

Precise Gravimetric Determinations of Dilution Factors

A dilution of a solution is the process of decreasing the massic concentration of a substance in a solution by the addition of more solvent. The magnitude of the dilution is given by a “dilution factor” D that relates the massic concentration of the starting and ending solutions. In radionuclidic metrology, the dilution is generally performed by taking a measured aliquot mass of a master solution, called M, with massic activity A_M , and adding to it a measured mass of a carrier solution, called C. The resultant solution, called S, has massic activity $A_S = A_M / D$. Often solutions M and C are designed to have comparable chemical compositions to avoid solution instability issues. In cases only involving small masses (< 5 g or thereabouts), the dilution factor can be determined from both pycnometer dispensed masses and from contained masses using the same microbalance. Of necessity, separate clean pycnometers must be used for each M and C solution. For convenience, these dilutions are frequently performed directly in flame-sealable 5-mL ampoules.

A suitable protocol is as follows:

Balance readings

m_1 = empty container

m_2 = pycnometer with C

m_3 = pycnometer after dispense C

m_4 = container + C

m_5 = pycnometer with M

m_6 = pycnometer after dispense M

m_7 = container + C + M

Solution mass differences

(with application of air buoyancy corrections and possible balance zero corrections)

$(m_2 - m_3)$ = dispensed mass of C

$(m_5 - m_6)$ = dispensed mass of M

$(m_4 - m_1)$ = contained mass of C

$(m_7 - m_4)$ = contained mass of M

$(m_2 - m_3) + (m_5 - m_6)$ = total dispensed mass

$(m_7 - m_1)$ = total contained mass

Apparent error differences in percent

$$\Delta_C = \left(\frac{m_4 - m_1}{m_2 - m_3} - 1 \right) 100$$

$$\Delta_M = \left(\frac{m_7 - m_4}{m_5 - m_6} - 1 \right) 100$$

$$\Delta_{\text{total}} = \left(\frac{(m_7 - m_1)}{(m_2 - m_3) + (m_5 - m_6)} - 1 \right) 100$$

Dilution factor

$$D = \frac{(m_7 - m_1)}{(m_5 - m_6)}$$

The dilution factor is determined by the ratio of the total mass as obtained from contained mass readings over the aliquot mass as obtained from the dispensed mass readings. This procedure provides a more accurate determination for that true amount of added aliquot and a better estimate for the total mass since it accounts for possible evaporation losses during the procedure. In general, the contained mass differences will reflect small evaporation losses compared to the dispensed mass differences. This results from the larger time interval between the two readings for contained mass difference and the larger opening on a container compared to the opening on the pycnometer tip. For an appreciation of possible evaporation losses, one can also calculate the dilution factors obtained from just the dispensed masses and from the contained masses for comparison.

The above 7-reading procedure does not provide for possible corrections for balance zero offsets. The balance zero could of course be examined after each step. This is rarely advisable, however, since it would substantially lengthen the amount of time for the procedure leading to increase evaporation losses. The extent that balance zeros be examined should be determined by each metrologist based on their own experience as obtained from data. A useful compromise is to examine and correct for balance zeros after reading m_4 and after reading m_7 in comparison to the initial zero before reading m_1 .

Whenever possible, good practice would require that any gravimetric dilution factor should be checked for consistency against radiometric measurements results, such as ratios of massic ion currents from aliquots of both solutions or from relative LS massic counting rates for the two solutions, M and S.

An example (using real data as obtained from a metrologist at NIST) for a dilution to 5 mL with approximately $D = 20$ follows.

Master solution M was contained in a 5-mL flame sealed ampoule. Masses of both M and C were dispensed with plastic aspirating pycnometers. Diluted solution S was prepared directly in another 5-mL ampoule for subsequent flame sealing. The employed balance was a Mettler AT-20 electronic microbalance. The gravimetric dilution factor was confirmed by concurrent ion chamber measurements of the solution S ampoule and another ampoule containing master solution M.

Balance readings (in grams)

$$m_1 = 4.766020$$

$$m_2 = 7.034976$$

$$m_3 = 2.205482$$

$$m_4 = 5.014768$$

$$m_5 = 6.310632$$

$$m_6 = 6.061656$$

$$m_7 = 9.844194$$

Mass differences (after corrections)

$$(m_2 - m_3) = 4.834360 \quad (\text{dispensed mass of C})$$

$$(m_5 - m_6) = 0.249230 \quad (\text{dispensed mass of M})$$

$$(m_4 - m_1) = 4.834428 \quad (\text{contained mass of C})$$

$$(m_7 - m_4) = 0.249002 \quad (\text{contained mass of M})$$

$$(m_2 - m_3) + (m_5 - m_6) = 5.083590 \quad (\text{total dispensed mass})$$

$$(m_7 - m_1) = 5.083430 \quad (\text{total contained mass})$$

Apparent error differences

$$\Delta_C = \left(\frac{m_4 - m_1}{m_2 - m_3} - 1 \right) 100 \% = -0.0915 \%$$

$$\Delta_M = \left(\frac{m_7 - m_4}{m_5 - m_6} - 1 \right) 100 \% = +0.0014 \%$$

$$\Delta_{\text{total}} = \left(\frac{(m_7 - m_1)}{(m_2 - m_3) + (m_5 - m_6)} - 1 \right) 100 \% = -0.0032 \%$$

Dilution factor

$$D = \frac{(m_7 - m_1)}{(m_5 - m_6)} = 20.3965$$

A useful way to examine the data is in tabular form, as below, where the percent differences Δ between dispensed and contained masses are compared along with a comparison of the computed contained and dispensed dilution factors (DF) to D .

	contained	dispensed	$\Delta / \%$
M	0.249002	0.249230	-0.0915
C	4.834428	4.834360	0.0014
total	5.083430	5.083590	-0.0031
<i>DF</i>	20.4152	20.3972	0.0884
% diff <i>D</i>	0.0916	0.0031	

The radiometrically-determined dilution factor that was obtained for this work was

$$D_R = 20.369 \pm 0.022 \ (\pm 0.11 \%),$$

which differs from the gravimetric D by 0.14 %. Though statistically equivalent, the difference, if real, might be attributed to possible evaporation losses during the dilution and during sealing of the ampoule.

Examination of these results indicates that there is no reason to believe that the dilution factor D was determined to better than about 0.1 %, so the relative standard uncertainty on the dilution factor is taken to be 0.1 %. All other uncertainty factors in the mass determinations (reproducibility, balance calibration, buoyancy correction, external effects, etc.) are either embodied within this estimate or negligible with respect to this magnitude.

It is important to recognize that precision (and underlying accuracy) in a dilution factor is dependent on the magnitude of the dilution, given by D , as well as on the aliquot mass of M used. In the above example, an aliquot of about 250 mg was used. Had the dilution been done with an aliquot of about 50 mg with the same total mass (for a dilution of $D = 100$), the uncertainty would have been decidedly larger.

Below are two further examples of dilutions using real data from the NIST Radioactivity Group. Both dilutions had relatively small dilution factors and were performed directly in 5-mL flame-sealed ampoules.

The first of these (Example 2) is for a dilution of ^3H tritiated-water standard with pure water. The mass results in tabular form (after application of all corrections) are:

$$D = \frac{5.270907}{1.224712} = 4.3038$$

	contained	dispensed	$\Delta / \%$
M	1.224581	1.224712	- 0.011
C	4.046326	4.046603	- 0.007
total	5.270907	5.271315	- 0.008
DF	4.30425	4.30412	+ 0.003
% diff D	+ 0.011	+ 0.008	

Example 3 is for a small dilution of a $^{99\text{m}}\text{Tc}$ solution, adjusted to obtain a specific massic counting rate for coincidence counting. These mass results (again after all corrections were applied) are:

$$D = \frac{4.114119}{1.802516} = 2.2824$$

	contained	dispensed	$\Delta / \%$
M	1.8032228	1.802516	- 0.016
C	2.311891	2.312170	- 0.012
total	4.114119	4.114686	- 0.014
DF	2.28280	2.28275	+ 0.002
% diff D	+ 0.016	+ 0.014	

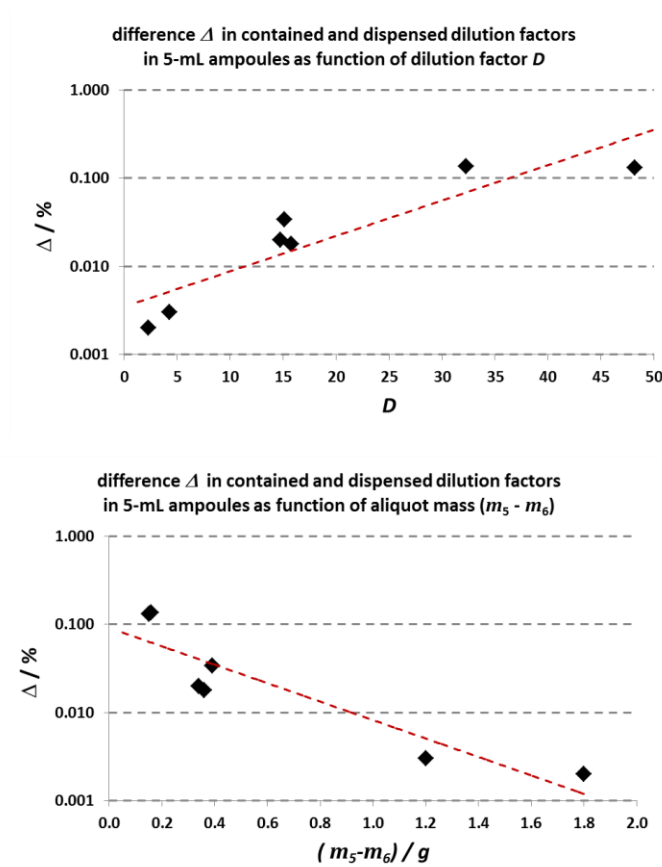
The gravimetric dilution factor was confirmed by relative LS counting rates from cocktails prepared with aliquots of solutions M and S. A value of $D_{\text{LS}} = 2.2851 \pm 0.0043$ ($\pm 0.19 \%$) was obtained, which differed from D by 0.12 %

This case and the earlier one in Example 1 demonstrates that radiometric methods are useful for confirming a gravimetric dilution factor (to detect gross blunders), but generally are much less precise than the gravimetric determination. This generalization, however, was not entirely true for Example 1. One must also appreciate that “too perfect” of agreement in results can occur because of fortuity of sampling from real distributions.

Examination of the results for Examples 2 and 3 reveal very similar precisions in both cases, essentially, agreements between dispensed and contained masses to about $\pm 0.01 \%$ or less. In part, this can be attributed to the relatively large aliquot masses $[(m_5 - m_6) > 1 \text{ g}]$ and small dilution factors ($D < 5$). The

results, however, can serve to illustrate an important point. The above two determinations (Examples 2 and 3), despite the similarities in results, were performed with two different microbalances; *viz.*, a Mettler M5 mechanical microbalance balance with built –in calibration weights and an optical scale for Example 2, and a Mettler AT20 electronic microbalance for the third example. And the two determinations were performed by the same metrologist approximately four years apart. The development of this type of data for THIS metrologist can result in the establishment of a canonical estimate for the uncertainty in determining a dilution factor in the range by THIS metrologist. In fact, based on several decades of work by THIS same metrologist, canonical values of $\pm 0.02\%$ to $\pm 0.1\%$ for the relative standard uncertainty in dilution factors in the range of $D = 2$ to $D = 50$ has been established. The canonical value must of course be checked for each dilution with data, such as that shown in the three examples.

The figure below shows data for the difference Δ in contained and dispensed dilution factors as function of both dilution factor D and solution M aliquot mass ($m_5 - m_6$) as obtained for seven different dilutions performed directly in 5-mL ampoules. The data were obtained by a single experienced metrologist over the course of five years for the purpose of evaluating a canonical uncertainty for that dilution procedure by THAT metrologist. All of the percent differences are in the same direction, reflecting more evaporation between the contained mass readings. From this it is evident that the uncertainty in the dilution factors varies over a substantial range and is dependent on the aliquot mass taken and magnitude of the dilution factor. Note that the ordinate is a logarithmic scale plotted against the mass and dilution factor abscissae. The red lines are only meant to direct the eye.



One may observe that the result in Example 1 appears to fall outside the stated range for the above stated canonical value based on revealed experience. The determination of Example 1 was real data obtained by another, less experienced, metrologist and the aliquot mass at 250 mg was less. In good practice, this metrologist should develop his own canonical expectations for the realistic uncertainty associated with his determinations of dilution factors.

From these examples, one can conclude that the weighing uncertainty in determining a dilution factor is not an uncertainty in mass, and that this uncertainty is likely to be as dependent on the experience, practices, and capability of the metrologist as on the balance characteristics *per se* and the experimental conditions. A good evaluation of the uncertainty in a dilution factor must take into consideration three factors: (i) the experience and training of the metrologist, (ii) the use of data actually obtained during the weighing; and (iii) the experimental design, which includes the masses to be taken, the containers, the balance, and the procedural steps.

The following fourth example, shown in the attached figure, illustrates a more complex design for performing a larger-volume dilution, such as needed for the preparation of a dispensing solution that is used to make a series of standards. It illustrates a realistic assessment of the uncertainty in preparing a 1-L solution with a dilution factor of approximately $D = 110$ from a master solution. An electronic microbalance (mettler AT20) was used to weigh the dispensed master solution (from two 5-mL ampoules) and a large capacity (3 kg) mechanical balance (Volland Jupiter 300) was used to obtain the contained mass of the master solution and the total solution mass. All appropriate air buoyancy corrections were applied for the masses that are shown at the various steps. The master solution dispensed mass from the ampoules was obtained from mass differences with an aspirating pycnometer. The weighing with the large capacity balance for each mass was based on the average of three readings. At the time of the measurements, both balances were “calibrated” (i.e., checked for possible calibration error) with OIML Class E1 standard weights in the exact mass ranges used for the determinations (single substitution with sensitivity weights). The large capacity balance was evaluated in the mass range of the empty bottle (605 g) and the mass range for the filled bottle (1681 g). Maximum deviation relative bias errors of < 0.0002 % and < 0.0003 %, respectively, were found. The microbalance was evaluated at the mass ranges for empty and filled pycnometer, with errors of less than < 0.0009% and < 0.0004 %, respectively. The mass data from the weighings follow:

$$D = \frac{1075.90761}{4.919196 + 4.858217} = 110.0401$$

	contained	dispensed	Δ / %
M	9.775785	9.777413	- 0.017
C	1066.13118	----	----
total	1075.90761	----	----
DF	110.0584	-----	----
% diff D	+ 0.017	----	

The relative difference in the dispensed and contained mass of the master solution (nominal 9.78 g) was found to be 0.017 %. The calculated gravimetric dilution factor was confirmed by LS measurements of aliquots of the two solutions to within 0.031%. The estimated relative standard uncertainty on the dilution factor was taken to be 0.025 %. This was in large part based on the experienced judgment of the metrologist for the replicate measurement repeatability and the zero-tare stability of the two balances (though confirmed by the present observations). In this example, the uncertainty on air buoyancy was negligible as was most of the other balance and environmental effects (non-linearity, sensitivity tolerance, temperature coefficient, etc). With this kind of data-based approach, there is no need to speculate on unquantifiable evaporation losses, electrostatic effects, or eccentricity, and no need to invoke any additional “method uncertainty”. Critiques may contend that this treatment is pessimistic and overestimates the likely uncertainty in the dilution factor. But reliance on just the given “balance” calibrations (of magnitudes < 0.001 %) would grossly underestimate what was really involved. The bigger contribution to the uncertainty in mass determinations often comes from real mass loss (or gain) effects (evaporation, transfers, condensation, dirt, etc) and not from balance characteristics. The uncertainty treatment shown here is actually driven by what was actually done, and not as theoretical expectations using manufacturer’s idealized data.

