Transferring the unit of mass between weights kept in air and in vacuum

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Abstract

In the current watt balance and crystal density measurements used to assign a value to the Planck constant h in terms of the international prototype of the kilogram $\mathfrak{K}$, the unit of mass has to be transferred from air to vacuum. In the future, when the kilogram has been redefined in terms of a fixed value of the Planck constant, the unit of mass has to be transferred from vacuum to air. This report describes how this mass transfer may be done in a way that enables evaluation of the standard uncertainty associated with the mass transfer.

1. Introduction

The unit of mass, kilogram is currently defined as the mass of the international prototype of the kilogram $\mathfrak{K}$ immediately after cleaning and washing using a specified procedure involving solvents and steam[1][2][3]. As the prototype $\mathfrak{K}$ is kept and used in humid air, a natural layer of adsorbed water on the surface of the artefact is contributing to the unit of mass. When measuring the Planck constant h in the current watt balance experiments or the Avogadro constant N_A in the current crystal density experiment, mass standards (weights) that are traceable to the prototype $\mathfrak{K}$ but used in vacuum are required. Once a new definition of the kilogram in terms of a fixed value of the Planck constant is in place, the kilogram will be realized in vacuum and needs to be transferred to air before being disseminated.

A gravimetric method is often used to measure the mass change due to water sorption/desorption associated with the transfer of weights between air and vacuum. This method uses at least two mass standards (known as sorption artefacts) having the same nominal values of mass and volume, the same surface finish, but a large difference in their surface areas. Based on the assumption that the sorption per unit area is the same for the two sorption artefacts, the change in sorption can be calculated from a measured change in mass difference between the two sorption artefacts when transferred between air and vacuum.

Experiments have shown that the sorption is not always reversible. The modelling described in this report accounts for that.

2. Modelling

Assume that sorption artefact S is cycled repeatedly between the two media air (A) and vacuum (B). The cycling is described by a media sequence $M = (\mathrm{A}, \mathrm{B}, \mathrm{A}, \mathrm{B}, \dots)$, so that $M_1 = \mathrm{A}$, $M_2 = \mathrm{B}$, $M_3 = \mathrm{A}$, etc. When the sorption artefact is transferred from medium M_i to medium M_{i+1} the mass of the artefact is assumed to change according to the model:

$$m_{\mathrm{S},i+1} = m_{\mathrm{S},i} + p_{\mathrm{S}} A_{\mathrm{S}} s_i, \qquad (1)$$

where

- $m_{S,i}$ is the mass of the artefact S in medium M_i,
- $m_{S,i+1}$ is the mass of the artefact S in medium M_{i+1},
- A_{S} is the geometrical surface area of the artefact S,

- s_i is the change in sorption per unit surface area of the artefact when transferred from medium M_i to medium M_{i+1},
- p_S is a factor for the sorption artefact S converting its geometric surface area to an effective surface area for the sorption.

Note that the quantity s_i may be negative or positive depending on the media between which the artefact is transferred.

If a set of N sorption artefacts $\mathrm{S}_1, \mathrm{S}_2, \ldots, \mathrm{S}_N$ are cycled between the two media, equation (1) is replaced by

$$\begin{gathered} m_{\mathrm{S}_1,i+1} = m_{\mathrm{S}_1,i} + p_{\mathrm{S}_1} A_{\mathrm{S}_1} s_i \\ m_{\mathrm{S}_2,i+1} = m_{\mathrm{S}_2,i} + p_{\mathrm{S}_2} A_{\mathrm{S}_2} s_i \\ \vdots \\ m_{\mathrm{S}_N,i+1} = m_{\mathrm{S}_N,i} + p_{\mathrm{S}_N} A_{\mathrm{S}_N} s_i \end{gathered} \qquad (2)$$

The successful use of sorption artefacts rely on the assumptions that the change in sorption s_i is the same for all sorption artefacts involved in the same transfer between media A and B. In order to test that assumption, at least three sorption artefacts need to be used. Up to now it has been usual practice to assume that the factors $p_{\mathrm{S}_1}, \ldots, p_{\mathrm{S}_N}$ are identical (and equal to 1 exactly). This implies that the sorption s_i is defined in terms of geometric area rather than in terms of effective area, and that the ratio of effective area to geometrical area is the same for all sorption artefacts in a set. The factors $p_{\mathrm{S}_1}, \ldots, p_{\mathrm{S}_N}$ can be interpreted as the ratios of effective area to geometric areas of the sorption artefacts. If the surface roughnesses of the artefacts have been measured, some information about these ratios is available. In that case, best estimates (larger than 1) and associated standard uncertainties may be assigned to the factors $p_{\mathrm{S}_1}, \ldots, p_{\mathrm{S}_N}$. If no information of the effective areas of the artefacts is available, variation in the surface finish of the sorption artefacts in a set may be taken into account by assigning a prior value 1 to all factors $p_{\mathrm{S}_1}, \ldots, p_{\mathrm{S}_N}$ but with non-zero standard uncertainties.

Assume that one weight M_A is permanently stored in air (medium A), and another weight M_B is permanently stored in vacuum (medium B); both weights have the same nominal mass values as the sorption artefacts $\mathrm{S}_1, \mathrm{S}_2, \ldots, \mathrm{S}_N$. The goal is to measure the mass m_B of the weight M_B stored in vacuum in terms of the mass m_A of the weight M_A stored in air, or vice versa. The volumes of the weights M_A and M_B are denoted V_A respectively V_B, and the volumes of the sorption artefacts $\mathrm{S}_1, \mathrm{S}_2, \ldots, \mathrm{S}_N$ are denoted $V_{\mathrm{S}_1}, V_{\mathrm{S}_2}, \ldots, V_{\mathrm{S}_N}$.

At stage i in the media sequence the sorption artefacts $\mathrm{S}_1, \mathrm{S}_2, \ldots, \mathrm{S}_N$ are compared with each other and with either the weight stored in air or the weight stored in vacuum. This comparison is modelled by

$$f_i \Delta \boldsymbol{I}_i = \boldsymbol{X}_i \boldsymbol{m}_i - \boldsymbol{diag}(\boldsymbol{a}_i) \boldsymbol{X}_i \boldsymbol{V} \qquad (3)$$

where

- $\boldsymbol{m}_i = (m_{\mathrm{A},}, m_\mathrm{B}, m_{\mathrm{S}_1,i}, \ldots, m_{\mathrm{S}_N,i})^T$ is a vector of the mass values of the weights and the sorption artefacts at stage i in the media sequence,
- $\boldsymbol{V} = (V_\mathrm{A}, V_\mathrm{B}, V_{\mathrm{S}_1}, \ldots, V_{\mathrm{S}_N})^T$ is a vector of the volume values of the mass and sorption artefacts involved in the comparisons,
- $\boldsymbol{X}_i$ is the design matrix according to which the mass and sorption artefacts have been compared at stage i in the media sequence,
- $\boldsymbol{a}_i$ is the vector of air densities measured for each mass comparison at stage i in the media sequence,

- $\Delta \boldsymbol{I}_i$ is the vector of indication differences measured for each mass comparison performed at stage i of the media sequence,
- f_i is the scale factor of the mass comparator at stage i of the media sequence.

When weighing is done in air ($M_i = \mathrm{A}$), the weight $\mathrm{M_B}$ stored in vacuum is not involved in the mass comparison, so if $M_i = \mathrm{A}$, then the elements of the second column of $\boldsymbol{X}_i$ are all zero. Similarly, when weighing are done in vacuum ($M_i = \mathrm{B}$), the weight $\mathrm{M_A}$ is not involved in the comparisons, so if $M_i = \mathrm{B}$, then the elements of the first column of $\boldsymbol{X}_i$ are all zero. The masses m_A and m_B are assumed to constant; this assumption is plausible only if the weight $\mathrm{M_A}$ is kept permanently in air, and the weight $\mathrm{M_B}$ is kept in permanent vacuum. When weighing is done in vacuum ($M_i = \mathrm{B}$), the air density is negligible, so if $M_i = \mathrm{B}$, then $\boldsymbol{a}_i = \boldsymbol{0}$.

The equations (2) and (3) form the necessary basis for transferring the unit of mass between air and vacuum. These equations are easily solved by the general method of least squares developed at DFM[4][5], known a s DFM-LSQ. To illustrate this, consider that the mass of the weight $\mathrm{M_A}$ kept in air is known, and that we want to measure the mass of the weight $\mathrm{M_B}$ kept in vacuum using two sorption artefacts $\mathrm{S_1}$ and $\mathrm{S_2}$. If the shortest possible media sequence $M = (\mathrm{A}, \mathrm{B})$ is applied, three mass differences may be measured in air,

$$f_1 \begin{pmatrix} \Delta I_{1,1} \\ \Delta I_{1,2} \\ \Delta I_{1,3} \end{pmatrix} = \begin{pmatrix} 1 & -1 & 0 \\ 1 & 0 & -1 \\ 0 & 1 & -1 \end{pmatrix} \begin{pmatrix} m_\mathrm{A} \\ m_{S_{1,1}} \\ m_{S_{2,1}} \end{pmatrix} - \begin{pmatrix} a_{1,1} & -a_{1,1} & 0 \\ a_{1,2} & 0 & -a_{1,2} \\ 0 & a_{1,3} & -a_{1,3} \end{pmatrix} \begin{pmatrix} V_\mathrm{A} \\ V_{S_{1,1}} \\ V_{S_{2,1}} \end{pmatrix}, \qquad (4)$$

and three mass differences may be measured in vacuum:

$$f_2 \begin{pmatrix} \Delta I_{2,1} \\ \Delta I_{2,2} \\ \Delta I_{2,3} \end{pmatrix} = \begin{pmatrix} 1 & -1 & 0 \\ 1 & 0 & -1 \\ 0 & 1 & -1 \end{pmatrix} \begin{pmatrix} m_\mathrm{B} \\ m_{S_{1,2}} \\ m_{S_{2,2}} \end{pmatrix}. \qquad (5)$$

The masses of the sorption artefacts in air and in vacuum are related to a single (negative) sorption coefficient s_1 through the equations

$$\begin{pmatrix} m_{S_{1,2}} \\ m_{S_{2,2}} \end{pmatrix} = \begin{pmatrix} m_{S_{1,1}} \\ m_{S_{2,1}} \end{pmatrix} + s_1 \begin{pmatrix} p_1 A_{S_1} \\ p_2 A_{S_2} \end{pmatrix} \qquad (6)$$

In this measurement there are $k = 6$ quantities, for which no prior information is available,

$$\boldsymbol{\beta} = (m_\mathrm{B}, m_{S_{1,1}}, m_{S_{2,1}}, m_{S_{1,2}}, m_{S_{2,2}}, s_1)^T, \qquad (7)$$

and $m = 16$ quantities

$$\boldsymbol{\zeta} = (f_1, f_2, \Delta I_{1,1}, .., \Delta I_{2,3}, m_\mathrm{A}, V_\mathrm{A}, V_{S_{1,1}}, V_{S_{2,1}}, A_{S_1}, A_{S_2}, p_1, p_2)^T \qquad (8)$$

for which we have best estimates $\boldsymbol{z}$ and an associated covariance matrix $\boldsymbol{\Sigma}$. Among the quantities $\boldsymbol{\beta}$ and $\boldsymbol{\zeta}$ there are $n = 8$ constraints on the form

$$f(\boldsymbol{\beta}, \boldsymbol{\zeta}) = \boldsymbol{0}, \qquad (9)$$

which are derived from equations (4),(5),and (6) by subtraction the right hand sides from the left hand sides of the equations. Following ref. [5], best estimates $\hat{\boldsymbol{\beta}}$ and $\hat{\boldsymbol{\zeta}}$ of the quantities $\boldsymbol{\beta}$ and $\boldsymbol{\zeta}$, as well as the associated covariance matrix, is found by minimising the chi-square function

$$\chi^2 = (\mathbf{z} - \boldsymbol{\zeta})^T \boldsymbol{\Sigma}^{-1} (\mathbf{z} - \boldsymbol{\zeta}) \qquad (10)$$

subject to the constraint $\boldsymbol{f}(\boldsymbol{\beta}, \boldsymbol{\zeta}) = \boldsymbol{0}$. The consistency of model and data should be checked by comparing the observed chi-square value

$$\chi^2_{\text{obs}} = (\boldsymbol{z} - \hat{\boldsymbol{\zeta}})^T \boldsymbol{\Sigma}^{-1} (\boldsymbol{z} - \hat{\boldsymbol{\zeta}}) \qquad (11)$$

with its expectation value, which is equal to the degrees of freedom ν of the least squares adjustment:

$$E[\chi^2] = \nu = n - k, \qquad (12)$$

where n is the number of constraints and k number of quantities, for which no prior information is available. Assuming that χ^2_{obs} is the outcome of a chi square distribution $\chi^2(\nu)$, consistency between data and model may be questioned if

$$p = \Pr\{\chi^2(\nu) > \chi^2_{\text{obs}}\} < p_c, \qquad (13)$$

where p is the probability that (by chance) the outcome of a chi-square distribution $\chi^2(\nu)$ is larger than the value actually observed, and p_c is a chosen level of significance. It is recommended to use a level of significance in the range $0.1 \leq p_c \leq 0.2$.

The larger the number of degrees of freedom are, the stronger is the consistency test expressed by equation (13). In the case described above, we have $\nu = 8 - 6 = 2$ degrees of freedom for the least squares adjustment; these two degrees of freedom would reduce to zero, if the two (redundant) mass comparison of the sorption artefacts in equations (4)(5) were omitted. Even if the two redundant mass comparisons were included, there would be no redundancy in the determination of the sorption coefficient. In order to obtain such redundancy, a third sorption artefact would have to be included. Assuming that the mass values m_{A} and m_{B} are constant, further redundancy would be obtained by expanding the media cycle from just two stages to three or more stages.

In addition to the general test for consistency described above, it is recommended to test for consistency between each measured value z_i in the array $\boldsymbol{z}$ with the corresponding adjusted value $\hat{\zeta}_i$ in the array $\hat{\boldsymbol{\zeta}}$. This is done by calculating the normalised deviations

$$d_i = \frac{z_i - \hat{\zeta}_i}{u(z_i - \hat{\zeta}_i)}, \qquad i = 1, \ldots, m. \qquad (14)$$

Measured values z_i for which $|d_i| > 2$ are potential outliers, although there is a probability of about 0.05 that this could happen by chance, assuming that d_i follows a normal distribution $\text{N}(0,1)$.

3. Analysis of sorption data

Unfortunately there are no data available for a mass transfer between mass and vacuum, which has been carried out using the recommended procedure. However, in a sorption comparison carried out in the task group CCM WGM TG 1, data were reported that have been used to demonstrate how the method works and how accurate it is.

In the TG1 sorption comparison three sorption artefact S_1, S_2, and S_3 were circulated among a number of participants. The sorption artefact S_1 was an integral weight of stainless steel identified as ‘71DD’, S_2 was a stack of two stainless steel discs identified as ‘Stack 1’, and S_3 was a stack of four stainless steel discs identified as ‘Stack 2’. The measured volumes and areas are listed in table 1.

	S_1	S_2	S_3
$V\,/\text{cm}^3$	126.7730	126.7737	126.7700
$u(V)/\text{cm}^3$	0.0011	0.0014	0.0010
$A\,/\text{cm}^2$	140.0	188.3	285.4
$u(A)/\text{cm}^2$	2.3	2.6	3.3

Table 1. Measured volumes and surface areas of sorption artefacts

	K48
$(m - 1\,\text{kg})/\text{mg}$	0.160
$u(m)/\text{mg}$	0.008
$V\,/\text{cm}^3$	46.4879
$u(V)/\text{cm}^3$	0.0005

Table 2. Mass correction and volume of Danish national prototype K48

Each participating laboratory did measurements in air (medium A) and vacuum (medium B) using a media cycle $M = (\mathrm{A}, \mathrm{B}, \dots, A)$ with at least one measurement in vacuum and two measurements in air. The laboratories compared the three sorption artefacts with each other in air and in vacuum, and with an unspecified reference standard kept in air. The sorption artefacts were not compared to a weight kept in continuous vacuum. At each stage in the media sequence, the laboratories reported the measured mass value of S_1 and the three mass differences measured by comparing S_1, S_2, and S_3. The average air densities associated with the mass comparisons in air were also reported.

In order to assess the uncertainty at which the mass of a national prototype kept in air could be transferred from air to vacuum, the indication differences, which would have been observed by comparing the integral sorption artefact S_1 with the Danish prototype K48 in air, were calculated using the air densities and mass values of S_1 reported by the laboratories, the volume of S_1 listed in table 1 and the mass m and volume V of the prototype listed in table 2. The calculation was done using equation (3) with $f_i = 1$ (exactly). Similarly, all reported mass differences measured in air were converted into indication differences.

Measurement data were reconstructed this way for five participating laboratories that provided the necessary information: BIPM, LNE, PTB, METAS, and INRIM. The reconstructed measurement data were analysed using DFM-LSQ. A common standard uncertainty $u(\Delta I) = 0.001$ mg were assigned to the reconstructed indication differences ΔI, and for the factors $p_{\mathrm{S}_1}, p_{\mathrm{S}_2}, p_{\mathrm{S}_3}$ used to describe variations in the sorption efficiencies of the surfaces of the sorption artefacts, a prior value equal to 1 with standard uncertainty $u(p) = 0.1$ was assigned to each sorption artefact.

The results of the analysis of the reconstructed measurement data are shown in figure 1 in the case of INRIM. The figure indicates that the sorption is not reversible; what is removed from the surface in the first transition from air to vacuum is less than that removed in the subsequent transitions from air to vacuum. Furthermore, more is added to the surface by the transfer from vacuum to air than that removed by the preceding transition from air to vacuum. As a result, the mass in air of the sorption artefacts increases from one stage in air to the next, and the same is true for the mass in vacuum. This is why it is recommended to compare the sorption artefacts with a weight permanently kept in vacuum as well as with a weight permanently kept in air. By doing so it can be tested if the mass difference between the weight kept in air and the weight kept in vacuum is constant within the measurement uncertainty.

In the case of INRIM, the degrees of freedom of the least squares analysis is $\nu = 21$, and the observed chi-square value is $\chi^2_{\mathrm{obs}} = 2.5$. In this case, there is no indication of inconsistencies between data and model. This is confirmed by the normalised deviations shown in figure 2, which all falls well within the range $|d_i| < 2$. If the prior uncertainties of the factors $p_{\mathrm{S}_1}, p_{\mathrm{S}_2}, p_{\mathrm{S}_3}$ are reduced by a factor of 10 (from $u(p) = 0.1$ to $u(p) = 0.01$), the observed chi-square value increases from $\chi^2_{\mathrm{obs}} = 2.5$ to $\chi^2_{\mathrm{obs}} = 11.1$, which also not larger than expected. However, the normalised deviations associated the surface areas $A_{\mathrm{S}_1}, A_{\mathrm{S}_2}, A_{\mathrm{S}_3}$ and the factors $p_{\mathrm{S}_1}, p_{\mathrm{S}_2}, p_{\mathrm{S}_3}$ fail to meet the criteria $|d_i| < 2$ by a significant margin $(2.4 < |d_i| < 3.1)$. This indicates that there is a significant difference in the sorption efficiencies of the surfaces of the three sorption artefacts. Had only two sorption artefacts been used, such a difference could not have been detected.

The standard uncertainties of the mass values found for the sorption artefacts in air is about 0.010 mg, whereas the standard uncertainties of the mass values found in vacuum are about 0.008 mg. This means that the uncertainty associated with the mass transfer from air to vacuum (or from vacuum to air) is about 0.006 mg.

Form the analysis of the data provided by BIPM, LNE, PTB, METAS, and INRIM in the CCM WGM TG1 sorption comparison, five sets of factors $p_{\mathrm{S}_1}, p_{\mathrm{S}_2}, p_{\mathrm{S}_3}$ were found for the circulated sorption artefacts S_1, S_2, and S_3. These five sets are shown in figure 3. It is noted that the five sets of values are consistent taking into account the associated standard uncertainties, and that sorption artefact S_2 seems to have a sorption efficiency that is about 10 % higher than S_1 and S_3.

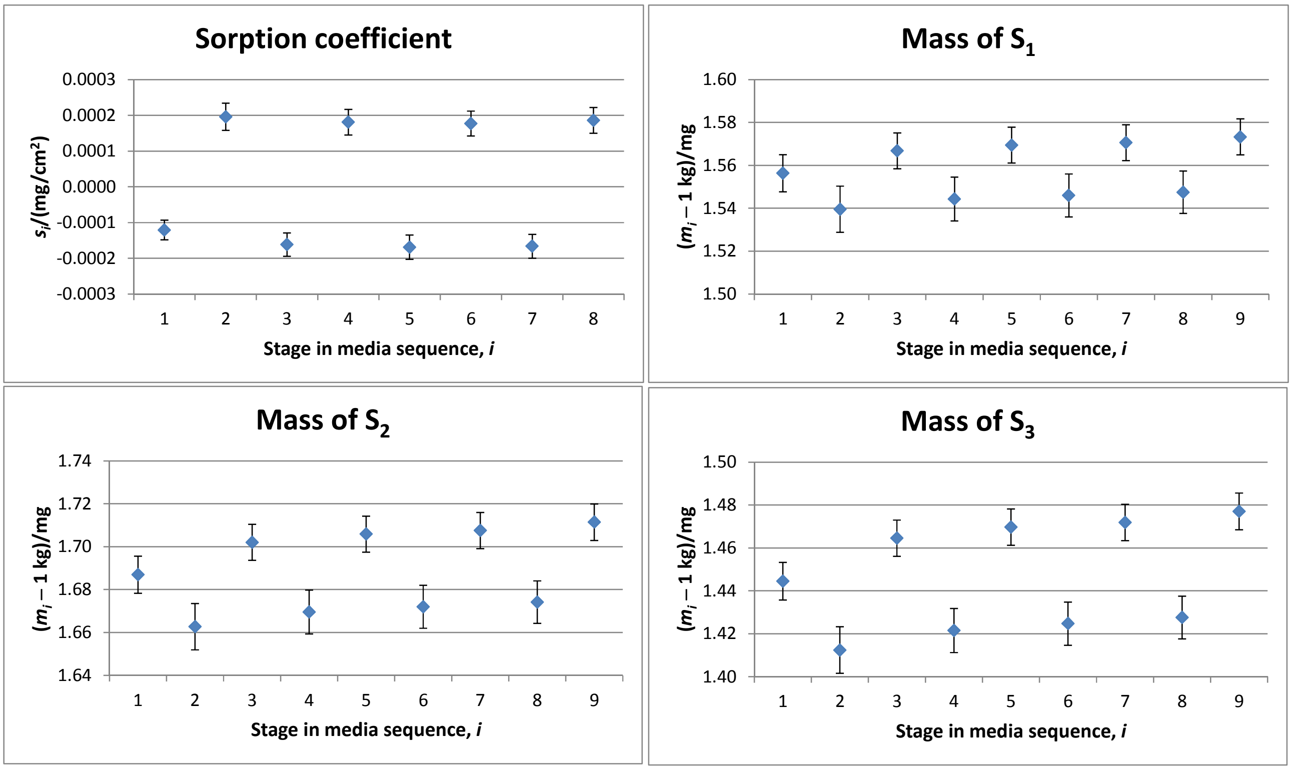

Figure 1. The sorption coefficients s_i and masses $m_{\mathrm{S}_1,i}, m_{\mathrm{S}_2,i}, m_{\mathrm{S}_3,i}$ of the sorption artefacts S_1, S_2, and S_3 measured by INRIM at the nine stages of the media sequence $M = (\mathrm{A, B, A, B, A, B, A, B, A})$, where medium A is air (odd values of stage index i) and B is vacuum (even values of stage index i). The error bars indicate standard uncertainties.

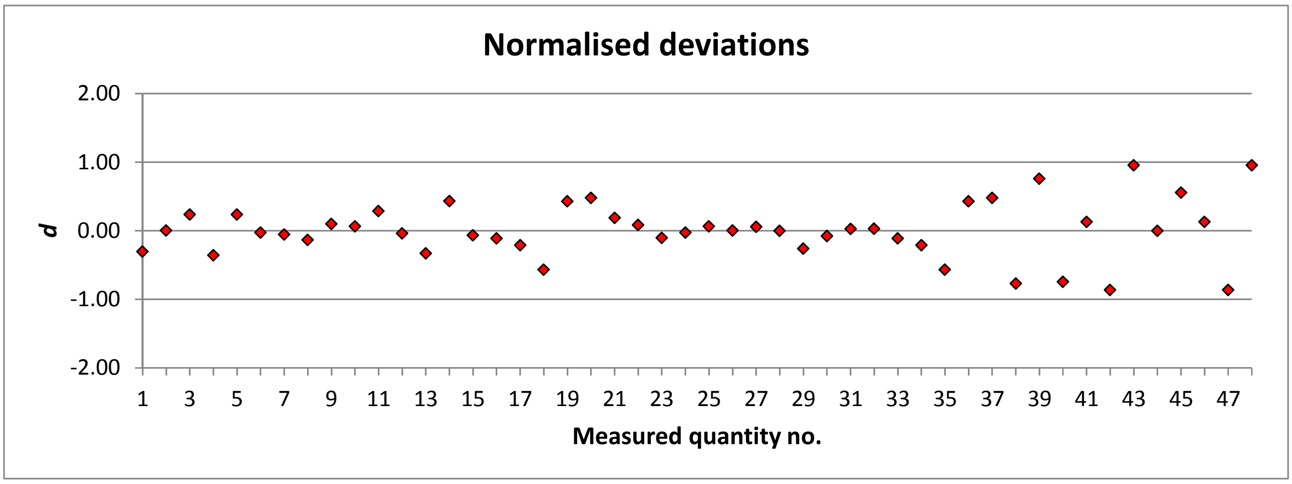

Figure 2. The normalised deviations associated with the 48 measured quantities involved in the least squares adjustment.

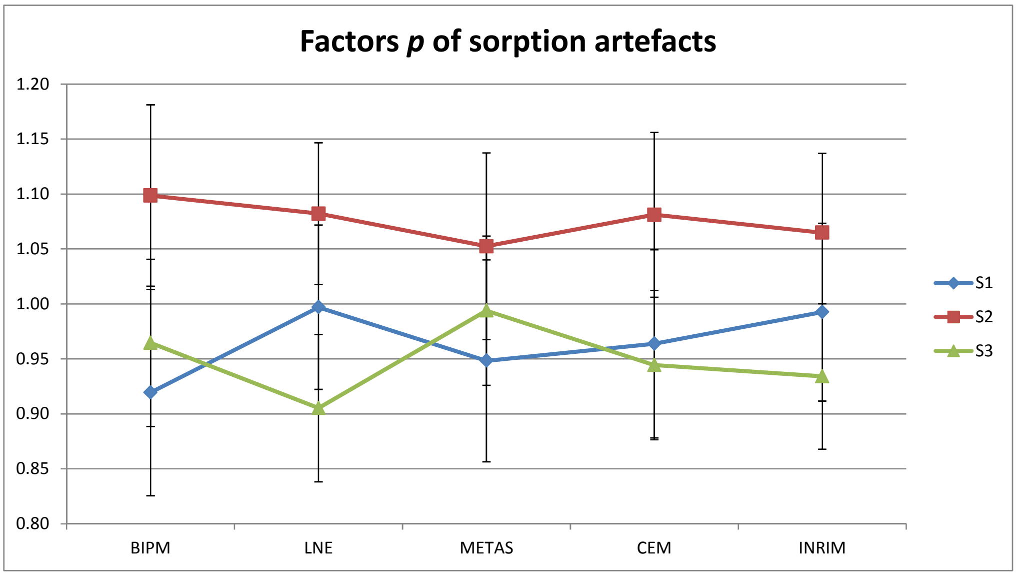

Figure 3. The factors $p_{S_1}, p_{S_2}, p_{S_3}$ measured by five laboratories for the same set of sorption artefacts S_1, S_2, and S_3. The error bars indicate standard uncertainties.

4. Simulation study

In order to validate the mass transfer from air to vacuum using the model described in section 2, a simulation study was carried out. The study involved one weight M_A permanently stored in air (medium A), one weight M_B permanently stored in vacuum (medium B), and $N = 3$ three sorption artefacts S_1, S_2, and S_3 cycled between air and vacuum using the media sequence $M = (A, B, A, B, A, B, A, B, A)$. At each stage in the media sequence, all six possible mass differences between the three sorption artefacts and the weight kept permanently in the media were assumed to be measured.

4.1. Simulation of data

In the first step, true values were assigned to the following quantities:

- The mass m_B of the weight kept permanently in vacuum.
- The mass m_A and volume V_A of the weight kept permanently in air.
- The volumes $V_{S_1}, V_{S_2}, V_{S_3}$, geometrical areas $A_{S_1}, A_{S_2}, A_{S_3}$, conversion factors $p_{S_1}, p_{S_2}, p_{S_3}$ and initial masses $m_{S_{1,1}}, m_{S_{2,1}}, m_{S_{3,1}}$ of the sorption artefacts S_1, S_2, and S_3.
- The air densities a_1, a_3, a_5, a_7, a_9 during mass comparisons in (assumed to be constant during mass comparisons at a given stage of the media sequence).
- The balance scale factors f_i.
- The eight sorption coefficients $s_1, \dots, s_8$.

Using equation (2), true mass values of the three sorption artefacts at stage 2 – 9 in the media sequence were calculated, and using equation (3) a total of $9 \times 6 = 54$ true differences $\Delta I_{1,1}, \dots, \Delta I_{9,6}$ were calculated.

In a second step a realistic standard deviation σ_i was assigned to each quantity ζ_i (except for the factors $p_{S_1}, p_{S_2}, p_{S_3}$), and a measured value z_i was draw from a normal distribution $N(\mu_i, \sigma_i^2)$, where μ_i

is the true value of the quantity ζ_i assigned or calculated in the first step. For the factors $p_{\mathrm{S}_1}, p_{\mathrm{S}_2}, p_{\mathrm{S}_3}$ measured values equal to 1 were assigned.

A total of twenty simulations simulation was carried out in four cases:

Case 1: Reversible sorption/desorption of the same amount of water (0.0001 mg/cm^2) at each media transfer.

Case 2: Reversible sorption/desorption as in Case 1, but a contamination of 0.010 mg was added to all three sorption artefacts in the transfer from media stage 4 (vacuum) to stage 5 (air) and not removed again.

Case 3: Irreversible sorption/desorption similar to that observed by INRIM in the sorption comparison described in section 3, see figure 1.

Case 4: Irreversible sorption/desorption as in Case 3, but a contamination of 0.010 mg was added to all three sorption artefacts in the transfer from media stage 4 (vacuum) to stage 5 (air) as in Case 2.

In each of the four cases, the same seed of the random number generator was used for the simulations. This means the sequence of random components is the same in each of the four cases; only the true values of the quantities are different.

For the mass of the weight kept in vacuum, a true value $m_{\mathrm{B}} = 1$ kg was assigned, and for the mass kept in air, the best estimates given in table 2 were used as true values of the mass m_{A} and volume V_{A} of the weight kept in air, whereas the standard uncertainties in table 2 were used as standard deviations for the simulation. For the sorption artefacts, the best estimates given in table 1 were used as true values of the volumes $V_{\mathrm{S}_1}, V_{\mathrm{S}_2}, V_{\mathrm{S}_3}$ and the geometrical areas $A_{\mathrm{S}_1}, A_{\mathrm{S}_2}, A_{\mathrm{S}_3}$, whereas the standard uncertainties in table 1 were used as standard deviations for the simulation; twenty sets of conversion factors $p_{\mathrm{S}_1}, p_{\mathrm{S}_2}, p_{\mathrm{S}_3}$ randomly selected from a normal distribution $\mathrm{N}(1, \sigma^2)$ with $\sigma = 0.1$ were used as true values, one set for each of the twenty simulations. As initial mass values $m_{S_{1,1}}, m_{S_{2,1}}, m_{S_{3,1}}$ of the sorption artefacts, the best estimates found by INRIM in the sorption comparison described in section 3 (see figure 1) were used as true values. The five air densities reported by INRIM in the sorption comparison were used as true values of the air densities a_1, a_3, a_5, a_7, a_9; the standard deviation used for the simulation of air densities was $\sigma = 0.000\,05\ \mathrm{kg/m^3}$. For simplicity, the values $f_i = 1$ (exactly) were selected for the balance scale factors. For the simulation of the indication differences ΔI, the standard deviation $\sigma = 0.001$ mg was used.

4.2. Analysis of simulated data

To each simulated value z_i of a quantity ζ_i (except the factors $p_{\mathrm{S}_1}, p_{\mathrm{S}_2}, p_{\mathrm{S}_3}$), a standard uncertainty $u(z_i) = \sigma_i$ was assigned. For the factors $p_{\mathrm{S}_1}, p_{\mathrm{S}_2}, p_{\mathrm{S}_3}$, the best estimate $p = 1$ and five different but common standard uncertainties $u(p)$ were assigned:

$$p_{S_1} = p_{S_2} = p_{S_1} = p = 1,$$

$$u(p_{S_1}) = u(p_{S_2}) = u(p_{S_1}) = u(p),\ \ u(p) \in \{0.2,\ 0.1,\ 0.05,\ 0.02,\ 0.01\}.$$

Each simulated set of data was analysed five times, one time for each standard uncertainty $u(p)$ assigned to the factors $p_{\mathrm{S}_1}, p_{\mathrm{S}_2}, p_{\mathrm{S}_3}$. Only one of the standard uncertainties $u(p)$ is equal to the standard deviation $\sigma = 0.1$ used to simulate values of the factors $p_{\mathrm{S}_1}, p_{\mathrm{S}_2}, p_{\mathrm{S}_3}$. Analyses with larger and smaller values of $u(p)$ were performed in order to assess the importance of selecting a realistic value of $u(p)$. A summary of the results of the analyses performed are shown in figure 4-7.

In case of completely reversible sorption/desorption (Case 1), the adjusted value of the mass m_B of the weight kept in air is fairly independent of the value of the uncertainty $u(p)$ assigned to the factors $p_{\mathrm{S}_1}, p_{\mathrm{S}_2}, p_{\mathrm{S}_3}$ in the least squares analysis, see figure 4. Only in the case $u(p) = 0.2$, where the uncertainty is overestimated by a factor of two, there are a few cases (simulation no. 14 and 19), where the adjusted values of the mass m_B are significantly different compared to the cases, where $u(p)$ is equal to or smaller than the standard deviation $\sigma = 0.1$ used for the simulation of the factors $p_{\mathrm{S}_1}, p_{\mathrm{S}_2}, p_{\mathrm{S}_3}$. The standard uncertainty $u(m_\mathrm{B})$, the value of which is indicated with error bars in figure 4, decreases as $u(p)$ decreases, but as there are other significant uncertainty contributions to $u(m_B)$, e.g. from the standard uncertainty $u(m_\mathrm{A}) = 0.0080$ mg assigned to the mass m_A of the reference weight kept in air, the decrease in $u(m_\mathrm{B})$ is predominant when $u(p)$ is reduced from $u(p) = 0.2$, where 0.8 mg $\leq u(m_\mathrm{B}) \leq$ 1.4 mg, to $u(p) = 0.1$, where 0.0096 mg $\leq u(m_\mathrm{B}) \leq$ 0.0103 mg. In the case $u(p) = 0.2$, the variation in the uncertainty $u(m_\mathrm{B})$ of the adjusted value of the mass m_B is very large, especially for those adjusted values of m_B that differs mostly from the true value. What happens in these cases is that the adjusted values of $p_{\mathrm{S}_1}, p_{\mathrm{S}_2}, p_{\mathrm{S}_3}$ are rather extreme in such a way that the differences of the effective sorption areas $p_{\mathrm{S}_1}A_{\mathrm{S}_1}, p_{\mathrm{S}_2}A_{\mathrm{S}_2}, p_{\mathrm{S}_3}A_{\mathrm{S}_3}$ becomes rather small, or even get the wrong sign. It should be noted that for all five standard uncertainties $u(p)$, the adjusted value of the mass m_B is consistent with the true value within $\pm 2u(m_\mathrm{B})$. The same is not true for the factors $p_{\mathrm{S}_1}, p_{\mathrm{S}_2}, p_{\mathrm{S}_3}$; for these factors the true values are only expected to be recovered, if the value of $u(p)$ is equal to or larger than the standard deviation $\sigma = 0.1$ used for the simulation of the true values of $p_{\mathrm{S}_1}, p_{\mathrm{S}_2}, p_{\mathrm{S}_3}$. The graphs in the right column of figure 4 confirm that. The graphs in the middle of figure 4 show that the test of consistence of data with model is almost independent of the value of the uncertainty $u(p)$ assigned to the factors $p_{\mathrm{S}_1}, p_{\mathrm{S}_2}, p_{\mathrm{S}_3}$. At first this might be seen as a paradox, since for small values of $u(p)$ the adjusted values of $p_{\mathrm{S}_1}, p_{\mathrm{S}_2}, p_{\mathrm{S}_3}$ differ significantly from the true values. The explanation is, however, that due to the significant uncertainty in the air buoyancy correction, the information about differences in the effective sorption areas $p_{\mathrm{S}_1}A_{\mathrm{S}_1}, p_{\mathrm{S}_2}A_{\mathrm{S}_2}, p_{\mathrm{S}_3}A_{\mathrm{S}_3}$ cannot be extracted from the measured mass differences when sorption/desorption is reversible.

Case 1: Reversible sorption/desorption

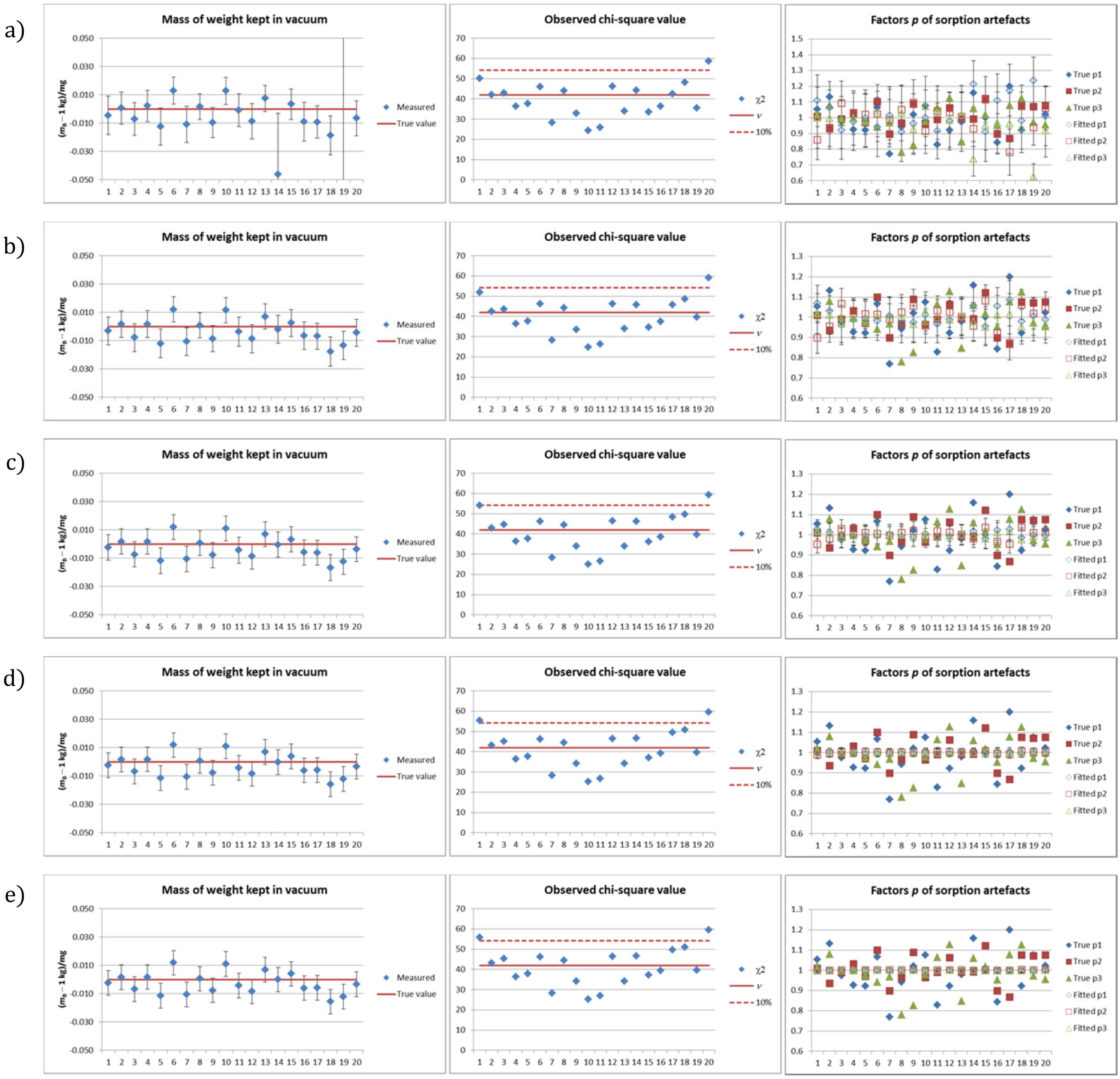

Figure 4. Results of the least squares analysis of twenty simulations in Case 1 with standard uncertainty a) $u(p) = 0.2$, b) $u(p) = 0.1$, c) $u(p) = 0.05$, d) $u(p) = 0.02$ and e) $u(p) = 0.01$ assigned to the factors $p_{\mathrm{S}_1}, p_{\mathrm{S}_2}, p_{\mathrm{S}_3}$. The graph to the left shows the adjusted values found for the mass m_{B} of weight kept in vacuum compared to its true value. The graph in the middle shows observed chi-square value χ^2_{obs} compared to the expectation value ν (full line) and the critical value corresponding to significance level $p_c = 10\ \%$ (broken line). The graph to the right shows the adjusted values (open dots) of the factors $p_{\mathrm{S}_1}, p_{\mathrm{S}_2}, p_{\mathrm{S}_3}$ compared to their true values (closed dots). Error bars indicate standard uncertainties.

Case 2: Reversible sorption/desorption + 0.01 mg contamination

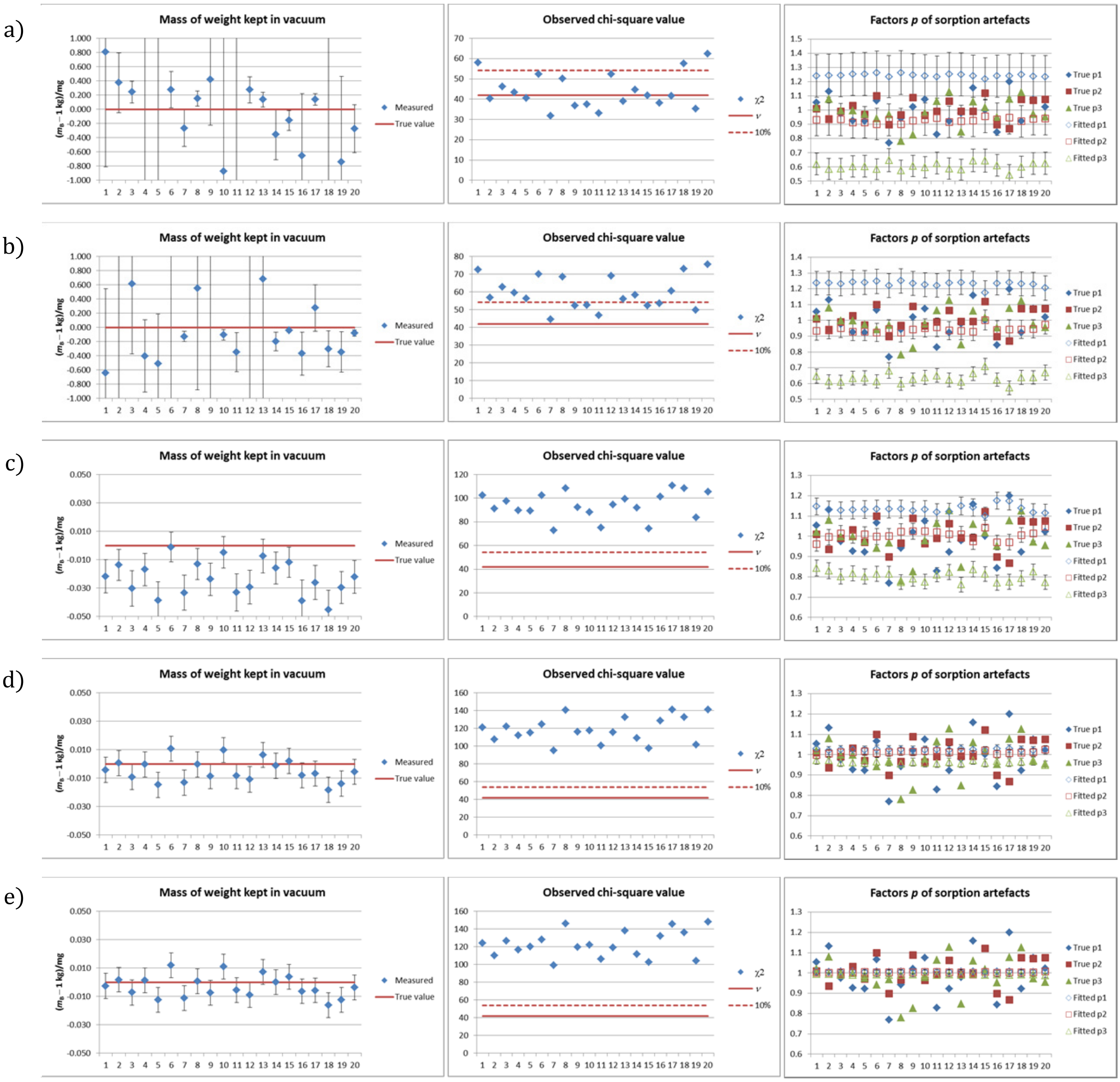

Figure 5. Results of the least squares analysis of twenty simulations in Case 2 with standard uncertainty a) $u(p) = 0.2$, b) $u(p) = 0.1$, c) $u(p) = 0.05$, d) $u(p) = 0.02$ and e) $u(p) = 0.01$ assigned to the factors $p_{S_1}, p_{S_2}, p_{S_3}$.

Case 3: Irreversible sorption/desorption

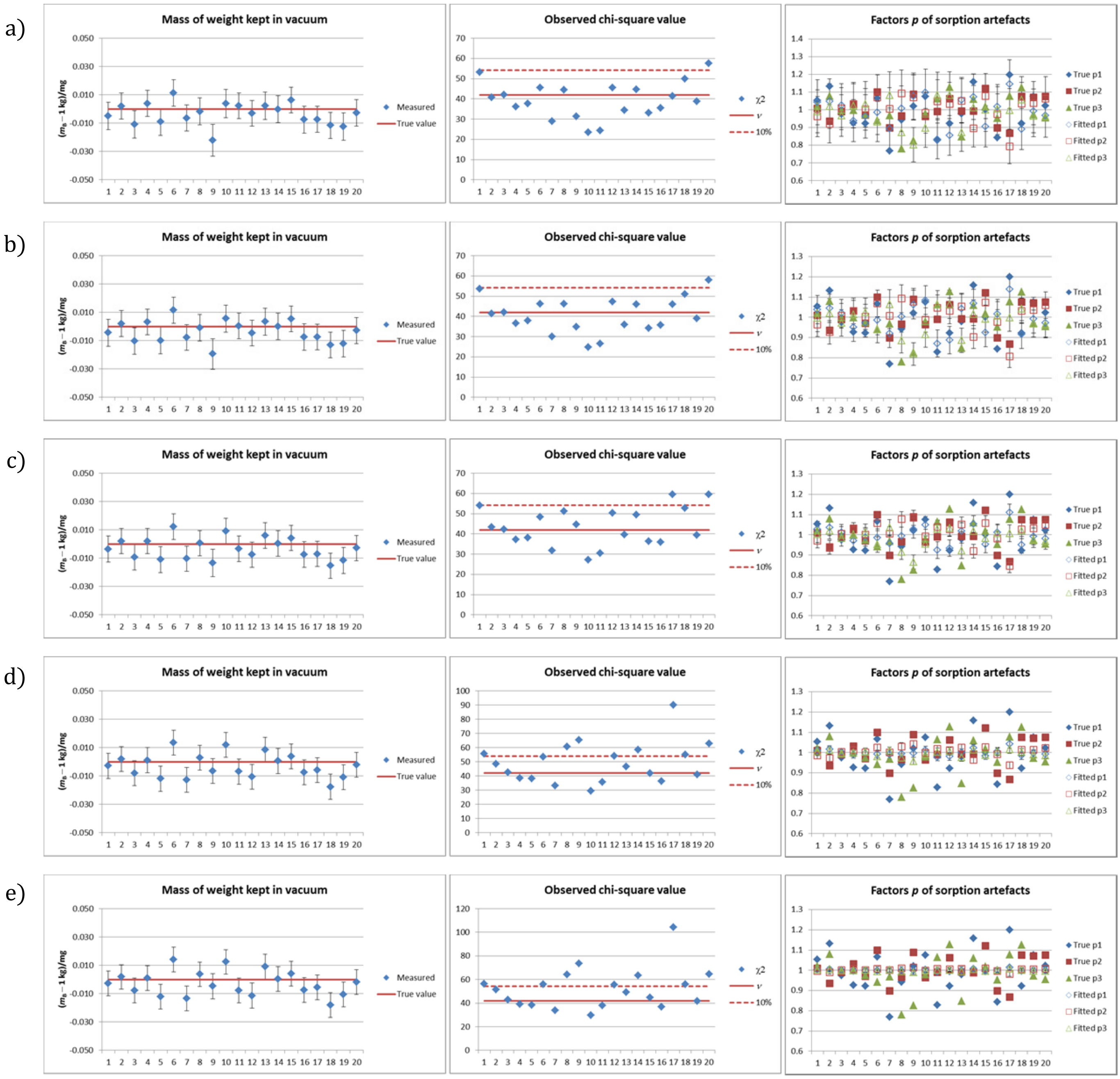

Figure 6. Results of the least squares analysis of twenty simulations in Case 3 with standard uncertainty a) $u(p) = 0.2$, b) $u(p) = 0.1$, c) $u(p) = 0.05$, d) $u(p) = 0.02$ and e) $u(p) = 0.01$ assigned to the factors $p_{S_1}, p_{S_2}, p_{S_3}$.

Case 4: Irreversible sorption/desorption + 0.01 mg contamination

Figure 7. Results of the least squares analysis of twenty simulations in Case 4 with standard uncertainty a) $u(p) = 0.2$, b) $u(p) = 0.1$, c) $u(p) = 0.05$, d) $u(p) = 0.02$ and e) $u(p) = 0.01$ assigned to the factors $p_{S_1}, p_{S_2}, p_{S_3}$.

In case 2, where the reversible sorption/desorption is disrupted by adding 0.010 mg contamination to all three sorption artefacts between stage 4 and 5 in the media cycle, it is only possible to obtain consistency between data and model if the adjusted values of the factors $p_{\mathrm{S}_1}, p_{\mathrm{S}_2}, p_{\mathrm{S}_3}$ are so that the differences in effective sorption areas $p_{\mathrm{S}_1}A_{\mathrm{S}_1}, p_{\mathrm{S}_2}A_{\mathrm{S}_2}, p_{\mathrm{S}_3}A_{\mathrm{S}_3}$ are close to zero. This is achieved if $p_{\mathrm{S}_1} \cong 1.2, p_{\mathrm{S}_2} \cong 1$ and $p_{\mathrm{S}_3} \cong 0.6$ as in the graph to the right of figure 5 a). That is, to achieve consistency a large value of $u(p)$ is required, such as $u(p) = 0.2$. However, as the differences in the effective sorption areas $p_{\mathrm{S}_1}A_{\mathrm{S}_1}, p_{\mathrm{S}_2}, A_{\mathrm{S}_2}p_{\mathrm{S}_3}A_{\mathrm{S}_3}$ are close to zero, the uncertainty $u(m_{\mathrm{B}})$ becomes extremely large as seen in the graph in the left in figure 5 a). For $u(p) = 0.05$, the uncertainty $u(m_{\mathrm{B}})$ reaches a useful level, but the adjusted values of m_{B} are significantly biased compared to the true value, see figure 5 c). For smaller values of $u(p)$, this bias disappears as seen in figure 5 d)-e). However, the results would not (and should not) be trusted by the experimenter, as the consistence test shows a significant inconsistency between data and model, which is due to the fact that a contamination of 0.010 mg was added between stage 4 and 5 in the media cycle without accounting for it in the model used to analyse the data.

Contamination of the sorption artefacts is a problem only if it is not uniformly distributed over the surfaces of the sorption artefacts. In fact, uniformly distributed contamination allows the ratios of the effective sorption areas to be measured fairly accurate. This is illustrated in Case 3, where uniform irreversible sorption/desorption has been assumed. As seen in the graphs in the left column of figure 6, the adjusted values of the mass m_{B} of the weight kept in vacuum are virtually independent of the value assigned to $u(p)$. The associated standard uncertainties $u(m_{\mathrm{B}})$ also have only little dependence of the value assigned to $u(p)$ in the least squares analysis; on the average it decreases from $u(m_{\mathrm{B}}) = 0.0096$ mg for $u(p) = 0.2$ to $u(m_{\mathrm{B}}) = 0.0087$ mg for $u(p) = 0.01$. In contrast to case 1, the test of consistency depends on the value assigned to $u(p)$, as seen in the graphs in the middle column of figure 6. However, even for $u(p) = 0.01$ the observed chi-square value falls below the critical value for a test of consistence at a 10 % level of significance in eleven out of twenty simulations. As shown in the graphs in the right column of figure 6, the adjusted values of the factors $p_{\mathrm{S}_1}, p_{\mathrm{S}_2}, p_{\mathrm{S}_3}$ are consistent with the true values as long as the uncertainty $u(p)$ is equal to or larger than the standard deviation $\sigma = 0.1$ used for the simulation. For $u(p) = 0.1$, the standard uncertainties associated with the factors $p_{\mathrm{S}_1}, p_{\mathrm{S}_2}, p_{\mathrm{S}_3}$ are about 30 % smaller in Case 3 than in Case 1. The reason is that the gain in mass of the sorption artefacts from one stage in given media to the next stage in the same media is measured by comparing the sorption artefacts with the weight stored in that media, which is assumed to have the same mass at all stages in the media cycle. The larger these mass gains are, the more information there would be regarding the values of the factors $p_{\mathrm{S}_1}, p_{\mathrm{S}_2}, p_{\mathrm{S}_3}$.

In case 4, the uniform irreversible sorption/desorption was disrupted by adding a 0.010 mg contamination to all sorption artefacts between stage 4 and stage 5 in the media cycle. As seen in the graphs in the left column of figure 7, this lead to a significant bias in the adjusted values of the mass m_{B} of the weight kept in vacuum, which is larger the larger the value assigned to $u(p)$ is. For $u(p) = 0.2$, the average bias is –0.0300 mg, and for $u(p) = 0.01$, the average bias is –0.0061 mg. For comparison, the average biases found in Case 3 were –0.0034 mg for $u(p) = 0.2$ and –0.0028 mg for $u(p) = 0.01$. As seen in the graphs in the right column of figure 7, the adjusted values of the factors $p_{\mathrm{S}_1}, p_{\mathrm{S}_2}, p_{\mathrm{S}_3}$ seek to reduce the differences in the effective sorption areas $p_{\mathrm{S}_1}A_{\mathrm{S}_1}, p_{\mathrm{S}_2}, A_{\mathrm{S}_2}p_{\mathrm{S}_3}A_{\mathrm{S}_3}$, just as in case 2. It is less pronounced in Case 4, however, due to the additional amount of information about the effective sorption areas. For the majority of the simulations, the chi-square test indicates the inconsistency between data and model created by adding the 0.010 mg contamination to the data without accounting for it in the model; see the graphs in the right column of figure 7.

5. Discussion

When transferring the unit of mass from air to vacuum, a traditional assumption has been that only water is adsorbed and desorbed, and that that the adsorption/desorption is reversible. The sorption comparison carried out in CMM WGM TG1 shows, that adsorption/desorption is irreversible in general, so that the sorption artefacts gain masses as they are repeatedly cycled between air and vacuum. The irreversibility seems to be most pronounced if the sorption artefacts are cleaned just before the media cycling experiment. After some cycles between air and vacuum, the sorption/desorption seems to approach reversibility, and the masses of the sorption artefacts tend to stabilize in air as well as in vacuum.

The simulation experiment shows that irreversibility of the sorption/desorption is in fact useful as it enables a measurement of the relative absorption efficiencies $p_{\mathrm{S}_1}, \dots, p_{\mathrm{S}_N}$ of the surfaces of a set of sorption artefacts $\mathrm{S}_1, \mathrm{S}_2, \dots, \mathrm{S}_N$. The quantities $p_{\mathrm{S}_1}, \dots, p_{\mathrm{S}_N}$ may therefore be determined by performing an air-vacuum cycling experiment on freshly cleaned sorption artefacts. Once these quantities have been measured, their values and associated covariance matrix could be used as input to the analysis of subsequent air-vacuum cycling experiments without cleaning of the sorption artefacts, where the irreversibility of the sorption/desorption process might be less pronounced.

In case of reversible sorption/desorption, at least three sorption artefacts are needed in order to test the hypothesis that the mass of the sorption is proportional to the geometrical area of the sorption artefacts. If a sorption artefact is made up of n discs (with spacers) having the same nominal mass, the uniformity of the sorption efficiencies among the discs could be tested in a separate air-vacuum cycling experiment in which the mass differences among the discs (with spacers) are measured in air and in vacuum.

The simulations were performed on an air-vacuum cycling experiment, in which the weight stored in air was a platinum-iridium standard, whereas the weight stored in vacuum and the sorption artefacts were made of stainless steel. This was done in order to evaluate the standard uncertainty with which the mass of a weight kept in vacuum could be measured in terms of a national prototype kept in air using the sorption standards circulated in the CCM WGM TG1 sorption comparison. This uncertainty turned out to be on the order of 0.010 mg and was actually dominated by the standard uncertainty 0.008 mg assigned to the prototype itself. The validity of this uncertainty can only be proven by performing a rather large number of air-vacuum cycling experiments (similar to the performed simulation) that leads to consistent mass values of the weight stored in vacuum, taking into account the measurement uncertainty. In such an experiment, the weight kept in air should have the same nominal volume as the sorption artefacts in order to reduce the uncertainty due to buoyancy effects when measuring in air. For the same reason should the volumes (or volume differences) of the sorption artefacts and the weight kept in air be measured with the smallest possible standard uncertainty.

6. Conclusion

A procedure for transferring the unit of mass between a weight kept in air and a weight kept in vacuum has been presented. The procedure involves the use of sorption artefacts that are repeatedly compared to the weight kept in air and to the weight kept in vacuum in an air-vacuum cycle. A model of the measurement based on homogeneous absorption/desorption has been described. The model has been tested on adapted measurement data provided by participants in a sorption comparison and on simulated data. The sensitivity to modelling errors has been tested by simulation as well.

It has been shown that a mass value in air having a standard uncertainty of 0.008 mg can be transferred to a mass value in vacuum with a standard uncertainty of 0.010 mg, which means that an uncertainty contribution of 0.006 mg from the air-vacuum transfer can be achieved, at least in principle. The model is based on the crucial assumption that sorption/desorption is homogenous over the surfaces of the sorption artefacts. If this assumption fails in reality, the mass value calculated for the weight kept in vacuum might be significantly biased. Although the proposed method for analysing the data from an air-vacuum cycling experiment includes a tool for testing the consistency among data and model, there is a rather large probability, that an invalid assumption might not be detected in a single air-vacuum cycling experiment.

7. References

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