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MASS MEASUREMENTS OF EVAPORATING ARTEFACTS

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Abstract: The mass measurement of the water content of a pycnometer is done in the same way as a mass measurement of a solid artefact. There are many types of pycnometers, among them there are the Gay-Lussac types, and within the latter there are those with an anti-evaporation cap and those without. Pycnometers without a cap let the water evaporate during the measurement process. Yet it is possible to measure the mass of the full pycnometer by extrapolating backward in time from the weighing measurements taken over a period of time. The analysis of the process is presented here as well as the advantages of using this method over the usual one of a single quick weighing of the artefact.

Keywords: Mass, Volume, Water

1. INTRODUCTION

It came to our attention, a few years ago, that the mass of a Gay-Lussac pycnometer filled with water was decreasing at a steady rate much faster than expected from normal evaporation from the overflow hole during the weighing process. The weighing scheme at that time was RTR repeated six times over a period of about 15 minutes.

We discovered that the evaporation process was caused by a wicking effect at the unpolished joint between the stopper and the container parts of the pycnometer. When the water level was down below the joint, the evaporation rate was back to normal, the expected rate for a small overflow hole.

The effect is so important that it could not be ignored during the weighing process of the pycnometer. It became evident to us that a simple quick weighing of the pycnometer, before any sign of evaporation appears, was far from a satisfactory measurement: it is a combination of the stabilisation time of the balance and the onset of the evaporation process; this is too large an uncertainty source for an appropriate weight measurement. We also discovered that the rate of evaporation varies from one measurement series to the other for the same pycnometer. It depends on the amount of wetting of the unpolished joint between the stopper and the main container. This wetting does have a very low reproducibility, hence the different rates of evaporation.

The procedure outlined in this paper illustrates how one can still make measurements during the evaporation and evaluate the exact weight of a pycnometer when it is filled and the overflow wiped. The idea is simple enough in principle: assuming the evaporation to be linear, the answer is given by a linear regression with extrapolation backward in time when the pycnometer is filled. Instead of fighting against the evaporation, it becomes an opportunity to estimate with a lower uncertainty the mass of water before the onset of evaporation, just after the pycnometer is filled. The proper estimation of the propagation of uncertainties is a little more complicated and the matter will be covered extensively here.

2. METHOD

After a pycnometer is filled with water and the overflow is wiped, it is weighed on a Mettler Toledo AT201 balance with a scheme RTR, repeated six times. As seen in Figure 1, the data corresponding to T, the Test, show evaporation with the weight decreasing linearly with time. The Reference R is almost horizontal, affected only by the small drift of the balance. Points on the ordinate axis t=0, defined when the pycnometer is filled, are, respectively, the extrapolations of R and T, Ro and To. The rate of evaporation is 4.3 µg/s.

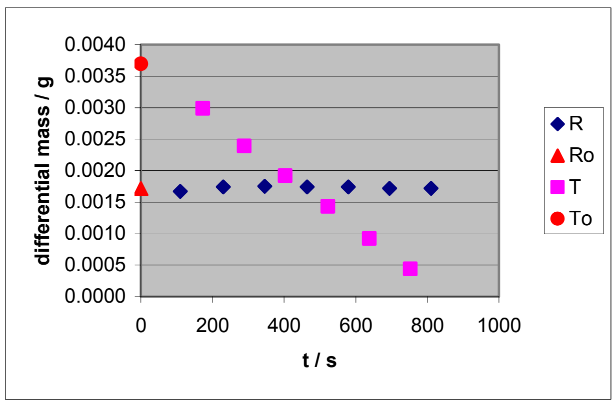

Figure 1 RTR weighing data

3. RESULTS

The value we are looking for is the difference:

$$d = \Delta m = m_{T0} - m_{R0} \,. \quad (1)$$

All subsequent calculations for the evaluation of the mass, absolute or conventional, start with a proper evaluation of Δm and its uncertainty.

Two least-square linear fits are done on each set of data, R for reference, and T for test (the filled pycnometer).

$$m_T\{t\} = m_{T0} + B_T t \quad (2)$$

and

$$m_R\{t\} = m_{R0} + B_R t \,. \quad (3)$$

The uncertainties of m_{T0} and m_{R0} are, respectively,

$$u\{m_{T0}\} = \sqrt{\frac{V_T\{m\}\sum t_i^2}{n_T \sum t_i^2 - \left(\sum t_i\right)^2}} \quad (4)$$

and

$$u\{m_{R0}\} = \sqrt{\frac{V_R\{m\}\sum t_i^2}{n_R \sum t_i^2 - \left(\sum t_i\right)^2}} \,, \quad (5)$$

where

$$V_T\{m\} = \frac{\sum\left(m_{Ti}\{\text{measured}\} - m_{T0} - B_T t_i\right)^2}{n_T - 2} \quad (6)$$

and

$$V_R\{m\} = \frac{\sum\left(m_{Ri}\{\text{measured}\} - m_{R0} - B_R t_i\right)^2}{n_R - 2} \,. \quad (7)$$

$V_T\{m\}$ and $V_R\{m\}$ are the estimated variances of the measurements. n_T and n_R are the numbers of measurements of R and T, respectively. The evaluation of the uncertainties $u\{B_T\}$ and $u\{B_R\}$, and the covariances between respectively m_{T0} and B_T on one side and m_{R0} and B_R on the other do not need to be evaluated if $t = 0$ coincides with the onset of evaporation when the pycnometer is filled.

In the particular example given in this paper, we present the following values, measurements and calculations.

$$n_T = 6$$
$$n_R = 7$$
$$V_T\{m\} = 1.3 \times 10^{-9}\ \text{g}^2$$
$$V_R\{m\} = 8.0 \times 10^{-10}\ \text{g}^2$$
$$B_T = -4.346\ (77) \times 10^{-6}\ \text{g/s}$$
$$B_R = 3.1\ (48) \times 10^{-8}\ \text{g/s}$$

and, finally,

$$m_{T0} = 0.003693\ (39)\ \text{g}$$
$$m_{R0} = 0.001711\ (25)\ \text{g}$$

with the difference

$$d = \Delta m = m_{T0} - m_{R0} = 0.001982\ (46)\ \text{g} \,.$$

Since the covariance between the two sets of measurements T and R is essentially zero, the variance of d is the sum of the variances of m_{T0} and m_{R0}. The only contribution to the variance would come from the balance. It cancels out while subtracting m_{R0} from m_{T0} since the covariant contribution of m_{R0} is negative. Furthermore, the uncertainty of the balance is included into $V\{m\}$.

It is worth noting that the uncertainty on the slope of the reference measurements, B_R, is larger than its value, which means that its value is essentially zero; the line is horizontal.

4. DISCUSSION

The example given here is from real measurements taken on a pycnometer used for the key comparison in flow CCM.FF-K4 [1]. They are typical. The first time this method was applied was for the regional comparison within the Sistema Interamericano de Metrología (SIM) SIM.M.FF-S1 [2], where one can compare the two methods as used then at the National Research Council (NRC).

The linearity of the evaporation allows a linear regression and a backward extrapolation in time to when the pycnometer is filled and ready for measurements. There is no need for a quick measurement before the onset of evaporation, which is an advantage since a minimum stabilization time is needed for the balance to give a proper measurement.

In the case of an evaporating pycnometer, the mass measurement is not the principal source of uncertainty. The uncertainty reported here is typical, $46\ \mu\text{g}$. There are other elements involved, temperature measurements in particular. This latter kind of source of uncertainty can be estimated by multiple series of "filling – mass measurements". In this particular case, the combined uncertainty is $950\ \mu\text{g}$, much greater than the contribution of the mass measurement.

An alternative procedure for measuring liquid volumes is to use pycnometers with an anti-evaporation cap, Figure 2. When the vapour pressure within the cap reaches its equilibrium, and if there is no leak, the evaporation from the pycnometer stops. Furthermore, there is no mass loss once the cap is put in place on the pycnometer.

Figure 2 Pycnometers with caps

This is illustrated in Figure 3. We let two pycnometers on respective pans of two balances for a few hours. One of the pycnometers has an anti-evaporation cap. The apparent increase in mass is due to the drift of the balance. This pycnometer does not show any mass loss, since there is no evaporation. The second pycnometer clearly shows a mass loss of 2.2×10^{-6} g/s due to evaporation.

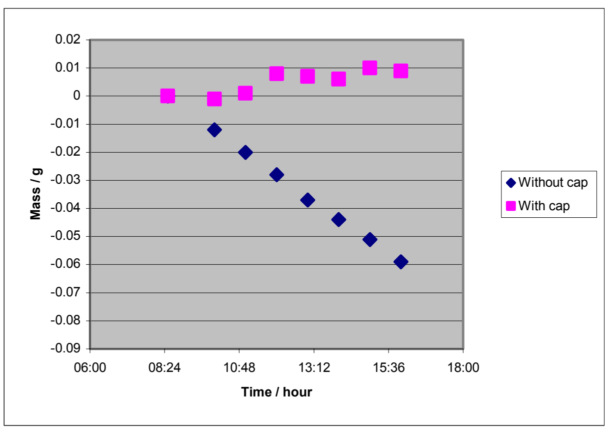

Figure 3 Pycnometers with and without a cap

Usual weighing methods, like RTR, for the pycnometer with a cap apply since there is no evaporation. Fortunately, one can find this kind of pycnometer on the market. The pycnometer without a cap presents a challenge due to mass loss caused by evaporation. This is the problem addressed in this paper. The method with backward extrapolation is to be preferred to avoid systematic errors, or offsets, due to an oversight of the evaporation.

This process of differential mass measurement between a Test T and a Reference R is not the final step towards mass measurement. Some calculations are needed from this point on, to provide the required absolute or conventional masses, or even the old concept of effective mass still used in some laboratories. These calculations involve the volume of the weights – reference and test –, the density of air, and the calibration of the balance.

As an example of calculation of volume, we give here the set of equations that provide the volume-to-contain of a pycnometer. The calculation is done with conventional masses. The volume is calculated from the difference between the conventional mass of the filled pycnometer $Mc_{\text{pyc+water}}$ and the empty pycnometer Mc_{pyc}:

$$V_{\text{water}} = \frac{0.99985\left(1-3\alpha\left(T-20\right)\right)\left(Mc_{\text{pyc+water}}-Mc_{\text{pyc}}\right)}{\rho_{\text{water}}\left\{T\right\}-1.2}$$

where

$V =$ volume content of the pycnometer

$\alpha =$ linear coefficient of thermal expansion of the pycnometer (8)

$T =$ temperature of measurement

$Mc_{\text{pyc\_water}} =$ conventional mass of filled pycnometer

$Mc_{\text{pyc}} =$ conventional mass of empty pycnometer

$\rho_{\text{water}}\left\{T\right\} =$ density of water, function of temperature

The conventional masses are evaluated from the balance measurements: test mass m_{T0} and reference mass m_{R0}. The mass of the empty pycnometer is first measured, then its mass filled with water. The same equation below applies for both measurements except that, for the filled pycnometer, the difference between test mass and reference mass is done by backward extrapolation as explained above.

$$d = m_{T0} - m_{R0} \tag{9}$$

where

$m_{T0} =$ balance reading for test mass

$m_{R0} =$ balance reading for reference mass

and

$$Mc_T = Mc_R + d + \frac{\left(\rho_a - 1.2\right)\left(V_T - V_R\right)}{0.99985} \tag{10}$$

where

$Mc_T =$ conventional mass of test (pycnometer empty or filled)

$Mc_R =$ conventional mass of reference weights

$\rho_a =$ density of air

$V_T =$ volume of test (approximate value to be refined)

$V_R =$ volume of reference weights ensemble

For the mass measurement of the filled pycnometer, V_T is equal to $V_{\text{pyc+water}}$. Since we are looking for $V_{\text{water}} = V_{\text{pyc+water}} - V_{\text{pyc}}$, it is like using the answer as an input parameter. Fortunately, an approximate value of V_T in equation (10) is sufficient. Then, when V_{water} is evaluated in equation (8), it can be used to refine the value of V_T for the filled pycnometer. This is an iterative process. It converges quickly, usually within two steps.

5. CONCLUSION

This paper shows that it is possible to make mass measurements of evaporating artefacts with an acceptable uncertainty budget. The problem of a variable mass artefact is easily solved if the evaporation leads to a linear change of mass. This is the solution we have presented here.

A pycnometer is a device to measure volume of liquid. There are two ways to solve the problem of evaporation through the stopper: 1) a mass measurement scheme like the one treated in this paper, and 2) a cap on the stopper to eliminate evaporation. Both methods may be adopted by any national laboratory.

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