

Review comments on MET-100289:

“Weighing uncertainties in source preparation” by V. Lourenco

Line-by-line specific comments will follow this overview of the paper and general comments.

This paper is well written and is well researched (with references) on the operation of modern electronic balances and on the effects of external influences on mass determinations. It inadequately treats how to realistically assess mass uncertainty obtained by weighing methods. The paper ignores the human element and reliance on real data. The uncertainty assessment approach given here is not based on any obvious measurement model, which in turn depends on the exact experimental procedures that are used. 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. Yet, these are the only considerations given in this paper.

My principal concern is that this paper treats the uncertainty assessment in weighing almost as a theoretical exercise using manufacturers idealized data, with almost no emphasis on the actual collection of observational data obtained by persons actually making the measurements, nor any mention that weighing is a skill requiring craftsmanship, a great deal of experience, and training by a master.

My greatest fear is that users of this document will take the uncertainty assessments in the two idealized examples and blindly use the results as typical. I can easily foresee that future ICRM papers will blindly invoke the exact uncertainty values given in these examples. In my mind, the magnitudes of the cited standard uncertainties, particularly for the 50 mg drop deposition, is grossly optimistic. Weighing uncertainties must rely on the judgment of experienced user as much as on any theoretical expectation that is rarely realized.

The paper also fails to address several important aspects and examples that are fairly critical considerations in source preparations for mass activity determinations. These include: (i) measurement of solution density is equally as important as knowing air density; (ii) comparison of “dispensed” and “contained” masses for validation purposes; (iii) an example on how to determine a gravimetric dilution factor (the 100-mL solution example is inadequate), and how to independently check it; (iv) gravimetric preparation of a large volume solution (as might be prepared for an international measurement comparison or for a series of standards) when two balances of different capacities are required; (v) inadequate emphasis on making balance “calibrations” (beyond the few words in Sect 5.4) in the exact mass range and at the time of

measurements; (v) failure to address that most of the uncertainty in weighing is embodied in the precision estimators of the massic activity when multiple sources are used (or at least SHOULD be used) and measured .

For purposes of full disclosure, I would like to point out that I was opposed to having a weighing uncertainty paper in the proposed collection. Firstly, the paper would certainly not be a treatise on mass determination since this is clearly outside our community's purview. Secondly, the mass uncertainty per se in radionuclidic metrology rarely occurs uncorrelated to the uncertainties in other parts of measurement methods employed, and the largest component of the weighing uncertainty (operator and environment effects) is of necessity largely if not wholly embodied in these other uncertainty assessments. Inasmuch as we are normally concerned with determinations of massic activity, it would make as much sense to have a separate paper in this same collection on the determination of time for rates (independent of the method used) as it would a weighing paper. The uncertainty in a mass determination due to weighing is more dependent on the weighing method employed and not on just the characteristics of the balance. I do not see this reflected in this paper, which almost exclusively covers balance effects.

I believe this paper should have covered in depth at least two very important and distinct operations; viz., source and solution preparations. It does not.

The first arises from the need to prepare very quantitative counting sources. This in fact is given as the title of the paper, but really isn't covered. Much of this topic is covered in the cited references, but is certainly not condensed in any useable form here. One must also appreciate the fact that most well-designed experiments would have the major weighing uncertainty embodied within other uncertainty components – such as in averaging massic counting rates over numerous sources having variable masses. The exception, of course, would be if only one counting source is prepared, which is never a good idea! One further appreciation is that no amount of words (insightful, clever, or not) in a document will ever suffice in the training of metrologists without hands-on mentoring by experienced master practitioners. And if this is needed, as I believe it is, then what role does the present document serve. The assignment of an uncertainty value to a mass determination is largely irrelevant if the measurement itself is dominated by mistakes, blunders, and uncontrolled experimental errors. For example, a document (and many exist) could spell out in excruciating detail exactly how to correctly perform double- or triple-substitution weighing in the few milligram range. I contend (and I have witnessed it) that any novice following these instructions is more likely to obtain an incorrect mass than if this untrained person just read the mass from single readings on an

electronic single-pan balance and would be much better served. This person could indeed go through all of the substitution steps – in cookbook fashion – and crank out a derived uncertainty from the data and would likely have a very erroneous result. This is the problem with rote formulations. It can bestow confidence and the appearance of rigor when none exists.

The second area of weighing, which has even more possible variations, involves the preparation of solutions and the performance of solution dilutions. Most of the above comments equally apply in these situations. Again, the mere assignment of uncertainty values outside the scope of what was exactly done for the given case is irrelevant. There is not just one way to do things, particularly for complex assays. For example, I suppose I could write a general protocol to cover the most common case of obtaining a dilution factor with confirmation by dispensed and contained mass comparisons, including a prescription for its uncertainty assessment. But then, I can similarly imagine that it might be blindly invoked for something where it doesn't apply. It all comes down to having well-designed experiments and well-executed procedures – performed with understanding. This paper certainly does not cover all of the conceivable designs that may be encountered and all of the operations that are commonplace in analytical solution chemistry. I contend that if anyone needs to read a paper to do these operations and to assign uncertainties on them, without the necessary educational background and requisite training from experienced masters, then they just shouldn't do the work.

Let us try to remember that an uncertainty number is not just picked out of the sky for a given component and it cannot be generalized as one oft sees done in ICRM papers without any evident analyses. It starts with the underlying experimental design and measurement model and then depends on what was actually done and what the data show. How do you generalize all this when I know for a fact that the uncertainty in mass determinations that I make can be quite different from that of my closest colleagues doing the same procedures on the same balances?

In short, where in this paper does it make it clear that a substantial part of the uncertainty assessment should come from actual data taken by the user?

Page 1

Line 18 – use “smallest” not lowest.

Line 20 ff – sentence that uncertainty comes from features of balance and that air buoyancy is “main bias effect” ignores the human factor entirely. The experience of the operator is probably the largest contributor to the accuracy. And the specific weighing method used by that operator drives that accuracy.

Line 31 – 100 g example needs a more important example, like determining dilution factor, or preparation of a standard solution.

Line 33 – yes, get uncertainties of 10^{-3} to 10^{-5} in the absence of all normal conditions (“disturbance factors”) and the absence of humans. This essentially dictates that it is not a realistic assessment.

Line 41—Not one mention is made in the abstract that the uncertainty assessment could (should) include actual observation data taken by a user!

Line 52 – very little of this paper actually addresses “source preparation”, not in terms of how the weighing comes into play with the actual steps in making the source

Line 54 – It is not apparent as to what is being cited from Ref (1). Is it the “but not only”?

Page2

Line 22—yes, good practice is needed and a proper balance, but what about the requirement for a TRAINED and EXPERIENCED person

Line 47 – what is meant by “non-automatic”. Does it refer to a human having to actually put things on and off the balance pan?

Page3

Line 37 – use “are” not is

Page 4

Line 3 – what is the meaning of “ $1-2 \times 10^{-6}/^{\circ}\text{C}$ ”? What is the numerator supposed to represent?

Line 60 --- which manufacturer?

Page 6

Line 15 – why is “Dilutions” part just dropped into this “good practice “ section when all the other parts address how to avoid certain effects

Line 24 – I’m not sure where I should bring this up, but surely somewhere in this section there should be at least a mention and discussion of comparing dispensed and contained masses, such as in filling an ampoule with solution by measuring the mass difference with plastic pycnometer and the mass difference between the unfilled and filled ampoule. On accounting for even worst cases evaporation losses, an operator can get a revealing look at how well the weighing procedure was done. Based on my experience, the grossly underestimated uncertainties given in the examples in this paper will be revealed for many laboratory workers doing weighing.

Line 39 – no mention of equal importance of having well known sample density. Over next two pages all the emphasis is given to getting the air density with not one mention of the need for knowing sample density.

Page 7

Figure 1 – looking at slope of the curve near specific gravity of 1 shows how important it is to know the density of solutions being measured.

Page 8

Line 53 – where did this 0.1 % number come from all of a sudden?

Line 57 – These balance “checks” are all fine and good, but what is exactly meant by this check. What is “prior to use” ? Every time? You mention that at LNE-LNHB you do a 8 point check from 5 mg to 5 g. When? Wouldn’t it be better to more closely examine over a smaller and more relevant range at the time of measurements. At NIST, for the most careful work, the balance calibration is actually checked at the weighing time with standard weights over the very small mass range of samples to be determined.

Page 9

Line 44 – the paper is now finally getting into some of the specifics of good weighing practice, mainly substitution weighing techniques. This should probably be given much greater emphasis, particularly in terms of doing calibration checks at the time of weighing.

Page 10

Line 10 – Ref (3) needs publisher information . NPL?

Line 13 – these comments are directed toward this entire section (pp 10 – 15) -- too much emphasis is placed on just taking manufacturer’s data for these components, which is nothing but the most idealized, unrealistic conditions.

Line 25 – shouldn’t this paper address how to “check the available data” to “build a realistic uncertainty budget.” I couldn’t agree more that it should all be based on observational data whenever possible, but this paper never tell us how to do this, just that we should!

Page 11

Line 8 – rectangular distributions can indeed be assumed, but why required?

Line 29 – deviations are ALWAYS observed under repeatability at the edge of the instruments sensitivity – and this should be measured and evaluated. And all persons doing weighings should have obtained such data and have a sense of typical and / or canonical values for their ability with specific operations.

Line 42 – Values of 40 μg ($m > 50 \text{ g}$) and 0.9 μg ($m > 2 \text{ g}$) may be “typical” in balance specification sheets, but are not realistic. Can the author actually present data for 10 replicate weighing of a solution in a sealed ampoule weighing about 7 grams that shows a relative precision of $10^{-5} \%$? And what is that “repeatability for the 50 mg drop? In Table 2 (p 17), you claim that it is $< 0.002 \%$. I do not believe that this is realistic in any way.

Line 54 – Indeed checks on “repeatability” should be performed – and this is the data that should be used for the assessment not some idealized theoretical value from a manufacturer’s specification sheet.

Page 12 – Again there should be no need to rely on idealized manufacturers claims and guarantees for non-linearity, if users actually base their results on observational calibration check data obtained over the small range that the weighings are performed.

line 23 – why “MUST” the data be treated as being rectangularly distributed? It can be, but it’s just a choice. In all cases this choice should be stated as one possible assumption. This should also be fixed in all other cases as well (page 11 line 7, page 12 line 51, page 13 line 29, page 15 line 47, etc..)

Page 13

Line 61 – eccentric load does not have to be ignored in the uncertainty treatment, and should not be for many of the substitution weighing methods. And it’s magnitude can again be assessed by actual observational data by users.

Page 14

Line 47 – this concept of “method uncertainty “ needs to be clarified as to what is meant.

Line 47 – evaporation is indeed a serious concern and should be assessed in some way. What exactly is meant by “resolution of the scale”?

Page 15

Line 3 – Clarify what exactly is to be done with the pycnometer between the steps of placing it on then pan and taking the reading, removing it from the pan, and replacing it on the pan for another reading.

Page 16

Line 26 – I don’t follow what is being done in this example. There are several possible ways of determining the mass of 100 mL of solution. Presumably, this solution is inside some sort of container. Is this example to represent the mass difference of the container with and without the solution? What if I want to determine this mass by dispensing? Nothing is clear or apparent in this example. Any uncertainty assessment is driven by the measurement model and exactly what was done. Without knowing how this 100 g mass was determined it is impossible to address its uncertainty.

Table 1 -- How can this budget cover every one of these possible cases. Would this identical budget be valid if I was to measure a stack of eleven 2-euro coins, which has a mass of approximately (100.0 ± 0.5) g? Based on the budget, I would think so.

Table 1 – the example is said to be for a “dilution factor evaluation”, but where is the calculation of the dilution factor which clearly requires two or more mass determinations and the uncertainty on the dilution factor?

Table 1 – units for the “standard uncertainty (k=1)” not given.

Table 1 – I do not know of any serious radionuclidic metrologist who believes that the mass of 100 g of solution (presumably in some vessel) can be determined with relative uncertainty of

0.0005 % and that this entire uncertainty is due to the uncertainty in the air buoyancy correction.

An addendum (at the end of this critique) follows that provides an example of a more realistic weighing uncertainty treatment for a gravimetric dilution factor determination.

Page 17

Line 13 – the “method” component (Table 2) requires some sort of clear definition. At present, it is vaguely explained and undefined. Is it really meant to be the prescription give on page 14 (line 47) as 3 times the “scale resolution” ? And how is the method component evaluated for example in Table 1

Table 2 – units for the “standard uncertainty ($k=1$)” not given

Table 2 – I do not know of any serious radionuclidic metrologist who believes that the mass of single 50 mg drop can be determined to < 0.01% relative uncertainty, without the measurement being performed by a very experienced person doing substitution weighing.

Line 59 – what is “the 0/00 range” ?

Page 18

Line 11 – Why is 0.05 % to 0.1 % “very conservative”? What data is available to support the contention that it is.

References – the excellent handbook by Jones & Schoonover could be included in the bibliography:

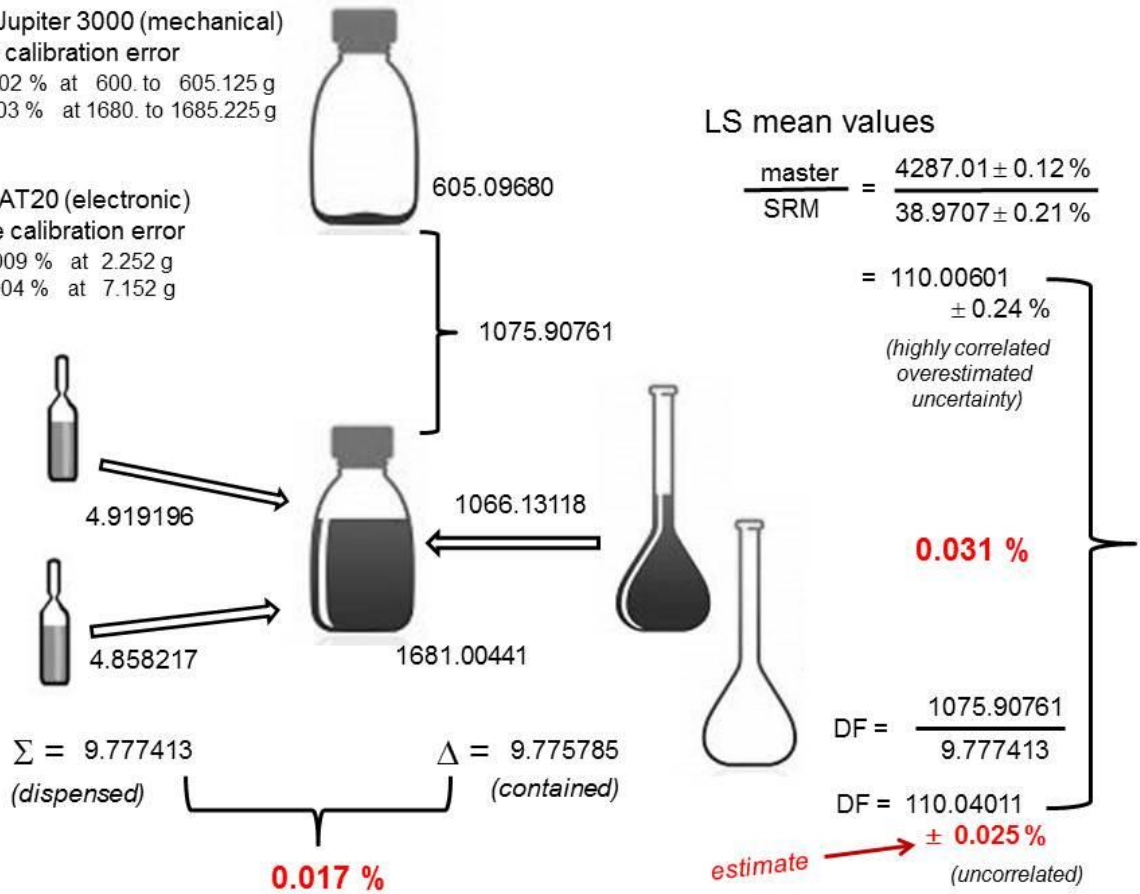
F.E. Jones, R.M. Schoonover , Handbook of Mass Measurement, CRC Press, 2002.

ADDENDUM

The attached figure is representative of a more realistic treatment of weighing uncertainties. It illustrates the preparation of a 1 liter solution with a dilution factor of approximately 110 from a master solution. An electronic microbalance was used to weigh the dispensed master solution (from two 5-mL ampoules) and a large capacity (3 kg) mechanical balance 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 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 uncertainty on the dilution factor was taken to be 0.025% . This was in large part based on the experienced judgment of the experimenter 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 were most of the other balance effects (non-linearity, sensitivity tolerance, temperature coefficient, etc) given at length in the author’s examples as dominant effects. There was no need to speculate on unquantifiable evaporation losses, electrostatic effects, or eccentricity, and no need to invoke an undefined “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 a theoretical exercise using manufacturer’s idealized data.

Voland Jupiter 3000 (mechanical)
balance calibration error
< 0.0002 % at 600. to 605.125 g
< 0.0003 % at 1680. to 1685.225 g

Mettler AT20 (electronic)
balance calibration error
< 0.0009 % at 2.252 g
< 0.0004 % at 7.152 g



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