SOP 4

Recommended Standard Operating Procedure
for
Weighing by Double Substitution

1 Introduction

1.1 Purpose

The double substitution procedure is one in which a standard and an unknown weight of equal nominal value are compared twice to determine the average difference between the two weights. Errors in any built-in weights or in the weighing instrument indications are minimized by using the weighing instrument as a comparator and by calibrating the weighing instrument indications over the range of use for the measurement with a sensitivity weight that has a known mass. Accordingly, the procedure is especially useful for calibrations of weights in OIML[1] Classes F_1 to M_3, ASTM[2] Classes 2 through 7, and forms the basis for advanced weighing designs used in SOP 5 and SOP 28 (See NISTIR 5672). The procedure incorporates two methods of measurement assurance: one is a mathematical check that evaluates the within-process repeatability and the other involves using a check standard to monitor the reference value(s) of the standard. This procedure may be used for any nominal values provided adequate standards and equipment are available. Detailed measurement ranges, standards, equipment, and uncertainties for this SOP are generally compiled in a separate document in the laboratory.

1.2 Prerequisites

1.2.1 Valid calibration certificates with appropriate values and uncertainties must be available for all of the standards used in the calibration. All standards must have demonstrated metrological traceability to the international system of units (SI), which may be to the SI through a National Metrology Institute such as NIST.

1.2.2 Standards must be evaluated to ensure that standard uncertainties for the intended level of calibration are sufficiently small. Reference standards should only be used to calibrate the next lower level of working standards in the laboratory and should not be used to routinely calibrate customer standards.

1.2.3 The weighing instrument must be in good operating condition with sufficiently small process standard deviation as verified by a valid control chart. When a new weighing instrument is put into service, preliminary

[1] OIML is the International Organization for Legal Metrology. Weight classes are published in OIML R 111, which is freely available at http://www.oiml.org.
[2] ASTM International (formerly the American Society for Testing and Materials) publishes the E617 standard for mass specifications and tolerances.

experiments must be conducted to ascertain initial performance quality and adequacy.

1.2.4 The operator must be trained and experienced in precision weighing techniques with specific training in SOP 2, SOP 4, SOP 29, GMP 4, and GMP 10.

1.2.5 Laboratory facilities must comply with the following minimum conditions to meet the expected uncertainty possible with this procedure and to comply with the balance manufacturer's operating conditions specified for the balance. Equilibration of balances and weights requires environmental stability of the laboratory within the stated limits for a minimum of 24 hours before a calibration.

Table 1. Environmental conditions.

Echelon[3]	Temperature Requirements During a Calibration	Relative Humidity (%)
II	Lower and upper limits: 18 °C to 23 °C Maximum changes: ± 2 °C / 12 h and ± 1.5 °C / h	40 to 60 ± 10 / 4 h
III	Lower and upper limits: 18 °C to 27 °C Maximum changes: ± 5 °C / 12 h and ± 3 °C / h	40 to 60 ± 20 / 4 h

Standards and test artifacts must be allowed to reach equilibration in or near the balance before commencing measurements. It is essential for the difference in temperature between the weights and the air inside the mass comparator to be as small as possible. Keeping the reference weight and the test weight inside, or next to, the mass comparator before and during the calibration can reduce this temperature difference.

2 Methodology

2.1 Scope, Precision, Accuracy

This method is applicable for all types of weighing instruments. The achievable precision and expanded uncertainty depend on the resolution, sensitivity, linearity, and other operating characteristics of the weighing instrument and the care exercised to make the required weighings. The accuracy achievable with this procedure depends on the accuracy of the calibration of the working standards and the accuracy obtained in the measurement process.

2.2 Summary

The weighing instrument is adjusted if necessary, to obtain measurement indications for all weighings that are within the range of the optical scale or digital

[3] Echelon II corresponds to weights of Classes OIML F_1 and F_2, ASTM Classes 2, 3 and 4. Echelon III corresponds to weights of Classes OIML M_1, M_2, and M_3, ASTM Classes 5, 6 and 7. This procedure does not provide adequate redundancy for OIML Classes E_1 or E_2, ASTM Classes 000, 00, 0, or 1 and SOP 5 or SOP 28 should be used.

indications without changing built-in weights, if present (this includes changing dials or the weighing platform masses). The standard and the test weight are each weighed twice. A small, calibrated weight, called a sensitivity weight, is added to the standard and unknown test weight in the latter two weighings to provide a determination of the sensitivity of the balance under the load conditions at the time of the intercomparison. All weighings are made at regularly spaced time intervals to minimize effects due to drift in the measurement process.

The double substitution procedure is the same for all weighing instruments, but the adjustment of the weighing instrument to prepare for the intercomparison and the selection of the sensitivity weight differs slightly depending upon the type of instrument used. When steps specific to a particular instrument are required, they are given in subsections of the procedure identified by a, b, and c along with the type of instrument.

2.3 Apparatus/Equipment Required

2.3.1 Precision analytical balance or mass comparator with sufficient capacity and resolution for the calibrations planned.

2.3.2 Calibrated working standards, of nominally equal mass to the unknown mass standards being calibrated. Calibrated tare weights are used as needed to ensure that the standard(s) and test artifacts are of equal nominal mass (See SOP 34 for suitable limits).

2.3.3 Calibrated sensitivity weights and tare weights selected to comply with the guidelines in SOP 34.

2.3.4 Uncalibrated weights to be used to adjust the balance to the desired reading range if needed.

2.3.5 Forceps to handle the weights, or gloves to be worn if the weights are moved by hand. Forceps and gloves must be selected to avoid damage or contamination of mass standards.

2.3.6 Stop watch or other timing device to observe the time of each measurement (calibration not required; this is used to ensure consistent timing of the measurement). If an electronic weighing instrument is used that has a means for indicating a stable reading, the operator may continue to time readings to ensure consistent timing that can minimize errors due to linear drift.

2.3.7 Calibrated barometer with sufficiently small resolution, stability, and uncertainty (See SOP 2, e.g., accurate to ± 66.5 Pa (0.5 mmHg)) to determine barometric pressure.[4]

2.3.8 Calibrated thermometer with sufficiently small resolution, stability, and uncertainty (see SOP 2, e.g., accurate to ± 0.10 °C) to determine air temperature.[4]

2.3.9 Calibrated hygrometer with sufficiently small resolution, stability, and uncertainty (see SOP 2, e.g., accurate to ± 10 percent) to determine relative humidity.[4]

2.4 Symbols

Table 2. Symbols used in this procedure.

Symbol	Description
S	standard reference weight
X	weight to be calibrated
S_c	check standard
t	small calibrated tare weight, A subscript *s* or *x* is used to indicate the weight(s) with which it is associated
sw	small calibrated weight used to evaluate the sensitivity of the balance
M	the mass (true mass) of a specific weight. Subscripts *s*, *x*, *t*, *sw* are used to identify the weight (equals Nominal plus Correction)
N	nominal value of a specific weight. Subscripts *s*, *x*, are used to identify the weight.
C	correction for a specific weight. Subscripts *s*, *x*, are used to identify the weight.
CM	the conventional mass of a specific weight. Subscripts *s*, *x*, *t*, *sw* are used to identify the weight.
ρ_a	density of air at time of calibration
ρ_n	density of normal air (1.2 kg/m^3)
ρ	density of masses; subscripts *s*, *x*, t_s, t_x, *sw* are used to identify the weight.

2.5 Procedure

2.5.1 Preliminary Procedure

2.5.1.1 Weights are visually inspected for cleanliness and damage. Follow the laboratory policy, including discussions with customers, to determine if and when standards will be cleaned, or where standards with inadequate cleanliness are returned without calibration and when "as found" and "as left" values will be obtained through duplicate calibrations.

[4]The barometer, thermometer, and hygrometer are used to determine the air density at the time of the measurement. The air density is used to make an air buoyancy correction. The limits specified are recommended for high precision calibration.

2.5.1.2 If cleaning weights, it is important to clean weights before any measurements are made, unless “as found’ data is to be measured, because the cleaning process will likely change the mass of the weight. Cleaning should not remove any significant amounts of weight material. Weights should be handled and stored in such a way that they stay clean. Before calibration, dust and any foreign particles shall be removed by blowing air across the surface with a clean bulb or by brushing with a clean soft bristled brush. Care must be taken not to change the surface properties of the weight (i.e., by scratching the weight). If a weight contains significant amounts of dirt that cannot be removed by the methods cited above, the weight or some part of it can be washed with clean alcohol, distilled water or other solvents. Weights with internal cavities should normally not be immersed in the solvent to avoid the possibility that the fluid will penetrate the opening. If there is a need to monitor the stability of a weight in use, the mass of the weight should, if possible, be determined before cleaning.

2.5.1.3 If weights are cleaned with solvents, they must be stabilized for the times given in the following table (better class weights need to stabilize for 7 to 10 days):

Table 3. Cleaning stabilization.

Weight class	F_1	F_2 to M_3
After cleaning with alcohol	1 to 2 days	1 hour
After cleaning with distilled water	1 day	1 hour

2.5.1.4 Prior to performing any calibration tests, the weights need to be equilibrated to the ambient conditions of the laboratory. In particular, weights of classes F_1 (or better) should be close to the temperature in the weighing area. The minimum times (in hours) required for temperature stabilization (depending on weight size, weight class and on the difference between the initial temperature of the weights and the room temperature in the laboratory) are shown in the table below (with appropriate documented evidence). As a practical guideline, a waiting time of 24 hours is recommended. If weights are extremely hot or cold, additional equilibration is required to address problems with varying surface moisture levels. Weights must be completely dry prior to calibration.

Table 4. Minimum equilibration times. [5]

ΔT[a]	Nominal Mass	OIML Class F_1 (time in h)	OIML Class F_2 to M_3 (time in h)
± 20 °C	1 000, 2 000, 5 000 kg	79	5
	100, 200, 500 kg	33	4
	10, 20, 50 kg	12	3
	1, 2, 5 kg	6	2
	100, 200, 500 g	3	1
	10, 20, 50 g	1	1
	< 10 g	1	0.5
± 5 °C	1 000, 2 000, 5 000 kg	24	1
	100, 200, 500 kg	10	1
	10, 20, 50 kg	4	1
	1, 2, 5 kg	3	1
	100, 200, 500 g	2	0.5
	< 100 g	1	0.5
± 2 °C	< 100 g to 5 000 kg	1	0.5
± 0.5 °C	< 100 g to 5 000 kg	0.5	0.5

[a]ΔT = Initial difference between weight temperature and laboratory temperature.

2.5.1.5 Conduct preliminary measurements to obtain an approximate value for the difference between the standard and the unknown, to identify where in the weighing instrument range the readings occur, to determine if tare weights are required, to determine the sensitivity weight to be used, and to determine the time interval required for the weighing instrument indication to stabilize. See NISTIR 6969, SOP 34 for specific instructions on evaluation of the need for and selection of tare weights and sensitivity weights.

Tare weights are rarely needed for mass standards that are within applicable tolerances. When unequal nominal weights are compared, tare weights are often required. When tare weights are required, carry tare weights, t_s and t_x, with the standard and the unknown, S and X, respectively. The tare weights must be calibrated standards with valid uncertainties that are included in the process of determining mass values and calibration uncertainties. The standard and its tare weight, $S + t_s$, should be "nearly the same mass" as the unknown with its tare weight, $X + t_x$. "Nearly the same mass" depends upon the balance used (See SOP 34, Table 1).

A sensitivity weight must be used on equal-arm balances, single-pan mechanical, and is usually used on electronic balances, to ensure that the measured differences between the standard(s) and unknown test items have valid accuracy and traceability (See SOP 34, Table

[5] Consider equivalent ASTM Classes for equilibration times.

2) (e.g., the optical/digital scale is *calibrated* each time the procedure is performed through the use of a sensitivity weight).

If the sensitivity of the balance has been analyzed and is periodically evaluated and found to introduce negligible errors or uncertainties according to SOP 34 and measurement requirements, the equations in Section 3 must be modified to eliminate the sensitivity factor to avoid "division by zero" errors in the calculations.

Sensitivity weights are selected to meet the criteria in SOP 34.

2.5.1.6 Determine whether optional sequence A or B will be used. Optional sequence A uses the standard on the balance for the first and fourth observations and the unknown on the balance for the second and third observations; this is often called the "SXXS" sequence. Optional sequence B starts with the unknown on the balance first and last with the standard on the balance for the second and third observations; this is often called the "XSSX" sequence. The primary advantage of sequence B is less handling of the mass standards. The advantage of sequence A is in the case where the unknown is a summation of weights that require careful arrangement on the balance pan only once. Option A is used in SOP 5 and SOP 28.

2.5.1.7 Adjust the single pan mechanical balance or the combination balance so the first two readings of the double substitution fall in the first quarter of the optical scale or digital indications. The zero adjustment and tare adjustment may be used. Small weights may be placed on the balance pan to reach the desired reading range. These weights remain on the pan throughout the double substitution and calibration is not required. Once the balance has been adjusted to the desired scale indication, neither the balance dials, the zero and tare adjustments, nor the small weights placed on the balance pan, are to be changed during the measurement.

2.5.1.8 If the balance is equipped with a pan arrestment mechanism, arrest the pan between each observation.

2.5.2 Measurement Procedure, Optional Sequence A (*SXXS*)

Table 5. Optional sequence A.

Measurement No.	**Weights on Pan**	**Observation**
1	$S + t_s$	O_1
2	$X + t_x$	O_2
3	$X + t_x + sw$	O_3
4	$S + t_s + sw$	O_4

All observations should be recorded on suitable data sheets such as those in the appendix or may be entered into computer software. Measure and record the laboratory ambient temperature, barometric pressure, and relative humidity before and after the mass measurements.

2.5.2.1 Observation 1. Place the standard weight(s), *S*, along with t_s (if applicable) on the balance pan. If equipped with a pan arrestment mechanism, release the balance pan. When the pan is released, time the interval or wait for the stability indicator and record observation O_1 once the balance indication has stabilized.

2.5.2.2 Observation 2. Remove weight(s) *S* and t_s (if present) and replace with test weight *X* and its tare weight, t_x (if applicable.) Release the pan, time the interval or wait for the stability indicator, and record observation O_2.

2.5.2.3 Observation 3. Add the sensitivity weight, *sw*, to the weights of observation 2. Pick up the largest weight on the pan to ensure consistent stabilization timing when needed. Release the pan, time the interval or wait for the stability indicator, and record observation O_3.

2.5.2.4 Observation 4. Remove weights *X* and t_x (if present) and replace with *S* and t_s (if applicable) on the balance pan. The sensitivity weight, *sw*, remains on the balance pan. Release the pan, time the interval or wait for the stability indicator, and record observation O_4.

2.5.2.5 Compare the two differences ($O_2 – O_1$) and ($O_3 – O_4$) to evaluate within process repeatability; they should not differ from one another by a laboratory determined limit (e.g., 2 standard deviations of the balance or 10 balance divisions are commonly used) for this process and load. If this difference is exceeded, reject the data and redo the measurements. Investigate possible causes of excess variability should within process repeatability exceed the limits.

2.5.2.6 Repeat 2.5.2.1 through 2.5.2.5 with a check standard, S_c. It is acceptable to begin with the check standard to ensure that the standards and process are in control, followed by the steps with the unknown standard, *X*.

2.5.3 Measurement Procedure, Optional Sequence B (*XSSX*)

Table 6. Optional Sequence B.

Measurement No.	Weights on Pan	Observation
1	$X + t_x$	O_1
2	$S + t_s$	O_2
3	$S + t_s + sw$	O_3
4	$X + t_x + sw$	O_4

Measurements for Option B are made as described in Option A except that X, S, t_x, and t_s are interchanged.

3 Calculations

3.1 If no air buoyancy correction is performed, calculate the conventional mass correction, C_{Sc}, for the check standard using the appropriate equation from 3.1.1 or 3.1.2, depending on the sequence used, and incorporate an uncorrected systematic uncertainty in the uncertainty calculations when using these equations due to the lack of performing air buoyancy corrections. Use the equations provided in SOP 2 to calculate the magnitude of the air buoyancy correction and treat it as a rectangular distribution. Calculate the value for the test weight correction using the same equations, but substitute X for the S_c subscript for the unknown in equations 3.1.1. and 3.1.2. as appropriate.

3.1.1 Optional Sequence A (*SXXS*)

$$C_{Sc} = C_s + CM_{t_s} - CM_{t_{Sc}} + \left[\frac{(O_2 - O_1) + (O_3 - O_4)}{2}\right]\left[\frac{CM_{sw}}{O_3 - O_2}\right] + N_s - N_{Sc} \qquad \text{Eqn. (1)}$$

3.1.2 Optional Sequence B (*XSSX*)

$$C_{S_c} = C_s + CM_{t_s} - CM_{t_{S_c}} + \left[\frac{(O_1 - O_2) + (O_4 - O_3)}{2}\right]\left[\frac{CM_{sw}}{O_3 - O_2}\right] + N_s - N_{S_c} \qquad \text{Eqn. (2)}$$

3.2 Mass Calculation with Air Buoyancy Correction

3.2.1 Calculate the air density, ρ_a, as described in the Appendix to SOP No. 2, Option B.

3.2.2 Calculate the mass M_{Sc} of the check standard using the mass of the standard weight(s), the tare weights, and the sensitivity weights, according to the optional sequence used.

3.2.2.1 Optional Sequence A (SXXS).

$$M_{Sc} = \frac{M_S\left(1-\frac{\rho_a}{\rho_S}\right)+M_{t_S}\left(1-\frac{\rho_a}{\rho_{t_s}}\right)-M_{t_{Sc}}\left(1-\frac{\rho_a}{\rho_{t_{Sc}}}\right)+\left[\frac{(O_2-O_1)+(O_3-O_4)}{2}\right]\left[\frac{M_{sw}\left(1-\frac{\rho_a}{\rho_{sw}}\right)}{O_3-O_2}\right]}{\left(1-\frac{\rho_a}{\rho_{Sc}}\right)}$$

Eqn. (3)

3.2.2.2 Optional Sequence B (XSSX).

$$M_{Sc} = \frac{M_S\left(1-\frac{\rho_a}{\rho_S}\right)+M_{t_S}\left(1-\frac{\rho_a}{\rho_{t_s}}\right)-M_{t_{Sc}}\left(1-\frac{\rho_a}{\rho_{t_{Sc}}}\right)+\left[\frac{(O_1-O_2)+(O_4-O_3)}{2}\right]\left[\frac{M_{sw}\left(1-\frac{\rho_a}{\rho_{sw}}\right)}{O_3-O_2}\right]}{\left(1-\frac{\rho_a}{\rho_{Sc}}\right)}$$

Eqn. (4)

3.2.3 Calculate the Conventional Mass[6] of S_c, CM_{Sc}.

$$CM_{Sc} = \frac{M_{S_c}\left(1-\frac{\rho_n}{\rho_{Sc}}\right)}{\left(1-\frac{\rho_n}{8.0}\right)}$$ Eqn. (5)

3.2.4 Calculate the Mass Correction of S_c.

$$C_{Sc} = M_{Sc} - N_{Sc}$$ Eqn. (6)

where N_{Sc} is the nominal value for *Sc* and ensure it is within statistical control or take suitable corrective action. The mass or conventional mass (depending on laboratory control charts) determined for the check standard should be plotted on the control chart and must lie within the control limits (see NISTIR 6969, SOP 9). If the value is not within limits, and the source

[6] Conventional Mass: "The conventional value of the result of weighing a body in air is equal to the mass of a standard, of conventionally chosen density, at a conventionally chosen temperature, which balances this body at this reference temperature in air of conventionally chosen density." The conventions are: artifact reference density 8.0 g/cm^3; reference temperature 20 °C; *normal* air density 0.0012 g/cm^3. Conventional mass was formerly called "Apparent Mass versus 8.0 g/cm^3" in the United States. *See OIML D28 (2004).*

of error cannot be found, measurement must be stopped until suitable corrective action is taken. Corrective action is demonstrated through evaluation of additional measurement results that are within limits.

3.2.5 Calculate the mass of the test weight, M_x, and its mass correction, C_x, using the equations in 3.2.2.1 or 3.2.2.2 where S_c is replaced by X. Calculate the mass correction C_x, as follows:

$$C_x = M_x - N_x \qquad \text{Eqn. (7)}$$

where N_x is the nominal value for X.

3.2.6 Calculate the Conventional Mass of X, CM_x. The conventional mass should be reported.

$$CM_x = \frac{M_x\left(1 - \frac{\rho_n}{\rho_x}\right)}{\left(1 - \frac{\rho_n}{8.0}\right)} \qquad \text{Eqn. (8)}$$

3.2.7 Calculate the Apparent Mass versus Brass only if requested. This value should only be provided when requested by the customer for use when calibrating mechanical balances that have been adjusted to this reference density. (This is rare.)

$$AM_{x\ vs\ brass} = \frac{M_x\left(1 - \frac{\rho_n}{\rho_x}\right)}{\left(1 - \frac{\rho_n}{8.3909}\right)} \qquad \text{Eqn. (9)}$$

4 Measurement Assurance

4.1 The process integrates a suitable check standard (See GLP 1, SOP 9, and SOP 30).

4.2 The check standard value is calculated and immediately entered on the control chart to verify that the mass is within established limits. All values must be entered in the control chart, even if failing this statistic, unless a mistake (i.e., typographical error) is identified and corrected, to ensure the variability obtained for the process is not unduly reduced over time.

A t-test may be incorporated to check the observed value of the check standard against the mean value using the following equation and a 95 % confidence level. The t-statistic is calculated for stability analysis. The observed value of the check standard is compared to the accepted mean value of the check standard and divided by the standard deviation for the check standard observations over time. This equation monitors stability over time but should not be used to assess for bias. A calculated t-value less than two is within the warning limits of the process. A calculated t-value between two and three represents a value between the warning limits and control/action limits. A calculated t-value exceeding three represents a value outside of the control/action limits and suitable action must be taken. Calculated values of the t-statistic may also be monitored over time to determine the presence of drift.

$$t = \frac{\left(S_c - \overline{S_c}\right)}{s_p} \qquad \text{Eqn. (10)}$$

4.3 Check standard measurement results obtained over time are used to calculate the standard deviation of the measurement process, s_p.

4.4 The mean value of the check standard over time is also compared to an appropriate reference value of the check standard with respect to their applicable expanded uncertainties to evaluate bias and drift over time. Excessive drift or bias must be investigated and followed with suitable corrective action. See SOP 9, Section 4.2 for assessment methodology.

4.5 Where SOP 9 is followed, and check standards are used for 2 to 3 nominal values per balance, more frequent calibration intervals may be needed to monitor the working standards and the larger standard deviation of the nominal values bracketing the nominal value should be used. If check standards were already checked on a given day and found to be in control, additional check standard measurements are not required.

5 Assignment of Uncertainty

The limits of expanded uncertainty, *U*, include estimates of the standard uncertainty of the mass standards used, u_s, estimates of the standard deviation of the measurement process, s_p, and estimates of the effect of other components associated with this procedure, u_o. These estimates should be combined using the root-sum-squared method (RSS), and the expanded uncertainty, *U*, reported with a coverage factor to be determined based on the degrees of freedom, which if large enough will be 2, (k = 2), to give an approximate 95 percent level of confidence. See SOP 29 for the complete standard operating procedure for calculating the uncertainty.

5.1 The expanded uncertainty for the standard, U, is obtained from the calibration certificate. The combined standard uncertainty, u_c, is used and not the expanded uncertainty, U, therefore the reported uncertainty for the standard will usually need to be divided by the coverage factor k. When multiple standards are used, see SOP 29 for evaluation of dependent and independent conditions and combining methods for the standard uncertainty of the standard. Tare weights used in determining the mass of unknown weights are treated as additional standards in the measurement process. Where the coverage factor or confidence interval is not given, the laboratory should either contact the calibration provider to obtain the correct divisor or use a value of $k = 2$, assuming that the expanded uncertainty was reported with an approximate 95 % confidence interval (95.45 %).

Check standards are not used to assign values to unknown weights; however, the uncertainty of calibration of the check standard may be used to assess the control status.

5.2 The value for s_p is obtained from the control chart data for check standards using double substitution measurements. Where the standard deviation is less than the balance resolution, the laboratory may round up to the value of the balance division or use one of the equations in 5.2.1 to determine the smallest standard deviation to be included in the uncertainty calculations. (See SOP No. 9.)

5.2.1 Where the standard deviation of the measurement process from the control chart is less than the resolution of the balance being used, the larger of the standard deviation of the process and one of the following estimates for repeatability is used to represent the standard deviation of the process:

5.2.1.1 If the laboratory prefers a more conservative approach, or when the current and representative degrees of freedom are less than 30, the larger of the control chart s_p and the result from Eqn. (11) should be used, where d is the smallest balance division. For example, if the balance division is 0.1 mg, the smallest standard deviation may be 0.06 mg. If the laboratory calculated standard deviation is 0.075 mg, then 0.075 mg is used. As the most conservative approach, the laboratory may also round up to the value of the balance division as noted earlier.

$$s_p = \frac{d}{\sqrt{3}} \approx 0.6d \qquad \text{Eqn. (11)}$$

5.2.1.2 When the laboratory has the confidence associated with a well characterized measurement process and has 30 or more degrees of freedom to represent the process, the larger of the control chart s_p and the result from Eqn. (12) may be used, where d is the smallest balance division. For example, if the balance division is 0.1 mg, the smallest standard deviation may be 0.03 mg. If the laboratory calculated standard deviation is 0.075 mg, then 0.075 mg is used. Use of Eqn. (12) is appropriate as the degrees of freedom approaches 30; the check standard calculated standard deviation is less than is calculated using Eqn. (11).

$$s_p = \frac{d}{2\sqrt{3}} \approx 0.3d \qquad \text{Eqn. (12)}$$

5.3 Uncertainty due to air buoyancy corrections and air density. Select one of the following options in priority preference for calculating and uncertainty associated with air buoyancy.

5.3.1 Option 1, preferred. Use the formulae provided in OIML R111 (2004), C.6.3-1, C.6.3-2, and C.6.3-3.

5.3.2 Option 2. Calculate the uncertainty by quantify estimated impacts associated with the uncertainties of the air temperature, barometric pressure, relative humidity, and the air density formula based on laboratory uncertainties and calculations given in NISTIR 6969, SOP 2 and the SOP being used. Note: this may be done using a simplified baseline "what if" approach or a Kragten analysis.[7]

5.3.3 Option 3. If buoyancy corrections are not performed, include an uncorrected systematic standard uncertainty due to the buoyancy effect using the equations for the magnitude of the air buoyancy correction per SOP 2 and use a rectangular distribution. This approach is not recommended for precision calibrations; however, if the resulting value from this approach is evaluated and does not significantly affect the expanded uncertainty, it may be adequate.

5.4 Uncertainty associated with the density of the standards and the unknown test weights, u_{ρ}. Uncertainties associated with the density of the standards used in the calibration may be incorporated into the estimated calculations in section 5.3.

5.5 Uncertainty associated with bias, u_d. Any noted bias that has been determined through analysis of control charts and round robin data must be less than limits

[7] A baseline "what if" approach calculates the estimated impact of each variable in the final measurement result by individually changing each variable of interest by the uncertainty quantity. See the EURACHEM/CITAC Quantitative Guide to Uncertainties in Analytical Methods (QUAM, 2012) for a discussion of Kragten spreadsheets.

provided in SOP 29 and may be included if corrective action is not taken. See SOP 2 and 29 for additional details.

5.6 Example components to be considered for an uncertainty budget table are shown in the following table.

Table 7. Example uncertainty budget table.

Uncertainty Component Description	Symbol	Source	Typical Distribution
Uncertainty of the standard mass(es) (5.1)	u_s	Calibration certificate	Normal divided by coverage factor
Accepted standard deviation of the process (5.2)	s_p	Control chart, standard deviation chart OR estimates when s_p is smaller than balance division	Normal
Uncertainty of the air buoyancy correction (5.3)	u_b	OIML R111	Rectangular
Air temperature (for air density)	u_t	SOP 2 or R111	Rectangular
Air pressure (for air density)	u_p	SOP 2 or R111	Rectangular
Air relative humidity (for air density)	u_{RH}	SOP 2 or R111	Rectangular
Air density (formula)	$u_{\rho a}$	SOP 2 or R111	Rectangular
Mass densities (5.4)	$u_{\rho m}$	Measured and reported value OIML R111 Table B.7 Typically, 0.03 g/cm^3 to 0.05 g/cm^3	Rectangular
Uncertainty associated with bias (5.5)	u_d	Control chart, proficiency tests	See SOP 29

5.7 Draft a suitable uncertainty statement for the certificate. For example:

The uncertainty reported is the root sum square of the standard uncertainty of the standard, the standard deviation of the process, and the uncertainty associated with the buoyancy corrections, multiplied by a coverage factor of 2 (k = 2) for an approximate 95 % confidence interval. Factors not considered in the evaluation: magnetism (weights not evaluated for magnetism specifications unless measurement aberrations are noted), balance eccentricity and linearity (these factors are considered as a part of the measurement process when obtaining the standard deviation of the process when using a check standard with adequate degrees of freedom).

NOTE: Where inadequate degrees of freedom are available, k, is determined using the appropriate degrees of freedom and the 95.45 % column in the table from Appendix A of NISTIR 6969, SOP 29.

6 Certificate

6.1 Report results as described in SOP No. 1, Preparation of Calibration Certificates. Report the mass (if requested by the customer), conventional mass, environmental conditions during the calibrations, mass density used (reported, measured, or assumed), and calculated expanded uncertainties with coverage factor(s).

6.2 Conformity assessments.

Evaluate compliance to applicable tolerances as needed or required by the customer or by legal metrology requirements. Decision criteria for uncertainty and tolerance evaluations include two components: 1) the expanded uncertainty, U, must be < 1/3 of the applicable tolerances published in ASTM E617 and OIML R111 documentary standards and 2) the absolute value of the conventional mass correction value plus the expanded uncertainty must be less than the applicable tolerance to confidently state that mass standards are in or out of tolerance. Compliance assessments must note the applicable documentary standard and which portions of the standard were or were not evaluated.

Appendix A

Double Substitution Data Sheet
(Optional Sequence A, *SXXS)*

Laboratory data and conditions:

			Before	After
Operator			Before	After
Date		Temperature		
Balance		Pressure		
Load		Relative Humidity		
Standard deviation of the process, from control chart, s_p		Degrees of Freedom		

Mass standard(s) data:

ID	Nominal	Mass Correction*	Expanded Unc: From cal. certificate	Unc: *k* factor	Density g/cm^3	Unc Density (k = 1)
S						
t_s						
X						
t_x						
S_c						
t_{Sc}						
sw						

*Mass Correction = *True Mass* if using buoyancy correction. Mass Correction = *Conventional Mass* if NOT using buoyancy correction. Density is used only with buoyancy corrections.

Observations:

Observation No.	Weights	Balance Observations, Units _____
Time:		
1 (O_1)	$S + t_s$	
2 (O_2)	$X + t_x$	
3 (O_3)	$X + t_x + sw$	
4 (O_4)	$S + t_s + sw$	
Time:		

Measurement Assurance (See Section 4.5):

Observation No.	Weights	Balance Observations, Units _____
Time:		
1 (O_1)	$S + t_s$	
2 (O_2)	$S_c + t_{Sc}$	
3 (O_3)	$S_c + t_{Sc} + sw$	
4 (O_4)	$S + t_s + sw$	
Time:		
Check Standard in Control?	_____Yes_____No	

Appendix B

Double Substitution Data Sheet
(Optional Sequence B, *XSSX*)

Laboratory data and conditions:

			Before	After
Operator				
Date		Temperature		
Balance		Pressure		
Load		Relative Humidity		
Standard deviation of the process, from control chart, s_p		Degrees of Freedom		

Mass standard(s) data:

ID	Nominal	Mass Correction*	Expanded Unc: From cal. certificate	Unc: k factor	Density g/cm^3	Unc Density (k=1)
S						
t_s						
X						
t_x						
S_c						
t_{Sc}						
sw						

*Mass Correction = *True Mass* if using buoyancy correction. Mass Correction = *Conventional Mass* if NOT using buoyancy correction. Density is used only with buoyancy corrections.

Observations:

Observation No.	Weights	Balance Observations, Units
Time:		
1 (O_1)	$X + t_x$	
2 (O_2)	$S + t_s$	
3 (O_3)	$S + t_s + sw$	
4 (O_4)	$X + t_x + sw$	
Time:		

Measurement Assurance (See Section 4.5):

Observation No.	Weights	Balance Observations, Units
Time:		
1 (O_1)	$S_c + t_{Sc}$	
2 (O_2)	$S + t_s$	
3 (O_3)	$S + t_s + sw$	
4 (O_4)	$S_c + t_{Sc} + sw$	
Time:		
Check Standard in Control?	_____Yes_____No	