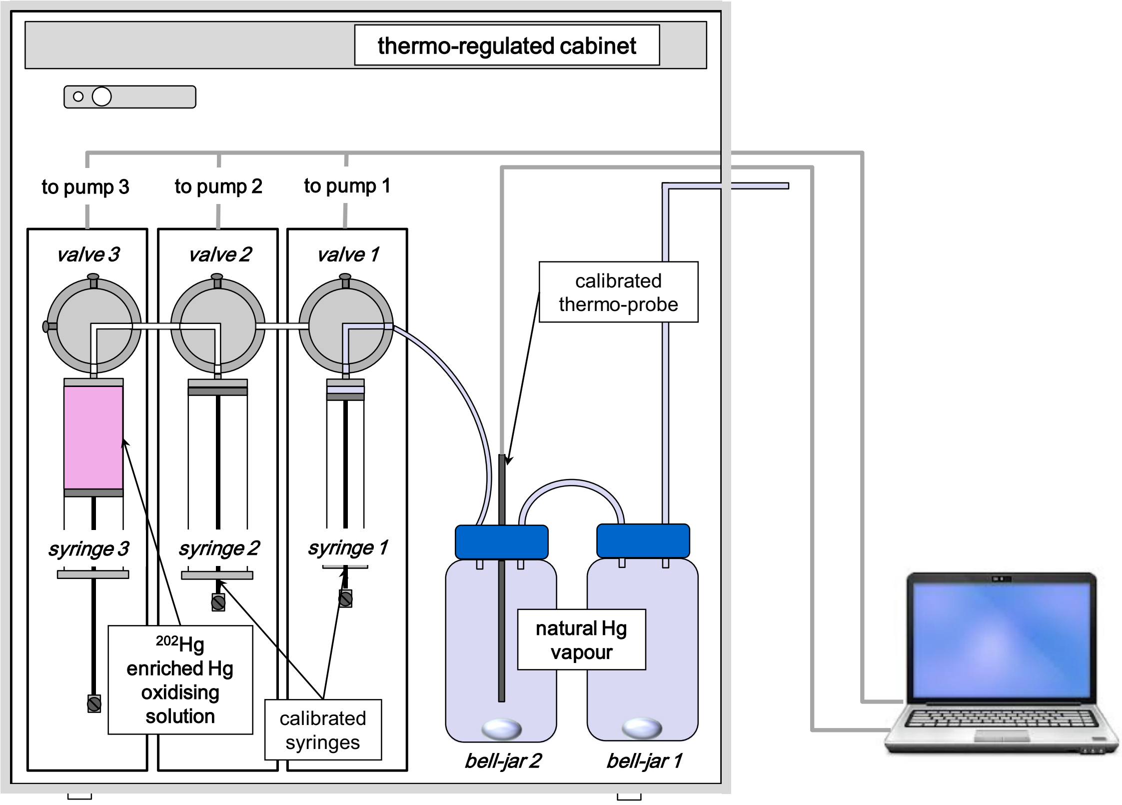

Fig. 1. Schematic description of the experimental setup applied in this study. The pumps are operated remotely and allow, under closed circuit conditions and through the use of calibrated syringes and automated 4-way valves, the quantitative trapping, transfer and mixing of the Hg vapour at saturation in air in the liquid phase for isotope dilution purposes. Enclosure into a thermo-regulated cabinet enables a strict control of the temperature conditions during the air sampling sequence.

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