GLP 1

Good Laboratory Practice
for the
Quality Assurance of the Measurement Process

Quality Assurance of the Measurement Process means establishing, documenting, implementing, and maintaining a quality system appropriate to the laboratory's scope of activities. Having such a system in place will allow the laboratory to know, within the limits of a measurement process, that a measurement is valid with respect to its traceability, accuracy, and precision.

The validity of tests and calibrations should be monitored with quality control procedures. Statistical techniques are used to record and monitor charted measurement results to permit the detection of trends. The metrologists and laboratory management should plan and review the results from quality assurance monitoring.

Other steps taken to ensure the quality of the measurement process may include, but are not limited to:

- the regular use of Standard Reference Materials (SRMs) and /or internal quality control using secondary reference materials;
- participation in interlaboratory comparisons (round robins);
- test replications with same and/or different methods;
- recalibration of retained items;
- correlation of different characteristics of an item; and
- proper calibration intervals.

Each measurement parameter in the laboratory's scope of activities should be reviewed and analyzed to determine the validity of the measurement process.

The standards and the measurement process for each parameter must be in a state of statistical control. Statistical control means that the variability of the measurement process is known and stable; when a process is in statistical control, we can assume that the reported measurement uncertainties are valid. The National Institute of Standards and Technology provides technical guidance and support to the State weights and measures laboratories to develop measurement control programs that provide measurement assurance. The objective of these programs is to evaluate the entire measurement process including:

- procedures;
- standards;
- equipment;
- personnel; and
- environment.

While other quality assurance programs could meet these objectives, the control programs developed for measurement assurance greatly increase the comprehensiveness of the program.

The State laboratories typically provide measurement services in the disciplines of mass, volume, and length. Some laboratories provide services in other measurement areas. Approximately 89 % of their workload is in mass standards calibration.[1] Mass calibration demands the greatest precision and is the first discipline for which a measurement assurance program was developed and implemented. Nevertheless, all measurement disciplines should have a measurement assurance system in place.

The most recent improvement in assuring the quality of each measurement parameter in the State Laboratories is the incorporation of a Process Measurement Assurance Program (PMAP).[2]

A measurement assurance program consists of duplicating the measurement process by including a check/control standard as surrogate for the test item. Measurements made throughout the year will show all the conditions that are likely to affect the measurement process and their combined effects. Controlled duplication of the process provides for the realistic evaluation of the variability of the measurement process as one of the components in the estimation of the measurement uncertainty.

Measurement results that are collected over several years may be statistically evaluated with current results being compared to results from previous years. Any observed problems or changes in the measurement results are investigated and if necessary, corrective action can be taken. Ongoing monitoring establishes a continuous, comprehensive, internal measurement assurance program in a State laboratory.

Data from internal measurement assurance programs is compared to the results of inter-laboratory comparisons (round robins) in which the laboratory participates as part of the Regional Measurement Assurance Program (RMAP) groups. (These groups consist of the metrologists of the State laboratories and their counterparts in private industry in a geographic region of the country. Six regional measurement assurance groups operate in the United States and its territories.)

The strength of the measurement assurance approach lies in its applicability to a wide variety of measurements with sufficient flexibility to permit each measurement control program to be tailored to the particular needs of a given measurement area. The sophistication of the control program depends on the criticality of the measurement.

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[1] State Laboratory Program Workload Survey, 1999, NIST/OWM & NCWM Metrology Subcommittee

[2] See NISTIR 6176 and SOP 30.

GLP 4

Good Laboratory Practice
for
Periodic Recalibration of State Standards

A number of States have provisions in their weights and measures laws that require the periodic submission of their State standards to NIST for calibration. Those provisions are based on an early version of the Model Law (1911), which was considered appropriate for the circumstances that prevailed prior to the establishment of the New State Standards Program by NIST. Periodic calibration is necessary on a regular, periodic basis, and also when measurement control results from internal control charts or external round robins indicate questionable data.

Standards of mass, volume, and length, fabricated from modern materials, kept in the controlled environment of a State metrology laboratory under the custody of trained metrologists, are generally stable and not subject to change. Moreover, the cooperative NIST-State audit programs often identify changes in ample time for corrective action in the unlikely event that such a change should occur. These same programs provide the necessary evidence of the ability to provide traceable measurement results at a level of confidence sufficient for the need.

Moreover, the process of packing, shipping, and unpacking exposes the standards to unnecessary hazards that could result in damage, compromising their integrity. The return and re-calibration could take several months causing an unavailability of State services that would be disruptive to the performance of the mission of the State laboratories.

In order to develop a policy for the guidance of and implementation by all 50 States regarding this subject, the following actions are recommended:

1. All States should recognize the fact that periodic return of their State standards to NIST for re-calibration is essential to comply with ISO/IEC 17025, GMP 11, and when: 1) data regarding traceability is unavailable; 2) charted measurement results indicate that the standards are out of control; 3) measurement results on round robins or performance tests are suspect; or 4) NIST advises the State of the need.

3. References to the periodic re-calibration of State standards in the law such as,

   "He (the director) shall maintain the State standards in good order and shall submit them, at least once in ten years, to the National Institute of Standards and Technology for calibration,"

   should be followed if present and may be amended to reflect a regular interval, plus identified needs. In lieu thereof, the wording of Sections 3 and 12 of the present Uniform Law may be substituted:

> SECTION 3. PHYSICAL STANDARDS. -- Weights and measures that are traceable to the U. S. prototype standards supplied by the Federal Government, or approved as being satisfactory by the National Institute of Standards and Technology, shall be the State primary standards of weights and measures, and shall be maintained in such calibration as prescribed by the National Institute of Standards and Technology. All secondary standards may be prescribed by the director and shall be verified upon their initial receipt and as often thereafter as deemed necessary by the director.
>
> SECTION 12. POWERS AND DUTIES OF THE DIRECTOR. -- The director shall:
>
> 12 (a) Maintain traceability of the State standards to the National Institute of Standards and Technology, *as evidenced by laboratory Recognition.*

The approach described above is recommended by NIST because each State that participates in the Weights and Measures Division Laboratory Recognition Program has the capability of evaluating its own State standards with the necessary documentation referencing the national standards. The Laboratory Recognition Program provides interaction between the State standards laboratories and NIST, ensuring satisfactory laboratory conditions suitable for primary standards in addition to the proper use of NIST procedures in standards calibration. Thus, each State program is evaluated and, if found in compliance, is Recognized as being capable of performing the measurements listed on the Certificate of Measurement Traceability.

GLP 9

Good Laboratory Practice
for
Rounding Expanded Uncertainties and Calibration Values

A calibration is not complete until the expanded uncertainty associated with the calibration is determined and reported. Each Standard Operating Procedure (SOP) includes information regarding the calculation of uncertainties. The expanded uncertainty is generally reported with approximately a 95 % confidence interval. The confidence interval is determined by multiplying a coverage factor (usually 2) times the root sum square of properly combined Type A and Type B evaluated components according to the ISO/IEC Guide to the Expression of Uncertainty in Measurement (GUM).

The steps for reporting corrections and uncertainties are as follows:

1. Round the uncertainty to two significant figures.
2. Round the correction/error to the last figure affected by the uncertainty.
3. Report the rounded correction and uncertainty.

Zeros, which follow a decimal point, when there are only zeros ahead of the decimal point, are not considered significant figures.

Rounding Rules

Use the following rules to round measurement data, consistent with its significance:

1. When the digit next beyond the one to be retained is less than five, keep the retained figure unchanged. For example: 2.541 becomes 2.5 to two significant figures.

2. When the digit next beyond the one to be retained is greater than five, increase the retained figure by one. For example: 2.453 becomes 2.5 to two significant figures.

3. When the digit next beyond the one to be retained is exactly five, and the retained digit is even, leave it unchanged; conversely if the digit is odd, increase the retained figure by one (even/odd rounding). Thus, 3.450 becomes 3.4 but 3.550 becomes 3.6 to two significant figures.

   Note: Even/odd rounding of numbers provides a more balanced distribution of results. Use of computer spreadsheets to reduce data typically follows the practice of rounding up.

4. When two or more figures are to the right of the last figure to be retained, consider them as a group in rounding decisions. Thus, in 2.4(501), the group (501) is considered to be greater than 5 while for 2.5(499), (499) is considered to be less than 5.

Several examples to illustrate the proper method of reporting corrections and uncertainties follow.

Example 1

Suppose the correction for a weight is computed to be 1.3578 mg and the uncertainty is 0.5775 mg. First, round the uncertainty to two significant figures, that is, 0.58 mg. Then state the correction as 1.36 mg. Notice that the uncertainty and the correction express the same number of decimal places. Report the correction as 1.36 mg ± 0.58 mg.

Example 2

The volume of a given flask is computed to be 2000.714431 mL and the uncertainty is 0.084024 mL. First, round the uncertainty to two significant figures, that is, 0.084 mL. (Do not count the first zero after the decimal point.) Round the calculated volume to the same number of decimal places as the uncertainty statement, that is, 2000.714 mL. Report the volume as 2000.714 mL ± 0.084 mL.

Example 3

The correction for a weight is computed to be 4.3415 mg and the uncertainty is 2.0478 mg. First, round the uncertainty to two significant figures, that is, 2.0 mg. (Notice that two significant figures are shown. The zero is a significant figure since it follows a non-zero number.) Then, round the correction to the same number of decimal places as the uncertainty statement, that is, 4.3 mg. Report the correction as 4.3 mg ± 2.0 mg.

Example 4

The correction for a weight is computed to be 285.41 mg and the uncertainty is 102.98 mg. Because this uncertainty is a large number, we first convert both values to the next larger commonly reported unit (i.e., 0.28541 g and 0.10298 g respectively). First, round the uncertainty to 0.10 g. (The first nonzero digit (1) is the first significant figure and the remaining digits are rounded to the nearest number following the first nonzero digit.) Then, round the correction to the point where the rounding occurred in the uncertainty statement. Round the correction to 0.29 g. Report the correction as 0.29 g ± 0.10 g.

Example 5

The correction for a weight is computed to be 285.41 mg and the uncertainty is 33.4875 mg. First, round the uncertainty to two significant figures, that is 33 mg. Then, round the correction to the same number of decimal places as the uncertainty statement, that is, 285 mg. Report the correction as 285 mg ± 33 mg.

Example 6

The length of a calibrated interval is computed to be 9.9994558 ft and the uncertainty is 0.0035617 in. First, make sure both values are reported in the same unit (i.e., convert the uncertainty to ft, 0.000296808 ft.) Then, round the value to two significant figures, that is, 0.00030 ft. Then, round the length of the interval to the same number of decimal places as the uncertainty value, that is, 9.99946 ft. Report the length of the interval as 9.99946 ft ± 0.00030 ft.

Rather than stating the uncertainty value with each correction, it is also proper to place the correction values in a column headed by the words "Correction" or "Error," etc., and place the uncertainties (without plus or minus signs) in a column headed "Expanded Uncertainty".

GLP 11

Good Laboratory Practice
for
Painting Cast Iron Weights

Large cast iron or steel weights should be painted both for their protection and to preserve their mass integrity. Unprotected weights are subject to corrosion. Furthermore, when corrosion is present, the extent and any changes resulting from it may be difficult to estimate.

Thin even coats of aluminum paint are recommended for this purpose. Spray applications are best if large weights or a number of small weights are to be painted. In preparation for painting, a weight should be cleaned and loose scale should be removed using a wire brush (DO NOT remove old paint and corrosion by means of sand blasting or pressure washing. Severe damage may result.). The painting should be done before the weights are calibrated or tolerance tested, unless arrangements are made to obtain "as found" values. If “as found” values are desired, two tests may be required.

Painting should be done in an area reserved for this purpose, or at least in a place which is removed from laboratory measurement operations. Painting operations must be in compliance with applicable safety standards. The weights should be protected from dust or dirt contamination while the coating is drying.

GMP 1

Good Measurement Practice
for
Reading Turning Points on an Equal-Arm Balance

The damping of the beam oscillations of an equal-arm balance is generally very slow. Consequently, it is practical to read the turning points (the highest and lowest value of the beam oscillation) on the graduated scale and use the sum of the turning points as the observation value rather than wait for the beam to come to rest. This GMP requires that the graduated scale be numbered such that adding weights to the left arm increases the readings.

Suppose the graduated scale has 20 graduations that are numbered from 0 to 20. The loads on the balance arms should be adjusted so that the sum of the turning points is approximately twice the midscale reading. In this example, the sum of the turning points should be within one division of twenty. Turning points should be estimated to at least 0.1 division in this example, which is typical of the Russell balance. This means that the final rest point is approximately 10, the midscale reading. Motion should be induced to the beam so that the turning points can be read easily. Care should be taken so that the beam does not hit limiting stops during its normal oscillation while turning points are being read. The amount of the beam oscillation is not critical although a span of from three to ten divisions is adequate.

Once motion has been induced for the beam oscillation, wait for at least one complete oscillation cycle for the beam motion to stabilize. After this time, the turning points can be read. The readings may begin with either the high or low turning point. The turning points for at least two consecutive oscillation cycles should be recorded. The turning points should reveal a consistent pattern of slow damping; that is, the turning points should gradually converge to the eventual rest point. For example, if the last high turning point was greater than the previous high turning point (assuming that the readings normally drop on successive readings), this would indicate that something has interfered with beam oscillation, hence the last reading was not valid with respect to the previous readings. Under these circumstances, turning points should continue to be read until a consistent damping pattern has been obtained. In some cases, the balance oscillation will dampen so slowly that the same readings may be obtained for several oscillations before a decrease is observed. These readings are valid and may be used to compute the sum of the turning points.

When at least four satisfactory turning points have been obtained (two high and two low turning points), all but the last three readings should be discarded. This will leave two high and one low turning point or vice versa. <u>The two readings for the high or low turning points, as the case may be, should be averaged and added to the single turning point to obtain the sum of the turning points</u>. The sum should be carried out to two decimal places if the second decimal place digit is nonzero. As an example, the following readings were obtained: 15.5, 4.3, 15.4, 4.4. The sum of the turning points is computed as $\left(\frac{4.3+4.4}{2}\right)+15.4=19.75$.

GMP 10

Good Measurement Practice
for
Understanding Factors Affecting Weighing Operations

Good laboratory techniques and practices, as well as good standards and balances, are required to obtain good mass measurements. Errors can arise from a variety of sources, such as balance drift, air currents, lack of thermal equilibrium, magnetic or electrostatic fields, and to manipulative skills using the balance. The magnitude and significance of these errors depends upon the laboratory environment, the balance, and the accuracy required for the measurement. Different methods of weighing are used to eliminate or reduce the effects of sources of error. Particular sources of error and ways to eliminate the errors are discussed with the weighing procedures. The accuracy required for a measurement and the criticality of the measurement often influence the choice of the weighing method used in the measurement. Regardless of the procedure used, several practices should be followed to promote good measurements.

Environment and Preparation

First, the balance should be installed in a laboratory having good temperature and humidity control. The requirements for temperature stability increase as more precision is needed in the measurement. For high precision measurement, the temperature should not vary by more than ± 1 °C in a 24 h period throughout the year and should vary by less than 0.5 °C during the course of any one measurement series (typically less than 1 h). General laboratory measurements can probably withstand temperature variations of ± 2 °C per day. Varying temperatures result in balance drift and in unequal temperatures for the air, balance, and objects to be weighed. The relative humidity should be maintained between 40 % and 60 %. If the relative humidity falls significantly below 40 %, electrostatic discharge may be generated both in and near the balance. This can result in erratic readings and make precision weighing impossible. If precision mass standards are cleaned, they should stabilize in the laboratory environment for seven to ten days.

Thermal and environmental equilibrium are critical for mass calibrations. This is why each mass SOP will provide instruction that the environment must be stable and the weights set in or near the balance for 24 hours prior to a calibration. The test objects, balances, reference standards, and air should all be in thermal equilibrium. When possible, the objects to be weighed and the reference standards should be placed either in the balance chamber or adjacent to the balance so all can come to the same thermal equilibrium. If there is a lack of thermal equilibrium, convection currents will be generated when an object is on the balance pan and an erroneous reading may result. These types of errors are likely to go unnoticed when check standards are handled the same way, so care must be taken to reduce the likelihood of their occurrence. Tests have shown that these types of errors depend upon the temperature differences among the objects and the balance, and on the geometry of the objects being weighed. On 20 g standards of greatly differing geometry, studies have shown that errors as large as 0.2 mg can occur for a 4 °C temperature difference among the standards and the balance. Errors as large as 3 mg have also been observed at 1 kg loads when standards were stored in a cabinet, and unknown test items near the balance where a temperature gradient of 2 °C was present (when the uncertainty was less than 0.1 mg).

The balance must be installed in an area free from air currents. Balances should be installed away from heating/cooling vents. It is not adequate to merely close vents when weighing because disrupting the temperature control system may result in temperature changes near the balances.

Handling Weights

The masses of standard weights or objects weighed can be affected significantly by the manner in which they are handled. Human contact can leave grease or oily films that affect the mass at the time of measurement and can even cause permanent damage due to corrosion.

Small weights should never be touched by hand, but handled using forceps, clean gloves, or swatches of cloth. In the latter case, the cloth must be lint free. Instructions for cleaning weights and for removing adhering foreign material are described in GMP 5.

Large weights of lower tolerance classes (NIST Class F) may be handled by bare hands. Large weights are a source of special problems. Fork lifts, portable cranes, hoists, or even overhead cranes may have to be used to move the weights within the laboratory and on or off the balances. Laboratory personnel must become expert in using such equipment, as necessary, to avoid damage to the laboratory facilities, to the balances used, and even to the weights themselves. Special hoist/crane hydraulics or multi-speed systems are available to gently set large weights in place on large comparators to avoid damage. The problem of temperature equilibrium for large weights is qualitatively the same as for small weights and needs consideration on an individual basis.

Large weights must be clean at the time of use, but cleaning may be a problem. Minimally, they should be inspected to ensure that foreign material is not present. Cleaning is addressed further in GMP 5.

Operation

Analytical balances are high precision instruments and should be operated carefully. Excessive shock can damage a balance. Avoid shock loading the balance. Gently place all weights in the center of the weighing pan/platform. The dials on mechanical balances should be turned slowly and gently. Careful balance operation will improve the repeatability of measurements.

Mechanical analytical balances are provided with partial and full release positions. The partial release position is used when determining if an unknown load will provide an on-scale reading. The balance beam has limited movement in this position. The partial release position provides some protection to the balance when the dialed-in weights are not close to the actual mass placed on the pan. It is good practice to arrest the pan each time a dial is being changed to protect the balance from shock loading. It is acceptable to change the dial representing the smallest built-in weights when in the partial release position because the small weight changes should not result in shock loading of the balance.

When releasing the pan to either the full or partial release position, the action should be done slowly and carefully. The objective is to minimize disturbances to the balance as much as possible.

Similarly, all loads should be placed on the balance pan carefully and centered on the pan.

When a mechanical balance is released, the beam goes through a series of oscillations. The frequency of these oscillations diminishes as time passes until they are almost imperceptible to the naked eye. At this point, optimal stabilization is achieved. This stabilization of the balance typically lasts for a very short period of time, after which the balance reading will usually drift. A similar situation occurs when a mass is placed on the pan of an electronic balance. Therefore readings should be taken at the precise moment of achieving balance stability. This interval between the releasing of a pan on a mechanical balance, or the placing of a mass on an electronic balance, and the reading of the observation, varies from balance to balance. Stabilization time differs for all balances, even among those of the same type and model. Knowledge of the instrument is critical to correctly establish this time interval. Although manufacturers will usually state this value, it is necessary for the metrologist to verify its reliability. Many electronic balances have a stability signal incorporated into the design, but this also must be verified. All measurements in a calibration should be performed at the same time interval, and within the shortest time possible.

All balances should be exercised before taking readings. A load equal to the load to be measured should be placed on the balance, a reading taken, and the pan arrested, if appropriate, or the weight removed from electronic balances. This operation should be repeated several times before readings are taken for measurement purposes. Once the balance has been "warmed-up", better repeatability will be achieved. Balances can be very accurate even when used without being exercised first, but improved results can be obtained by going through a "warm-up" procedure. If the larger variation present in initial weighings on a balance that has not been exercised is not significant to the measurement, the warm-up procedure may be minimized.

To determine the repeatability of measurements when a balance has not been exercised versus its performance after being exercised, and to determine how much warm-up time is required, begin measurements starting with the unexercised balance and record the readings. Repeat a series of measurements until you have obtained several measurements after the balance has been exercised. This test can be repeated over several days using the same objects and the results compared. The readings obtained when using an unexercised balance are likely to show a slightly larger variation than those obtained after the balance has been exercised. Balance drift is likely to be larger initially and then reach a steady state when the balance has been "warmed-up".

Comparison Weighing - Mechanical Balance

For mass calibrations, the unknown object must be compared to a known mass standard. Comparison weighing eliminates the errors of the built-in weights, reduces disturbances during the measurement because dial settings are not changed during the measurement, and can cancel the effect of drift by selecting the appropriate weighing design. Comparing the unknown, *X*, to a standard, *S*, eliminates the built-in weights from the measurement: thus, the built-in weights act only as counterweights; they do not affect the difference measured between *X* and *S*. Consequently, the dial settings must not be changed during a comparison measurement; otherwise the built-in weights would be part of the measurement.

When comparison measurements are made on a single pan mechanical balance, all readings are taken from the optical scale. The unknown and the standard must have nearly the same mass so that the difference between them can be measured on the optical scale. If the masses of the unknown and the standard are significantly different, small mass standards are used as tare weights with either the unknown or the reference standard or both to obtain an observed mass difference that is significantly less than one-fourth the range of the optical scale.

As part of a comparison measurement, the mass value of a scale division is determined by performing a sensitivity determination. The small mass standard used as part of the weighing design to calibrate the optical scale is called the sensitivity weight and should have a mass between 1/5 and 1/2 the range of the optical scale, inclusive. Additionally, the mass of the sensitivity weight should have a mass that is at least twice the observed mass difference between the standard and the unknown. Since the maximum size of the sensitivity is limited to one-half the range of the optical scale, it may be necessary to carry tare weights with the standard and the unknown to ensure that the observed difference between them is less than one-half the mass of the sensitivity weight. The value of the sensitivity weight should include the correction plus its nominal value. For high precision calibrations, the inclusion of the air buoyancy correction for the sensitivity weight is critical. See GMP 14 for detailed guidance on the selection of sensitivity weights.

The first readings for the standard and the unknown in a comparison on a single pan balance should fall in the first quarter of the optical scale, but well ahead of zero, so the balance drift will not result in negative values for any readings. Although negative numbers may be used in calculations, they are avoided to simplify calculations and reduce calculation errors. Because the sensitivity weight may have a mass as large as one-half the range of the optical scale and the measured difference between the standard and the unknown may be as large as one-fourth the range of the optical scale, it is necessary to obtain the first two readings in the first quarter of the optical scale so all readings will remain on-scale for the measurement. In this way it is not necessary to change the dial settings to measure the difference between the standard and the unknown.

Comparison Weighing - Electronic Balance

Measurements made on a full electronic balance are simplified because there are no built-in weights to consider. Although many electronic balances are equipped with a built-in calibration weight, the weight is not involved in the comparison weighing.

The principles for comparison weighing on a full electronic balance are the same as when using a single pan mechanical balance. The balance indications are used to measure the mass difference between the standard and the unknown, and a sensitivity weight is used to establish the mass value for a digital division on the balance. Since there are no built-in weights in the full electronic balance, the entire range of the digital indications can be considered for "optical scale" of the balance.

For comparison weighing the standard and the unknown should be "nearly the same mass." Since a full electronic balance has a much larger range for indicating mass values, the masses do not have to be as close together as when a mechanical balance is being used. When using an electronic balance, the difference in mass between the standard and unknown should be less than 0.05 % of the balance capacity. Tare weights that are known standards should be used if the masses are not sufficiently close together. The sensitivity weight used to determine the mass per digital division should have a mass that is at least 10 to 20 times the mass difference between the standard and the unknown but not exceeding 1 % of the balance capacity. For high precision weighing, air buoyancy corrections must be made for all objects used in the intercomparison.

Magnetic and Electrostatic Fields

Care must be taken when weighing magnets or objects having electrostatic charges. A magnetic field will likely affect results of a mass measurement. A magnet is attracted to ferromagnetic materials in the balance and balance chamber. The magnetic field may also affect the magnetic field generated in an electronic balance that utilizes the principle of magnetic force restoration as its method of measurement.

Weights made of ferromagnetic material can become magnetized during manufacture or during use if they are placed in a strong magnetic field. Magnetized weights can result in measurement errors that may go undetected. If a measurement problem is suspected, the weights should be checked for magnetism and may have to be rejected if excessively magnetized.

If magnets or magnetized material must be weighed, the material should be placed in a magnetically shielded container to prevent the magnetic field from generating measurement errors. If balance design and conditions permit, an alternative is to position the magnetized material a relatively large distance from the balance pan using a non-ferromagnetic object on the pan to serve as a platform for the magnetic. Since the strength of the magnetic field drops off at a rate of the cube of the distance from the magnetic, it may be possible to effectively isolate the magnet from other ferromagnetic material in the balance.

Electrostatic fields can also cause errors in measurements. If there is a static charge in a mechanical balance, the balance may give erratic readings and lack repeatability. If the object being weighed has a significant electrostatic charge, it may result in measurement errors and may leave a static charge on the balance. Electrostatic charges are of particular concern when plastic containers are placed on the balance.

Care should be taken to remove electrostatic charges from objects being weighed by grounding the objects, if necessary, before placing them on the balance. To prevent the build-up of static electricity in a balance, the relative humidity in the laboratory should be maintained between 40 % and 60 %. The water vapor in the air will serve to drain off electrostatic charges from the balance.

Balances utilizing the magnetic force restoration principle for weighing should be checked to verify that the magnetic field generated by the magnetic cell in the balance does not exist around the balance pan. If the shielding of the magnetic cell is inadequate, measurement errors may occur when weighing ferromagnetic objects or when the balance is placed on a surface comprised of ferromagnetic material.

GMP 11

Good Measurement Practice
for
Assignment and Adjustment of Calibration Intervals for Laboratory Standards

1. Introduction

1.1. Purpose

Measurement processes are dynamic systems and often deteriorate with time or use. The design of a calibration system would be incomplete without some established means of determining how often to calibrate instruments and standards. A calibration performed only once establishes a one-time reference of uncertainty. Recalibration detects uncertainty growth and serves to reset values while keeping a bound on the limits of errors. A properly selected interval assures that an item will receive recalibration at the proper time. **Proper calibration intervals allow specified confidence intervals to be selected and they support measurement traceability.** The following practice establishes calibration intervals for standards and instrumentation used in measurement processes.

1.2. Prerequisites

1.2.1. Calibration history for laboratory standards

1.2.2. Expected tolerance limits if applicable

1.3. Safety

1.3.1. No outstanding safety concerns

2. Methodology

2.1. Summary

Recommended calibration intervals are based on various examples of traceability as described in GMP 13. As data is collected and evaluated, the laboratory technical manager may adjust the calibration intervals to ensure that measurement results are not invalidated by the intervals selected.

2.2. Apparatus

None.

2.3. Procedure

2.3.1. Identification of Parameters

Critical Parameters
Components that contribute more than 25 % of a measurement's uncertainty are identified as critical parameters. To ensure an accurate evaluation of performance, calibration intervals are determined to meet a 99 % reliability target. Critical parameters are checked and defined below:

Mass Critical Parameters (The example provided below corresponds to Option A in Mass Traceability in GMP 13.)

Balance Performance

Balance performance in Echelon 1 weighing processes is evaluated in every measurement series. An F-test ratio evaluates the observed standard deviation of the process against the accepted standard deviation of the process. The balance performance component is also tested with a check standard in each weighing series. The check standard value is evaluated with a t-test by compared the observed value to the accepted reference value. All other weighing processes have incorporated measurement control procedures and control charts that are evaluated as data is collected.

Mass Standards

Mass standards are dynamic with use. Wear, contamination and other factors can cause drift from accepted values. Thus, the following intervals have been set:

Table 1. Calibration intervals for mass standards

Item	Initial Cal Interval (months)	Source
P1. kg + P1.. kg	48	NIST
C1. kg + C1.. kg	(alternating 2 years) 48	NIST
P30 kg - P2 kg	12	Lab
P500 g - P1 mg	6	Lab
C500 g - C1 mg	6	Lab
W25 kg - W1 mg	12	Lab
P Pound Standards	24	Lab
W Pound Standards	12	Lab
P = primary; C = check/control; W = working standards		

Length Critical Parameters

Length Comparison Performance

The measurement performance of each length calibration is evaluated with a check standard (when performing tape-to-tape comparison).

Initial Length Intervals

Length standards are dynamic with use. Wear, contamination and other factors can cause drift from accepted values. The following intervals have been set due to these factors:

Table 2. Calibration intervals for length standards

Item	Initial Cal Interval (months)	Source
100 ft Tape #1	60	NIST
100 ft Tape #2	60	NIST
25 ft or 7 m Tape	60	NIST
18 in Steel Rule	120	NIST
Length Bench	24 (if used or moved)	Lab

Volume Critical Parameters (Example shown corresponds to Option A for volume calibration in GMP 13.)

Volume Comparison Performance

The measurement performance of a volume transfer calibration is evaluated in each use with a repeatability check. Use of check standards is the preferred method for evaluating the measurement process over time. Traceability for volume standards may be established through gravimetric calibrations using traceable mass standards.

Initial Volume Intervals

Volume standards are dynamic with use. Wear, contamination and other factors can cause drift from accepted values. Calibration intervals are as follows:

Table 3. Calibration intervals for volume standards

Item	Initial Cal Interval (months)	Source
P100 gal standard	60	NIST
P25 gal standard *	60	Lab
P5 gal standard *	12	Lab
Glassware- Autopipetes 5 L to 100 mL	120	Lab
*Gravimetric calibration for volumes 5 gallon or smaller, and all "slicker plate" standards. Laboratory must be qualified for performing gravimetric calibrations. Volume transfer is acceptable above 5 gallon. *May be a "slicker plate" type. None are hand-held, "dump" style, test measures.		

Temperature Critical Parameters

Temperature Comparison Performance

The measurement performance of each temperature comparison calibration is evaluated with a check standard and can be verified periodically using triple point cells, melting point cells, and ice baths (using documented procedures).

Initial Intervals

Temperature standards are dynamic with use. Shock, contamination and other factors can cause drift from accepted values. Recalibration intervals are as follows:

Table 4. Calibration intervals for temperature standards

Item	Initial Cal Interval (months)	Source
25.5 ohm SPRT	36	NIST
100 ohm PRT′s	12	Lab
Standard Thermistor	12	Lab
Check Standards	6	Lab
Liquid-in-glass standards	6	Lab

Secondary Parameters

Components that contribute less than 25 % but more than 1 % of a measurement's uncertainty are identified as secondary parameters. Secondary parameters are assigned calibration intervals designed to meet a 95 % reliability target. Secondary parameters are defined below:

Mass and Gravimetric Volume Secondary Parameters

Environmental Measurement Equipment

Table 5. Calibration intervals for environmental equipment

Item	Initial Calibration Interval (months)	Source
Barometer	12	NIST
Hygrometer	24	NIST
Thermometer	12	Lab

Length Secondary Parameters - No secondary parameters.

Volume Secondary Parameters

Water Temperature Measuring Device

Table 6. Calibration intervals for volume secondary parameters

Item	Initial Cal Interval (months)	Source
Thermometer	12	Lab

Temperature Secondary Parameters - No secondary parameters.

3. Calculations

3.1. Initial Intervals

3.1.1. Assignment of Initial Intervals

Assignment of initial intervals is based on these recommendations. Subsequent intervals may be adjusted based on analysis of Check standard data that is recorded on control charts. The initial interval is equivalent to the amount of time that passes before a metrologist makes the first observation of a result lying outside the warning limits of the chart when the investigation yields no apparent correctable cause. Warning limits are established at ± 2 standard deviations of the measurement process around the accepted value of the check standard.

3.1.2. Absence of Control Charts

If no control charts are available, the laboratory’s Technical Manager will assign the initial interval based on engineering evidence, manufacturer′s specifications, NIST recommendations, and experience.

3.2. Adjustment of Intervals

3.2.1. Intervals will be adjusted when determined to be necessary by the laboratory's Technical Manager.

3.2.2. The intervals will be adjusted by taking the following factors into consideration as appropriate:

- calibration history;
- measurement assurance data;
- data for the population of similar equipment;
- NIST recommendations;
- statistical analysis methods; and
- manufacturer's recommendations.

4. Assignment of Uncertainty

The uncertainty associated with the establishment of calibration intervals is not included as a part of the uncertainties associated with the respective measurement SOPs. See SOP 29 for calculating uncertainties for standards and the instruments.

GMP 12

Good Measurement Practice
on
Standard Operating Procedure Selection

Good laboratory practices, use of proper standards and equipment, and selection of standard operating procedures are essential for providing calibration results with accurate and traceable values with appropriate and suitable uncertainties. The following matrix recommends SOPs based on the parameter, type of test items, and level of uncertainty needed.

Parameter	Test Item	Recommended SOP
Mass		
	Railroad test cars	SOP 27, Railroad Test Cars using a Master Track Scale
	Weight carts	SOP 33, Calibration of Weight Carts (References SOP 4 and SOP 7)
HB 105-1, Class F ASTM, OIML	Class F Class 5, 6, 7 Class M1, M2, M3 e.g., 10 kg to 250 kg (≥500 lb) cast iron 1 mg to 5 kg (1 µlb to 10 lb) stainless steel	SOP 8, Modified Substitution - may be used if expanded uncertainty is less than 1/3 of the tolerance SOP 7, Single Substitution - to be used, as a minimum, if conditions given for SOP 8 cannot be met NOTE: Balances and standards must be selected properly for these conditions to be met.
ASTM, OIML	Class 3, 4 (P) Class F1, F2 e.g., 1 kg kit, 100 g kit	SOP 7, Single Substitution - may be used if expanded uncertainty is less than 1/3 of the tolerance. If uncertainty is greater than 1/3 of the tolerance, then use SOP 4. SOP 4, Double Substitution - to be used for buoyancy corrections and if expanded uncertainty is less than 1/3 of the tolerance Modified SOP 4/5, to be used to incorporate measurement control into SOP 4 NOTE: Balances and standards must be selected properly for these conditions to be met.
ASTM, OIML	Class 1, 2 (S, S-1) Class E2 for use in balance calibration	SOP 5, 3-1 Weighing Design (preferred) Modified SOP 4/5, to be used to incorporate measurement control with SOP 4

Parameter	Test Item	Recommended SOP
ASTM, OIML	Class 0, 1 (S) Class E1 for use as laboratory standards	Weighing Designs per TN 952, TN 844, IR 5672, SOP 28, with appropriate check standards
	Volume	
HB 105-2	Glass flasks	SOP 16, Volume Transfer (acceptable, SOP 14 preferred)
HB 105-3	20 L test measures (5 gal or 10 gal)	SOP 18, Volume Transfer (single delivery from slicker plate type standard; if glass standards SOP 19)
HB 105-3	Large graduated neck type provers - used for meter verification	SOP 19, Volume Transfer for Graduated Neck Type Provers
HB 105-4	LPG provers	SOP 21, Volume Transfer for LPG Provers
HB 105-7	Dynamic Small Volume Provers	SOP 26, Waterdraw Calibration of Dynamic Small Volume Provers
	Laboratory standards Glassware: burets, pipetes, flasks	SOP 13, Gravimetric Calibration with a Single Pan Mechanical Balance OR SOP 14, Gravimetric Calibration with an Electronic Balance
	Laboratory standards Laboratory slicker plate standards	SOP 14, Gravimetric Calibration with an Electronic Balance OR SOP 15, Gravimetric Calibration with an Equal Arm Balance
	Micropipetes	SOP 13, Gravimetric Calibration with a Single Pan Mechanical Balance OR SOP 14, Gravimetric Calibration with an Electronic Balance
HB 105-3	Large graduated neck type provers - used as laboratory standards	SOP 19, Volume Transfer for Graduated Neck Type Provers OR SOP 14, Gravimetric Calibration with an Electronic Balance OR SOP 15, Gravimetric Calibration with an Equal Arm Balance

Parameter	Test Item	Recommended SOP
Length		
	Tapes	SOP 11, Tape to Tape OR SOP 12, Bench Method (lower uncertainties)
	Rigid Rules	SOP 10, Rigid Rule
	Pi Tapes	SOP 23, Pi Tape Calibration
Liquid-in-Glass Thermometers		
HB 105-6	Field standards for weights and measures	SOP 25
Timing Devices		
HB 105-5	Field standards for weights and measures	SOP 24
Traffic Speed Gun Tuning Forks		
	For highway official use	SOP 22

Parameter	Process	Recommended SOP
Measurement Assurance		
All Process Measurement Assurance	SOP 30	Use of process measurement assurance programs
Mass	SOP 5, 28	Use of check standards in procedure TN 952, TN 844, NISTIR 5672
Mass	SOP 4, 6, 7, 8	SOP 9
Length	SOP 10, 11, 12, 23	Redundancy built into procedures
Volume	SOP 13, 14, 15, 16, 18, 19, 21, 26	SOP 17, laboratory check standards OR SOP 20, range charts
Temperature	SOP 25	Use of check standards in procedure
Uncertainty		
All parameters	All SOPs	SOP 29, Calculation of Uncertainty

GMP 13

Good Measurement Practice
for
Ensuring Traceability

1. Introduction

1.1 Purpose

Traceability is defined as "the property of a result of a measurement or the value of a standard whereby it can be related to stated references, usually national or international standards, through an unbroken chain of comparisons all having stated uncertainties".[1] Traceability ensures that the measurements are accurate representations of the specific quantity subject to measurement, within the uncertainty of the measurement.

To ensure traceability, suitably calibrated standards that are appropriately maintained and cared for, proper standard operating procedures, continuous measurement control, surveillance, and suitable documentation must all be present.

Test numbers issued by NIST should not be used nor required as proof of the adequacy or traceability of a test or measurement. Having a NIST number does not provide evidence that the measurement value provided by another organization is traceable. (See section 1.3.3.)

1.2 Prerequisites

Traceability can be characterized by the following essential elements:

1.2.1 *Unbroken chain of comparisons.* A documented system of comparisons going back to a standard acceptable to the parties, usually a national or international standard;

1.2.2 *Measurement uncertainty.* The measurement uncertainty for each step in the traceability chain must be calculated according to defined methods and must be stated so that an overall uncertainty for the whole chain may be calculated (see SOP 29);

1.2.3 *Documentation.* Each step in the chain must be performed according to documented and generally acknowledged procedures (see GMP 12) and the results must be documented (i.e., in a calibration report, see SOP 1);

---

[1] ISO VIM, 2nd ed., 1993, definition 6.10

1.2.4 *Competence.* The laboratories or bodies performing one or more steps in the chain must supply evidence of technical competence (e.g., by maintaining appropriate training records, participating in interlaboratory comparisons, and by demonstrating that they are accredited by a recognized accreditation body);

1.2.5 *Realization of SI Units.* The primary national, international or intrinsic standards must be primary standards for the realization of the SI units;

1.2.6 *Periodic recalibration.* Calibrations of standards (and equipment where appropriate) must be repeated at established (may be defined through measurement assurance) and appropriate intervals to preserve the traceability of the standard over time and use (see GLP 4, GMP 11); and

1.2.7 *Measurement assurance.* A proper measurement assurance program must be established to ensure the validity of the measurement process and the accuracy of standard used (see SOP′s 9, 17, 20, 30).

1.3 Responsibility

1.3.1 *Provider.* Providing support for the claim of traceability of the result of a measurement or value of a standard is the responsibility of the calibration provider. Calibration reports and certificates must contain a traceability statement.

1.3.2 *User.* Assessing the validity of a claim of traceability is the responsibility of the user of that result or value. Verifying claims of traceability often includes obtaining a calibration directly from a national metrology institute or another laboratory that has achieved recognition or accreditation through a recognized accrediting body.

1.3.3 *Use of, or reference to, official test numbers of a national metrology institute.* Having an authentic test number does not provide assurance or evidence that the measurement value provided by another organization is traceable. Not only must there be an unbroken chain of comparisons, but each measurement must be accompanied by a statement of uncertainty associated with the value. Test report numbers should not be used nor required as proof of the adequacy or traceability of a test or measurement. National and international standards dealing with test and measurement quality requirements, such as ANSI/NCSL Z 540-1, ISO 10012, ISO/IEC 17025 and the ISO 9000 series do not require the use or reporting of specific test numbers to establish traceability.

1.4 Safety

No outstanding safety concerns

2. Methodology

2.1 Summary

Traceability is maintained through comparison to appropriate standards with suitable procedures and measurement uncertainties. Procedures are outlined in SOPs and GMPs. Examples of possible hierarchies of the standards leading to the traceability of a calibration are provided in this document.

2.2 Procedure

The charts in this GMP show examples of the traceability hierarchy for mass, length, volume, and temperature measurement disciplines. Each laboratory must define the exact traceability system in their operating quality manual. (A worksheet is included as an Appendix to help in the definition of the traceability system.)

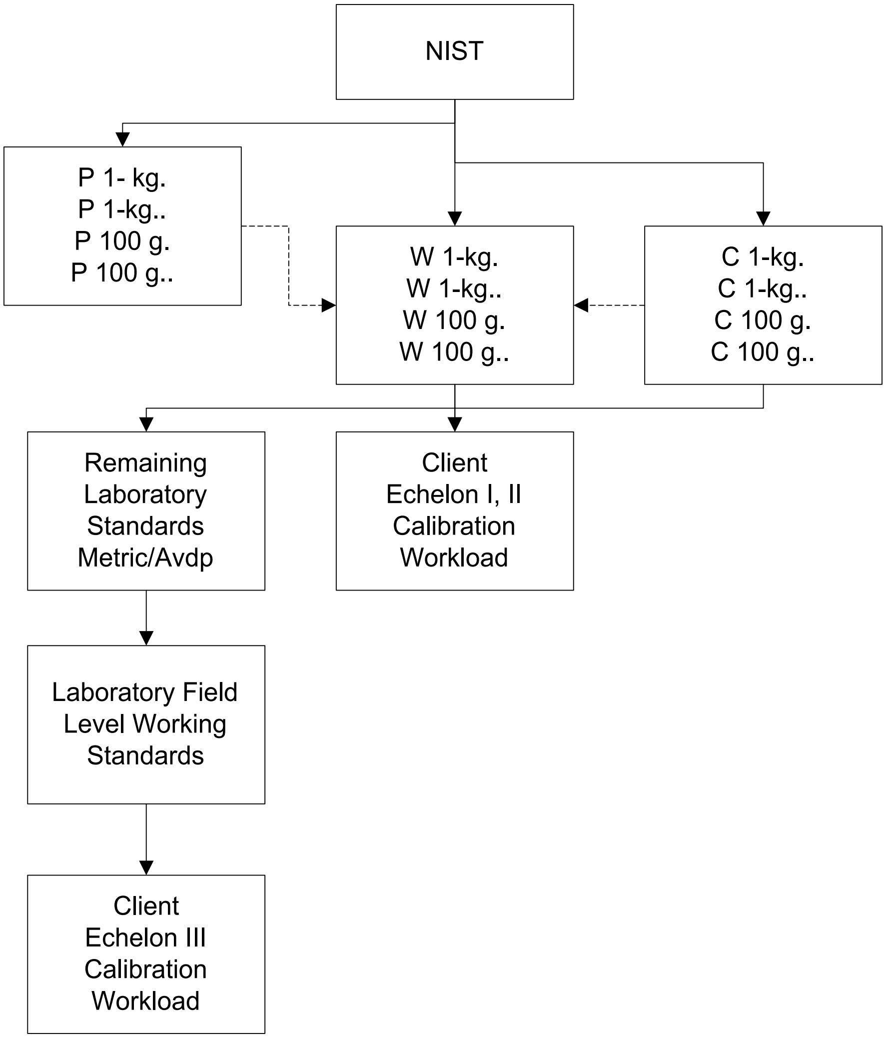
3. Calculations

There are no calculations in this GMP.

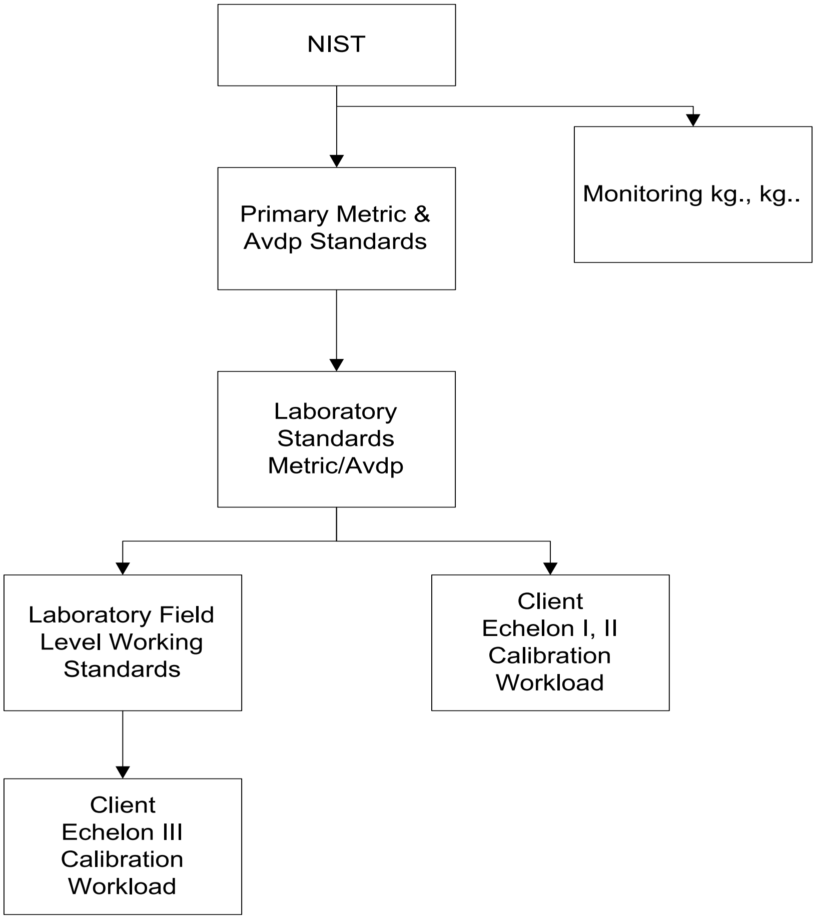
4. Assignment of Uncertainty

The uncertainty associated with reported calibration values is included within the uncertainty analysis for each SOP and in SOP 29, Calculating and Reporting Uncertainties.

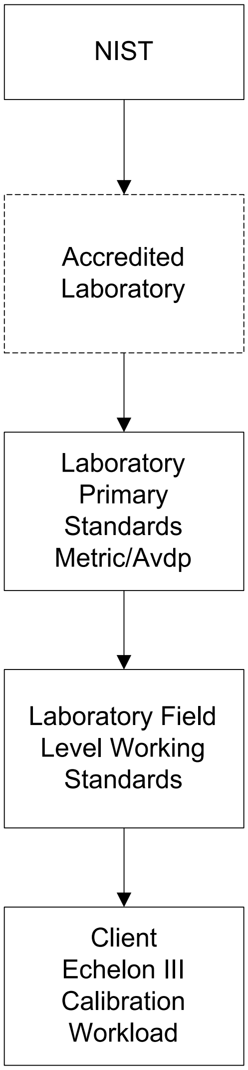
Mass - Option A



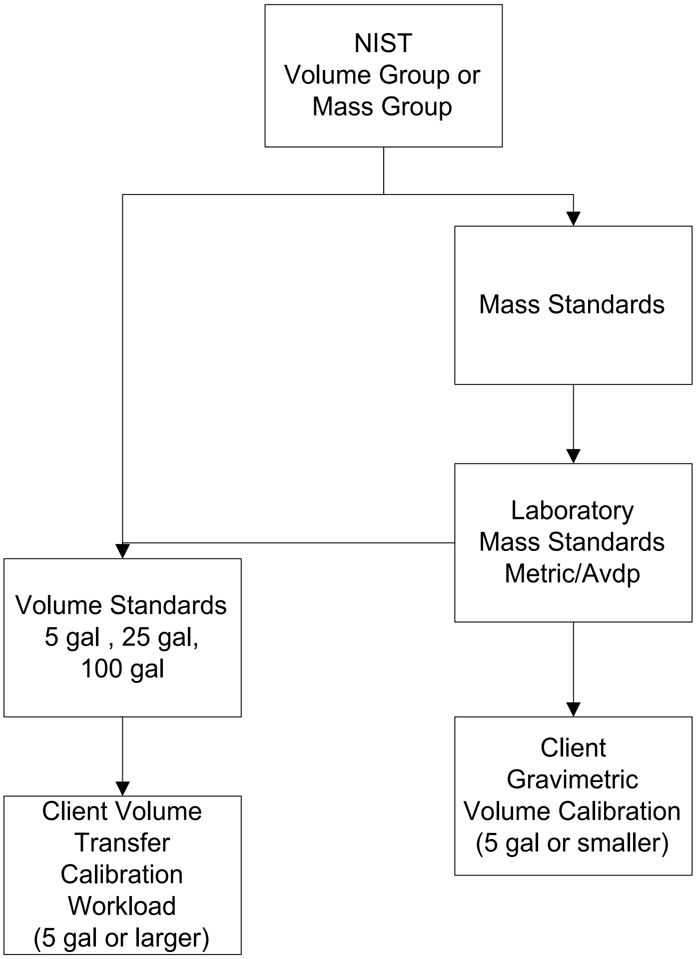
Mass - Option B



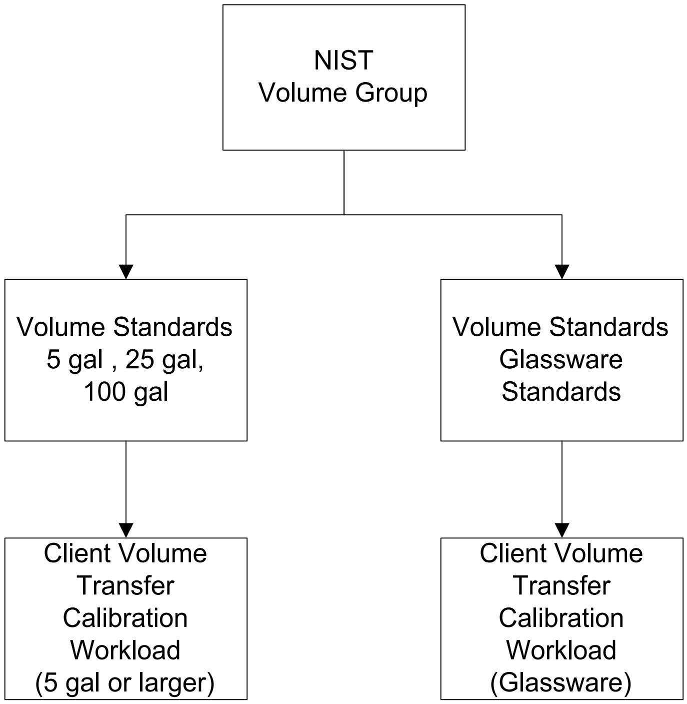
Mass - Option C



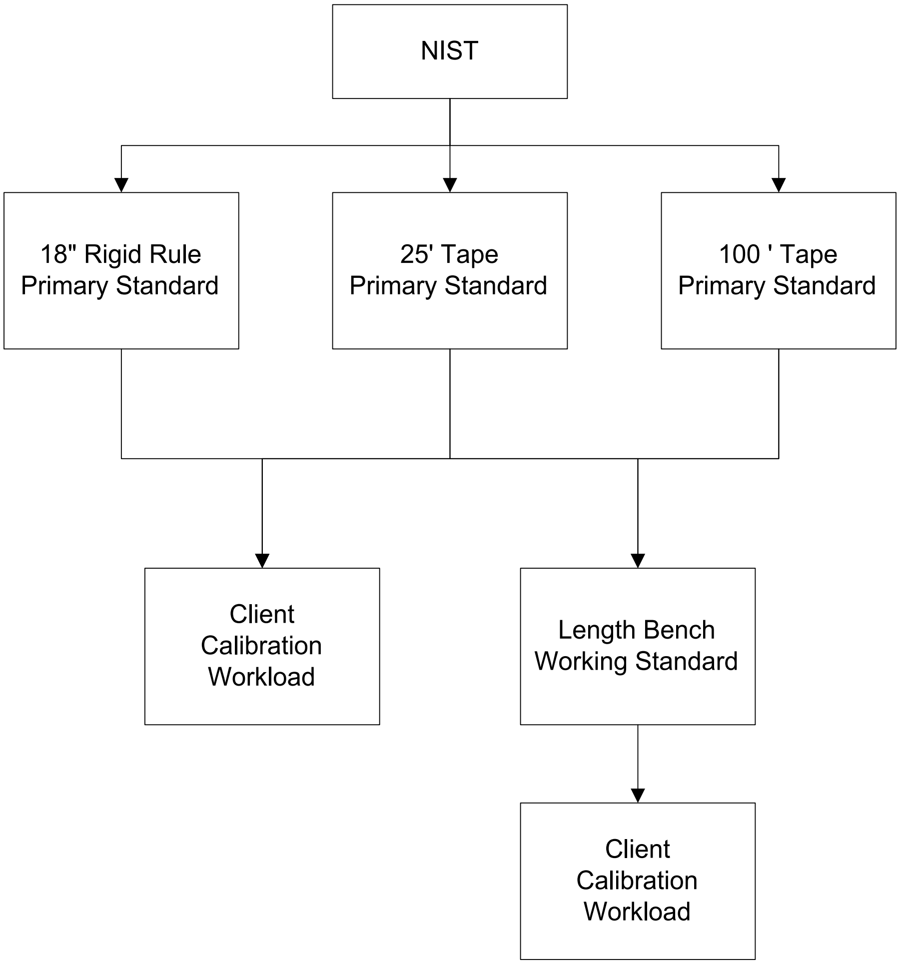
Volume - Option A



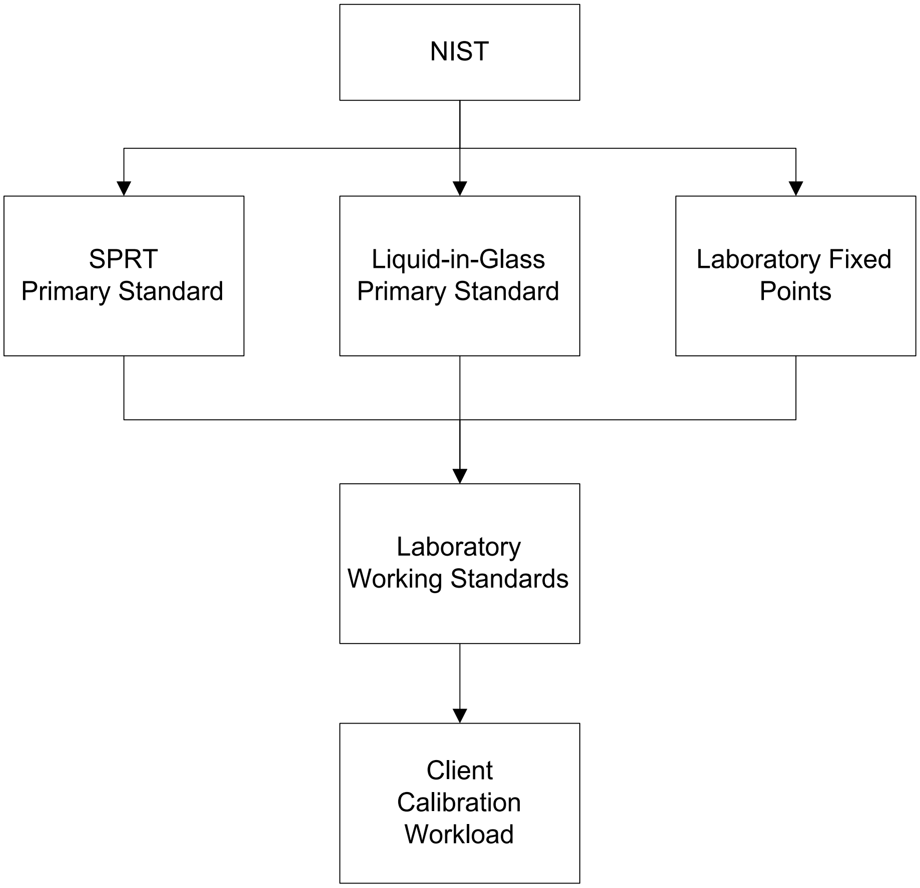
Volume - Option B



Length


NIST
18" Rigid Rule Primary Standard
25' Tape Primary Standard
100 ' Tape Primary Standard
Client Calibration Workload
Length Bench Working Standard
Client Calibration Workload

Temperature



Appendix A - Traceability worksheet

Parameter: Mass, Volume, Length, Temperature, Other

P		**Metric (g, L, m, °C)**	**Cal. date**	**Cal. Lab**	**Interval**
	Range				
		Customary (lb, gal, ft, °F)			
	Range				

W		**Metric (g, L, m, °C)**	**Cal. date**	**Cal. Lab**	**Interval**
	Range				
		Customary (lb, gal, ft, °F)			
	Range				

S_c		**Metric (g, L, m, °C)**	**Cal. date**	**Cal. Lab**	**Interval**
	Range				
		Customary (lb, gal, ft, °F)			
	Range				

GMP 14

Good Measurement Practice
for the
Selection and Use of Sensitivity Weights in Weighing Procedures

1. Introduction

Mass calibration procedures are based on comparing the unknown mass, *X*, to a standard mass, *S*, utilizing the balance as a comparator. This comparison relies on the accuracy of balance indications. Most balance indications are not accurate enough for precision mass calibrations, and they tend to drift with time. Drift can often be assumed to be linear over a short period. Concerns over balance inaccuracy and drift result in two possible causes of errors in mass determination procedures. Inaccuracy of the balance indications can be corrected by incorporating a sensitivity weight in the procedure that calibrates the range of use of the optical scale (mechanical balances) or of the digital indications (electronic balances). Errors due to drift can be minimized by using the correct comparison method, selecting a suitable sensitivity weight, and by consistent timing within the procedure. The proper selection of procedures (GMP 12), the adherence to those procedures, and equal time intervals between weighing operations will allow the measured difference between *X* and *S* to be corrected for inaccuracy of the balance indications and for balance drift.

1.1. Purpose

The following practice will guide you through the process of selecting and using a correct sensitivity weight for mass determination procedures.

1.2. Prerequisites

1.2.1. Verify that valid calibration certificates are available for the masses to be used as standards, sensitivity weights, and tare weights.

1.2.2. Verify that weight-handling equipment is available and in good operational condition.

1.2.3. Verify that the operator is familiar with the design and the operation of the balances and familiar with weighing procedures.

1.3. Safety

1.3.1. Handling of large or small weights can represent a hazard to either the weights or personnel if the weights are dropped.

2. Methodology

2.1. Summary

A sensitivity weight is selected to calibrate the balance over the range to be used in the measurement procedure. Minimizing the difference in mass values between *X* and *S* is critical when choosing an appropriate sensitivity weight. Therefore, tare weights may be necessary whenever the difference in mass values is significant. Minimizing the difference between *X* and *S* works to our benefit since the range of the measurements is minimized and reduces potential errors that can be introduced by nonlinearity of the balance.

2.2. Apparatus

2.2.1. Sensitivity weights with accurate and traceable calibration values.

2.2.2. Tare weights with accurate and traceable calibration values.

2.2.3. Clean forceps to handle the weights, or gloves to be worn if the weights are to be moved by hand.

2.3. Procedure for selection

2.3.1. Conduct preliminary measurements to determine the approximate mass value for the difference between the standard and the unknown ($X - S$).

2.3.2. Define the range of use for the balance to be used:

2.3.2.1. Equal arm – number of scale divisions

2.3.2.2. Mechanical – optical scale

2.3.2.3. Combination – digital indications

2.3.2.4. Fully electronic – capacity

2.3.2.5. Comparators – digital indications

2.3.3. Determine the need for tare weights if the difference between *X* and *S* exceeds the values shown in Table 1.

Table 1. Maximum allowed difference between *X* and *S*

Balance	(*X* – *S*)
Equal arm	balance each other within one division on the scale
Mechanical	1/10 optical scale
Combination	1/10 digital range
Fully electronic	0.05 % capacity
Comparator	1/10 digital range

2.3.4. Select tare weights, if necessary, making sure that the difference between *X* and *S*, with the appropriate tare weights, do not exceed the values shown in Table 1.

2.3.5. Select a sensitivity weight according to Table 2.

Table 2. Selection of Sensitivity Weight

Balance	Procedure	Sensitivity Weight
Equal Arm	SOP 3, 5, 6, 7, 8, 28	change turning points by 20 %
Mechanical	SOP 4, 5, 7, 28 SOP 8	≥4 times (*X* – *S*); ≤ ½ optical scale ≈ ¼ optical scale
Combination Electro-mechanical	SOP 4, 5, 7, 8, 28	≥4 times (*X* – *S*); ≤ ½ digital Range
Fully Electronic	SOP 4, 5, 7, 28 SOP 8	≤ 1 % capacity 2 times the applicable tolerance
Comparator*	SOP 4, 5, 7, 8, 28	≥4 times (*X* – *S*); < ½ digital range

*A sensitivity weight is not required if the electronic mass comparator that is used has been tested (with supporting data available) to determine that the balance has sufficient accuracy, resolution, repeatability, and stability so that no advantage is gained using a sensitivity weight. For example, any possible errors must be less than the last digit retained in the expanded uncertainty. When a mass comparator is used without a sensitivity weight, the sensitivity must be periodically verified and documented (e.g., prior to each use).

2.4. Use of sensitivity weight

The sensitivity weight is used to ensure that the mass differences determined with the optical scale, or electronic range, have valid accuracy and traceability. The sensitivity weight calibrates the range of use of the balance used for making the mass determinations. Using a sensitivity weight provides us with a sensitivity value in terms of mass units per division.

$$sensitivity = \frac{mass\ units}{divisions} = \frac{M_{sw}}{deflection}$$

Where M_{sw} represents the mass of the sensitivity weight.

3. Calculations

No special calculations are associated with this practice. See each mass SOP for calculation of sensitivity within the procedure.

4. Uncertainty

No uncertainty calculations are associated with this practice. See the appropriate SOP for the calculations of uncertainty. (The uncertainty of the sensitivity weight does not need to be included in calculations of uncertainty since the uncertainty value is distributed across the range of use. However, it does no harm to incorporate it in uncertainty calculations when spreadsheets are set up to handle all of the data.)

SOP 1

Recommended Standard Operations Procedures for Preparation of Test/Calibration Reports

1. Introduction

   1.1. Test/calibration reports are the visible outputs of the testing laboratory. They should be prepared with utmost care to ensure that they accurately convey all information pertaining to the testing so that reports may be used with maximum benefit by all concerned. Carefully prepared test reports will contain or refer to all information necessary to justify the test results.

   1.2. The test report may consist of filling in the blanks in a form in the case of a routine measurement. A more detailed report, including narrative information, may be required for special calibrations or tests.

   1.3. Regardless of the final form, the test report must contain the basic information described in the following sections.

2. Content

   2.1. Title (e.g., “Test Report” or “Report of Calibration”).

   2.2. Name and address of the laboratory, or location at which tests were performed.

   2.3. Unique identification of the test report or calibration certificate, and on each page an identification in order to ensure that the page is recognized as part of the test report or calibration certificate, and a clear identification of the end of the report or certificate.

   2.4. Name and address of the client.

   2.5. Method used – Describe how test was made by reference to SOP(s). In the absence of SOP’s, brief but informative descriptions of the methodology should be included. Information describing deviations from previously agreed upon procedure must also be included.

   2.6. Description of, the condition of, and unambiguous identification of the item calibrated. A laboratory number should be assigned and attached to each test item at the time of its acceptance for testing. The use of the laboratory number will facilitate the internal control of test items during the testing process.

   2.7. Date of receipt of calibration item where this is critical to the validity and application of the results, and the date of performance of calibration.

2.8. Calibration results with the units of measurement in tabular or other convenient form. (When an instrument has been repaired or adjusted the calibration results before and after repair or adjustment, if available, are reported.)

2.9. Identify standards used and their traceability to national standards.

2.10. Conditions (e.g., environmental) under which the calibrations were made that have an influence on the measurement results.

2.11. Where relevant, a statement of compliance/non-compliance with requirements and/or specifications. Compliance refers to all criteria, both specifications and tolerances, of a referenced standard and not just portions (e.g., compliance to tolerance only).

2.12. A statement of the estimated measurement uncertainty, components that were considered and included, a rationale for their inclusion, and the coverage factor and estimated confidence interval.

2.13. Where appropriate and needed, opinions and interpretations.

2.14. Additional information which may be required by specific methods, clients or groups of clients.

2.15. Name, title, and signature of person authoring the report or certificate. Other signatures may be required, at the discretion of the laboratory director. Each signer accepts his/her share of responsibility for the contents of the report.

2.16. Where relevant, a statement to the effect that the results relate only to the items tested or calibrated.

2.17. Hard copies of test reports should also include the page number and total number of pages.

2.18. A statement specifying that the test report or calibration certificate shall not be reproduced except in full, without written approval of the laboratory.

3. Recording

3.1. File all test reports in a systematic manner for ease of retrieval, as necessary.

3.2. Retain copies of all test reports for a minimum period of five years, until superseded by a subsequent report, or as stated in the laboratory quality manual, or until deemed by the laboratory director as having no future value.

APPENDIX A - Sample Format

Recommended Format for Report of Test

Report of Test

Issued by
Name of Testing Laboratory
Laboratory Report No. ______________

Test Item(s)/Lab No(s): ____

Submitted by:____

Date: ____

Purpose of Test: ____

____

Test Results*:

As Found	After Adjustment

____

Reference Information:

Test Method: ____

Traceability: ____

Uncertainty Statement: ____

Conditions of Test: ____

Data
Reference: ____

Test Results Approved by (name, title, date): ____

*Report, as appropriate

The results stated on this report relate only to the items specifically identified.
This test report or calibration certificate shall not be reproduced except in full, without written approval of the laboratory.

APPENDIX B – Sample Format

Recommended Format for Calibration Certificate

A B C COMPANY

123 Utopia Street
Anywhere, USA

Report of Calibration

Report Number:

Name of Device:

Model: Serial No:

Submitted by:

Calibration (date) ___________.
The ambient conditions were _____ °C, ____ % relative humidity and ____ mm Hg Barometric pressure.
The item tested was/was not in tolerance at time of calibration. Adjustments are noted and any out of tolerance data are attached.

Data:

Nominal Value	Correction or Error	Expanded Uncertainty

The primary standards to which the above data are traceable are identified in this report. The calibration of these standards is traceable to the National Institute of Standards and Technology. The cycling and certification of all standards of measurement at this facility meet the requirements of ISO/IEC 17025.

Name of Standard	Traceability Reference	Calibration Date	Next Calibration Due

Test Method: ____

Uncertainty Statement: ____

Test Results Approved by (name, title, date): ____________________________________

The results stated on this report relate only to the items specifically identified.
This test report or calibration certificate shall not be reproduced except in full, without written approval of the laboratory.

APPENDIX C - Example

BUREAU OF STANDARDS
PO Box 12345
City, State 12345-1234

COMPLIANT CALIBRATION LABORATORY
123 Some Ave.
City, State 12312-1231

REPORT OF CALIBRATION
FOR
1 kg to 10 mg weight kit
(Twenty-one metric weights)

Maker: DENTROM LAKE
Serial No.: 27269

Lab Test No. : TI-01-056
NMI Test No.: 822/1234

SUBMITTED BY

YOUR CUSTOMER, INC.
Customer's Address
City, State

Nominal (g)	**Conventional Mass (g)**	**Conventional Mass Correction (mg)**	**Expanded Uncertainty (mg)**
1 000	1 000.000 82	0.82	0.92
500	500.000 71	0.71	0.53
300	299.999 87	- 0.13	0.27
200	200.000 67	0.67	0.18
100	100.000 411	0.411	0.091
50	50.000 318	0.318	0.051
30	30.000 117	0.117	0.028
20	19.999 987	- 0.013	0.023
10	10.000 011	0.011	0.018
5	5.000 022	0.022	0.015
3	3.000 112	0.112	0.013
2	1.999 965	- 0.035	0.012
1	1.000 117	0.117	0.010
0.500	0.500 013 2	0.013 2	0.005 1
0.300	0.300 022 3	0.022 3	0.004 8
0.200	0.200 001 7	0.001 7	0.004 3
0.100	0.100 001 3	0.001 3	0.004 2
0.050	0.050 001 8	0.001 8	0.004 0
0.030	0.030 001 1	0.001 1	0.003 7
0.020	0.020 000 9	0.000 9	0.003 3
0.010	0.009 999 7	- 0.000 3	0.003 1

The data in the above table of this report only applies to those items specifically listed on this report.

Uncertainty statement:
The combined standard uncertainty includes the standard uncertainty reported for the standard, the standard uncertainty for the measurement process, the standard uncertainty for any uncorrected errors associated with buoyancy corrections, and a component of uncertainty to account for any observed deviations from NIST values that are less than surveillance limits. The combined standard

uncertainty is multiplied by a coverage factor of 2 to give an expanded uncertainty, which defines an interval having a level of confidence of approximately 95 percent. The expanded uncertainty presented in this report is consistent with the 1993 ISO Guide to the Expression of Uncertainty in Measurement. The expanded uncertainty is not to be confused with a tolerance limit for the user during application.

Traceability statement:

The Standards of the Compliant Calibration Laboratory are traceable to the National Metrology Institute, and are part of a comprehensive measurement assurance program for ensuring continued accuracy and measurement traceability within the level of uncertainty reported by this laboratory. The laboratory test number identified above is the unique report number to be used in referencing measurement traceability for artifacts identified in this report only.

Supplemental Information

Description of artifacts submitted for testing:

Twenty one metric weights from 1 kg to 10 mg, marked ASTM Class 4. Weights from 1 kg to 1 g: two-piece weights, with assumed density of 8.0 g/cm^3. Weights from 500 mg to 50 mg: sheet weights, with assumed density of 16.6 g/cm^3. Weights from 30 mg to 10 mg: sheet weights, with assumed density of 2.7 g/cm^3.

Conditions of artifacts submitted for testing:

Artifacts showed evidence of improper handling. Fingerprints and dents were visible on the surface of the weights.

Treatment of artifacts prior to testing:

Artifacts were cleaned with cheesecloth and ethyl alcohol. Thermal equilibrium time/conditions: ten days next to balances in mass lab.

Equipment & Standards:

Balance	Range	Stds Used	Calibration due
AT1005	1 kg to 200 g	Set H	2/31/2002
AT106	100 g to 10 g	Set H	2/31/2002
UMT5/6	5 g to 10 mg	Set H	2/31/2002

Assumed Density of Reference Standards:

1 kg to 1 g: 7.94 g/cm^3 500 mg to 10 mg: 8.41 g/cm^3

Procedure used:

Double Substitution (NIST HB 145, SOP 4)

Environmental conditions at time of test:

Temperature: 20.1 °C to 20.2 °C Barometric Pressure: 752.7 mmHg Relative Humidity: 43.35 % to 43.40 %

Date artifacts were received: February 15, 2001 Date of report preparation: March 3, 2002

Date of test: February 25, 2001

Due date per customer's request: February 25, 2002

Josh Balani II

Test performed by: Josh Balani II
Metrology Expert

Member: ARMAP
NCSLI
NCWM
ASQ

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ACCREDITED

SOP 2

Recommended Standard Operations Procedure for Applying Air Buoyancy Corrections

1. Introduction

1.1. Purpose

If uncorrected, the effect of air buoyancy on the objects being compared is frequently the largest source of error in mass measurement. This SOP provides the equations to be used to correct for the buoyant effect of air. The significance of the air buoyancy correction depends upon the accuracy required for the measurement, the magnitude of the air buoyancy correction relative to other sources of error in the overall measurement process, and the precision of the mass measurement. An air buoyancy correction should be made in all high accuracy mass determinations. The gravimetric volume procedure uses a high accuracy mass determination with the corresponding buoyancy corrections. The Appendix to this SOP provides a brief theoretical discussion of this subject.

1.2. Prerequisites

1.2.1. Verify that (true) mass values or corrections are available for the standards used in the measurement process. The calibration values for the mass standards must be traceable to NIST.

1.2.2. Verify that the thermometer, barometer, and hygrometer used have been calibrated and are in good operating condition as verified by periodic tests or cross-checks with other standards.

2. Methodology

2.1. Scope, Precision, Accuracy

This procedure is applicable to all weighings using a comparison of mass standards. The precision will depend upon the accuracy of the thermometer, barometer, and hygrometer used to determine the air density. When the calculations for the air density and air buoyancy corrections are made, a sufficient number of decimal places must be carried so the error due to the rounding of numbers is negligible relative to the error in the measurement process. Typically, carrying six to eight decimal places is sufficient, but depends upon the precision of the measurement.

2.2. Apparatus/Equipment Required[1]

2.2.1. Barometer accurate to ± 66.5 Pa (0.5 mm Hg) to determine air pressure.

2.2.2. Thermometer accurate to ± 0.10 °C to determine air temperature.

2.2.3. Hygrometer accurate to ± 10 % to determine relative humidity.

2.3. Estimating the Magnitude of the Air Buoyancy Correction

2.3.1. Estimate the magnitude of the air buoyancy correct, *MABC*, using the following formula:

$$MABC = (\rho_a - \rho_n)(V_x - V_s)$$

2.3.2. The equation may also be represented as follows:

$$MABC = m_o(\rho_a - \rho_n)\left(\frac{1}{\rho_x} - \frac{1}{\rho_s}\right)$$

Table 1. Variables for *MABC* equation

Variable	Description of Variable
ρ_a	air density at the time of the measurement in mg/cm^3
ρ_n	density of "normal" air; i.e., 1.2 mg/cm^3
m_o	nominal mass (in grams)
V_x	volume of the unknown weight, *X* in cm^3
V_s	volume of the reference standard, *S* in cm^3
ρ_s	density of reference standard, *S* in g/cm^3
ρ_x	density of unknown weight, *X* in g/cm^3

The relative magnitude of the correction can be compared to the expanded measurement uncertainty to determine the importance of the air buoyancy correction and the uncertainty components for a particular measurement.

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[1] 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 accuracies specified are recommended for high precision calibration. Less accurate equipment can be used with only a small degradation in the overall accuracy of the measurement.

2.4. Procedure

2.4.1. Record the temperature, pressure, and relative humidity at the start and at the end of the measurement process as near the location of the measurement as necessary and practical. If these parameters change significantly during the measurement process, it may be necessary to wait for more stable operating conditions or to use average values to compute the air density. Use of the average environmental values may influence the uncertainty of the measurement result and must be evaluated for significance.

2.4.2. Determine the air density using the equation given in Section 8 of the Appendix to this SOP.

3. Calculations

3.1. Calculate the mass, M_x, of the unknown weight, X, using the following equation, where d represents the "difference" obtained with buoyancy corrections applied to the sensitivity weight.

$$M_x = \frac{M_s\left(1 - \frac{\rho_a}{\rho_s}\right) + d}{\left(1 - \frac{\rho_a}{\rho_x}\right)}$$

If tare weights were carried with X and/or S, use the following equation:

$$M_x = \frac{M_s\left(1 - \frac{\rho_a}{\rho_s}\right) + d + M_{t_s}\left(1 - \frac{\rho_a}{\rho_{t_s}}\right) - M_{t_x}\left(1 - \frac{\rho_a}{\rho_{t_x}}\right)}{\left(1 - \frac{\rho_a}{\rho_x}\right)}$$

Table 2. Variables not previously defined

Variable	Description of Variable
d	measured difference between X and the reference standard, S, using one of the weighing designs given in other SOPs
M_s	[true] mass of the reference standard
M_{t_s}	[true] mass of the tare weights carried with S
M_{t_x}	[true] mass of the tare weights carried with X
ρ_S	density of the reference standard, S
ρ_x	density of the unknown standard, X
ρ_{t_s}	density of the tare weights carried with S
ρ_{t_x}	density of the tare weights carried with X

3.2. If reporting the conventional mass[2], CM_x, compute it using the following.

$$CM_x = \frac{M_x\left(1 - \frac{0.0012}{\rho_x}\right)}{\left(1 - \frac{0.0012}{8.0}\right)}$$

3.3. If reporting the apparent mass, AM_x, versus brass, compute it using the following.

$$AM_{x\,vs\,brass} = \frac{M_x\left(1 - \frac{0.0012}{\rho_x}\right)}{\left(1 - \frac{0.0012}{8.3909}\right)}$$

3.4. The conventional and apparent mass values are related by the following:

$$CM_x = \frac{AM_{x\,vs\,brass}\left(1 - \frac{0.0012}{8.3909}\right)}{\left(1 - \frac{0.0012}{8.0}\right)}$$

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[2] 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: reference density 8.0 g/cm^3; reference temperature 20 °C; *normal* air density 0.0012 g/cm3. Conventional mass was formerly called “Apparent Mass versus 8.0 g/cm^3” in the United States. *See OIML IR 33 (1973, 1979), under revision.*

4. Assignment of Uncertainty

The uncertainty in determining the air buoyancy correction is usually negligible relative to the precision of the measurement process itself. Consequently, the uncertainty for the measurement is based upon the uncertainty for the measurement process used. The uncertainty in the air density equation as given in numerous periodicals is 0.0012 mg/cm^3 (or about 0.1 % of normal air density.)

Table 3. Tolerances for measurements related to air density estimation

	Uncertainty of air density values in % of air density		
Variable	± 0.1 % of air density	± 1.0 % of air density	Recommended (Section 2.2)
Air pressure (Pa)	± 101	± 1010	± 66.5
Air pressure (mm Hg)	± 0.76	± 7.6	± 0.5
Air temperature (°C)	± 0.29	± 2.9	± 0.1
Relative Humidity (%)	± 11.3	....	± 10

Appendix A

Based on "The Basic Theory of Air Buoyancy Corrections"

by Richard S. Davis[3]

1. Introduction

In performing measurements of mass, the balance or scale used acts as a force transducer. The force produced by an object to be weighed in air has two components: one proportional to the mass of the object, and the other proportional to its volume. The latter component, or buoyant force, may under some circumstances be large enough to require correction. The following shows under what circumstances buoyancy corrections are required as well as how they are made.

2. Scope

The method for applying buoyancy corrections presented below applies to mass measurements made in air. The density of air is computed from auxiliary measurements of temperature, pressure and relative humidity after which the buoyancy corrections are calculated directly from the Principle of Archimedes. The following weighing situations are considered.

2.1. Two-Pan Balance

2.2. Single-Pan Balance

2.2.1. With Built-In Weights

2.2.2. With Electronic Control

3. Summary of Method

In general, buoyancy corrections are applied to mass measurements by calculating the difference in volume between the unknown weight and the standard, multiplying this volume difference by the density of air at the balance or scale, and adding the product to the mass of the standard. The density of air is computed from an equation of state using measured values for the temperature, pressure and relative humidity of the air.

4. Significance and Use

Buoyancy corrections generally must be applied when determining the mass of an unknown object to high accuracy. The corrections may become important even at modest

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[3] Richard S. Davis, formerly of the National Institute of Standards and Technology, Mass Group.

accuracies if the unknown object whose mass is to be determined has a density that differs widely from that of the standards (weighing of water, for example). Many mass standards are calibrated in terms of a so-called "apparent mass" [conventional mass] scale (See Chapter 7.3, Handbook 145). Use of this scale does not indiscriminately eliminate the need for buoyancy corrections as is sometimes assumed.

5. Terminology

5.1. Weighing by Substitution

Substitution weighing is the procedure by which one determines the assembly of standard weights that will produce nearly the same reading on a one-pan balance as does the unknown object. The balance thus serves as a comparator. A two-pan balance may be used in this mode if one of the pans contains a counterpoise and the standards and unknown are substituted on the second pan. (See SOP No. 3.)

5.2. Mass

The term "mass" is always used in the strict Newtonian sense as a property intrinsic to matter. Mass is the proportionality constant between a force on a material object and its resulting acceleration. This property is sometimes referred to as "true mass", "vacuum mass", or "mass in vacuum" to distinguish it from conventional [apparent] mass.

5.3. Conventional [Apparent] Mass[4]

The mass of material of a specified density that would exactly balance the unknown object if the weighing were carried out at a temperature of 20 °C in air of density 0.0012 g/cm^3. The mass, M_N, of an object, N, is related to its apparent mass $M_{N,A}$ by the equation:

$$M_{N,A} = \frac{M_N\left(1 - \frac{0.0012}{\rho_N}\right)}{\left(1 - \frac{0.0012}{\rho_B}\right)}$$

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[4] Pontius, P. E., Mass and Mass Values, NBS Monograph 122, 1974, pp 12-23, 26-33 described the concept of apparent mass. The term conventional mass is described by OIML R 33, the Conventional Value of Mass in Air.

Table A-1. Variables for conventional (apparent) mass equation

Variable	Description
ρ_N	density of the object *N* at 20 °C in g/cm^3
ρ_B	density of the conventional (apparent) mass scale at 20 °C in g/cm^3

There are at present two apparent mass scales in wide use. The older is based on ρ_B = 8.4000 g/cm^3 at 0 °C with a coefficient of volumetric expansion of 0.000054/ °C and the more recent (Conventional Mass) specifies ρ_B = 8.0000 g/cm^3 at 20 °C. The quantity $M_{N,A}$ is a function of the particular conventional or apparent mass scale, which has been used in its calculation. OIML IR 33 only recognizes Conventional Mass.

5.4. Sensitivity

The response of a balance under load to an additional small weight:

$$sensitivity = \frac{M_{sw} - \rho_a V_{sw}}{\Delta R} = \frac{M_{sw}\left(1 - \frac{\rho_a}{\rho_{sw}}\right)}{\Delta R}$$

Table A-2. Variables for sensitivity equation

Variable	Description
sensitivity	balance sensitivity (mass per division)
M_{sw}	mass of the small, additional weight
ρ_a	density of the air
ρ_{sw}	density of the small, additional weight
V_{sw}	volume of the small, additional weight
ΔR	change in balance reading due to the addition of the small weight, balance deflection

6. Apparatus

In order to ascertain the density of air at the balance, the following measuring instruments are necessary: thermometer, barometer, and hygrometer. Ideally, these instruments should be placed in or next to the balance case (as near the measurement location as is practical). It may only be practical for the thermometer or temperature sensor to actually be placed inside the balance chamber. A calculator or computer will be extremely useful for this procedure.

7. Procedure

Weigh the unknown object as directed by the balance manufacturer or in accordance with accepted procedure. Record the temperature, pressure and relative humidity of the air in the balance at the time of weighing. Do not correct the barometric pressure to sea level.

8. Calculation

8.1 Air density, Option A (Option B is preferred)

The density of air, in g/cm^3, can be *approximated for lesser accuracy* from the following formula:[5]

$$\rho_a = \left\{ \frac{0.464\,60\left[P - \left(0.003\,796\,0\ U\ e_s \right) \right]}{\left(273.15 + t \right)} \right\} \text{x}\, 10^{-3} \qquad (1)$$

Table A-3. Variables for air density equation

Variable	Description
ρ_a	density of air, g/cm^3
P	barometric pressure, mm Hg
U	% relative humidity, entered as a whole number
t	temperature, °C
e_s	$1.314\,6 \text{ x } 10^9 \text{ x } e^{[-5\,315.56/(t + 273.15)]}$

Note: e_s can be written as follows in a spreadsheet and in some calculators:
1.3146E9*@EXP(-5315.56/(t+273.15))

Small errors (of order 0.01 %) in this equation occur for locations well above sea level or under conditions in which the concentration of carbon dioxide differs greatly from the global average. See the references for a more general formulation of the equation.

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[5] Jones, F.E., "The Air Density Equation and the Transfer of the Mass Unit," Journal of Research, National Institute of Standards and Technology, Vol. 83, 1978, p. 419.

8.2. Air density, Option B – Preferred

The density of air should be calculated with the following formula.[6]

$$\rho = \frac{pM_a}{ZRT}\left(1 - 0.3780\, x_v\right)$$

$$x_v = \left(h/100\right) f\, \frac{\rho_{sv}}{p}$$

$$Z = 1 - \frac{p}{T}\left[a_0 + a_1 t + a_2 t^2 + \left(b_0 + b_1 t\right)x_v + \left(c_0 + c_1 t\right)x_v^{\,2}\right] + \frac{p^2}{T^2}\left(d + e x_v^{\,2}\right)$$

Table A-4. Variables for CIPM air density equation

Variable	Description
M_a	molar mass of the air within laboratory 28.963 5 x 10^{-3} kg/mol
p	ambient barometric pressure in Pascal
T	ambient temperature in Kelvin
R	universal gas constant: 8.314 510 J mol^{-1} K^{-1}
h	relative humidity in %
f	1.000 62 + (3.14 x 10^{-8}) p + (5.6 x 10^{-7})t^2
t	ambient temperature in degrees Celsius
p_{sv}	1 Pascal x exp (AT^2 + BT + C + D/T)
A	1.237 884 7 x 10^{-5} K^{-2}
B	-1.912 131 6 x 10^{-2} K^{-1}
C	33.937 110 47
D	-6.343 164 5 x 10^{3} K
a_0	1.581 23 x 10^{-6} K Pa^{-1}
a_1	-2.933 1 x 10^{-8} Pa^{-1}
a_2	1.104 3 x 10^{-10} K^{-1} Pa^{-1}
b_0	5.707 x 10^{-6} K Pa^{-1}
b_1	-2.051 x 10^{-8} Pa^{-1}
c_0	1.989 8 x 10^{-4} K Pa^{-1}
c_1	-2.376 x 10^{-6} Pa^{-1}
d	1.83 x 10^{-11} K^2 Pa^{-2}
e	-0.765 x 10^{-8} K^2 Pa^{-2}

Calculate the density of air at the balance during the weighing. Then determine the mass of the unknown, M_x, as follows:

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[6] CIPM References: Giacomo, P. Metrologia 18: 33-40 (1982), Davis, R.S., Metrologia 29: 67-70 (1992).

8.3 If a two-pan balance is used:

$$M_x = M_s + \rho_a \left(V_x - V_s \right) + \mathit{sensitivity}\ \Delta M_{opt} \qquad (3a)$$

or

$$M_x = \frac{M_s \left(1 - \dfrac{\rho_a}{\rho_s} \right) + \mathit{sensitivity}\ \Delta M_{opt}}{\left(1 - \dfrac{\rho_a}{\rho_x} \right)} \qquad (3b)$$

or

$$M_x = \frac{M_s - \rho_a V_s + \mathit{sensitivity}\ \Delta M_{opt}}{\left(1 - \dfrac{\rho_a}{\rho_x} \right)} \qquad (3c)$$

Table A-5. Variables not previously defined

Variable	Description
M_x	mass of the unknown object
M_s	mass of the standard weights
ρ_S	density of the standard weights, $\frac{M_S}{V_S}$
ΔM_{opt}	off-balance indication read on the optical scale
V_x	volume of the unknown object
V_s	volume of the standard weights
ρ_x	density of the unknown object, $\frac{M_X}{V_X}$

Volumes and densities are, in general, a function of temperature. The thermal coefficients of volumetric expansion of the unknown object and the standard may be significant in very accurate work.[7] The coefficient of volumetric expansion is usually estimated as three times the linear coefficient of expansion of the weight material.

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[7] In general, $V(t) = V_{20} [1 + ß(t - 20\ °C)]$ where t is the temperature of the weight, V_{20} is the volume at 20 °C, and ß is the coefficient of volumetric expansion.

The error in M_x incurred by ignoring the buoyancy correction is $\rho_a (V_x - V_s)$. To estimate quickly whether such an error is of consequence in a particular measurement, (assume $\rho_a = 1.2 \times 10^{-3} g/cm^3$).

If the mass and volumes of the standards have been adjusted to a conventional mass scale, then

$$M_x \approx \frac{CM_s\left(1 - \dfrac{\rho_a}{\rho_B}\right) + sensitivity\ \Delta M_{opt}}{\left(1 - \dfrac{\rho_a}{\rho_x}\right)} \qquad (4)$$

Table A-6. Variables not previously defined

Variable	Description
CM_s	conventional mass of the standard
The symbol ≈ signifies an approximation	

8.4 If a single-pan balance with built-in weights is used, it is probable that the built-in weights have been adjusted on an apparent mass or conventional mass scale[8]. Determine which apparent mass scale has been used and calculate the mass of the unknown from the equation

$$M_x \approx \frac{M_D\left(1 - \dfrac{\rho_a}{\rho_B}\right) + sensitivity\ M_{opt}}{\left(1 - \dfrac{\rho_a}{\rho_x}\right)} \qquad (5)$$

Table A-7. Variables not previously defined

Variable	Description
M_D	mass indicated by dial or digital readings
M_{opt}	mass indicated on the optical scale when present

If the balance has been used only as a comparator, that is, to compare the mass of the unknown object with that of some external standard, then:

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[8] Schoonover, R. M. and Jones, F. E., "Air Buoyancy in High-Accuracy Weighing on Analytical Balances," Anal. Chem., 53, 1981, p. 900.

$$M_x = M_s + \rho_a \left(V_x - V_s \right) + sensitivity\, \Delta M'_{opt}$$

Table A-8. Variable not previously defined

Variable	Description
$\Delta M'_{opt}$	difference in optical scale reading between observations of the standard and the unknown

For some balances, operation requires that the user restore the balance to null by means of a manually controlled dial. The portion of the mass reading controlled by this dial should be treated, for purposes of buoyancy corrections, as an optical scale.

8.5 If a single-pan balance with full-range electronic control is used, the following should be noted. As part of its calibration, the electronic gain has been adjusted by means of a weight of known mass. For example, if the range of electronic control is 100 g, the electronics have been adjusted so that a 100-g standard weight produces an indication of precisely 100 g. This procedure effectively builds an apparent mass calibration into the balance. The reference density of the apparent mass scale is the density of the standard mass used for the calibration and the reference air density is the air density at the time of calibration.

The mass of an unknown object weighed on the balance is then

$$M_x = \frac{M_R \left(1 - \dfrac{\rho_a}{\rho_c} \right)}{\left(1 - \dfrac{\rho_a}{\rho_x} \right)} \qquad (6)$$

Table A-9. Variables not previously defined

Variable	Description
M_R	readout displayed on the balance
ρ_a	density of air at the time of balance calibration
ρ_c	density of the standard used to calibrate the balance (or ρ_B if the apparent [conventional] mass of the standard was used instead of the true mass

If the balance includes both an electronic control system and built-in weights, the buoyancy considerations for the built-in weights are as described in section 8.2 and the considerations for the electronically determined mass are those given directly above.

8.6 Top-loading balances may be considered a form of single-pan balance and the appropriate procedure for buoyancy correction followed.

9. Precision

The contribution of the random error of the evaluation of air density to the precision of mass measurement may be estimated as follows:

For mechanical balances, or electronic balances used in weighing by substitution, the contribution is:

$$\delta\rho_a \left(V_x - V_s \right)$$

Table A-10. Variables for above equation

Variable	Description
$\delta\rho_a$	random error of evaluation of ρ_a
V_s	volume of standards, if weighing by substitution $V_s = M_D / D_B$, if using the built-in weights on a single pan balance.
V_x	volume of object weighed

The quantity, $\delta\rho_a$ will have contributions from the measurements of temperature, pressure and relative humidity which are required for the calculation of ρ_a. Equation (1) may be used to estimate the effects of imprecision in measurements of P, t, and U. It is unrealistic to expect $\delta\rho_a/\rho_a$ ever to be less than 0.05 % even using the best techniques available.

10. Accuracy

Inattention to problems of buoyancy most often results in systematic errors. For a substitution weighing, for example, the buoyancy correction is of the order of $\rho_a(V_x - V_s)$. While this quantity may be significant to a measurement, day-to-day variation in ρ_a (usually no more than 3 %) may not be noticeable and hence need not be measured. For the most accurate work, not only must ρ_a be accurately determined, but the volumes of the unknown and standard may have to be measured to better than 0.05 % - the minimum systematic uncertainty attainable in the calculation of ρ_a.

If the standards have been calibrated in terms of conventional mass, complete neglect of buoyancy corrections will produce an error in the measured result M_x of order:

$$CM_s \left[\left(1.2\,x\,10^{-3} - \rho_a \right) \left(\frac{1}{\rho_s} - \frac{1}{\rho_B} \right) + \left(\frac{\rho_B - \rho_x}{\rho_B} \right) \left(\frac{\rho_a}{\rho_x} \right) \right] \qquad (7)$$

This error is often unacceptably large.

Use of equation (4), on the other hand, introduces only an error of approximately

$$CM_s\left(1.2\,x\,10^{-3}\;-\;\rho_a\right)\left(\frac{1}{\rho_s}-\frac{1}{\rho_B}\right) \qquad (8)$$

It is a requirement for manufacture that the actual density of standard weights be near enough to the assumed density of the apparent mass scale to which they are adjusted that the magnitude of (8) will always be small under normal conditions in laboratories near sea level.

The fact that there are two apparent mass scales widely used - one based on density 8.0 g/cm^3 and an older one based on 8.4 g/cm^3 - means that some caution is required on the part of the user. Conventional mass is generally preferred and reported for all calibrations where mass standards will be used to calibrate weighing instruments. For the most accurate work, the apparent mass scale should be abandoned in favor of substitution weighing with standards of known mass and volume.

The user must decide the accuracy required of the particular mass measurement and choose a buoyancy correction technique commensurate with that accuracy.

The same considerations, which apply to the accuracy of buoyancy corrections in weighing by substitution, are easily extended to the other types of weighing indicated above.

There are many factors, which affect the accuracy of a mass measurement. The above has dealt only with those arising from problems of buoyancy.

Appendix B

Examples

Example 1:

The weight set of Table B-1 is used with an equal-arm balance to find the mass of a piece of single-crystal silicon. The following weights were used to balance the silicon: 10 g, 3 g. The balance pointer showed the silicon side to be light by 3.5 divisions. The 10 mg weight of Table 1 was used to find the sensitivity of the balance. When the weight was added, the pointer moved 10.3 divisions. At the time of the weighing, the following measurements were taken:

P = 748.1 mm Hg

t = 22.3 °C

U = 37 % relative humidity

What is the mass of the silicon?

Answer:

From Eq. 1, or Table B-2, calculate

$$e_s = 1.314\,6\,x\,10^9\ x\ e^{\left(\frac{-5\,315.56}{(22.3\ +\ 273.15)}\right)} = 20.194\ \text{mm Hg}$$

$$\rho_a = \left\{ \frac{0.464\,60\left[748.1 - (0.003\,796\,0)(37)(20.2)\right]}{(273.15 + 22.3)} \right\} 10^{-3}$$

$\rho_a = 1.171\ 94 \text{ x } 10^{-3}$ g/cm^3

The density of silicon at 20 °C is 2.329 1 g/cm^3 and its coefficient of linear expansion is 0.000 002 6 /°C.

Make use of Eq. 3c and Table B-1.

$$M_s = 10.000\,126\,4 + 3.000\,045\,9 = 13.000\,172\ \text{g}$$

$$V_s = (1.267 + 0.380) = 1.647\ \text{cm}^3$$

Calculate the sensitivity:

$$\text{sensitivity} = \frac{0.010\,003\,g - (0.003\,70)(1.172\,x\,10^{-3})}{10.3}$$

$$\text{sensitivity} = \frac{(0.009\,999)}{10.3} = 0.000\,971\,\text{g/division} = 0.971\,\text{mg/division}$$

$$M_x = \frac{[13.000172 - (1.647)(1.172\,x\,10^{-3})] + [(0.971\,x\,10^{-3})(-3.5)]}{\left(1 - \frac{1.172\,x\,10^{-3}}{2.3291}\right)}$$

M_x = 13.001 385 g

Note that the thermal expansion is insignificant in this example.

Example 2:

Let us again consider the weighing performed in Example 1. This time, all we know about our weight set is that it has been adjusted to the 8.4 apparent mass scale at the best available commercial tolerance.

Using Eq. (4),

$$M_x = \left\{ \frac{\left[13.00\left(1 - \frac{1.172\,x\,10^{-3}}{8.3909}\right)\right] + \left[0.010\left(1 - \frac{1.172\,x\,10^{-3}}{8.3909}\right)\right]\left(\frac{-3.5}{10.3}\right)}{\left(1 - \frac{1.172\,x\,10^{-3}}{2.3291}\right)} \right\}$$

M_x= 13.001 329 g

For routine weighing, it is sometimes satisfactory to assume that the temperature is 20 °C and the density of air is 1.2 x 10^{-3} g/cm^3. Had this been done, the computed value for the silicon would be

$$M_x = \left\{ \frac{\left[13.00\left(1 - \frac{1.2\,x\,10^{-3}}{8.3909}\right)\right] + \left[0.010\left(1 - \frac{1.2\,x\,10^{-3}}{8.3909}\right)\right]\left(\frac{-3.5}{10.3}\right)}{\left(1 - \frac{1.2\,x\,10^{-3}}{2.3291}\right)} \right\}$$

M_x = 13.001 442 g

which is within 100 µg of the answer found in Example 1.

Example 3:

Another piece of silicon is measured on a single-pan microbalance. The balance weights were adjusted by the manufacturer to the conventional mass scale. The sensitivity of the balance has been determined to be exactly 1.000. This particular laboratory is well above sea level. At the time of the weighing, the following measurements were recorded:

P = 612.3 mm Hg

t = 23.4 °C

U = 23 % relative humidity

The balance reading was 15.00 g on the built-in weights and 0.000 358 g on the optical screen. What is the mass of the silicon?

Answer:

First, calculate e_s and ρ_a:

e_s = 21.59 mm Hg

$\rho_a = 0.956 \text{ x } 10^{-3}$ g/cm^3

Then, use Eq. 5:

$$M_x = \frac{\left(15.00 + 0.000\,358\right)\left(1 - \dfrac{0.956\,x\,10^{-3}}{8.0}\right)}{\left(1 - \dfrac{0.956\,x\,10^{-3}}{2.3291}\right)}$$

M_x = 15.004 724 g

Example 4:

The built-in weights in Example 3 are actually stainless steel of density 7.78 g/cm^3 at 20 °C. What is the approximate error caused by using the apparent mass scale?

Answer:

Using (7), the error is approximately

$$15\ g\left(0.2\ x\ 10^{-3}\ g/cm^{3}\right)\left(\frac{1}{7.78\ g/cm^{3}}-\frac{1}{8.0\ g/cm^{3}}\right)=11\ \mu g$$

This discrepancy, though larger than the precision of the best analytical balances, is actually well within the tolerance of Class 1 weights.

Table B-1. Example of calibration report data

Mass (g)	Uncertainty (g)	Vol at 20 °C (cm^3)	Coefficient of Expansion
100.00094070	0.00002535	12.67439	0.000045
50.00046277	0.00001550	6.33719	0.000045
30.00029259	0.00001361	3.80232	0.000045
20.00015779	0.00001113	2.53487	0.000045
10.00012644	0.00001330	1.26744	0.000045
5.00004198	0.00000688	0.63372	0.000045
3.00004588	0.00000459	0.38023	0.000045
2.00000627	0.00000333	0.25349	0.000045
1.00001438	0.00000300	0.12674	0.000045
0.49995376	0.00000160	0.03012	0.000020
0.29996145	0.00000115	0.01807	0.000020
0.19994984	0.00000087	0.01205	0.000020
0.09996378	0.00000091	0.00602	0.000020
0.04998659	0.00000072	0.00301	0.000020
0.02999100	0.00000077	0.00181	0.000020
0.02000570	0.00000066	0.00741	0.000069
0.01000277	0.00000086	0.00370	0.000069
0.00499706	0.00000070	0.00185	0.000069
0.00300299	0.00000076	0.00111	0.000069
0.00200197	0.00000066	0.00074	0.000069
0.00100083	0.00000086	0.00037	0.000069

Table B-2. e_s approximation in terms of temperature

Temperature (°C)	e_s (mm Hg)
18	15.48
18.5	15.97
19	16.48
19.5	17
20	17.54
20.5	18.09
21	18.65
21.5	19.23
22	19.83
22.5	20.44
23	21.07
23.5	21.72
24	22.38
24.5	23.07
25	23.77
25.5	24.49
26	25.23
26.5	25.99
27	26.77
27.5	27.57
28	28.39
28.5	29.23
29	30.09
29.5	30.98

SOP No. 4

Recommended Standard Operations Procedure
for
Weighing by Double Substitution Using a Single-Pan Mechanical Balance, a Full Electronic Balance, or a Balance with Digital Indications and Built-In Weights

1.0 Introduction

1.1. Purpose

The double substitution procedure is one in which a standard and an unknown weight are intercompared twice to determine the average difference between the two weights. Errors in any built-in weights or in the balance indications are eliminated by using the balance only as a comparator and by calibrating the balance indications over the range of use for the measurement with a sensitivity weight. Accordingly, the procedure is especially useful for high accuracy calibrations. The procedure does not incorporate measurement control steps to ensure the validity of the standards and the measurement process; additional precautions must be taken.

1.2. Prerequisites

1.2.1. Verify that valid calibration certificates are available for the standards used in the test.

1.2.2. Verify that the standards to be used have sufficiently small standard uncertainties for the intended level of calibration. Primary standards should not be used at this level.

1.2.3. Verify that the balance is in good operating condition with sufficiently small process standard deviation as verified by a valid control chart or preliminary experiments to ascertain the performance quality when a new balance is put into service.

1.2.4. Verify that the operator is experienced in precision weighing techniques and has had specific training in SOP 2, SOP 4, SOP 29, GMP 4, and GMP 10.

1.2.5. Verify that the laboratory facilities comply with the following minimum conditions to meet the expected uncertainty possible with this procedure.

Table 1. Environmental conditions

Echelon	Temperature	Relative Humidity (percent)
II	20 °C to 23 °C, a set point ± 2 °C, maximum change 1.0 °C/h	40 to 60 ± 10 / 4 h
III	18 °C to 27 °C, maximum change 2.0 °C/h	40 to 60 ± 20 / 4 h

2. Methodology

2.1. Scope, Precision, Accuracy

This method is applicable to all weighings utilizing a mass comparator, a single-pan mechanical balance, a full electronic balance, or a balance that combines digital indications with the use of built-in weights (combination balance). The precision will depend upon the sensitivity of the balance 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 precision of the intercomparison.

2.2. Summary

The balance is adjusted if necessary, to obtain balance indications for all measurements that will be within the range of the optical scale or digital indications of the balance without changing the dial settings for the built-in weights, if present. The standard and the test weight are each weighed. A small, calibrated weight, called a sensitivity weight, is added to the test weight and these are weighed. The standard and the same sensitivity weight are then weighed. The latter two weighings provide both second weighings of the standard and the test weight as well as 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 average out any effects due to instrument drift.

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

2.3. Apparatus/Equipment Required

2.3.1. Precision balance with sufficient capacity and sensitivity for the calibrations planned.

2.3.2. Calibrated working standard and sensitivity weights with recent calibration values that are traceable to NIST.

2.3.3. Calibrated small standard weights with recent calibration certificates and values traceable to NIST to be used as tare weights.

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

2.3.5. Forceps to handle the weights, or gloves to be worn if the weights are moved by hand.

2.3.6. Stop watch or other timing device to observe the time of each measurement.

2.3.7. Calibrated barometer accurate to ± 66.5 Pa (0.5 mm Hg) with recent calibration values traceable to NIST to determine air pressure.

2.3.8. Calibrated thermometer accurate to ± 0.10 °C with recent calibration values traceable to NIST to determine air temperature.

2.3.9. Calibrated hygrometer accurate to ± 10 percent with recent calibration values traceable to NIST to determine relative humidity.[1]

2.4. Symbols

Table 2. Symbols used in this procedure

Symbol	Description
S	standard reference weight
X	weight to be calibrated
t	small calibrated tare weight, A subscript s or x is used to indicate the larger weight 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	the nominal value of a specific weight. Subscripts s, x, are used to identify the weight.
C	the 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

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[1] 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 accuracies specified are recommended for high precision calibration. Less accurate equipment can be used with only a small degradation in the overall accuracy of the measurement.

Symbol	Description
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. Place the test weight and standards in the balance chamber or near the balance overnight to permit the weights and the balance to attain thermal equilibrium.

2.5.1.2. Conduct preliminary measurements to obtain an approximate value for the difference between the standard and the unknown, to determine where the readings occur on the balance, to determine if tare weights are required, to determine the sensitivity weight that must be used, and to determine the time interval required for the balance indication to stabilize.

Tare weights are rarely needed for high precision mass standards. If 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 evaluated in the process of determining 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 GMP 14, Table 1). Select t_s and t_x such that the difference in mass between $S + t_s$ and $X + t_x$ is:

a. Single-pan mechanical balance - less than $\frac{1}{10}$ the range of the optical scale.

b. Full electronic balance - less than 0.05 percent of the balance capacity.

c. Combination balance - less than $\frac{1}{10}$ the range of the digital indications.

d. Mass comparator – less than $\frac{1}{10}$ digital range

A sensitivity weight must be used on equal-arm balances, and is normally used on single-pan mechanical and electronic balances, to ensure that the measured differences determined through the use of the optical scale or electronic range have valid accuracy and traceability (See GMP 14, Table 2). (e.g., The optical scale is *calibrated* each time the procedure is performed through the use of a sensitivity weight). The uncertainty of the sensitivity weight does not generally need to be included in calculations of uncertainty since the uncertainty value is distributed across its range of use.

If a sensitivity weight will be used, select one that is:

a. Single-pan balance - between ¼ and ½ the range of the optical scale, and at least 4 times the mass difference between *X* and *S*.

b. Full electronic balance - at least 4 times the mass difference between *X* and *S*, but not exceeding 1 percent of the balance capacity.

c. Combination balance - between ¼ and ½ the range of the digital indications, and at least 4 times the mass difference between *X* and *S*.

d. Mass comparator – at least 4 times the mass difference between *X* and *S*, but not exceeding ½ of the digital range.

A sensitivity weight is not required if the electronic mass comparator that is used has been tested (with supporting data available) to determine that the balance has sufficient accuracy, resolution, repeatability, and stability so that no advantage is gained through the use of a sensitivity weight. For example, any possible errors must be less than what contributes to the uncertainty. When a mass comparator is used without a sensitivity weight, the sensitivity must be periodically verified and documented.

2.5.1.3. Determine which optional sequence will be used, A or B. 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.

2.5.1.4. Adjust the single pan 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. Once the balance has been adjusted to the desired position, 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.

2.5.1.5. 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 3. 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. Record the laboratory ambient temperature, barometric pressure, and relative humidity.

2.5.2.1. Observation 1. Place the standard weight(s), S, along with t_s on the balance pan. If equipped with a pan arrestment mechanism, release the balance pan. When the pan is released, start the stop-watch and record observation O_1 once the balance indication has stabilized.

2.5.2.2. Observation 2. Remove weight(s) S and t_s and replace with test weight X and its tare weight, t_x. Release the pan, time the interval, and record observation O_2.

2.5.2.3. Observation 3. Add the sensitivity weight, sw, to the weights of observation 2. Release the pan, time the interval, and record observation O_3.

2.5.2.4. Observation 4. Remove weights X and t_x and replace with S and t_s. The sensitivity weight, sw, remains on the balance pan. Release the pan, time the interval, and record observation O_4.

2.5.2.5. Compare the two differences ($O_2 – O_1$) and ($O_3 – O_4$); they should not differ from one another by more than 2 standard deviations of the balance for this process and load. If this difference is exceeded, reject the data and redo the measurements. Investigate possible causes of excess variability if measurements do not agree within these limits.

2.5.2.6. If repeated double substitutions are performed, the values between successive trials should not differ from one another by more than ± 2 standard deviations of the balance for this process and load. If this difference is exceeded, reject the data and take a new series of measurements that do so agree.

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

Table 4. 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. No air buoyancy correction. Calculate the conventional mass correction, C_x, for the test weight as follows, according to the optional sequence used. In each case, the conventional mass corrections for the standard weight(s), C_s, the conventional mass of the tare weights, CM_{t_s} and CM_{t_x}, and the conventional mass of the sensitivity weight, CM_{sw}, are included. The symbols N_s and N_x refer to the nominal values of *S* and *X*, respectively. If no tare weights, and equal nominal values are used, those terms may all be deleted from the equations.

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3.1.1. Optional Sequence A (*SXXS*)

$$C_x = C_s + CM_{t_s} - CM_{t_x} + \left[\frac{(O_2 - O_1) + (O_3 - O_4)}{2} \right] \left[\frac{CM_{sw}}{O_3 - O_2} \right] + N_s - N_x$$

3.1.2. Optional Sequence B (*XSSX*)

$$C_x = C_s + CM_{t_s} - CM_{t_x} + \left[\frac{(O_1 - O_2) + (O_4 - O_3)}{2}\right]\left[\frac{CM_{sw}}{O_3 - O_2}\right] + N_s - N_x$$

3.2. Air Buoyancy Correction

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

3.2.2. Calculate the mass M_x of the test weight, and its mass correction C_x 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*)

$$M_x = \frac{M_s\left(1 - \frac{\rho_a}{\rho_s}\right) + M_{t_s}\left(1 - \frac{\rho_a}{\rho_{t_s}}\right) - M_{t_x}\left(1 - \frac{\rho_a}{\rho_{t_x}}\right) + \left[\frac{(O_2 - O_1) + (O_3 - O_4)}{2}\right]\left[\frac{M_{sw}\left(1 - \frac{\rho_a}{\rho_{sw}}\right)}{O_3 - O_2}\right]}{\left(1 - \frac{\rho_a}{\rho_x}\right)}$$

3.2.2.2. Optional Sequence B (*XSSX*)

$$M_x = \frac{M_s\left(1 - \frac{\rho_a}{\rho_s}\right) + M_{t_s}\left(1 - \frac{\rho_a}{\rho_{t_s}}\right) - M_{t_x}\left(1 - \frac{\rho_a}{\rho_{t_x}}\right) + \left[\frac{(O_1 - O_2) + (O_4 - O_3)}{2}\right]\left[\frac{M_{sw}\left(1 - \frac{\rho_a}{\rho_{sw}}\right)}{O_3 - O_2}\right]}{\left(1 - \frac{\rho_a}{\rho_x}\right)}$$

3.2.3. Calculate the mass correction C_x, as follows:

$$C_x = M_x - N_x$$

where N_x is the nominal value for *X*.

3.2.4. Calculate the conventional mass[2] of X, CM_x. It is recommended that the conventional mass be reported.

3.2.4.1. Conventional mass

$$CM_x = \frac{M_x\left(1 - \frac{\rho_n}{\rho_x}\right)}{\left(1 - \frac{\rho_n}{8.0}\right)}$$

3.2.5. If requested, the apparent mass versus the reference density of brass may be calculated. This value should only be used when calibrating mechanical balances that have been adjusted to this reference density.

3.2.5.1. Apparent mass versus brass

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

4. Measurement Assurance

4.1. Duplicate the process with a suitable check standard (See GLP 1, SOP 9, SOP 30, and Sec. 7.4)

4.2. Plot the check standard value and verify that it is within established limits; a t-test may be incorporated to check observed value against accepted value.

4.3. The mean of the check standard is used to evaluate bias and drift over time.

4.4. Check standard observations are used to calculate the standard deviation of the measurement process, s_p.

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

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[2] 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: reference density 8.0 g/cm^3; reference temperature 20 °C; *normal* air density 0.0012 g/cm3. Conventional mass was formerly called "Apparent Mass versus 8.0 g/cm^3" in the United States. *See OIML IR 33 (1973, 1979), under revision.*

(RSS), and the expanded uncertainty, *U*, reported with a coverage factor of two (k=2), to give us 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 report. 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.

5.2. The value for s_p is obtained from the control chart data for check standards using double substitution measurements. (See SOP No. 9.)

5.3. Other standard uncertainties usually included at this calibration level include uncertainties associated with calculation of air density and standard uncertainties associated with the density of the standards used.

5.4. The expanded uncertainty, *U*, must be ≤ 1/3 of the tolerance applicable as per ASTM E617-97 and OIML R111 to classify mass standards.

6. Report

Report results as described in SOP No. 1, Preparation of Calibration/Test Reports.

Appendix
Double Substitution Data Sheet
(Optional Sequence A)
SXXS

Laboratory data and conditions:

Operator			
Date		Temperature	
Balance		Pressure	
Nominal Load		Relative Humidity	
Standard deviation of the process, from control chart, s_p			

Mass standard(s) data:

ID	Nominal	Mass Correction*	Expanded Unc: From cal. report	Unc: k factor	Density g/cm^3
S					
X					
sw					
t_s					
t_x					

*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 (Duplication of the Process):

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:		

Note: dotted line represents decimal point

Appendix
Double Substitution Data Sheet
(Optional Sequence B)
XSSX

Laboratory data and conditions:

Operator			
Date		Temperature	
Balance		Pressure	
Load		Relative Humidity	
Process standard deviation from control chart, s_p			

Mass standard(s) data:

ID	Nominal	Mass Correction*	Expanded Unc: From Cal. report	Unc: k factor	Density g/cm^3
X					
S					
sw					
t_x					
t_s					

*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 (Duplication of the Process):

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:		

Note: dotted line represents decimal point.

Example: With Buoyancy Corrections
Double Substitution Data Sheet
(Optional Sequence A)
SXXS

Laboratory data and conditions:

Operator	HO		
Date	8/24/86	Temperature	22.3 °C
Balance	M5SA	Pressure	753.5 mm Hg
Nominal Load	10 g	Relative Humidity	45 %
Standard deviation of the process, from control chart, s_p			0.002 9 mg

Mass standard(s) data:

ID	Nominal	Mass Correction*	Expanded Unc: From Cal. Rpt. (mg)	Unc: k factor	Density g/cm^3
S	10 g	-0.679 mg	0.014 mg	3	8.00
X	10 g	TBD	TBD	2	7.84
sw	5 mg	-0.0227 mg	0.000 28	2	8.5
t_s	---	---	---	---	---
t_x	---	---	---	---	---
S_c	10 g	0.321 mg	0.025 mg	2	8.0

*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 mg
Time: 8:35 AM		
1 (O_1)	$S + t_s$	1 ⋮ 268
2 (O_2)	$X + t_x$	1 ⋮ 821
3 (O_3)	$X + t_x + sw$	6 ⋮ 798
4 (O_4)	$S + t_s + sw$	6 ⋮ 245
Time: 8:47 AM		

Measurement Assurance (Duplication of the Process):

Observation No.	Weights	Balance Observations, Units
Time: 9:00 AM		
1 (O_1)	$S + t_s$	1 ⋮ 270
2 (O_2)	$S_c + t_{Sc}$	2 ⋮ 271
3 (O_3)	$S_c + t_{Sc} + sw$	7 ⋮ 248
4 (O_4)	$S + t_s + sw$	6 ⋮ 248
Time: 9:10 AM		

Note: dotted line represents decimal point

Calculate the air density (SOP 2):

$\rho_a = 1.179\ 5$ mg/cm³ $= 0.001\ 179\ 5$ g/cm³

Use equation 3.2.2.1 for optional sequence A (*SXX*S) with buoyancy corrections[3]:

$$M_x = \frac{M_s\left(1 - \frac{\rho_a}{\rho_s}\right) + M_{t_s}\left(1 - \frac{\rho_a}{\rho_{t_s}}\right) - M_{t_x}\left(1 - \frac{\rho_a}{\rho_{t_x}}\right) + \left[\frac{(O_2 - O_1) + (O_3 - O_4)}{2}\right]\left[\frac{M_{sw}\left(1 - \frac{\rho_a}{\rho_{sw}}\right)}{O_3 - O_2}\right]}{\left(1 - \frac{\rho_a}{\rho_x}\right)}$$

$$\mathrm{M_X} = \frac{9.999321\left(1 - \frac{0.0011795}{8.0}\right) + 0 - 0 + \left[\frac{(1.821 - 1.268) + (6.798 - 6.245)}{2}\right]\left[\frac{0.0049773\left(1 - \frac{0.0011795}{8.5}\right)}{6.798 - 1.821}\right]}{\left(1 - \frac{0.0011795}{7.84}\right)}$$

$$\mathrm{M_x} = \frac{(9.997\,8461 + 0.000\,552\,957)}{0.99984949} = 9.999\,9041\,\mathrm{g}$$

Calculate the mass (*true mass*) correction:

$C_x = M_x - N_x$

$C_x = 9.999\ 904\ 1$ g $-$ 10 g $=$ $-0.000\ 095\ 9$ g $=$ $-0.095\ 9$ mg

Calculate the conventional mass value:

$$CM_x = \frac{M_x\left(1 - \frac{\rho_n}{\rho_x}\right)}{\left(1 - \frac{\rho_n}{8.0}\right)}$$

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[3] Keep in mind that these equations may be truncated for the purpose of this example and minor differences may be seen in the ending decimal places due to the use of calculators or spreadsheets.

$$CM_x = \frac{9.999\,9041 \left(1 - \frac{0.001\,2}{7.84} \right)}{0.999\,850}$$

$$CM_x = \frac{9.999\,9041 \; (0.999\,846\,9)}{0.999\,850} = 9.999\,873\,51\,\text{g}$$

$C_x = CM_x - N_x$

$C_x = 9.999\ 873\ 51$ g $-$ 10 g

$C_x = -\ 0.000\ 126\ 49$ g $=$ $-\ 0.126\ 49$ mg

Calculate the uncertainty for the calibration:

$U = u_c * 2$

$$u_c = \sqrt{u_s^{2} + s_p^{2} + u_o^{2}}$$

The uncertainty for the standard, U, must be divided by the k factor to determine the u_s.

$$u_c = \sqrt{(0.004\,667)^2 + (0.002\,9)^2 + (0.000\,000\,032)^2}$$

$u_c = 0.005\ 494\ 623\ 6\ mg$

$U = 0.005\ 494\ 623\ 6 * 2 = 0.010\ 989\ 247\ 3\ mg$

Uncertainty Statement

The uncertainty reported is the root sum square of the standard uncertainty of the standard, the standard deviation of the process, and an uncorrected systematic error for lack of buoyancy corrections, multiplied by a coverage factor of 2 (k=2) for an approximate 95 percent confidence interval. Factors not considered in the evaluation: magnetism (weights are considered to meet 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).

Compliance Evaluation

We have to evaluate the correction with its expanded uncertainty to determine if the weight is in tolerance or not. The magnitude of the expanded uncertainty has to be less than 1/3 of the tolerance to be able to perform that evaluation, according to ASTM E617-97 and OIML R111.

Load = 10 g

ASTM E617		OIML R111	
Class	Tolerance (mg)	Class	Tolerance (mg)
0	0.025	E_1	0.020
1	0.050	E_2	0.060
2	0.054	F_1	0.20

If we look at three times the uncertainty: 0.011 mg x 3 = 0.033 mg, we realize that the uncertainty complies with the 1/3 rule for ASTM classes 1, 2, and OIML classes E_2, F_1.

Next, we look at the correction with the uncertainty: -0.126 mg ± 0.011 mg.

We can see that the absolute value of the correction is within: $0.115 \le C_x \le 0.137$, therefore, it only complies with OIML class F_1.

Reporting

The conventional mass correction and uncertainty would be reported as follows:

$C_X = -0.126$ mg $\pm$ 0.011 mg

Example: Without Buoyancy Corrections
Double Substitution Data Sheet
(Optional Sequence B)
XSSX

Laboratory data and conditions:

Operator		HO	
Date	8/24/86	Temperature	22.3 °C
Balance	CB 100	Pressure	753.5 mm Hg
Load	30 g & 1 troy oz	Relative Humidity	45 %
		Process standard deviation from control chart, s_p	0.018 mg

Mass standard(s) data:

ID	Nominal	Mass Correction*	Expanded Unc: From cal. report	Unc: k factor	Density g/cm^3
S	30 g	0.407 mg	0.022 mg	3	8
X	1 t oz	TBD	TBD	2	7.84
sw	50 mg	-0.084 00 mg	0.000 65 mg	2	8.5
t_s	1.1 g	0.359 6 mg	0.006 3 mg	3	8.04
t_x	None	---	---	---	---
S_c	30 g	0.907 mg	0.030 mg	2	8

*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 mg
Time: 9:00 AM		
1 (O_1)	$X + t_x$	20 ⁞ 93
2 (O_2)	$S + t_s$	17 ⁞ 21
3 (O_3)	$S + t_s + sw$	67 ⁞ 08
4 (O_4)	$X + t_x + sw$	70 ⁞ 81
Time: 9:05 AM		

Measurement Assurance (Duplication of the Process):

Observation No.	Weights	Balance Observations, Units
Time: 9:15 AM		
1 (O_1)	$S + t_s$	20 ⁞ 95
2 (O_2)	$S_c + t_{Sc}$	21 ⁞ 45
3 (O_3)	$S_c + t_{Sc} + sw$	71 ⁞ 32
4 (O_4)	$S + t_s + sw$	70 ⁞ 83
Time: 9:20 AM		

Note: dotted line represents decimal point

Use equation 3.1.2 for optional sequence B (*XSSX*) with NO buoyancy corrections[4]:

$$C_x = C_s + CM_{t_s} - CM_{t_x} + \left[\frac{(O_1 - O_2) + (O_4 - O_3)}{2} \right] \left[\frac{CM_{sw}}{O_3 - O_2} \right] + N_s - N_x$$

Note: be careful to combine like units only!

$$C_x = 0.407 \text{ mg} + 1.100\,359\,6 \text{ g} - 0 + \left[\frac{(20.93 - 17.21) + (70.81 - 67.08)}{2} \right] \left[\frac{49.916 \text{ mg}}{67.08 - 17.21} \right] + 30 \text{ g} - 1 \text{ t oz}$$

$$C_x = 0.407 \text{ mg} + 1.100\,359\,6 \text{ g} - 0 + 3.728\,435\,9 \text{ mg} + 30 \text{ g} - 31.103\,47\,68 \text{ g}$$

$C_x =$ *1 104.495 036* mg – *1.103 476 8* g

$C_x =$ *1.018 236* mg

Calculate the uncertainty for the calibration:

$U = u_c * 2$

$$u_c = \sqrt{u_s^2 + s_p^2 + u_o^2}$$

The uncertainty for the standard, *U*, must be divided by the k factor for the standard and the tare weight to determine each u_s. The additional uncertainty for not performing the air buoyancy correction can be determined using the magnitude of the air buoyancy correction from SOP 2.

$$u_c = \sqrt{(0.007\,33)^2 + (0.002\,1)^2 + (0.018)^2 + (0.001\,6)^2}$$

u_c = 0.019 617 15 mg

U = 0.019 617 15 * 2 = 0.039 234 mg

The conventional mass correction and uncertainty would be reported as follows:

C_x = 1.018 mg ± 0.039 mg

OR

C_x = 0.000 032 7 t oz ± 0.000 001 3 t oz

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[4] Keep in mind that these equations may be truncated for the purpose of this example and minor differences may be seen in the ending decimal places due to the use of calculators or spreadsheets.

SOP No. 7

Recommended Standard Operations Procedure for Weighing by Single Substitution Using a Single-Pan Mechanical Balance, a Full Electronic Balance, or a Balance with Digital Indications and Built-In Weights

1.0 Introduction

1.1. Purpose

In the single substitution procedure a standard and an unknown weight are intercompared once to determine the difference in weights. Errors in any built-in weights or in the balance indications are eliminated by using the balance only as a comparator and by calibrating the balance indications over the range of use for the measurement with a sensitivity weight. This procedure is suitable for calibration when moderate accuracy is required and as a single substitution, does not eliminate errors due to drift. The procedure does not incorporate measurement control steps to ensure the validity of the standards and the measurement process; additional precautions must be taken.

1.2. Prerequisites

1.2.1. Verify that valid calibration certificates are available for the standards used in the test.

1.2.2. Verify that the standards to be used have sufficiently small standard uncertainties for the intended level of calibration. Primary standards should not be used at this level.

1.2.3. Verify that the balance that is used is in good operating condition with sufficiently small process standard deviation as verified by a valid control chart or preliminary experiments to ascertain its performance quality when a new balance is put into service.

1.2.4. Verify that the operator is experienced in precision weighing techniques and has had specific training in SOP 2, SOP 7, SOP 29, GMP 4, and GMP 10.

1.2.5. Verify that the laboratory facilities meet the following minimum conditions to meet the expected uncertainty possible with this procedure.

Table 1. Environmental conditions

Echelon	Temperature	Relative Humidity (%)
II	20 °C to 23 °C, a set point ± 2 °C, maximum change 1.0 °C/h	40 to 60 ± 10 / 4 h
III	18 °C to 27 °C, maximum change 2.0 °C/h	40 to 60 ± 20 / 4 h

2. Methodology

2.1. Scope, Precision, Accuracy

This method is applicable to all weighings utilizing a single-pan mechanical balance, a full electronic balance, or a balance that combines digital indications with the use of built-in weights (combination balance). The precision depends upon the sensitivity of the balance and the care exercised in making the required weighings. The accuracy achievable with this procedure depends on the accuracy of the calibration of the working standards and the precision of the intercomparison.

2.2. Summary

The balance is adjusted, if necessary, to obtain balance indications for all measurements that will be within the range of the optical scale or digital indications of the balance without changing the dial settings for the built-in weights, if present. The standard and the test weight are each weighed. A small, calibrated weight, called a sensitivity weight, is added to the test weight and these are weighed

The single substitution procedure is the same for all of the balances mentioned above, but the adjustment of the balance to prepare for the intercomparison and the selection of the sensitivity weight differ slightly depending upon the balance used. When steps specific to a particular balance are required, they are given in subsections of the procedure identified by a, b, and c along with the balance type.

2.3. Apparatus/Equipment Required

2.3.1. Precision balance with sufficient capacity and sensitivity for the calibrations planned.

2.3.2. Calibrated working standard and sensitivity weights with recent calibration values that are traceable to NIST.

2.3.3. Calibrated small standard weights with recent calibration values that are traceable to NIST to be used as tare weights.

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

2.3.5. Forceps to handle the weights, or gloves to be worn if the weights are moved by hand.

2.3.6. Stop watch or other timing device to observe the time of each measurement.

2.3.7. Calibrated barometer accurate to ± 66.5 Pa (0.5 mm Hg) with recent calibration values that are traceable to NIST to determine air pressure.

2.3.8. Calibrated thermometer accurate to ± 0.10° C with recent calibration values that are traceable to NIST to determine air temperature.

2.3.9. Calibrated hygrometer accurate to ± 10 % with recent calibration values that are traceable to NIST to determine relative humidity.[1]

2.4. Symbols

Table 2. Symbols used in this procedure

Symbol	Description
S	standard weight
X	weight calibrated
t	small calibrated tare weight, A subscript *s* or *x* is used to indicate the larger weight 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	the nominal value of a specific weight. Subscripts *s*, *x*, are used to identify the weight.
C	the 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

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[1] 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 accuracies specified are recommended for high precision calibration. Less accurate equipment can be used with only a small degradation in the overall accuracy of the measurement.

2.5. Procedure

2.5.1. Preliminary Procedure

2.5.1.1. Place the test weight and standards in the balance chamber or near the balance overnight to permit the weights and the balance to attain thermal equilibrium.

2.5.1.2. Conduct preliminary measurements to obtain an approximate value for the difference between the standard and the unknown, to determine where the readings occur on the balance, to determine if tare weights are required, to determine the sensitivity weight that must be used, and to determine the time interval required for the balance indication to stabilize.

Tare weights are rarely needed for high precision mass standards. If 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 evaluated in the process of determining 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 GMP 14, Table 1). Select t_s and t_x such that the difference in mass between $S + t_s$ and $X + t_x$ is:

a. Single-pan mechanical balance - less than $\frac{1}{10}$ the range of the optical scale.

b. Full electronic balance - less than 0.05 % of the balance capacity.

c. Combination balance - less than $\frac{1}{10}$ the range of the digital indications.

A sensitivity weight must be used on equal-arm balances, and is normally used on single-pan mechanical and electronic balances, to ensure that the differences determined through the use of the optical scale or electronic range have valid accuracy and traceability. (e.g., The optical scale is *calibrated* each time the procedure is used through the use of a sensitivity weight). The uncertainty of the sensitivity weight does not need to be included in calculations of uncertainty since the uncertainty value is distributed across the range of use.

If a sensitivity weight will be used, select one that is (See GMP 14, Table 2):

a. Single-pan balance - between ¼ and ½ the range of the optical scale, and at least 4 times the mass difference between X and S.

b. Full electronic balance - at least 4 times the mass difference between X and S but not exceeding 1 % of the balance capacity.

c. Combination balance - between ¼ and ½ the range of the digital indications, and at least 4 times the mass difference between X and S.

2.5.1.3. Determine whether optional sequence A or B will be used. Optional sequence A uses the standard on the balance for the first observation and the unknown on the balance for the second and third observations; this is often called the "*SXX*" sequence. Optional sequence B starts with the unknown on the balance first and with the standard on the balance for the second and third observations; this is often called the "*XSS*" sequence.

2.5.1.4. Adjust the single pan balance or the combination balance so the first two readings of the single 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 single substitution. Once the balance has been adjusted to the desired position, 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.

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

2.5.2. Measurement Procedure, Optional Sequence A (*SXX*)

Table 3. 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

All observations should be recorded on suitable data sheets, such as those in the appendix. Record the laboratory ambient temperature, barometric pressure, and relative humidity.

2.5.1.1. Observation 1. Place the standard weight(s), S, along with t_s on the balance pan. If equipped with a pan arrestment mechanism, release the balance pan. When the pan is released, start the stop-watch and record observation O_1 once the balance indication has stabilized.

2.5.1.2. Observation 2. Remove weight(s) S and t_s and replace with test weight X and its tare weight, t_x. Release the pan, time the interval, and record observation O_2.

2.5.1.3. Observation 3. Add the sensitivity weight, sw, to the weights of observation 2. Release the pan, time the interval, and record observation O_3.

2.5.1.4. If repeated single substitutions are performed, the values between successive trials should not differ from one another by more than ± 2 sd of the balance. If this difference is exceeded, reject the data and take a new series of measurements that will so agree.

2.5.3. Measurement Procedure, Optional Sequence B (*XSS*)

Table 4. 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

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. No air buoyancy correction. Calculate the conventional mass correction, C_x, for the test weight as follows, according to the optional sequence used. In each case, the conventional mass corrections for the standard weight(s), C_s, the conventional mass of the tare weights, CM_{t_s} and CM_{t_x}, and the conventional mass of the sensitivity weight, CM_{sw}, are included. The symbols N_s and N_x refer to the nominal values of S and X, respectively. If no tare weights, and equal nominal values are used, those terms may all be deleted from the equations.

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3.1.1. Optional Sequence A (*SXX*)

$$C_x = C_s + CM_{t_s} - CM_{t_x} + (O_2 - O_1)\left[\frac{CM_{sw}}{(O_3 - O_2)}\right] + N_s - N_x$$

3.1.2. Optional Sequence B (*XSS*)

$$C_x = C_s + CM_{t_s} - CM_{t_x} + (O_1 - O_2)\left[\frac{CM_{sw}}{(O_3 - O_2)}\right] + N_s - N_x$$

3.2. Air Buoyancy Correction

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

3.2.2. Calculate the mass of the test weight, M_x, and its mass correction C_x 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 (*SXX*)

$$M_x = \frac{M_s\left(1 - \frac{\rho_a}{\rho_s}\right) + M_{t_s}\left(1 - \frac{\rho_a}{\rho_{t_s}}\right) - M_{t_x}\left(1 - \frac{\rho_a}{\rho_{t_x}}\right) + (O_2 - O_1)\left[\frac{M_{sw}\left(1 - \frac{\rho_a}{\rho_{sw}}\right)}{(O_3 - O_2)}\right]}{\left(1 - \frac{\rho_a}{\rho_x}\right)}$$

3.2.2.2. Optional Sequence B (*XSS*)

$$M_x = \frac{M_s\left(1 - \frac{\rho_a}{\rho_s}\right) + M_{t_s}\left(1 - \frac{\rho_a}{\rho_{t_s}}\right) - M_{t_x}\left(1 - \frac{\rho_a}{\rho_{t_x}}\right) + (O_1 - O_2)\left[\frac{M_{sw}\left(1 - \frac{\rho_a}{\rho_{sw}}\right)}{(O_3 - O_2)}\right]}{\left(1 - \frac{\rho_a}{\rho_x}\right)}$$

3.2.3. Calculate the mass correction C_x, as follows:

$$C_x = M_x - N_x$$

where N_x is the nominal value for *X*.

3.2.4. Calculate the conventional mass[2] of *X*, CM_x. It is recommended that the conventional mass be reported.

3.2.4.1. Conventional mass

$$CM_x = \frac{M_x\left(1 - \frac{\rho_n}{\rho_x}\right)}{\left(1 - \frac{\rho_n}{8.0}\right)}$$

3.2.5. If requested, the apparent mass versus the reference density of brass may be calculated. This value should only be used when calibrating mechanical balances that have been adjusted to this reference density.

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[2] 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: reference density 8.0 g/cm^3; reference temperature 20 °C; *normal* air density 0.0012 g/cm3. Conventional mass was formerly called "Apparent Mass versus 8.0 g/cm^3" in the United States. *See OIML IR 33 (1973, 1979), under revision.*

3.2.5.1. Apparent mass versus brass

$$\mathrm{AM}_{x\ \mathrm{vs\ brass}} = \frac{\mathrm{M}_x\left(1 - \frac{\rho_n}{\rho_x}\right)}{\left(1 - \frac{\rho_n}{8.3909}\right)}$$

4. Measurement Assurance

4.1. Duplicate the process with a suitable check standard (See GLP 1, SOP 9, SOP 30, and Sec. 7.4)

4.2. Plot the check standard value and verify that it is within established limits; a t-test may be incorporated to check observed value against accepted value.

4.3. The mean of the check standard is used to evaluate bias and drift over time.

4.4. Check standard observations are used to calculate the standard deviation of the measurement process, s_p.

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 of two (k=2), to give us an approximate 95 % 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 report. 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.

5.2. The value for s_p is obtained from the control chart data for check standards using single substitution measurements. (See SOP No. 9.)

5.3. Other standard uncertainties usually included at this calibration level include uncertainties associated with calculation of air density and standard uncertainties associated with the density of the standards used.

5.4. Evaluation of compliance. The expanded uncertainty, *U*, must be ≤ 1/3 of the tolerance applicable as per ASTM E 617-97 and OIML R 111 if compliance statements are used

6. Report

Report results as described in SOP No. 1, Preparation of Calibration/Test Reports.

Appendix
Single Substitution Data Sheet
(Optional Sequence A)
SXX

Laboratory data and conditions:

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

Mass standard(s) data:

ID	Nominal	Mass Correction	Unc: From cal. report	Unc: k factor	Density g/cm^3
S					
X					
sw					
t_s					
t_x					

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:

Measurement #	Weights	Balance Observations, Units __________
Time:		
1 (O_1)	$S + t_s$	
2 (O_2)	$X + t_x$	
3 (O_3)	$X + t_x + sw$	
Time:		

Measurement Assurance (Duplication of the Process):

Measurement #	Weights	Balance Observations, Units __________
Time:		
1 (O_1)	$S + t_s$	
2 (O_2)	$S_c + t_{Sc}$	
3 (O_3)	$S_c + t_{Sc} + sw$	
Time:		

Note: dotted line represents decimal point.

Appendix
Single Substitution Data Sheet
(Optional Sequence B)
XSS

Laboratory data and conditions:

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

Mass standard(s) data:

ID	Nominal	Mass Correction	Unc: From cal. report	Unc: k factor	Density g/cm^3
X					
S					
sw					
t_s					
t_x					

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:

Measurement #	Weights	Balance Observations, Units _________
Time:		
1 (O_1)	$X + t_x$	
2 (O_2)	$S + t_s$	
3 (O_3)	$S + t_S + sw$	
Time:		

Measurement Assurance (Duplication of the Process):

Measurement #	Weights	Balance Observations, Units _________
Time:		
1 (O_1)	$S + t_s$	
2 (O_2)	$S_c + t_{Sc}$	
3 (O_3)	$S_c + t_{Sc} + sw$	
Time:		

Note: dotted line represents decimal point.

Example: Without Buoyancy Corrections
Single Substitution Data Sheet
(Optional Sequence A)
SXX

Laboratory data and conditions:

Operator	HO		
Date	8/27/86	Temperature	22.6 °C
Balance	H 20	Pressure	751.7 mm Hg
Load	50 g	Relative Humidity	50 %
Standard deviation of the process, from control chart, s_p			0.018 mg

Mass standard(s) data:

ID	Nominal	Mass Correction	Unc: From cal. report	Unc: k factor	Density g/cm^3
S	50 g	0.255 mg	0.033 mg	3	8.00
X	50 g				7.95
sw	50 mg	-0.084 mg	0.000 85 mg	2	8.5
t_s					
t_x					
S_c	50 g	0.315 mg	0.045 mg	2	8.00

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:

Measurement #	Weights	Balance Observations, Units mg
Time:	3:40 PM	
1 (O_1)	$S + t_s$	12 ¦ 62
2 (O_2)	$X + t_x$	12 ¦ 51
3 (O_3)	$X + t_x + sw$	62 ¦ 37
Time:	3:45 PM	

Measurement Assurance (Duplication of the Process):

Measurement #	Weights	Balance Observations, Units mg
Time:	3:50 PM	
1 (O_1)	$S + t_s$	12 ¦ 67
2 (O_2)	$S_c + t_{Sc}$	12 ¦ 73
3 (O_3)	$S_c + t_{Sc} + sw$	62 ¦ 60
Time:	3:55 PM	

Note: dotted line represents decimal point.

Calculation of Conventional Mass

Use equation 3.1.1 for optional sequence A (*SXX*) without buoyancy corrections[3]:

Since no tare weights were used and equal nominal values were used, the equation may be simplifies as follows:

$$C_x = C_s + (O_2 - O_1)\left[\frac{CM_{sw}}{(O_3 - O_2)}\right]$$

$$\mathrm{C_x} = 0.255\,\mathrm{mg} + (12.51 - 12.62)\left[\frac{49.916\,\mathrm{mg}}{(62.37 - 12.51)}\right]$$

$$C_x = 0.255\ \mathrm{mg} + (-0.110\ 124)\ \mathrm{mg}$$

$$C_x = 0.144\ 876\ \mathrm{mg}$$

Calculation of Uncertainty

Calculate the uncertainty for the calibration:

$$\mathrm{U} = \mathrm{u_c} * 2$$

$$u_c = \sqrt{u_s^2 + s_p^2 + u_o^2}$$

The uncertainty for the standard from the calibration report (or data sheet) must be divided by the k factor to determine the u_s. Refer to SOP 29 for the use of multiple standards. An additional uncertainty for not performing the air buoyancy correction can be determined using the magnitude of the air buoyancy correction from SOP 2.

$$u_c = \sqrt{(0.011)^2 + (0.018)^2 + (0.0010)^2}$$

$$u_c = 0.021\ 330\ 7\ \mathrm{mg}$$

$$U = 0.021\ 330\ 7 * 2 = 0.042\ 661\ 5\ \mathrm{mg}$$

Uncertainty Statement

The uncertainty reported is the root sum square of the standard uncertainty of the standard, the standard deviation of the process, and an uncorrected systematic error for lack of 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 are considered to meet magnetism specifications unless measurement aberrations are noted), balance eccentricity and

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[3] Keep in mind that these equations may be truncated for the purpose of this example and minor differences may be seen in the ending decimal places due to the use of calculators or spreadsheets.

linearity (these factors are considered as a part of the measurement process when obtaining the standard deviation of the process).

Compliance Evaluation

You may need to evaluate the conventional mass correction and its uncertainty to determine if a weight is or is not within specified tolerances. The magnitude of the expanded uncertainty must be less than 1/3 of the tolerance to be able to perform that evaluation, according to ASTM E 617-97 and OIML R111 documentary standards.

Load = 50 g

ASTM E 617		OIML R111	
Class	Tolerance (mg)	Class	Tolerance (mg)
1	0.12	E_2	0.10
2	0.25	F_1	0.30

If we look at three times the calculated expanded uncertainty: 0.043 mg x 3 = 0.129 mg, we observe that the uncertainty complies with the 1/3 rule for ASTM Class 2, and OIML Class F_1 but not ASTM Class 1 or OIML Class E_2.

Next, the weight value is considered to be within tolerance when the absolute value of its error plus its uncertainty, do not exceed the tolerance established for the particular class of weight.

Value and uncertainty: *0.145* mg ± *0.043* mg.
0.145 mg + 0.043 mg = 0.188 mg (upper limit of the value, or error bar if graphed)
0.145 mg – 0.043 mg = 0.102 mg (lower limit of the value, or error bar if graphed)

We can see that the correction of 0.145 is within these limits: $0.102 \leq C_x \leq 0.188$, therefore, the value also complies with ASTM Class 2 and OIML Class F_1, and a compliance statement may be included on the calibration report.

Reporting

The conventional mass correction and uncertainty are reported as follows:

C_x = *0.145* mg ± *0.043* mg

SOP No. 8

Recommended Standard Operations Procedure
for
Medium Accuracy Calibration of Mass Standards
by
Modified Substitution

1. Introduction

1.1. This SOP describes procedures to be followed for determining whether or not mass standards are within the tolerances specified for a particular class of standards (e.g., NIST Class F, ASTM Class 5, 6, 7 or OIML Classes M_1, M_2, and M_3) where the uncertainty is much smaller than the tolerance application. The described procedures permit the metrologist to report that the weights under test were compared against a reference standard with the results reported on the laboratory report form. The comparison is important because the built-in weights of a balance do not represent laboratory standards unless they have been formally calibrated. If a State law or other regulation requires that field weights be compared against the State (or reference) standards, this procedure can be used to fulfill this requirement. It is suitable for calibration when moderate accuracy is required, and does not eliminate errors due to drift. The procedure does not incorporate measurement control steps to ensure the validity of the standards and the measurement process; additional precautions must be taken. The expanded uncertainty with this procedure must be ≤ 1/3 of the tolerance per ASTM and OIML standards. If uncertainty to tolerance ratios are greater than recommended, SOP 7 (single substitution) or SOP 4 (double substitution) is preferred.

Note: If you use SOP 8, you are most likely using working standards that are equivalent to your customer's weights. If this is the case, the working standards should be at a higher level of calibration than the weights being calibrated with them. Therefore, you will need a better balance and procedure to calibrate your working standards than the one used to calibrate your customer's weights.

1.2. Prerequisites

1.2.1. Verify that valid calibration values are available for the standards used in the test.

1.2.2. Verify that the working standards to be used have sufficiently small standard uncertainties for the intended level of calibration. Primary standards should not be used at this level.

1.2.3. Verify that the balance that used is in good operating condition with sufficiently small process standard deviation as verified by a valid control chart or preliminary experiments to ascertain the performance quality when a new balance is put into service.

1.2.4. Verify that the operator is experienced in precision weighing techniques and has had specific training in SOP 7, SOP 8, SOP 29, and GMP 10.

1.2.5. Verify that the laboratory facilities meet the following minimum conditions to meet the expected uncertainty possible with this procedure.

Table 1. **Environmental conditions**

Echelon	Temperature	Relative Humidity (%)
III	18 °C to 27 °C, maximum change 2.0 °C/h	40 to 60 ± 20 / 4 h

2. Methodology

2.1. Scope, Precision, Accuracy

This method is applicable to all lower echelon mass calibration (tolerance testing) provided that the uncertainty requirements can be met. The achievable precision using this procedure is appropriate, provided the expanded uncertainty of the measurement is no more than one-third of the permissible tolerance of the mass standard tested. The accuracy achievable with this procedure depends on the accuracy of the calibration of the working standards and the precision of the intercomparison.

2.2. Summary

The mass to be tested is compared with a calibrated working standard by a modified substitution procedure. The comparison may be made using a single-pan, an equal-arm, or a fully-electronic balance. The reference standard is placed on the balance to obtain a convenient reference point and a sensitivity test is conducted. The error (departure from nominal value) of the weight tested is determined by comparing its reading to the reading obtained for the reference standard. A weight is considered to be within tolerance when the absolute value of its error plus its uncertainty does not exceed the tolerance established for the particular class of weight.

2.3. Apparatus/Equipment

2.3.1. Single-pan, equal arm, or full-electronic balance with sufficient capacity for the load tested and with readability equal to or less than one-tenth of the acceptable tolerance tested.

2.3.2. Mass standards calibrated with an expanded uncertainty of one-tenth or less than the tolerance tested. The calibration values must be traceable to NIST.

2.3.3. Calibrated sensitivity weights.

2.3.4. Uncalibrated counterweights, *T*, of approximately the same mass as the standard weights (for option C).

2.4. Procedure - Option A

Use of Single-Pan Balance

2.4.1. Select a reference standard of the same nominal value as the weight under test. Place the standard on the balance pan. Adjust the optical scale reading (See GMP No. 4) to approximately midscale using uncalibrated tare weights and the balance's coarse and fine Zero controls. This setting must not be altered during a measurement sequence. Record the reading as O_1.

2.4.2. Add a sensitivity weight equal to approximately one-quarter full scale reading and record reading as O_2.

2.4.3. Calculate the value of a scale division using the equation in 3.2. If it is within ± 2 % of nominal value (usual case) the nominal value of a division can be used for tolerance testing.

2.4.4. Remove the sensitivity weight and adjust the optical scale to account for corrected value of standard used.

Example: Suppose that the nominal range of the optical scale is 100 mg and that the reference standard has a correction of -2.5 mg. The optical scale is adjusted to read 47.5 mg when the standard is on the pan. Under this condition, the reading 50.0 mg represents the nominal mass of the reference standard.

2.4.5. Remove the Standard.

2.4.6. Place the weight to be tested on the balance pan, read the optical scale and record reading as X_n. The error in the weight is the amount by which the indication deviates from the mid-scale reading. If the weight indication is more than the mid-scale value, the weight is heavy by the indicated difference; if the indication is less than the mid-scale value, the weight is light.

2.4.7. After several weights have been tested (no more than 10), put the standard on the balance pan and record the reading. The difference between this indication and the previous one for the standard indicates a balance drift. This drift will normally be very small. If the drift exceeds 10 % of the tolerance applicable to the weights under test or affects a measurement result to the extent that a weight may be out of tolerance, the measurement should be repeated and more frequent checks of the standard should be made or a more appropriate procedure should be used.

2.4.8. Readjust the optical scale at any time that a significant difference is observed when rechecking a standard.

2.4.9. Calculate the mass correction for the unknown weights using the appropriate equation in Section 3.

2.5. Procedure - Option A_1

Use of Single-Pan Balance

2.5.1. Select a reference standard of the same nominal value as the weight under test. Place the standard on the balance pan. Adjust the optical scale reading (See GMP No. 4) to midscale using uncalibrated tare weights and the balance's coarse and fine Zero controls. This setting must not be altered during a measurement sequence. Record the reading as O_1.

2.5.2. Add a sensitivity weight equal to approximately one-quarter full scale reading and record reading as O_2.

2.5.3. Calculate the value of a scale division using the equation in 3.2. If the sensitivity is within ± 2 % of nominal value (usual case) of the scale division, the nominal value of a division may be used.

2.5.4. Remove the sensitivity weight and re-adjust the optical scale to obtain a midscale indication, if the indication has changed from that set in 2.5.1.

2.5.5. Remove the Standard.

2.5.6. Place the weight to be tested on the balance pan, read the optical scale and record the indication as X_n. The error in the weight is the amount by which the indication deviates from the mid-scale reading. If the weight indication is more than the mid-scale value, the weight is heavier than the standard by the indicated difference; if the indication is less than the mid-scale value, the weight is lighter than the standard.

2.5.7. After several weights have been tested (no more than 10 without rechecking the standard) put the standard on the balance pan and record the reading. The difference between this indication and the previous one for the standard indicates a balance drift. This drift will normally be very small. If the drift exceeds 10 % of the tolerance applicable to the weights under test or affects a measurement result to the extent that a weight may be out of tolerance, the measurement should be repeated and more frequent checks of the standard should be made or a more appropriate procedure should be used.

2.5.8. Readjust the optical scale at any time that a significant difference is observed when rechecking a standard.

2.5.9. Calculate the correction of the unknown using the equation

$$C_x = C_s + (X_n - O_1).$$

2.6. Procedure - Option B

Use of Full Electronic Balance

2.6.1. Select a reference standard of the same nominal value as the weight under test. Place the standard on the pan. Zero the balance and record reading as O_1.

2.6.2. Add a calibrated sensitivity weight (sw ≥ 2 times the tolerance but not exceeding 1 % of the balance capacity) and record the reading as O_2. Verify whether the nominal scale division is within ± 2 % of nominal value of the scale division using the equation in 3.2. If so, the nominal value of the scale division may be used.

2.6.3. Remove sensitivity weight and zero the balance so weight differences, *d*, can be read directly from the balance indications.

2.6.4. Remove all weights from the balance pan.

2.6.5. Place the weight to be tested on the balance pan. Record the reading as X_n.

2.6.6. After several weights have been tested (no more than 10 without rechecking the standard) recheck the zero as in 2.5.3 and record the reading. The difference between this indication and the previous one for the standard indicates a balance drift. This drift will normally be small. If the drift exceeds 10 % of the tolerance applicable to the weights under test or affects a measurement result to the extent that a weight may be out of tolerance, the measurement should be repeated and more frequent checks of the standard should be made or a more appropriate procedure should be used.

2.6.7. Readjust the zero at any time that a significant difference is observed when rechecking a standard.

2.6.8. Calculate the mass correction for each weight using the equation

$$C_x = C_s + (X_n - O_1) = C_s + X_n \text{ (when } O_1 \text{ is zeroed)}$$

2.7. Procedure - Option C

Use of Equal Arm Balance

2.7.1. Select a reference standard of the same nominal value as the weight under test. Place the standard on the left balance pan together with small, calibrated weights equal to the correction required for the standard, provided it is light. If (and only if) the standard is heavy, do nothing further at this point but follow instructions in 2.6.4. Add sufficient counterweights to the right pan to obtain a sum of turning points of approximately twice midscale value. If necessary, number the graduated scale such that adding weights to the left pan will increase the balance reading. Record the sum of the turning points as 0_1.

2.7.2. Add an appropriate calibrated sensitivity weight to the left pan and record the sum of the turning points as 0_2. Calculate the sensitivity,

$$sensitivity = \frac{CM_{sw}}{\left(O_2 - O_1\right)}$$

where CM_{sw} is the conventional mass of the sensitivity weight.

2.7.3. Remove all weights from the left pan.

2.7.4. Place weight to be tested on the left pan. If the standard used in 2.6.1 was heavy, add small correction weights to the left pan, equivalent to the correction required for the standard. Add small, calibrated tare weights as required to left or right pan to obtain an approximate balance and record the sum of the turning points as X_n.

2.7.5. Calculate the mass correction of the weight tested as follows.

2.7.5.1. If added tare weights are placed on the left pan (t_x).

$$C_x = (X_n - O_1)\left[\frac{CM_{sw}}{(O_2 - O_1)}\right] - CM_{t_x}$$

2.7.5.2. If added tare weights are placed on the right pan (t_s)

$$C_x = (X_n - O_1)\left[\frac{CM_{sw}}{(O_2 - O_1)}\right] + CM_{t_s}$$

2.7.6. After several weights have been tested (no more than 10 without rechecking the standard), recheck the turning point 0_1, as described in 2.6.1. Only a small difference should be observed. If the difference exceeds 2 % of the sum of the turning points in O_1, the measurement should be repeated and more frequent checks of the standard should be made or a more appropriate procedure should be used.

2.8. Tolerance Evaluation

2.8.1. Compare the correction plus the expanded uncertainty of the weight tested with the tolerance for the class of weights to which it belongs. If the absolute value of the correction plus the expanded uncertainty is numerically smaller than the tolerance, the weight is considered to be within tolerance. If the correction is larger than permissible, the weight is considered to be outside the tolerance and appropriate action should be taken. It is recommended that weights whose absolute value of the correction exceeds 75 % of the tolerance limit be adjusted.

Table 2. Example of Weighing Sequence

Measurement No.	Weights on Pan	Observation
1	S	O_1
2	$S + sw$	O_2
3	S	O_3
4	X_1	O_4
5	X_2	O_5
6	X_3	O_6
7	X_4	O_7
8	X_5	O_8
9	X_6	O_9
10	X_7	O_{10}
11	X_8	O_{11}
12	X_9	O_{12}
13	S_c	O_{13}
14	S	O_{14}

3. Calculations

3.1. Air buoyancy corrections are generally *not* made with the modified substitution. Calculate the conventional mass correction, C_x, for the test weight as follows, according to the optional sequence used. In each case, the conventional mass corrections for the standard weight(s) are included.

Table 3. Symbols used

Symbol	Description
CM_i	conventional mass of weight *i*
N_s	nominal value of *S*
N_x	nominal value of *X*

3.2. Evaluate the sensitivity of the balance:

$$sensitivity = \frac{CM_{sw}}{(O_2 - O_1)}$$

If the sensitivity error is less than 2 % of the nominal value of a division on the optical scale or the electronic range of operation, proceed with the modified substitution. If the sensitivity error is greater, SOP 7, Single Substitution may be acceptable.

3.3. Calculate the mass correction of each unknown weight as follows if the correction for the standard IS NOT used in setting a reference point on the balance:

$$C_x = C_s + d$$

$$C_x = C_s + (X_n - O_1)$$

Note: If an electronic balance is used and zeroed with the standard on the balance, O_1 is "0" and d becomes the X_n balance reading.

3.4. Calculate the mass correction of each unknown weight as follows if the correction for the standard IS used in setting a nominal reference point on the balance:

$$C_x = (X_{\text{balance reading}} - N_{\text{nominal reference point}})$$

Note: In this case the standard and its correction are used to artificially *set* a perfect nominal reference point for use in comparing the unknown weights.

3.5. If tare weights and unequal nominal values are used, use the following equation for modifying section 3.3:

$$C_x = C_s + CM_{ts} - CM_{tx} + (X_n - O_1) + N_s - N_x$$

4. Measurement Assurance

4.1. Duplicate the process with a suitable check standard (See GLP 1, SOP 9, SOP 30, and Sec. 7.4)

4.2. Plot the check standard value and verify that it is within established limits; a t-test may be incorporated to check observed value against accepted value.

4.3. The mean of the check standard is used to evaluate bias and drift over time.

4.4. Check standard observations are used to calculate the standard deviation of the measurement process, s_p.

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 of two (k=2), to give us an approximate 95 % 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 report. 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.

5.2. Standard deviation of the measurement process from control chart performance (See SOP No. 9.) The value for s_p is obtained from the control chart data for check standards using modified substitution measurements.

5.3. Other standard uncertainties usually included at this calibration level include uncertainties associated with lack of performing buoyancy corrections and can be determined using the equation given in SOP 2 for the magnitude of the air buoyancy correction. Buoyancy corrections are not generally needed at the uncertainty level this procedure is designed for.

5.4. The expanded uncertainty, *U*, must be ≤ 1/3 of the tolerance applicable as per ASTM E617-97 and OIML R111.

6. Report

Report results as described in SOP No. 1, Preparation of Calibration/Test Reports.

Appendix
Modified Substitution Data Sheet

Laboratory data and conditions:

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

Mass standard(s) data:

ID	Nominal	Mass Correction*	Expanded Unc: From cal. Report	Unc: k factor	Density g/cm^3
S					
X					
sw					
t_x					
t_s					

*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		
2 (O_2)	$S + sw$		
		Error < 2 % of optical scale or electronic range? Yes No	
3 (O_3)	S		
4 (O_4)	X_1		
5 (O_5)	X_2		
6 (O_6)	X_3		
7 (O_7)	S_c		
8 (O_8)	S		
Time:		Drift < 1/10 Tol. ?: Yes No	

Up to 10 unknown weights may be checked with this procedure if the drift is less than 1/10 of the tolerance.

Appendix

Modified Substitution Data Sheet

Laboratory data and conditions:

Operator	GH		
Date	9/30/96	Temperature	22.5 °C
Balance	PM 2000 MC (2300 g)	Pressure	747.5 mmHg
Load	5 lb	Relative Humidity	45 %
Standard deviation of the process, from control chart, s_p			0.85 mg

Mass standard(s) data:

ID	Nominal	Mass Correction	Expanded Unc: From cal. Report	Unc: k factor	Density g/cm^3
S	5 lb	7.5 mg	0.50 mg	3	7.85
X	5 lb				7.85
sw	5 g	0.000 002 g			
t_x	None				
t_s	None				
S_c	5 lb	2.4 mg	0.73 mg	2	7.95

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

Observations:

Observation No.	Weights	Balance Observations, Units 0.001 g
Time: 11:00 am		
1 (O_1)	S	0000
2 (O_2)	$S + sw$	4999
Error < 2 % of optical scale or electronic range? **Yes** No		
3 (O_3)	S	0000
4 (O_4)	X_1	0205
5 (O_5)	X_2	0104
6 (O_6)	X_3	- 0089
7 (O_7)	S_c	- 0005
8 (O_8)	S	0003
Time: 11:20 am	Drift < 1/10 Tol. ?: **Yes** No	

Up to 10 unknown weights may be checked with this procedure if the drift is less than 1/10 of the tolerance.

Sensitivity guidelines indicate a sensitivity weight, greater than or equal to 2 times the tolerance (460 mg) but not exceeding 1 % of the balance capacity (23 g). For a 5 lb load, the Class F tolerance is 230 mg so a 5 g weight was selected.

A 2 % sensitivity error in a 5 gram range would allow readings between 4.900 g and 5.100 g in the sensitivity test. Calculate the sensitivity:

$$sensitivity = \frac{5.000\,002\ g}{4.999\ \text{div}} = 1.000\,200\,4\ \text{g/div}$$

which deviates less than 2 % of the nominal value of a division.

The drift observed was 3 mg and is less than 1/10 of the tolerance and 23 mg could be allowed, so the error for each nominal weight may be calculated as follows.

$$\text{C}_{\text{x}_1} = 7.5\ \text{mg} + (\ 205\ \text{mg - 0}\ ) = 212.5\ \text{mg}$$

$$\text{C}_{\text{x}_2} = 7.5\ \text{mg} + (\ 104\ \text{mg - 0}\ ) = 111.5\ \text{mg}$$

$$\text{C}_{\text{x}_3} = 7.5\ \text{mg} + (\ \text{-}\ 89\ \text{mg - 0}\ ) = \text{-}\ 81.5\ \text{mg}$$

$$\text{C}_{\text{Sc}} = 7.5\ \text{mg} + (\ \text{-}5\ \text{mg - 0}) = 2.5\ \text{mg}$$

Calculate the uncertainty for the calibration:

$U = u_c * 2$

$$u_c = \sqrt{u_s^{\,2} + s_p^{\,2} + u_o^{\,2}}$$

The uncertainty for the standard must be divided by the k factor for the standard and the tare weight to determine each u_s. The additional uncertainty for not performing the air buoyancy correction can be determined using the magnitude of the air buoyancy correction from SOP 2. Since the working standard was previously calibrated with buoyancy corrections and is the same density as the unknown weights, the uncertainty for the buoyancy correction drops out of the equation.

$$u_c = \sqrt{(\ 0.167\ )^2 + (\ 0.85\ )^2}$$

u_c = 0.866 19 mg

U = 0.866 19 * 2 = 1.732 38 mg

The expanded uncertainty is less than 1/3 of the tolerance (76 mg) so the unknown weights can either be reported as “within tolerance” or the values and uncertainties can be reported. The value plus the uncertainty for the first unknown X_1 is within 25 % of the Class F tolerance, therefore it is desirable to adjust the weight closer to nominal value, although based on the tolerances and uncertainties, and it can be claimed as “within tolerance.”

SOP No. 9

Recommended Standard Operating Procedure
for
Control Charts for Calibration of Mass Standards

1. Introduction

1.1. This SOP describes procedures for the development of control charts and their use for demonstrating attainment of statistical control of a mass calibration process.

1.2. Prerequisites

The use of this SOP requires that appropriate apparatus, methodology, and standards are available, and that the laboratory thoroughly understands the basic principles of the measurement process used and has had sufficient experience to perform the necessary operations required for the measurements of concern.

2. Summary

An appropriate check standard (or control standard) is incorporated into the measurement process and weighed at established intervals, the results are plotted on an $\bar{x}$ (X-bar) chart. The abscissa (x) represents the sequence of measurements and the ordinate (y) the measured values. A central line is drawn, indicating the mean ($\bar{x}$) of the measured values and control limits are indicated within which the results of measurements are expected to be randomly distributed, based on statistical considerations. The system is considered to be in statistical control when the individual values are within the designated limits. The system is considered to be out of control if an excessive number of values are present outside established limits, unusual trends are observed, or if the mean exceeds the control limits. The statistical information on which the control limits are based can be used to calculate confidence limits for measurements made while the system is demonstrated to be stable and in a state of statistical control.

3. Procedure

3.1. Definition of Monitored System

The monitored system is considered to consist of the balance, the standard operating procedure, the laboratory environment, the check standard or control standard, the operator, and any other sources that contribute to the variance or bias of the measurement data. Any of the above that can be considered to be constant or negligible contributors to the variance may be consolidated and monitored by a single control chart. Any that cannot be so considered (for example: different standard, different balance, different SOP) may require separate control charts.

The variability of balance precision that is load dependent must be considered. For many balances, precision is a function of load, and a distinct control chart is required (in principle) for every load tested. This is not always feasible, except in the case of SOP 5 or 28 where check standards are incorporated into the measurement process. Hence, control charts used for measurement assurance and evaluation of measurement uncertainty are generally satisfactory if developed using data from check standards at two or three intervals for each balance appropriately spaced within the range of balance use, or at least with one check standard for each decade. On balances where few nominal values (loads) are tested, a control chart should be established for each load.

3.2. Selection, Care, and Calibration of Check Standards

3.2.1. A check standard used in high precision calibration measurement must be stable and normally be comparable to the primary standard or to the typical calibration work, depending on what is being monitored. For lower order calibrations, the check standard should simulate the laboratory's primary standards to the extent feasible. It should be calibrated with an expanded uncertainty equal to or better than the precision of the process being monitored. All check standards should be cared for in the same way as primary standards to prevent their damage or deterioration. Lower order check standards should be recalibrated at regular intervals according to Good Measurement Practice (GMP) 11 on Setting and Adjusting Calibration Intervals.

Table 1. Recommended check standards for typical test situations

Balance	Range of Measurement	Check Standard(s)
Echelon III (Class F) SOP 7, 8	5000 lb to 0.001 lb	2 to 3 values per balance OR 1 chart per load
Echelon II SOP 3, 4, 6, 7	5000 lb to 0.001 lb and 1000 kg to 1 mg	2 to 3 values per balance OR 1 check standard per decade
SOP 5	typically 1 kg to 1 mg	each nominal value incorporates a check standard
SOP 28	typically 1 kg to 1 mg	1 check standard per decade (e.g., 1 kg, 100 g, 10 g, 1 g, 100 mg, 10 mg, 1 mg)

3.3. Establishing Control Chart Parameters

3.3.1. The control chart parameters consist of the central line, the best estimate of the mean of measurements of the check standard, and control (or “action”) and warning limits that represent probabilistic limits for the distribution of results around the central line. These parameters are evaluated on the basis of a reasonable number of initial measurements and updated as additional measurement data are accumulated.

3.3.2. Make at least seven (minimum number) and preferably 12 or more, independent measurements of the check standard under the same conditions that will be used to make routine measurements. No two measurements should be made on the same day. This is necessary to estimate the long-term standard deviation to the extent feasible. To make statistically valid decisions or calculate uncertainties based on this data, 25 to 30 points are necessary.

Calculate the mean, $\bar{x}$ and the estimate of the standard deviation, s in the conventional manner.

Establish the control chart parameters as follows:

Central Line = $\bar{x}$
Upper Control/Action Limit = $\bar{x} + 3s$
Upper Warning Limit = $\bar{x} + 2s$
Lower Warning Limit = $\bar{x} - 2s$
Lower Control/Action Limit = $\bar{x} - 3s$

Control chart parameters for Echelon III (Class F or other) may be completed as follows to track practical limits:

Central Line = $\bar{x}$
Upper Control/Action Limit = $\bar{x}$ *+ 1/4 tolerance*
Upper Warning Limit = $\bar{x}$ *+ 1/10 tolerance*
Lower Warning Limit = $\bar{x}$ *- 1/10 tolerance*
Lower Control/Action Limit = $\bar{x}$ *- 1/4 tolerance*

3.3.3. Upgrading Control Chart Parameters

Upgrade control chart parameters when a significant amount of additional data is available or when the previously determined parameters are no longer pertinent due to changes in the system.

Note: Ordinarily, upgrading is merited when the amount of new data is equal to that already used to establish the parameters in use, or when at least seven additional data points have been recorded.

Calculate $\bar{x}$ and s for the new set of data and examine for significant differences from the former using the t-test and F-test, respectively. If the tests fail and results are significantly different, determine the reason for the difference, if possible, and decide whether corrective action is required. If data does not agree within statistical limits, establish new parameters using the most recent data and note the reasons for not using previous data. If no significant differences between the data sets are found, pool all data and calculate new control chart parameters based on all existing data.

3.4. Frequency of Measurement

The check standard should be measured and plotted with sufficient frequency to minimize the risk of loss of data during the period from last-known-in to first-known-out of control condition. It is good practice to measure the check standard at least once during each period when a set of test measurements is made. For critical calibrations or those of highest accuracy, it is desirable to alternate measurements of test items and check standards, but for real-time evaluation it is preferable to incorporate the check standard in the calibration design as in SOP 5 or SOP 28.

Whenever there has been a long period of inactivity, it is good practice to make a series of measurements of the check standard and to plot the results on a control chart to demonstrate attainment of statistical control prior to resuming measurements with that specific calibration system.

Control charts should be updated as close to real time as feasible to effectively monitor the measurement process to prevent the possible release of questionable data resulting in recall.

4. Use of Control Charts

4.1. Monitoring a Measurement Process

Use the following criteria to interpret control chart results.

4.1.1. If plotted points are stable and randomly distributed within the warning limits, decide that the system is in control.

4.1.2. If a plotted point is outside the warning limits but within the control limits, investigate the presence of calculation errors. If none were made, re-measure the check standard. The re-measured value must be within the warning limits to merit the decision of "in control". If the results are not within limits, consider the measurement process "out of control". Reject all data obtained since last "in-control" measurement and take corrective action (hence “action” limit). Accept no further data until the system is demonstrated to be in-control as indicated by at least two successive measurements of the check standard within the warning limits.

If a plotted point is outside the control limits and arithmetically correct, the system is considered to be out of control. Data are rejected, corrective actions must be taken and re-attainment of statistical control demonstrated, as above, before data may be accepted.

4.2. Transfer of Measurement Statistics

4.2.1. Absence of a significant difference between the central line and the accepted value for the check standard may be considered as evidence of insignificant bias at the level of confidence of the statistical test used. This conclusion is valid, as long as the system remains in control. On occasion, small differences (less than 1 s) from unknown sources will be obvious over time and the value observed for the bias should be incorporated into the uncertainty per SOP 29.

4.2.2. The estimate of the standard deviation of the process, s_p, used to establish the control limits may be used to calculate confidence intervals for all pertinent measurements made while the system is in control. However, see SOP 29 for calculation of measurement uncertainty using the process variability, s_p. The value of the test weight is said to be within the limits

$$\overline{y} \pm U$$

where $\overline{y}$ represents the mean of the measurements on the test weight and $U = k * \sqrt{u_S^2 + s_P^2 + u_O^2}$, with the value of k determined by the confidence level required for the interval.

Note:. For $n \geq 30, k \rightarrow z$.

SOP No. 29

Standard Operating Procedure
for the
Assignment of Uncertainty

1. Introduction

1.1. Purpose

Laboratories performing calibrations that meet ISO/IEC Guide 25, ISO/IEC 17025, or ANSI/NCSL Z 540-1-1994 must report uncertainties in conformance with the 1993 *ISO Guide to the Expression of Uncertainty in Measurement (*hereafter called the *GUM)*. This SOP provides instruction for the laboratory to meet this requirement.

1.2. Prerequisites

1.2.1. Calibration certificates with valid uncertainties must be available for all standards.

1.2.2. Statistical data regarding the calibration measurement process must be available; preferably from measurement control programs within the laboratory.

1.2.3. Knowledge of the technical basis for the measurement is critical for completeness in uncertainty evaluation. This can be obtained through brainstorming, experimentation, interlaboratory comparisons, cause and effect diagrams and the like. Flow charts at the end of this SOP show a number of common factors affecting measurements in the areas of mass, length, and volume.

2. Methodology

2.1. Scope, Precision, Accuracy

Each measurement made in a laboratory has a corresponding uncertainty assigned to the calibration value. The uncertainty is directly related to the measurement parameter (scope), range of the measurement, the equipment or measurement process being used (affecting precision), and the standards available with associated uncertainties.

2.2. Summary

This uncertainty analysis process follows the following steps:
1) the measurement process is clearly specified;
2) uncertainty sources are identified and characterized;
3) uncertainty sources are quantified;
4) uncertainty sources are converted to standard uncertainties;
5) the combined uncertainty is calculated;
6) the expanded uncertainty is calculated;
7) the expanded uncertainty is evaluated against appropriate tolerance or calibration limits; and
8) measurement results are reported.

Special methods for handling bias/errors are addressed as well.

3. The Process of Measurement Uncertainty Estimation

3.1. Step 1. Specify the process.

Clearly specify the measurement process in question, including the item being measured and the input quantities upon which it depends. This will usually require a quantitative expression related to the process. Where possible, you may reference an SOP or other method description along with the specific standards and measurement assurance process that is used to adequately complete this step.

3.2. Step 2. Identify and characterize uncertainty sources.

Identify all possible sources of uncertainty in a comprehensive list, characterizing them based on the evaluation method that will be used to quantify them (Type A, statistical methods or Type B, scientific judgement) and to categorize them based on their relatedness with something such as a flow chart (shown as Appendices), a cause and effect diagram, or an uncertainty budget table. Using the expression identified in 3.1 provides a good starting point. All of the parameters in this expression may have an uncertainty associated with them. When there are discrete steps in the measurement process, additional uncertainties may be associated with each.

What follows are the most common uncertainties associated with metrological measurements. Keep in mind that this list is exhaustive. Each item listed below is identified as a standard uncertainty u, when determined using Type B methods of evaluation and a standard uncertainty s, when determined with Type A methods of evaluation (statistical methods). Each standard uncertainty is further defined by an arbitrary subscript related to the source for ease in remembering that source.

3.2.1. Standard uncertainty from the measurement *process*, s_p, (Type A evaluation).

3.2.1.1. Standard deviation from a measurement assurance chart or control chart.

The value for s_p is obtained from the control chart limits and the current knowledge that the measurements are in a state of statistical control. This will have to be ascertained by measuring at least one check standard during the course of the current measurements.

3.2.1.2. Standard deviation from a series of measurements.

Measure a stable test object at least seven times, no two measurements of which may be made on the same day. Calculate the standard deviation in the conventional manner. The latter is the value of s_p, keeping in mind that it does not fully represent the measurement process under all typically encountered conditions.

Note: Repetitive measurements made on the same day estimate only the short-term standard deviation of the process.

3.2.2. Standard uncertainty for the *standards*, u_s (Type B evaluation).

3.2.2.1. When using standards calibrated by another laboratory.

The information for the standards comes from the calibration report, generally reported as an expanded uncertainty with its coverage factor (k). The expanded uncertainty is simply divided by k to obtain the combined uncertainty for the standard, u_c, which represents the u_s when used in your laboratory.

3.2.2.2. When using a standard calibrated in your laboratory (Type B evaluation).

If the standard was calibrated in your own laboratory, calculate the combined standard uncertainty, u_c, at k=1 and use that as the standard uncertainty for the standard, u_s.

3.2.2.3. When using more than one standard (Type B evaluation).

When more than one standard is used in a calibration, the standard uncertainty for each, u_{s1}, u_{s2}, u_{s3}, etc., is included in the RSS equation if the standards have had independent calibrations. When calibrations are performed at the same time, the standards may be dependent, so the standard uncertainties may be added ($u_{s1} + u_{s2}$) to determine a value to represent u_s. (This will be the case with two 1 kg standards that were calibrated at the same time using a weighing design and subsequently used together as standards (restraints) in a weighing design.)

3.2.3. Standard uncertainty due to *other* factors, u_o (Type B evaluation.)

These are factors related to the measurement equation, but distinct from the standard uncertainties associated with the process and the standards. These items are often much smaller in a well-controlled process than the standard uncertainties associated with the process and the standards. Examples are given in the flow charts.

The laboratory must carefully consider any other components of uncertainty that might contribute to the uncertainty of the measurement. In mass measurements, these might include effects from the magnitude of air buoyancy corrections as discussed in SOP 2, when these corrections are not made, or the uncertainty from the calculation of air density when buoyancy corrections are made (also discussed in SOP 2).

Additionally, the laboratory should include any other components that are not negligible, such as the uncertainty associated with the density of the standards, the density of the unknown test items, effects due to lack of thermal equilibrium during the test, or known and quantified effects due to magnetized mass standards. Each component that is considered should be included as an additional standard uncertainty u_{o1}, u_{o2}, u_{o3}, etc., and included in the RSS equation when data shows these factors to be significant. Note that components of uncertainty are not limited to those mentioned. Documentation of each component evaluated should be maintained to complete the documentation required by ISO/IEC 17025.

3.2.4. Standard uncertainty due to factors *unrelated* to the measurement process, u_u.

These are factors that may be related to characteristics of the items being testing or of the standard and are usually minimized in well-known and controlled measurement processes.

3.2.5. Special uncertainties from other sources (Type B evaluations). Includes bias or unidentified errors.

It is a general requirement of the GUM that corrections be applied for all recognized and significant systematic effects. Where a correction is applied based on a bias, an estimate of the associated uncertainty must then be included in the uncertainty analysis. Due to the various approaches present in the metrology system, several examples and possible approaches are presented in the section on calculating the combined or expanded uncertainties. At this stage, a determination must be made with regard to 1) identifying cause and 2) level of significance.

3.2.5.1. Identifying cause.

If the cause can be identified, it is usually corrected or applied to the measurement equation. In some cases, it is not possible to unarguably define the cause without exhaustive studies that provide little benefit. In those cases, the significance level must be evaluated.

3.2.5.2. Significance level.

When there is little to be gained from exhaustive studies on the measurement process to identify bias or potential errors, a test of significance may be conducted to determine alternative approaches for incorporating the bias into the uncertainty calculations.

In deciding whether a known bias can reasonably be included in the uncertainty, the following approach may be followed:

3.2.5.2.1. Estimate the combined uncertainty without considering the relevant bias.

3.2.5.2.2. Evaluate whether or not the bias is less than two times the combined uncertainty (i.e., $bias < 2\sqrt{u_s^2 + s_p^2 + u_o^2}$).

3.2.5.2.3. If the bias is less than twice the combined uncertainty, it may be included in the uncertainty using one of several approaches that must clearly be communicated in the report.

3.2.5.2.4. If the bias is larger than twice the combined uncertainty, the error must be investigated further prior to providing calibration data.

If the deviations show that a standard is out of control, it should not be used for calibration until corrective action has been taken and the value for the standard is verified as being within criteria limits.

$$criteria\ \mathrm{lim}it : \left| \bar{x}_{lab} - \mathrm{x}_{\mathrm{ref}} \right| < 2\, u_c$$

If these differences are smaller than the criteria limits, investigation and corrective action may be unrealistic. If the deviations are less than the surveillance limits shown above, and corrective action is not taken, the deviations may be included in the uncertainty statement following one of several options given in the following section. In ALL cases, the method used to incorporate bias must be clearly reported.

3.2.5.3. Adding the bias to the expanded uncertainty (e.g., used in PMAP software). In this case, the bias is simply added to the expanded

$$U + \text{bias} = (u_c * k) + \text{bias}$$

uncertainty and is reported as such.

3.2.5.4. Example when uncertainties for the laboratory data and the reference data are considered equivalent (e.g., laboratory data is compared to another laboratory's data).

In this case, a rectangular distribution is considered where the value might possibly be anywhere within the range shown for each laboratory data point. This method is referenced in section 4.6 of NIST Technical Note 1297. This approach may also be used in the case where a standard is predictably drifting with use over time. In this case, a mid-range value is chosen and u_d (uncertainty for *differences*) is calculated as follows:

$$u_d = \frac{\text{bias}}{2}\frac{1}{\sqrt{3}} \quad \text{or more simply: } 0.29\text{ d, where d is the bias}$$

3.2.5.5. Example when uncertainties for the laboratory data are considered secondary to a reference value (e.g., the difference between the laboratory data and NIST data). This method was originally published in 1994.

In this case, a reference value is given precedence over the laboratory data and a mid-range value is not chosen. The extreme value is more probable. In this case, the following equation may be used:

$$u_d = \frac{\text{bias}}{\sqrt{3}} \quad \text{or more simply : } 0.577\text{ d, where d is the bias}$$

3.3. Step 3. Quantify uncertainty estimates

All uncertainty estimates identified in the previous step must be quantified in units that represent the measured values. Type A methods of evaluation usually provide quantified estimates in the units of interest.

Type B methods of evaluation may be conducted with spreadsheets using the basic expression identified in the SOP or identified when the process was specified. Scenario testing can be done to determine the impact and quantify specific variables on the final measured quantity. The knowledge gained in this step often proves useful in identifying potential areas of improvement.

3.4. Step 4. Convert all factors to standard uncertainties

In those cases where the uncertainty factors were determined statistically (Type A methods), the standard deviation is used to represent the standard uncertainty. In other cases, estimates must be made to ensure that the quantified uncertainties represent "one-standard-deviation" values or a k=1 coverage level. The appropriate distribution factor must be used when converting values.

3.5. Step 5. Calculate the combined uncertainty

The combined standard uncertainty, u_c, includes the standard uncertainty reported for the standards used, u_s, the standard uncertainty of the measurement process, s_p, the standard uncertainty from other sources, u_o, which includes all other factors the laboratory considers significant, the standard uncertainty due to factors related to the measured item but unrelated to the measurement process, $u_{u,}$ and finally, the standard uncertainty due to bias or differences, $u_{d,}$ when u_d is included. The standard uncertainties are combined using the root-sum-of-the-squares (RSS) method as follows:

$$u_c = \sqrt{s_p^2 + u_s^2 + u_o^2 + u_u^2 + u_d^{\,2}}$$

Table 1. Symbol descriptions

Symbol	Description
U	Expanded uncertainty
u_c	combined standard uncertainty
s_p	standard uncertainty (standard deviation) of the "process"
u_s	standard uncertainty of the "standard"
u_o	standard uncertainty of "other factors"
u_u	standard uncertainty of factors "unrelated" to the measurement process
u_d	standard uncertainty of "differences" (may be treated in different ways)
k	coverage factor

3.6. Step 6. Calculate the expanded uncertainty

The combined standard uncertainty is then multiplied by a coverage factor, *k*, equal to 2 or 3, as chosen by the laboratory, to provide a level of confidence of approximately 95 % or 99 %, respectively. This procedure is based on the Central Limit Theorem and in most cases allows the use of 2 or 3 to provide an approximate 95 % or 99 % level of confidence. The equation used to determine the expanded uncertainty is as follows:

$$U = u_c * k$$

where $k = 2$ or $k = 3$.

3.7. Step 7. Evaluate the expanded uncertainty

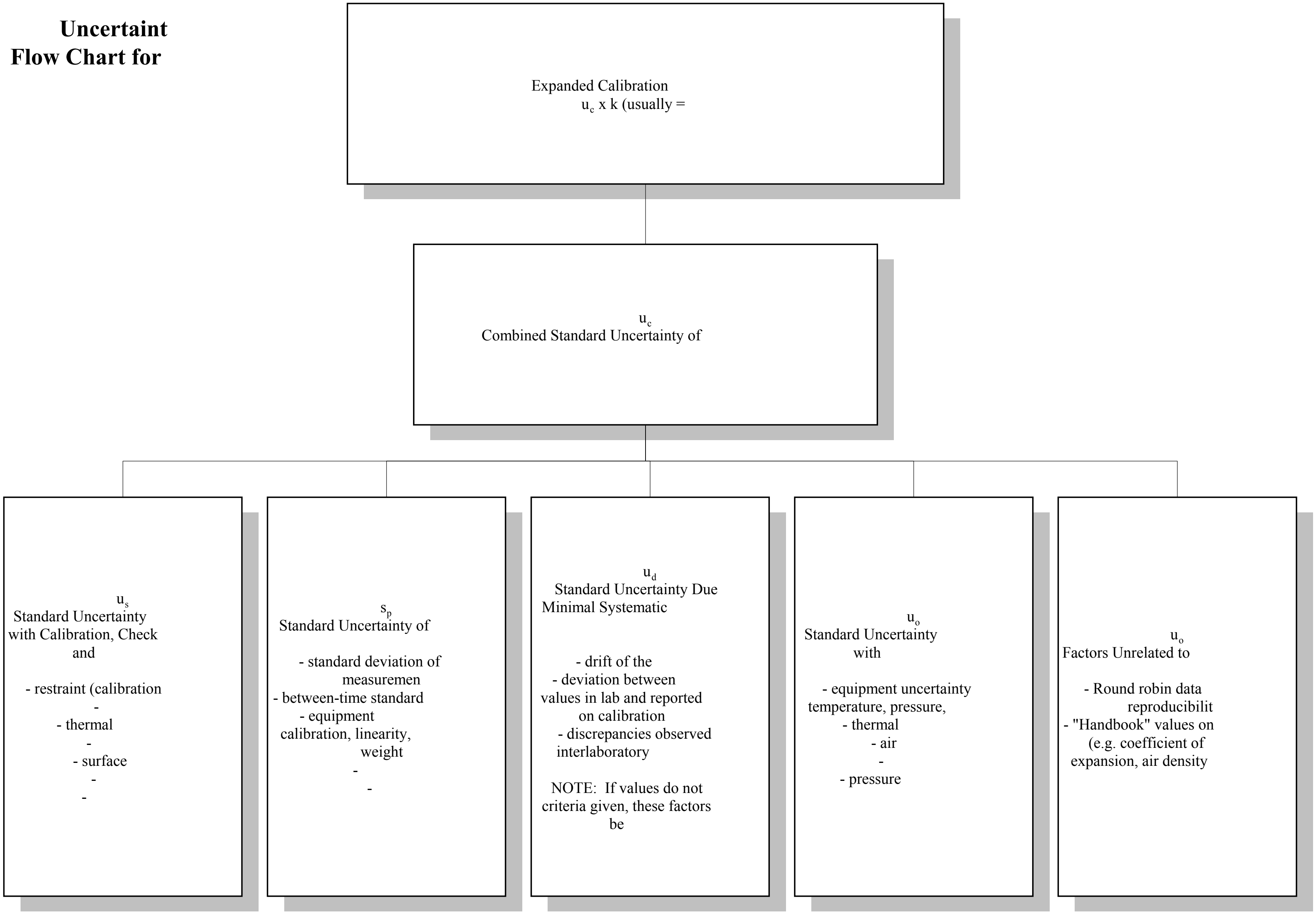
The expanded uncertainty may be evaluated against established criteria such as tolerance limits. For mass standards, the specifications clearly state that the expanded uncertainty must be less than 1/3 of the tolerance.

3.8. Step 8. Report the uncertainty

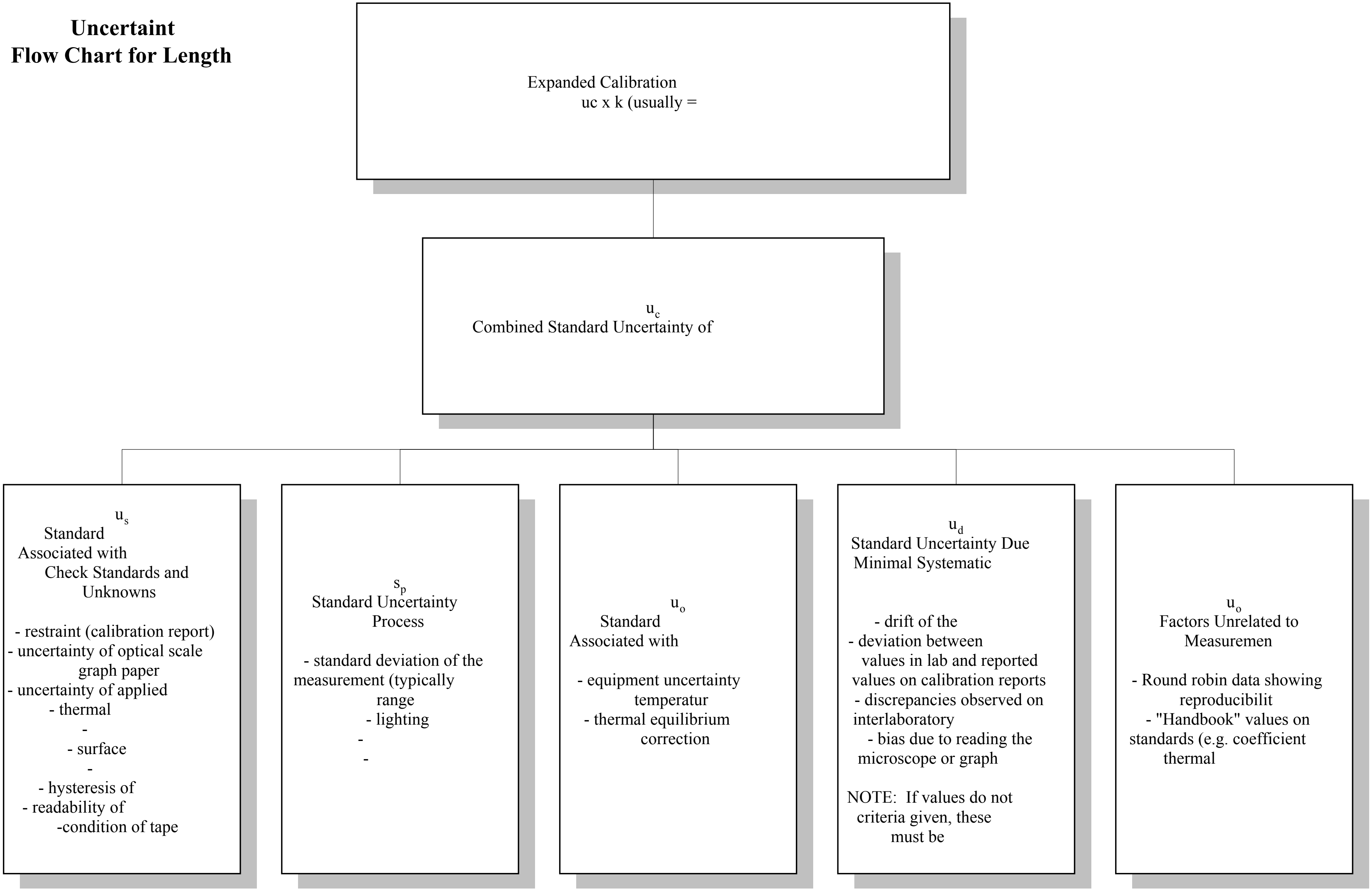
Once the uncertainty has been calculated, a statement such as the following is reported:

The combined standard uncertainty includes the standard uncertainty reported for the standard, for the measurement process, and for any observed deviations from reference (e.g., NIST) values, which are less than surveillance limits. The combined standard uncertainty is multiplied by *k*, a coverage factor of (2, 3) to give the expanded uncertainty (which defines an interval with an approximate (95, 99) % level of confidence).

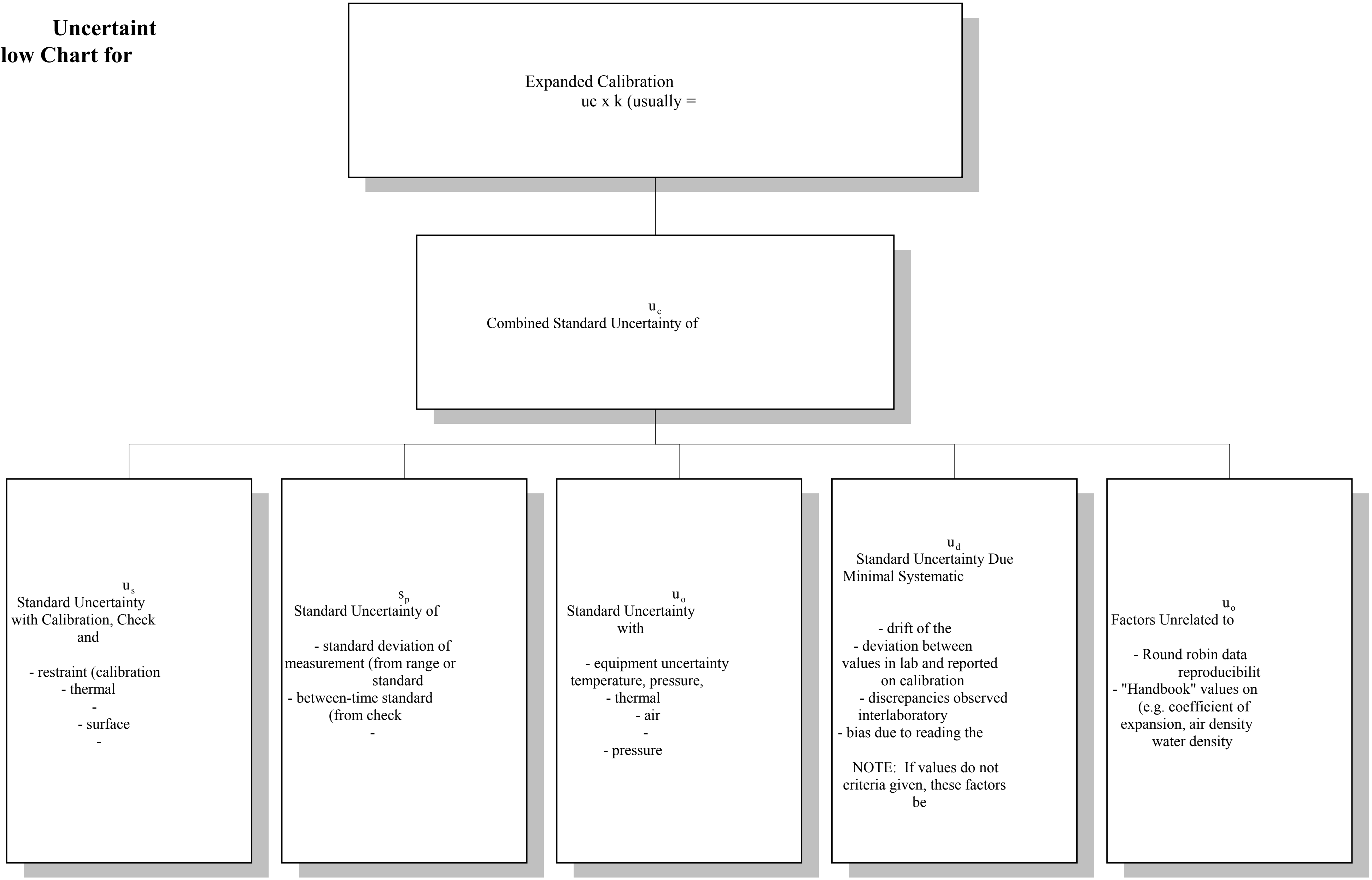
Uncertaint Flow Chart for



Uncertaint
Flow Chart for Length



Uncertaint
Flow Chart for



SOP 30

Recommended Standard Operating Procedure for a Process Measurement Assurance Program

1. Introduction

1.1. Purpose

The Process Measurement Assurance Program (PMAP) is used for the control and surveillance of measurement performance using check standards in measurement and calibration procedures. Incorporation of these measurement control steps ensures the validity of the measurement process and the standards used. The variables used in calculation and assignment of uncertainty can be determined and controlled by the use of this Standard Operating Procedure (SOP).

1.2. Prerequisites

1.2.1. A Standard Operating Procedure that describes and provides rigor and consistency in the calibration process.

1.2.2. Check standards that represent the items to be calibrated. These check standards should be stable and their values should be established with accuracy, since they will be used to control the uncertainty in the calibration process. Check standard values are to be determined by NIST or inside the laboratory with a procedure one level higher than the calibration process to be controlled.

1.2.3. The operator must be experienced in the calibration process and the standard operating procedure for the calibration to which this method is applied. The operator should also have had specific training on SOP 29 (uncertainty identification and calculations).

1.2.4. A calculating system for statistical control that performs standard deviations, control limits, “F” and “t” tests, root-sum-of-the-squares (RSS), and control charting. It is recommended that a computer program be used for efficiency, consistency, and uniformity.

2. Methodology

2.1. Scope, Precision, Accuracy

This method can be used on any measurement or calibration process where a check standard can be substituted for, or measured as, the item being calibrated. The method duplicates the standard operating procedure with the check standard serving as a surrogate for the item being calibrated. The results of these check standard measurements are recorded, charted, and analyzed to establish the measurement capability and to set process control limits, called reference limits. The reference limits are used to establish process uncertainties and to control future measurement performance.

2.2. Summary

Process Measurement Assurance Program (PMAP) is used for determining and controlling the measurement process uncertainty as the calibration is performed. The uncertainty includes effects of the measurement instrument, the operator, the procedure, the standards, and the environment. Each application is modeled to meet the following objective for determining and controlling uncertainties 1) in the measurement process; 2) in the calibration standards; or 3) in both the process and the standards.

The check standard is selected to evaluate the standard deviation of the process (s_p), other process uncertainties (u_o) such as material density or air density accuracy, and possible bias (u_d) of the process (see SOP 29). Reference measurements for the check standard are performed after calibrating the calibration standards and after the servicing of the measurement instrument.

Control measurements of the check standard are graphed for visual examination of process performance and are evaluated against control reference limits.

Statistical tools, ‘F’ and ‘t’ tests, determine if there are process changes in variability and bias (systematic error). These tests are used when process performance is questionable; when current data is evaluated to establish new reference control limits; and when evaluating uncertainty statements.

2.3. Apparatus/Equipment Required

2.3.2. A calibration process that meets the requirements of the standard operating procedure (SOP).

2.3.3. A check standard that has been selected to evaluate the established objectives of: the 1) measurement process uncertainty; 2) the calibration standards; or 3) both the process and the standards.

2.3.4. A data input, statistical calculating, and control charting system to provide analysis of measurement control data. (i.e., special software package or spreadsheet)

2.4. **Table 1. Symbols description**

Symbol	**Description**
S_c	Control measurement of check standard
S_{cs}	Accepted value of check standard
U	Expanded Uncertainty (of the process)
u_c	Combined standard uncertainty
u_s	Standard uncertainty of the standard
u_o	Standard uncertainty of other factors
u_d	Standard uncertainty of differences
s_p	Standard deviation of the process
k	Coverage factor

2.5. Procedure

2.5.1. Preliminary Procedure

2.5.1.1. Model the Calibration Process

Set objectives for the PMAP application. These objectives will establish the value of the check standard, the check standard measurement procedure, and influence the frequency of control measurements of the check standard. Objectives may be: 1) Determine the standard deviation of the process (s_p); 2) Determine the Expanded Uncertainty (U); 3) Measure the value of the calibration standard uncertainty (u_s). The model may allow any one objective or a combination of the objectives to be established with a single PMAP application and PMAP control chart.

Diagram the process to clarify the measurement steps and determine the approach that will achieve the established objectives. When determining and controlling the expanded uncertainty (U), evaluate the range of use of the process to ensure that the check standard values will determine the variability and the maximum bias that result from the process and the calibration standard. Determining and controlling expanded uncertainty requires duplicating the calibration process and determining where in the process to insert the control measurement using the check standard. When the objective of PMAP is to control the uncertainty of the calibration standard (u_s), the PMAP measurement may vary from the calibration process to allow inserting the check standard measurement close to the measurement of the calibration standard (see appendix, Model SOP 8). Diagram the calibration process to establish how many check standards and PMAP applications are required to meet objectives. Also, diagram the process to determine where in the process to insert the control measurements of the check standard.

2.5.1.2. Select and Calibrate Check Standard

For calibration process uncertainty determination and control, select a check standard that approximates the item to be calibrated. The selected check standard should be selected to evaluate maximum random variation (s_p) and bias of the process. The check standard selected should also be used to evaluate other objectives (u_o) of the specific calibration process. For multiple ranges of use, a check standard and PMAP application will be required for various portions of the range. For example, Double Substitution (SOP 4) will require, at a minimum, a check standard for each decade (1000 g, 100 g, 10 g, 1 g, 100 mg, and 10 mg) on each balance used. The selected check standard should be calibrated to establish its accepted value (S_c) with an uncertainty level sufficient to control the calibration process uncertainty. The calibration of the check standard must be completed using a standard which is independent of the calibration standard that the PMAP process is designed to control.

For control of the calibration standard, use a check standard that is not part of routine measurement and that will evaluate the changes in the calibration standard’s accepted value, not the maximum random variation of the process. The check standard used to control the calibration standard should be used less frequently (less than ¼ as often) than the calibration standard. For example, in (SOP 28), using Design A.1.2 (a 4-1 weighing design) at 1000 g, requires the selection of a 1000 g check standard that is measured less frequently than the item under test in order to evaluate the two 1000 g calibration standards. The selected check standard should be calibrated using a calibration standard other than the calibration standard(s) it will be controlling.

2.5.2. Establish Control Measurements for Reference Limits

2.5.2.1. Control measurements to establish initial reference limits may be made at any time to verify current measurement process performance. But to achieve control of calibration standards accuracy and measurement instrument capability, the control measurements should be made just after calibration of the calibration standards and servicing of the measurement instrument. Any significant change in the calibration status can then be detected by the performance change in the reference limits data.

2.5.2.2. Make the control measurement by duplicating the calibration process with the check standard substituted for the calibrated item. Make an observation of the check standard (S_c) and determine its measured value by completing calculations as described in the calibration SOP.

2.5.2.3. Record the measured value (S_c) and plot it on the control chart and evaluate it with reference to the accepted value of the check standard. Record date, time, and information tags with data.

2.5.2.4. Evaluate the bias (difference) between the mean of the measured S_c values and the accepted value for S_c from its calibration report.

Bias (deviation) of check standard = Observed mean of S_c - Accepted S_c

2.5.2.5 Repeat the control measurement at various intervals to sample environmental change and other factors than can affect measurement performance. Although a control chart and some statistical control can be established with as few as seven to 12 measurements, a minimum of twenty-five is recommended for estimates and control of uncertainties

2.5.3 Create and Prepare Control Charts

2.5.3.1 Construct a graph with the deviation of the check standard measurements on the y-axis and chronological date and time (or observation number) on the x-axis. The accepted value of the check standard (S_c) is identified near the center of the chart. The y-axis of the control chart should extend plus and minus three standard deviations from the mean $(\bar{x})$ of the control measurements. All control measurements are charted as deviation from the accepted value of the check standard (S_c)

2.5.3.2 Establish control chart parameters by calculating the mean and the estimate of the standard deviation (s_p) of the check standard reference measurements (S_c).

Control chart parameters are as follows:

$\text{Reference Line} = \text{Accepted } S_c$

$\text{Mean Line} = \bar{x} \text{ of Observed } S_c \text{ data}$

$\text{3s Action Limits} = \bar{x} + 3\,(s_p)$

$\text{2s Warning Limits} = \bar{x} + 2\,(s_p)$

$\text{Process Bias} = \text{Mean of Observed } S_c - \text{Accepted } S_c$

2.5.4 Establish Reference Limits and Process Uncertainty

2.5.4.1 Establish reference control limits (as described in 2.5.3.2) by calculating control limits and process bias using the control measurements obtained when calibration standards and measurement instruments are calibrated. These limits are to be stored and used as a reference for future control measurements. Future control measurements should be control-charted and tested against these limits for “in” or “out” of control status. This reference data will also be statistically used to periodically evaluate process and calibration standard performance for change from the calibrated reference status.

2.5.4.2 Establish the Expanded Uncertainty (U) by using the reference data, calibration standard uncertainty (u_s), and any other uncertainty (u_o) not covered by the reference data.

$$u_c = \sqrt{(s_p)^2 + (u_s)^2 + (u_o)^2 + (u_d)^2}$$

$$U = k * u_c$$

According to the PMAP model, s_p, u_o, and u_d are evaluated by comparison with the reference data. The uncertainty for the standard, u_s, and, in some situations, additional u_o are included in PMAP calculation of the process expanded uncertainty (U).

2.5.5 Make PMAP Control Measurement

2.5.5.1 Control measurements of the check standard should be made periodically to ensure that the current measurement performance remains in control of the established reference limits. Control measurements should be tested for “in” or “out” of control status and charted on the control chart. The frequency of the control measurements is dependent on the objective of the PMAP application.

When the objective is to determine and control the calibration process uncertainties, control measurements should be made during the calibration process to ensure the calibration results are accurate and within reference uncertainty statements. Control measurements should be made prior to returning calibrated items to the customer. A minimum of 25 control measurements are required within the calibration period or interval assigned to the calibration standards and the calibration process.

When the objective is to control calibration standards, working standards, or primary standards, the frequency of control measurements should be less than ¼ the use of the standard being controlled. The reduction in measurements ensures that the check standard receives less use and wear than the standard being controlled. Control measurements are charted and the Process Bias (observed mean value – accepted) is evaluated to detect any significant change in the calibration standard being controlled.

2.5.6 Evaluate Process Performance at Specific Intervals

2.5.6.1 Examine each control measurement data point as it is charted. Evaluate each data point for its control status and investigate causes for out of control data. Analyze the measurement process uncertainty, including the process standard deviation (s_p), process bias, and other uncertainties quarterly or every five to ten data points to ensure that significant changes in uncertainties do not occur.

2.5.6.2 Evaluate current performance using the control measurements described in 2.5.5 to establish the current standard deviation of the process (s_p), process bias and other uncertainties. Perform each evaluation at specific calibration intervals established by the calibration of standards and service of the measurement instrument. This evaluation, referred to as “calibration” of the process, is performed at intervals that will ensure detection of changes in the calibration uncertainty statements.

2.5.6.3 Use statistical tools at specific calibration intervals to evaluate current data performance to reference data that was established at calibration of standards and at the service of the measurement instrument. This evaluation will assist in deciding when to recalibrate calibration standards and service the measurement instrument.

Use the F test to evaluate if a significant change in (s_p) performance has occurred.

$$F\ test = \frac{(s_{p\ \mathrm{large}})^2}{(s_{p\ \mathrm{small}})^2}$$

The current and previously established reference standard deviations are compared and evaluated using F test table values based on degrees of freedom in the measurements.

Use the t-test to evaluate if a significant change in measurement process bias has occurred.

$$t\ test = \frac{(Bias_{\ \mathrm{new}}) - (Bias_{\ \mathrm{old}})}{\sqrt{\frac{(s_{p\ \mathrm{new}})^2}{n_{\ \mathrm{new}}} + \frac{(s_{p\ \mathrm{old}})^2}{\mathrm{n}_{\ \mathrm{old}}}}}$$

The current (new) and previous (old) reference bias is compared and evaluated using t test table values based on the degrees of freedom in the measurements.

2.5.6.4. Take action based on the results of statistical evaluation. If F and t tests reveal no significant change in process performance, use the current data analysis to establish new process reference limits, control chart and uncertainty statements (as described in 2.5.3 and 2.5.4). If the process has a stable history, it is permissible to pool the current data with previous reference limits to establish new reference limits, control chart, and uncertainty statements. Continue control measurements until the next calibration interval.

If F and t tests reveal significant change in the measurement process, investigate the specific cause. If the cause for the change cannot be identified and corrected, then collect new reference data to establish new reference limits and process uncertainties. If a specific cause is found and corrected, and subsequent control measurements indicate an “in-control” status, continue collecting control measurements and test against established reference limits until the next calibration interval.

2.5.7. Continue the measurement assurance procedure as described in 2.5.2 through 2.5.6 to determine and control the measurement process capability.

Significant changes in the measurement process capability can result from the following:

- measurement procedure change;
- measurement instrument change;
- calibration standards change; and/or
- location change.

These changes can require repeating the PMAP procedure (from 2.5 through 2.5.6).

8. STATISTICAL TECHNIQUES

Statistics are used in metrology to summarize experimental data, to provide the basis for assessing its quality, and to provide a basis for making probabilistic decisions in its use. The essential basic statistical information for describing a simple data set is:

The mean of the set,	$\bar{x}$
The standard deviation of the set,	s
The number of individuals in the set,	n

If the set is a random sample of the population from which it was derived, if the measurement process is in statistical control, and if all of the observations are independent of one another, then s is an estimate of the population standard deviation, σ, and $\bar{x}$ is an unbiased estimate of the mean, μ.

The population consists of all possible measurements that could have been made under the test conditions for a stable test sample. In this regard, the metrologist must be aware that any changes in the measurement system (known or unknown) could possibly result in significant changes in its operational characteristics, and, hence the values of the mean and standard deviation. Whenever there is doubt, statistical tests should be made to determine the significance of any apparent differences before statistics are combined.

The following discussion reviews some useful statistical techniques for interpreting measurement data. In presenting this information, it is assumed that the reader is already familiar with basic statistical concepts. For a detailed discussion of the following techniques and others not presented here, it is recommended that the reader consult NIST Handbook 91 - Experimental Statistics, by Mary G. Natrella [19]. That handbook also contains comprehensive statistical tables from which the tables contained in Chapter 9 of this publication were taken.

8.1 Estimation of Standard Deviation from a Series of Measurements on a Given Object

Given n measurements $x_1, x_2, x_3, \ldots\ldots, x_n$

Mean, $\bar{x} = \dfrac{(x_1 + x_2 + x_3 + \ldots + x_n)}{n}$

Standard deviation estimate, $s = \sqrt{\dfrac{\sum(x_n - \bar{x})^2}{n-1}}$

The estimate, s, is based on n-1 degrees of freedom

8.2 Estimation of Standard Deviation from the Differences of k Sets of Duplicate Measurements

Given k differences of duplicate measurements, d_1, d_2, d_3, …, d_k, a useful formula for estimating the standard deviation is:

$s_d = \frac{\sum d_i^2}{2k}$ where s_d is based on k degrees of freedom.

Note that $d_1 = \bar{x}_i' - \bar{x}_i''$, for example.

The values d_1, d_2 etc., may be differences of duplicate measurements of the same sample (or object) at various times, or they may be the differences of duplicate measurements of several similar samples (or objects).

8.3 Estimation of Standard Deviation from the Average Range of Several Sets of Measurements

The range, R, is defined as the difference between the largest and smallest values in a set of measurements.

Given R_1, R_2, R_3, …, R_k

Mean, $\overline{R} = \frac{\left(R_1 + R_2 + R_3 + \ldots + R_k\right)}{k}$

Standard deviation can be estimated by the formula, $s_R = \frac{\overline{R}}{d_2^*}$

The value of d_2^* will depend on the number of sets of measurements used to calculate s_R, and on the number of measurements in each set, i.e., 2 for duplicates, 3 for triplicates, etc. Consult a table such as Table 9.1 for the appropriate value of d_2^* to use. The effective number of degrees of freedom for s_R is in the table.

8.4 Pooling Estimates of Standard Deviations

Estimates of the standard deviation obtained at several times may be combined (pooled) to obtain a better estimate based upon more degrees of freedom. The following equation may be used for this purpose:

$s_p = \sqrt{\frac{(n_1 - 1)s_1^2 + (n_2 - 1)s_2^2 + (n_3 - 1)s_3^2 + \ldots + (n_k - 1)s_k^2}{(n_1 - 1) + (n_2 - 1) + (n_3 - 1) + \ldots + (n_k - 1)}}$ where

s_p will be based on $(n_1 - 1) + (n_2 - 1) + (n_3 - 1) + \ldots + (n_k - 1)$ degrees of freedom.

8.5 "Within" and "Between" Standard Deviation

Estimation of the within-series, s_w, and between-series, s_b standard deviation, (also referred to as short-term and long-term standard deviations in the applications described here) is an important way to characterize a measurement process. The former provides guidance as to how many repetitions of a measurement are required to obtain a result on a single occasion with a given precision, while the latter is a better estimate of the precision of replication (reproducibility) of a result on various occasions and is a more realistic evaluation of measurement variability.

To estimate these standard deviations, sets of measurements may be made on several occasions. To simplify the calculations, each set should consist of the same number of measurements. For most measurements, it is recommended that duplicate measurements be made on at least 12 separate occasions when estimating s_w and s_b.

Given k sets of duplicate measurements made on k occasions the following table and calculation can be made.

Table 8.1

Occasion	Measured Values		Range	Mean
1	x_1'	x_1''	R_1	$\frac{(x_1' + x_1'')}{2} = \bar{x}_1$
2	x_2'	x_2''	R_2	$\frac{(x_2' + x_2'')}{2} = \bar{x}_2$
3	x_3'	x_3''	R_3	$\frac{(x_3' + x_3'')}{2} = \bar{x}_3$
.	.	.	.	.
.	.	.	.	.
.	.	.	.	.
k	x_k'	x_k''	R_k	$\frac{(x_k' + x_k'')}{2} = \bar{x}_k$

1. Calculate $\bar{R} = \frac{(R_1 + R_2 + R_3 + ... + R_k)}{k}$
2. Calculate $s_w = s_R - \frac{\bar{R}}{d_2^*}$

Note: One may use the procedure of 8.2 to calculate s_w if preferred.

3. Calculate s_x as follows:

$$\bar{\bar{x}} = \frac{(\bar{x}_1 + \bar{x}_2 + \bar{x}_3 + \ldots + \bar{x}_k)}{k}$$

$$s_{\bar{x}} = \sqrt{\frac{\Sigma(\bar{x}_k - \bar{\bar{x}})^2}{k-1}}$$

4. Calculate s_b (for the case of duplicate measurements)

$$s_b = \sqrt{s_x^2 - \frac{s_w^2}{2}}$$

Note that s_b is an estimate of the long term component of the standard deviation of a single measurement. The long term standard deviation of the mean of *n* measurements taken at a single occasion is estimated by:

$$s_b(\bar{x}_n) = \sqrt{s_b^2 - \frac{s_w^2}{n}}$$

Important note: Do not use this approach for handling within-series and between-time standard deviations with the Mass Code. Separate formulas are available for that application.

8.6 Confidence Interval for the Mean

The estimation of the confidence interval for the mean of *n* measurements is one of the most frequently used statistical calculations. The formula used will depend on whether the population standard deviation,σ, is known or whether it is estimated on the basis of measurements of a sample(s) of the population.

Using Population Standard Deviation, σ

Strictly speaking, σ, is never known for a measurement process. However, the formula for use in such a case is:

$$\bar{x} \pm \frac{z\sigma}{\sqrt{n}}$$

Variable	Description
$\bar{x}$	sample mean
s	known standard deviation
n	number of measurements of sample
z	standard normal variate, depending on the confidence level desired

For 95 % confidence $z = 1.960$; for 99.7 % confidence $z = 3.0$.
For other confidence levels, see Table 9.2

Using Estimate of Standard Deviation, s

In the usual situation, s is known, based on υ degrees of freedom and the formula for use is:

$$\bar{x} \pm \frac{ts}{\sqrt{n}}$$

Variable	Description
$\bar{x}$	sample mean
s	estimate of standard deviation
n	number of measurements on which the mean is based
t	Student's *t* value, based on the confidence level desired and the υ degrees of freedom associated with *s* (see Table 9.3).

Note that $t \rightarrow z$ as $n \rightarrow \infty$. For many practical purposes, the standard deviation may be considered as known when estimated by at least 30 degrees of freedom.

8.7 Confidence Interval for σ

The standard deviation, σ, is ordinarily not known but is, instead, an estimated value based on a limited number of measurements, using procedures such as have been described above. Such estimates may be pooled, as appropriate, to obtain better estimates. In any case, the uncertainty of the estimated value of the standard deviation may be of interest and can be expressed in the form of a confidence interval, computed as indicated below.

The interval is asymmetrical because the standard deviation is ordinarily underestimated when small numbers of measurements are involved due to the fact that large deviations occur infrequently in a limited measurement process. Indeed, it is the general experience of metrologists that a few measurements appear to be more precise than they really are.

The basic information required to compute the interval is an estimate of the standard deviation, s, and the number of degrees of freedom on which the estimate is based. The relationships to use are:

Lower limit	$B_L s$
Upper limit	$B_U s$
Interval	$B_L s$ to $B_U s$

The values for B_L and B_U depend upon the confidence level and degrees of freedom associated with s. Values for use in calculating the confidence level are given in Table 9.7. A more extensive table (Table A-20) is available in NIST Handbook 91 [19].

8.8 Statistical Tolerance Intervals

Statistical tolerance intervals define the bounds within which a percentage of the population is expected to lie with a given level of confidence. For example, one may wish to define the limits within which 95 % of measurements would be expected to lie with a 95 % confidence of being correct. The interval is symmetrical and is computed using the expression

$$\bar{x} \pm ks$$

where k depends on three things

Variable	Description
p	the proportion or percentage of the individual measurements to be included
γ	the confidence coefficient to be associated with the interval
n	the number of measurements on which the estimate, s, is based

Table 9.6 may be used to obtain values for k for frequently desired values of γ and p. A more extensive table is Table A-6 found in NIST Handbook 91 [19].

8.9 Comparing Estimates of a Standard Deviation (F Test)

The F-test may be used to decide whether there is sufficient reason to believe that two estimates of a standard deviation differ significantly. The ratio of the variances (square of the standard deviation) is calculated and compared with tabulated values. Unless the computed ratio is larger than the tabulated value, there is no reason to believe that the observed standard deviations are significantly different.

The F ratio is calculated using the equation

$$F = \frac{s_L^2}{s_S^2}$$

where s_L is the numerically larger value and s_S is the smaller value of the two estimates under consideration.

The critical value of F depends on the significance level chosen for the decision (test) and the number of degrees of freedom associated with s_L and s_S, respectively.

Table 9.4 contains critical values for F at the 95 % level of confidence. The tabulated values of F are not expected to be exceeded with 95 % confidence on the basis of chance alone. As an example, if both the numerator and the denominator values for s were each based on 9 degrees of freedom, an F value no larger than 4.03 is expected with 95 % confidence, due to the uncertainties of the s values, themselves. Table A-5 of NIST Handbook 91 [19] contains values for F for other confidence levels.

The F-test is useful for comparing the precision of methods, equipment, laboratories, or metrologists, for example. An inspection of Table 9.4 shows that when either of the values of s is based on a small number of degrees of freedom, the F value is large. Consequently, the significance of decisions based on small changes in precision can be supported statistically only by a relatively large number of measurements. If such changes are suspected, but the data requirement is difficult to meet, the decision may need to be made on the basis of information about the measurement process itself.

The F-test is also useful for deciding whether estimates of the standard deviation made at various times differ significantly. Such questions need to be answered when deciding on whether to revise control limits of a control chart, for example.

8.10 Comparing a Set of Measurements with a Given Value

The question may arise as to whether a measured value agrees or significantly disagrees with a stated value for the measured object. The evaluation can be based on whether or not the confidence interval for the measured value encompasses the stated value. The confidence interval is calculated using the expression

$$\bar{x} \pm \frac{ts}{\sqrt{n}}$$

as previously described in Section 8.6. In using this expression, n represents the number of measurements used to calculate the mean, $\bar{x}$, and t depends on the degrees of freedom, υ, associated with s and the confidence level needed when making the decision. Note that one may use historical data for estimating s, such as a control chart for example, in which case υ will represent the degrees of freedom associated with establishment of the control limits and may be considerably larger than $n-1$.

8.11 Comparing Two Sets of Measurements with Regard to Their Means

This discussion is concerned with deciding whether the means of two measured values, $_A$ and $_B$, are in agreement. The data sets used for this purpose may consist of the following:

$$\begin{array}{cc} \bar{x}_A & \bar{x}_B \\ s_A & s_B \\ n_A & n_B \end{array}$$

The first question to be resolved is whether s_A and s_B can be considered to be different estimates of the same standard deviation or whether they do, indeed, differ. An F test may be used for this purpose. However, it will be recalled that this is not sensitive to small real differences, so the decision may need to be based on physical considerations, such as the known stability of the measurement process, for example.

Case I

Confirming (or assuming) that s_A and s_B are not significantly different, they are pooled, as already described (but repeated here for convenience) and used to calculate a confidence interval for the difference of the means. If this is larger than the observed difference, there is no reason to believe that the means differ. The steps to follow when making the calculation described above are:

Step 1. Choose α , the level of significance for the test

Step 2. Calculate the pooled estimate of the standard deviation, s_{p}

$$s_p = \sqrt{\frac{(n_A - 1)s_A^2 + (n_B - 1)s_B^2}{(n_A - 1) + (n_B - 1)}}$$

s_{p} will be estimated with $n_{\mathrm{A}} + n_{\mathrm{B}} - 2$ degrees of freedom

Step 3. Calculate the respective variances of the means

$$v_A = \frac{s_A^2}{n_A} \text{ and } v_B = \frac{s_B^2}{n_B}$$

Step 4. Calculate the uncertainty of $|\mathrm{X_A} - \mathrm{X_B}| = \Delta$

$$U_\Delta = t\sqrt{(V_A + V_B)}$$

using a value for t based on $\frac{\alpha}{2}$ and $\upsilon = n_A + n_B - 2$.

Step 5. Compare U_Δ with Δ

If $U_\Delta \geq \Delta$, there is no reason to believe that Δ is significant at the level of confidence chosen.

Case II

Confirming (or assuming) that s_A and s_B are significantly different, their individual values are used to calculate U_Δ as outlined below.

Step 1. Choose α, the level of significance for the test.

Step 2. Calculate the respective variances of the means.

$$v_A = \frac{s_A^2}{n_A} \text{ and } v_B = \frac{s_B^2}{n_B}$$

Step 3. Calculate the uncertainty of $\left|\mathrm{X_A} - \mathrm{X_B}\right| = \Delta$

$$U_\Delta = t^* \sqrt{(V_A + V_B)}$$

using a value for t^* based on $\frac{\alpha}{2}$ and f, the effective number of degrees of freedom calculated as described in Step 4.

Step 4. Calculate f, the effective number of degrees of freedom as follows:

$$f = \left(\frac{(V_A + V_B)^2}{\frac{V_A^2}{n_A + 1} + \frac{V_B^2}{n_B + 1}} \right) - 2.$$

Step 5. Compare U_Δ with Δ.
If $U_\Delta \geq \Delta$, there is no reason to believe that Δ is significant at the level of confidence chosen.

8.12 Use of Random Numbers

Conducting operations in random sequences can avert problems of bias that might stem from a particular order of operations. For example, in the measurement of a series of items, it might be difficult to determine whether systematic trends in the measured values were due to differences in the items or to measurement system drift unless the items were measured in random order.

Use of tables of random numbers is a convenient means for randomizing measurement operations. The operations, test objects, and other matters requiring randomization may be assigned serial numbers. The order of selection is then determined by use of a random number table, as described below. When the number of operations or test items is less than 100, a table such as Table 9.11, reproduced from NIST Handbook 91 [19], may be used conveniently. One may start from any arbitrarily selected position in the table and proceed from it in any pre-determined arbitrary manner. If the first number encountered is not that of one of any item, ignore it and proceed until a valid match is encountered. This becomes the first item in the sequence. Continuing in the same manner, items are selected in the sequence in which their serial numbers are encountered ignoring the repetition of previously identified items. The procedure is continued until all items have been randomly selected.

As an example, select 10 specimens (numbered 01 to 10) in random order. Start from a randomly selected place, say column 2, row 5 of Table 9.11. Proceed from this point along the table as one would read a book. The starting number is 14, which is not usable. The first useful number encountered is 08, the next 03, and so on. Using the procedure described above, the following random order was found:

<table>
<tr><th colspan="10">Specimen No.</th></tr>
<tr><td>08</td><td>03</td><td>09</td><td>05</td><td>06</td><td>02</td><td>07</td><td>10</td><td>04</td><td>01</td></tr>
<tr><th colspan="10">Order</th></tr>
<tr><td>1</td><td>2</td><td>3</td><td>4</td><td>5</td><td>6</td><td>7</td><td>8</td><td>9</td><td>10</td></tr>
</table>

9. Reference Tables

Table 9.1 Use of Range to Estimate Standard Deviation

Number of Sets of Replicates k	Factor Degrees of Freedom	Number of Replicates in a Set				
		2	3	4	5	6
1	d_2^*	1.41	1.91	2.24	2.48	2.67
	υ	1.00	1.98	2.93	3.83	4.68
3	d_2^*	1.23	1.77	2.12	2.38	2.58
	υ	2.83	5.86	8.44	11.1	13.6
5	d_2^*	1.19	1.74	2.10	2.36	2.56
	υ	4.59	9.31	13.9	18.4	22.6
10	d_2^*	1.16	1.72	2.08	2.34	2.55
	υ	8.99	18.4	27.6	36.5	44.9
15	d_2^*	1.15	1.71	2.07	2.34	2.54
	υ	13.4	27.5	41.3	54.6	67.2
20	d_2^*	1.14	1.70	2.07	2.33	2.54
	υ	17.8	36.5	55.0	72.7	89.6
∞	d_2^*	1.13	1.69	2.06	2.33	2.53
$\overline{R}/d_2^* \rightarrow \sigma$						

Intermediate values for d_2^* and υ may be obtained by interpolation, or from the reference from which this table was adapted.

Example: If 10 sets of measurements were made and each set consisted of two measurements (duplicates), the value for d_2^* is 1.16; if 15 sets of measurements were made and each set consisted of three measurements (triplicates) the value for d_2^* is 1.71.

Adapted from Lloyd S. Nelson, J. Qual. Tech. 7 No. 1, January 1975.

Table 9.2 Z-Factors for Two-sided Confidence Intervals for the Normal Distribution

Confidence Level, %	Z Factor
50	0.68
67	1.00
75	1.15
90	1.645
95	1.960
95.28	2.000
99.00	2.575
99.74	3
99.993 4	4
99.999 95	5
$100 - 10^{-9}$	6
$100 - 10^{-12}$	7
$100 - 10^{-15}$	8
$100 - 10^{-18.9}$	9
$100 - 10^{-23}$	10

Table 9.3 Student t-Variate

*	80 %	90 %	95 %	98 %	99 %	99.73 %
df	$t_{0.90}$	$t_{0.95}$	$t_{0.975}$	$t_{0.99}$	$t_{0.995}$	$t_{0.9985}$
1	3.078	6.314	12.706	31.821	63.657	235.80
2	1.886	2.920	4.303	6.965	9.925	19.207
3	1.638	2.353	3.182	4.541	5.841	9.219
4	1.533	2.132	2.776	3.747	4.604	6.620
5	1.476	2.015	2.571	3.365	4.032	5.507
6	1.440	1.943	2.447	3.143	3.707	4.904
7	1.415	1.895	2.365	2.998	3.499	4.530
8	1.397	1.860	2.306	2.896	3.355	4.277
9	1.383	1.833	2.262	2.821	3.250	4.094
10	1.372	1.812	2.228	2.764	3.169	3.957
11	1.363	1.796	2.201	2.718	3.106	3.850
12	1.356	1.782	2.179	2.681	3.055	3.764
13	1.350	1.771	2.160	2.650	3.012	3.694
14	1.345	1.761	2.145	2.624	2.977	3.636
15	1.341	1.753	2.131	2.602	2.947	3.586
16	1.337	1.746	2.120	2.583	2.921	3.544
17	1.333	1.740	2.110	2.567	2.898	3.507
18	1.330	1.734	2.101	2.552	2.878	3.475
19	1.328	1.729	2.093	2.539	2.861	3.447
20	1.325	1.725	2.086	2.528	2.845	3.422
25	1.316	1.708	2.060	2.485	2.787	3.330
30	1.310	1.697	2.042	2.457	2.750	3.270
40	1.303	1.684	2.021	2.423	2.704	3.199
60	1.296	1.671	2.000	2.390	2.660	3.130
∞	1.282	1.645	1.960	2.326	2.576	3.00

* Columns to be used in calculating corresponding two-sided confidence interval. From: NBS Handbook 91 p. T-5; Last column from B.J. Joiner, J. Research NBS.

Table 9.4 Critical values for the F-Test, $F_{0.975}$

n_1 = degrees of freedom for numerator n_2 = degrees of freedom for denominator

n1 n2	1	2	3	4	5	6	7	8	9	10	12	15	20	24	30	40
1	647.8	799.5	864.2	899.6	921.8	937.1	948.2	956.7	963.3	968.6	976.7	984.9	993.1	997.2	1001	1006
2	38.51	39.00	39.17	39.25	39.30	39.33	39.36	39.37	39.39	39.40	39.41	39.43	39.45	39.46	39.46	39.47
3	17.44	16.04	15.44	15.10	14.88	14.73	14.62	14.54	14.47	14.42	14.34	14.25	14.17	14.12	14.08	14.04
4	12.22	10.65	9.98	9.60	9.36	9.20	9.07	8.98	8.90	8.84	8.75	8.66	8.56	8.51	8.46	8.41
5	10.01	8.43	7.76	7.39	7.15	6.98	6.85	6.76	6.68	6.62	6.52	6.43	6.33	6.28	6.23	6.18
6	8.81	7.26	6.60	6.23	5.99	5.83	5.70	5.60	5.52	5.46	5.37	5.27	5.17	5.12	5.07	5.01
7	8.07	6.54	5.89	5.52	5.29	5.12	4.99	4.90	4.82	4.76	4.67	4.57	4.47	4.42	4.36	4.31
8	7.57	6.06	5.42	5.05	4.82	4.65	4.53	4.43	4.36	4.30	4.20	4.10	4.00	3.95	3.89	3.84
9	7.21	5.71	5.08	4.72	4.48	4.32	4.20	4.10	4.03	3.96	3.87	3.77	3.67	3.61	3.56	3.51
10	6.94	5.46	4.83	4.47	4.24	4.07	3.95	3.85	3.78	3.72	3.62	3.52	3.42	3.37	3.31	3.26
11	6.72	5.26	4.63	4.28	4.04	3.88	3.76	3.66	3.59	3.53	3.43	3.33	3.23	3.17	3.12	3.06
12	6.55	5.10	4.47	4.12	3.89	3.73	3.61	3.51	3.44	3.37	3.28	3.18	3.07	3.02	2.96	2.91
13	6.41	4.97	4.35	4.00	3.77	3.60	3.48	3.39	3.31	3.25	3.15	3.05	2.95	2.89	2.84	2.78
14	6.30	4.86	4.24	3.89	3.66	3.50	3.38	3.29	3.21	3.15	3.05	2.95	2.84	2.79	2.73	2.67
15	6.20	4.77	4.15	3.80	3.58	3.41	3.29	3.20	3.12	3.06	2.96	2.86	2.76	2.70	2.64	2.59
16	6.12	4.69	4.08	3.73	3.50	3.34	3.22	3.12	3.05	2.99	2.89	2.79	2.68	2.63	2.57	2.51
17	6.04	4.62	4.01	3.66	3.44	3.28	3.16	3.06	2.98	2.92	2.82	2.72	2.62	2.56	2.50	2.44
18	5.98	4.56	3.95	3.61	3.38	3.22	3.10	3.01	2.93	2.87	2.77	2.67	2.56	2.50	2.44	2.38
19	5.92	4.51	3.90	3.56	3.33	3.17	3.05	2.96	2.88	2.82	2.72	2.62	2.51	2.45	2.39	2.33
20	5.87	4.46	3.86	3.51	3.29	3.13	3.01	2.91	2.84	2.77	2.68	2.57	2.46	2.41	2.35	2.29
21	5.83	4.42	3.82	3.48	3.25	3.09	2.97	2.87	2.80	2.73	2.64	2.53	2.42	2.37	2.31	2.25
22	5.79	4.38	3.78	3.44	3.22	3.05	2.93	2.84	2.76	2.70	2.60	2.50	2.39	2.33	2.27	2.21
23	5.75	4.35	3.75	3.41	3.18	3.02	2.90	2.81	2.73	2.67	2.57	2.47	2.36	2.30	2.24	2.18
24	5.72	4.32	3.72	3.38	3.15	2.99	2.87	2.78	2.70	2.64	2.54	2.44	2.33	2.27	2.21	2.15
25	5.69	4.29	3.69	3.35	3.13	2.97	2.85	2.75	2.68	2.61	2.51	2.41	2.30	2.24	2.18	2.12
26	5.66	4.27	3.67	3.33	3.10	2.94	2.82	2.73	2.65	2.59	2.49	2.39	2.28	2.22	2.16	2.09
27	5.63	4.24	3.65	3.31	3.08	2.92	2.80	2.71	2.63	2.57	2.47	2.36	2.25	2.19	2.13	2.07
28	5.61	4.22	3.63	3.29	3.06	2.90	2.78	2.69	2.61	2.55	2.45	2.34	2.23	2.17	2.11	2.05
29	5.59	4.20	3.61	3.27	3.04	2.88	2.76	2.67	2.59	2.53	2.43	2.32	2.21	2.15	2.09	2.03
30	5.57	4.18	3.59	3.25	3.03	2.87	2.75	2.65	2.57	2.51	2.41	2.31	2.20	2.14	2.07	2.01
40	5.42	4.05	3.46	3.13	2.90	2.74	2.62	2.53	2.45	2.39	2.29	2.18	2.07	2.01	1.94	1.88
60	5.29	3.93	3.34	3.01	2.79	2.63	2.51	2.41	2.33	2.27	2.17	2.06	1.94	1.88	1.82	1.74
120	5.15	3.80	3.23	2.89	2.67	2.52	2.39	2.30	2.22	2.16	2.05	1.94	1.82	1.76	1.69	1.61
∞	5.02	3.69	3.12	2.79	2.57	2.41	2.29	2.19	2.11	2.05	1.94	1.83	1.71	1.64	1.57	1.48

For use for a one-tailed test of equality of standard deviation estimate at 2.5 % level of confidence, or for a two-tailed test at 5 % level of confidence.

Table 9.5 Critical values for the F-Test, $F_{0.99}$

υ_1 = degrees of freedom for numerator υ_2 = degrees of freedom for denominator

υ_2 \ υ_1	1	2	3	4	5	6	7	8	9	10
10	10.04	7.56	6.55	5.99	5.64	5.39	5.20	5.06	4.94	4.85
11	9.65	7.21	6.22	5.67	5.32	5.07	4.89	4.74	4.63	4.54
12	9.33	6.93	5.95	5.41	5.06	4.82	4.64	4.50	4.39	4.30
13	9.07	6.70	5.74	5.21	4.86	4.62	4.44	4.30	4.19	4.10
14	8.86	6.51	5.56	5.04	4.69	4.46	4.28	4.14	4.03	3.94
15	8.68	6.36	5.42	4.89	4.56	4.32	4.14	4.00	3.89	3.80
16	8.53	6.23	5.29	4.77	4.44	4.20	4.03	3.89	3.78	3.69
17	8.40	6.11	5.18	4.67	4.34	4.10	3.93	3.79	3.68	3.59
18	8.29	6.01	5.09	4.58	4.25	4.01	3.84	3.71	3.60	3.51
19	8.18	5.93	5.01	4.50	4.17	3.94	3.77	3.63	3.52	3.43
20	8.10	5.85	4.94	4.43	4.10	3.87	3.70	3.56	3.46	3.37
22	7.95	5.72	4.82	4.31	3.99	3.76	3.59	3.45	3.35	3.26
24	7.82	5.61	4.72	4.22	3.90	3.67	3.50	3.36	3.26	3.17
26	7.72	5.53	4.64	4.14	3.82	3.59	3.42	3.29	3.18	3.09
28	7.64	5.45	4.57	4.07	3.75	3.53	3.36	3.23	3.12	3.03
30	7.56	5.39	4.51	4.02	3.70	3.47	3.30	3.17	3.07	2.98
35	7.42	5.27	4.40	3.91	3.59	3.37	3.20	3.07	2.96	2.88
40	7.31	5.18	4.31	3.83	3.51	3.29	3.12	2.99	2.89	2.80
45	7.23	5.11	4.25	3.77	3.45	3.23	3.07	2.94	2.83	2.74
50	7.17	5.06	4.20	3.72	3.41	3.19	3.02	2.89	2.78	2.70
55	7.12	5.01	4.16	3.68	3.37	3.15	2.98	2.85	2.75	2.66
60	7.08	4.98	4.13	3.65	3.34	3.12	2.95	2.82	2.72	2.63
65	7.04	4.95	4.10	3.62	3.31	3.09	2.93	2.80	2.69	2.61
70	7.01	4.92	4.07	3.60	3.29	3.07	2.91	2.78	2.67	2.59
75	6.99	4.90	4.05	3.58	3.27	3.05	2.89	2.76	2.65	2.57
80	6.96	4.88	4.04	3.56	3.25	3.04	2.87	2.74	2.64	2.55
85	6.94	4.86	4.02	3.55	3.24	3.02	2.86	2.73	2.62	2.54
90	6.93	4.85	4.01	3.53	3.23	3.01	2.84	2.72	2.61	2.52
95	6.91	4.84	3.99	3.52	3.22	3.00	2.83	2.70	2.60	2.51
100	6.90	4.82	3.98	3.51	3.21	2.99	2.82	2.69	2.59	2.50
105	6.88	4.81	3.97	3.50	3.20	2.98	2.81	2.69	2.58	2.49
110	6.87	4.80	3.96	3.49	3.19	2.97	2.81	2.68	2.57	2.49
115	6.86	4.79	3.96	3.49	3.18	2.96	2.80	2.67	2.57	2.48
120	6.85	4.79	3.95	3.48	3.17	2.96	2.79	2.66	2.56	2.47
∞	6.63	4.61	3.78	3.32	3.02	2.80	2.64	2.51	2.41	2.32

For use for a one-tailed test of equality of standard deviation estimate at 2.5 % level of confidence, or for a two-tailed test at 2 % level of confidence.

Table 9.6 Factors for Two-sided Tolerance Intervals for the Normal Distribution

	γ = 0.95					γ = 0.99				
P n	0.75	0.90	0.95	0.99	0.999	0.75	0.90	0.95	0.99	0.999
2	22.858	32.019	37.674	48.430	60.573	114.363	160.193	188.491	242.300	303.054
3	5.922	8.380	9.916	12.861	16.208	13.378	18.930	22.401	29.055	36.616
4	3.779	5.369	6.370	8.299	10.502	6.614	9.398	11.150	14.527	18.383
5	3.002	4.275	5.079	6.634	8.415	4.643	6.612	7.855	10.260	13.015
6	2.604	3.712	4.414	5.775	7.337	3.743	5.337	6.345	8.301	10.548
7	2.361	3.369	4.007	5.248	6.676	3.233	4.613	5.488	7.187	9.142
8	2.197	3.136	3.732	4.891	6.226	2.905	4.147	4.936	6.468	8.234
9	2.078	2.967	3.532	4.631	5.899	2.677	3.822	4.550	5.966	7.600
10	1.987	2.839	3.379	4.433	5.649	2.508	3.582	4.265	5.594	7.129
11	1.916	2.737	3.259	4.277	5.452	2.378	3.397	4.045	5.308	6.766
12	1.858	2.655	3.162	4.150	5.291	2.274	3.250	3.870	5.079	6.477
13	1.810	2.587	3.081	4.044	5.158	2.190	3.130	3.727	4.893	6.240
14	1.770	2.529	3.012	3.955	5.045	2.120	3.029	3.608	4.737	6.043
15	1.735	2.480	2.954	3.878	4.949	2.060	2.945	3.507	4.605	5.876
16	1.705	2.437	2.903	3.812	4.865	2.009	2.872	3.421	4.492	5.732
17	1.679	2.400	2.858	3.754	4.791	1.965	2.808	3.345	4.393	5.607
18	1.655	2.366	2.819	3.702	4.725	1.926	2.753	3.279	4.307	5.497
19	1.635	2.337	2.784	3.656	4.667	1.891	2.703	3.221	4.230	5.399
20	1.616	2.310	2.752	3.612	4.614	1.860	2.659	3.168	4.161	5.312
21	1.599	2.286	2.723	3.577	4.567	1.833	2.620	3.121	4.100	5.234
22	1.584	2.264	2.697	3.543	4.523	1.808	2.584	3.078	4.044	5.163
23	1.570	2.244	2.673	3.512	4.484	1.785	2.551	3.040	3.993	5.098
24	1.557	2.225	2.651	3.483	4.447	1.764	2.522	3.004	3.947	5.039
25	1.545	2.208	2.631	3.457	4.413	1.745	2.494	2.972	3.904	4.985
26	1.534	2.193	2.612	3.432	4.382	1.727	2.469	2.941	3.865	4.935
27	1.523	2.178	2.595	3.409	4.353	1.711	2.446	2.914	3.828	4.888

From: NBS Handbook 91, p T-11

Table 9.7 Factors for Computing Two-sided Confidence Limits for α (Part 1)

Degrees of Freedom	$\alpha = 0.05$		$\alpha = 0.01$		$\alpha = 0.001$	
	S_U	S_L	S_U	S_L	S_U	S_L
1	17.79	0.3576	86.31	0.2969	844.4	0.2480
2	4.859	0.4581	10.70	0.3879	33.29	0.3291
3	3.183	0.5178	5.449	0.4453	11.65	0.3824
4	2.567	0.5590	3.892	0.4865	6.938	0.4218
5	2.248	0.5899	3.175	0.5182	5.085	0.4529
6	2.052	0.6143	2.764	0.5437	4.128	0.4784
7	1.918	0.6344	2.498	0.5650	3.551	0.5000
8	1.820	0.6513	2.311	0.5830	3.167	0.5186
9	1.746	0.6657	2.173	0.5987	2.894	0.5348
10	1.686	0.6784	2.065	0.6125	2.689	0.5492
11	1.638	0.6896	1.980	0.6248	2.530	0.5621
12	1.598	0.6995	1.909	0.6358	2.402	0.5738
13	1.564	0.7084	1.851	0.6458	2.298	0.5845
14	1.534	0.7166	1.801	0.6549	2.210	0.5942
15	1.509	0.7240	1.758	0.6632	2.136	0.6032
16	1.486	0.7808	1.721	0.6710	2.073	0.6116
17	1.466	0.7372	1.688	0.6781	2.017	0.6193
18	1.448	0.7430	1.658	0.6848	1.968	0.6266
19	1.432	0.7484	1.632	0.6909	1.925	0.6333
20	1.417	0.7535	1.609	0.6968	1.886	0.6397
21	1.404	0.7582	1.587	0.7022	1.851	0.6457
22	1.391	0.7627	1.568	0.7074	1.820	0.6514
23	1.380	0.7669	1.550	0.7122	1.791	0.6568
24	1.370	0.7709	1.533	0.7169	1.765	0.6619
25	1.360	0.7747	1.518	0.7212	1.741	0.6668

From: NBS Handbook 91, p T-34

Table 9.7 Factors for Computing Two-sided Confidence Limits for α (Part 2)

Degrees of Freedom	α = 0.05		α = 0.01		α = 0.001	
	S_U	S_L	S_U	S_L	S_U	S_L
26	1.351	0.7783	1.504	0.7253	1.719	0.7130
27	1.343	0.7817	1.491	0.7293	1.698	0.6758
28	1.335	0.7849	1.479	0.7331	1.679	0.6800
29	1.327	0.7880	1.467	0.7367	1.661	0.6841
30	1.321	0.7909	1.457	0.7401	1.645	0.6880
31	1.314	0.7937	1.447	0.7434	1.629	0.6917
32	1.308	0.7964	1.437	0.7467	1.615	0.6953
33	1.302	0.7990	1.428	0.7497	1.601	0.6987
34	1.296	0.8015	1.420	0.7526	1.588	0.7020
35	1.291	0.8089	1.412	0.7554	1.576	0.7052
36	1.286	0.8062	1.404	0.7582	1.564	0.7083
37	1.281	0.8085	1.397	0.7608	1.553	0.7113
38	1.277	0.8106	1.390	0.7633	1.543	0.7141
39	1.272	0.8126	1.383	0.7658	1.533	0.7169
40	1.268	0.8146	1.377	0.7681	1.523	0.7197
41	1.264	0.8166	1.371	0.7705	1.515	0.7223
42	1.260	0.8184	1.365	0.7727	1.506	0.7248
43	1.257	0.8202	1.360	0.7748	1.498	0.7273
44	1.253	0.8220	1.355	0.7769	1.490	0.7297
45	1.249	0.8237	1.349	0.7789	1.482	0.7320
46	1.246	0.8253	1.345	0.7809	1.475	0.7342
47	1.243	0.8269	1.340	0.7828	1.468	0.7364
48	1.240	0.8285	1.335	0.7847	1.462	0.7386
49	1.237	0.8300	1.331	0.7864	1.455	0.7407
50	1.234	0.8314	1.327	0.7882	1.449	0.7427

From: NBS Handbook 91, p. T-34

Table 9.8 Density of Air-free Water in g/cm^3 as a Function of Celsius Temperature

T	**0.0 °C**	**0.1 °C**	**0.2 °C**	**0.3 °C**	**0.4 °C**	**0.5 °C**	**0.6 °C**	**0.7 °C**	**0.8 °C**	**0.9 °C**
0.0	0.999 840	0.999 846	0.999 853	0.999 859	0.999 865	0.999 871	0.999 877	0.999 883	0.999 888	0.999 893
1.0	0.999 899	0.999 903	0.999 908	0.999 913	0.999 917	0.999 921	0.999 925	0.999 929	0.999 933	0.999 937
2.0	0.999 940	0.999 943	0.999 946	0.999 949	0.999 952	0.999 954	0.999 956	0.999 959	0.999 961	0.999 963
3.0	0.999 964	0.999 966	0.999 967	0.999 968	0.999 969	0.999 970	0.999 971	0.999 971	0.999 972	0.999 972
4.0	0.999 972	0.999 972	0.999 972	0.999 971	0.999 971	0.999 970	0.999 969	0.999 968	0.999 967	0.999 965
5.0	0.999 964	0.999 962	0.999 960	0.999 958	0.999 956	0.999 954	0.999 951	0.999 949	0.999 946	0.999 943
6.0	0.999 940	0.999 937	0.999 933	0.999 930	0.999 926	0.999 922	0.999 918	0.999 914	0.999 910	0.999 906
7.0	0.999 901	0.999 896	0.999 892	0.999 887	0.999 881	0.999 876	0.999 871	0.999 865	0.999 860	0.999 854
8.0	0.999 848	0.999 842	0.999 835	0.999 829	0.999 822	0.999 816	0.999 809	0.999 802	0.999 795	0.999 787
9.0	0.999 780	0.999 773	0.999 765	0.999 757	0.999 749	0.999 741	0.999 733	0.999 725	0.999 716	0.999 707
10.0	0.999 699	0.999 690	0.999 681	0.999 672	0.999 662	0.999 653	0.999 643	0.999 634	0.999 624	0.999 614
11.0	0.999 604	0.999 594	0.999 583	0.999 573	0.999 562	0.999 552	0.999 541	0.999 530	0.999 519	0.999 507
12.0	0.999 496	0.999 485	0.999 473	0.999 461	0.999 449	0.999 437	0.999 425	0.999 413	0.999 401	0.999 388
13.0	0.999 376	0.999 363	0.999 350	0.999 337	0.999 324	0.999 311	0.999 297	0.999 284	0.999 270	0.999 256
14.0	0.999 243	0.999 229	0.999 215	0.999 200	0.999 186	0.999 172	0.999 157	0.999 142	0.999 128	0.999 113
15.0	0.999 098	0.999 083	0.999 067	0.999 052	0.999 036	0.999 021	0.999 005	0.998 989	0.998 973	0.998 957
16.0	0.998 941	0.998 925	0.998 908	0.998 892	0.998 875	0.998 858	0.998 841	0.998 824	0.998 807	0.998 790
17.0	0.998 773	0.998 755	0.998 738	0.998 720	0.998 702	0.998 684	0.998 666	0.998 648	0.998 630	0.998 612
18.0	0.998 593	0.998 575	0.998 556	0.998 537	0.998 519	0.998 500	0.998 480	0.998 461	0.998 442	0.998 422
19.0	0.998 403	0.998 383	0.998 364	0.998 344	0.998 324	0.998 304	0.998 284	0.998 263	0.998 243	0.998 222
20.0	0.998 202	0.998 181	0.998 160	0.998 139	0.998 118	0.998 097	0.998 076	0.998 055	0.998 033	0.998 012
21.0	0.997 990	0.997 968	0.997 947	0.997 925	0.997 903	0.997 881	0.997 858	0.997 836	0.997 814	0.997 791
22.0	0.997 768	0.997 746	0.997 723	0.997 700	0.997 677	0.997 654	0.997 630	0.997 607	0.997 584	0.997 560
23.0	0.997 536	0.997 513	0.997 489	0.997 465	0.997 441	0.997 417	0.997 392	0.997 368	0.997 344	0.997 319
24.0	0.997 294	0.997 270	0.997 245	0.997 220	0.997 195	0.997 170	0.997 145	0.997 119	0.997 094	0.997 068
25.0	0.997 043	0.997 017	0.996 991	0.996 966	0.996 940	0.996 913	0.996 887	0.996 861	0.996 835	0.996 808
26.0	0.996 782	0.996 755	0.996 728	0.996 702	0.996 675	0.996 648	0.996 621	0.996 593	0.996 566	0.996 539
27.0	0.996 511	0.996 484	0.996 456	0.996 428	0.996 401	0.996 373	0.996 345	0.996 316	0.996 288	0.996 260
28.0	0.996 232	0.996 203	0.996 175	0.996 146	0.996 117	0.996 088	0.996 060	0.996 031	0.996 001	0.995 972
29.0	0.995 943	0.995 914	0.995 884	0.995 855	0.995 825	0.995 795	0.995 765	0.995 736	0.995 706	0.995 676
30.0	0.995 645	0.995 615	0.995 585	0.995 554	0.995 524	0.995 493	0.995 463	0.995 432	0.995 401	0.995 370
31.0	0.995 339	0.995 308	0.995 277	0.995 246	0.995 214	0.995 183	0.995 151	0.995 120	0.995 088	0.995 056
32.0	0.995 024	0.994 992	0.994 960	0.994 928	0.994 896	0.994 864	0.994 831	0.994 799	0.994 766	0.994 734
33.0	0.994 701	0.994 668	0.994 635	0.994 602	0.994 569	0.994 536	0.994 503	0.994 470	0.994 436	0.994 403
34.0	0.994 369	0.994 336	0.994 302	0.994 268	0.994 234	0.994 201	0.994 167	0.994 132	0.994 098	0.994 064
35.0	0.994 030	0.993 995	0.993 961	0.993 926	0.993 891	0.993 857	0.993 822	0.993 787	0.993 752	0.993 717
36.0	0.993 682	0.993 647	0.993 611	0.993 576	0.993 541	0.993 505	0.993 469	0.993 434	0.993 398	0.993 362
37.0	0.993 326	0.993 290	0.993 254	0.993 218	0.993 182	0.993 146	0.993 109	0.993 073	0.993 036	0.993 000
38.0	0.992 963	0.992 926	0.992 889	0.992 852	0.992 815	0.992 778	0.992 741	0.992 704	0.992 667	0.992 629
39.0	0.992 592	0.992 554	0.992 517	0.992 479	0.992 442	0.992 404	0.992 366	0.992 328	0.992 290	0.992 252

*Based on the work of H. Wagenbreth and W. Blanke, PTB - Mitteilingen 6-71.
Reference equations for Air-Saturated or Air-Free distilled water may be used but reference source should be noted.

Table 9.9 Density of Air, g/cm^3, as Function of Temperature and Air Pressure[*]

Barometric Pressure			Temperature, °C					
kPa	**mbar**	**mm Hg**	**18**	**20**	**22**	**24**	**26**	**28**
77.33	773	580	0.000 92	0.000 92	0.000 91	0.000 91	0.000 90	0.000 90
79.99	800	600	0.000 95	0.000 95	0.000 94	0.000 93	0.000 93	0.000 92
82.66	827	620	0.000 99	0.000 98	0.000 97	0.000 96	0.000 96	0.000 95
85.33	853	640	0.001 02	0.001 01	0.001 00	0.001 00	0.000 99	0.000 98
87.99	880	660	0.001 05	0.001 04	0.001 03	0.001 03	0.001 02	0.001 01
90.66	907	680	0.001 08	0.001 07	0.001 07	0.001 06	0.001 05	0.001 04
93.33	933	700	0.001 11	0.001 10	0.001 10	0.001 09	0.001 08	0.001 07
95.99	960	720	0.001 14	0.001 14	0.001 13	0.001 12	0.001 12	0.001 10
98.66	987	740	0.001 18	0.001 17	0.001 16	0.001 15	0.001 14	0.001 13
101.32	1013	760	0.001 21	0.001 20	0.001 19	0.001 18	0.001 17	0.001 17
103.99	1040	780	0.001 24	0.001 23	0.001 22	0.001 21	0.001 21	0.001 20
106.66	1067	800	0.001 27	0.001 26	0.001 25	0.001 24	0.001 24	0.001 23

Computed for air at 50 % relative humidity

*Equations to compute the density of air at any pressure, temperature, and relative humidity are given in Section 8 of the Appendix to SOP No. 2 and are preferred for all precision mass and volume calibrations.

Table 9.10 Density and Coefficient of Expansion

Material	**Density**	**Coefficient of Expansion**		
	g/cm^3	**Linear (/°C)**	**Cubical (/°C)**	**Cubical (/°F)**
Aluminum	2.7	0.000 024	0.000 069	0.000 038 *(not suitable for provers)*
Brass	8.4 at 0 °C 8.390 9 at 20 °C	0.000 019	0.000 054	
Cast iron	7.0 7.2	0.000 010	0.000 030	
Copper		0.000 017	0.000 050	
Diamond		0.000 001 18	0.000 003 5	
Fused silica (quartz)		0.000 000 5	0.000 001 6	
Glass, borosilicate (T1CA)			0.000 010	
Glass, borosilicate (T1CB)			0.000 015	
Glass, soda-lime			0.000 025	
Gold	18.0		0.000 043	
Invar		0.000 000 4	0.000 001 2	
Lead	11.34	0.000 029	0.000 087	
Length bench		0.000 010 6		
Mercury			0.000 018	
Nichrome	8.39		0.000 039	
Nichrome V	8.5		0.000 039	
Platinum		0.000 011	0.000 027	
Polycarbonate plastic			0.000 45	
Polypropylene plastic			0.000 24	
Polystyrene plastic			0.000 21	
Steel, stainless (mass)	7.84, 7.95, 8.0		0.000 045	
Steel, stainless (provers)		0.000 018	0.000 047 7	0.000 026 5
Steel, tape, mild		0.000 0116	0.000 033 5	
Steel, pressure vessel, low carbon				0.000 016
Steel, prover, low carbon		0.000 012	0.000 033 5	0.000 018 6
Steel, terne plate		0.000 012	0.000 035	0.000 019 5
Tantalum	16.6		0.000 020	
Water (20 °C)			0.000 21	

Reference values for cubical coefficient of expansion given in per °F are provided as reference for prover calibrations used for petroleum products where the reference temperature is 60 °F.

Table 9.11 A Short Table of Random Numbers

46	96	85	77	27	92	86	26	45	21	89	91	71	42	64	64	58	22	75	81	74	91	48	46	18
44	19	15	32	63	55	87	77	33	29	45	00	31	34	84	05	72	90	44	27	78	22	07	62	17
34	39	80	62	24	33	81	67	28	11	34	79	26	35	34	23	09	94	00	80	55	31	63	27	91
74	97	80	30	65	07	71	30	01	84	47	45	89	70	74	13	04	90	51	27	61	34	63	87	44
22	14	61	60	86	38	33	71	13	33	72	08	16	13	50	56	48	51	29	48	30	93	45	66	29
40	03	96	40	03	47	24	60	09	21	21	18	00	05	86	52	85	40	73	73	57	68	36	33	91
52	33	76	44	56	15	47	75	78	73	78	19	87	06	98	47	48	02	62	03	42	05	32	55	02
37	59	20	40	93	17	82	24	19	90	80	87	32	74	59	84	24	49	79	17	23	75	83	42	00
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67	59	28	25	47	89	11	65	65	20	42	23	96	41	64	20	30	89	87	64	37	93	36	96	35
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39	91	63	18	38	27	10	78	88	84	42	32	00	97	92	00	04	94	50	05	75	82	70	80	35
74	62	19	67	54	18	28	92	33	69	98	96	74	35	72	11	68	25	08	95	31	79	11	79	54
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06	36	63	06	15	03	72	38	01	58	25	37	66	48	56	19	56	41	29	28	76	49	74	39	50
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16	94	85	82	89	07	17	30	29	89	89	80	98	36	25	36	53	02	49	14	34	03	52	09	20
04	93	10	59	75	12	98	84	60	93	68	16	87	60	11	50	46	56	58	45	88	72	50	46	11
95	71	43	68	97	18	85	17	13	08	00	50	77	50	46	92	45	26	97	21	48	22	23	08	32
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80	20	32	80	98	00	40	92	57	51	52	83	14	55	31	99	73	23	40	07	64	54	44	99	21
13	50	78	02	73	39	66	82	01	28	67	51	75	66	33	97	47	58	42	44	88	09	28	58	06
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71	20	03	30	79	25	74	17	78	34	54	45	04	77	42	59	75	78	64	99	37	03	18	03	36
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50	54	73	81	91	07	81	26	25	45	49	61	22	88	41	20	00	15	59	93	51	60	65	65	63
49	33	72	90	10	20	65	28	44	63	95	86	75	78	69	24	41	65	86	10	34	10	32	00	93
11	85	01	43	65	02	85	69	56	88	34	29	64	35	48	15	70	11	77	83	01	34	82	91	04
34	22	46	41	84	74	27	02	57	77	47	93	72	02	95	63	75	74	69	69	61	34	31	92	13

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