SOP 17

Standard Operating Procedure for Control Charts of Laboratory Owned Check Standards for Calibration of Measuring Flasks or Small Provers using Volume Transfer Methods[1]

1 Introduction

1.1 Purpose

This procedure may be used to develop and maintain control charts to monitor the statistical control of the volume transfer method for calibration of measuring flasks or 5 gallon test measures, especially when using the Standard Operating Procedures (SOP 16 or 18) for this purpose. The same principles may be applied to the development of control charts for other calibration procedures.

1.2 Prerequisites

1.2.1 The procedure to be monitored must match the calibration procedure that is used.

1.2.2 A clean quality assurance reference flask (QARF), suitable check standard (see 3.1), or a 5 gallon check standard must be available. Verify the cleanliness of the vessel or take corrective actions.

2 Summary

A reference volumetric flask (or a series of such) or check standard is obtained and calibrated several times initially to establish a reliable mean value and to estimate the standard deviation of calibration. All such calibrations are made using SOP 16, 18, or an equivalent procedure. Directions for preparing and using an $\bar{x}$ and an R control chart are given. The $\bar{x}$ control chart monitors the process with respect to both the standard and the variability, while the R control chart monitors its short-term precision. When the calibration process is determined to be in a state of statistical control, the calibrations made at that time may be considered to be valid and the process standard deviation may be used, as appropriate, to calculate the uncertainty for the calibrations using SOP 29.

Note: If a full evaluation of the process bias is desired, it is best if the reference value of the QARF or check standard are provided by an independent laboratory such as NIST or a laboratory accredited to perform volume calibrations, preferably using gravimetric methods.

1 Non-SI units are predominately in common use in State legal metrology laboratories, and/or the petroleum industry for many volumetric measurements, therefore non-SI units have been used to reflect the practical needs of the laboratories performing these measurements as appropriate.

3 Equipment

3.1 A quality assurance reference flask(s) (QARF) or check standard is required, constructed of similar materials and design as the standards under calibration. A 1 pt and a ½ gal flask or a 2 pt and 1 qt flask are recommended for glass flasks when monitoring SOP 16 (or other suitable volumetric standards that match the range of items calibrated by the laboratory). A 5 gal check standard is recommended for monitoring SOP 18.

3.2 All equipment designated in SOP 16 or SOP 18 as appropriate.

4 Procedure

4.1 Initial Measurements

4.1.1 Calibrate the QARF or 5 gallon check standard a minimum of 12 times to establish the baseline chart. A calibration is defined as the result of duplicate measurements as required by the SOP (i.e., a complete test consists of two runs). Calibrations may be made on successive days, but no two complete tests should be made on any single day. Note: 25 to 30 points are recommended to determine uncertainties.

4.1.2 Tabulate the measurement data using the notation and a form such as the one contained in the Appendix of this SOP. The data may be maintained in a spreadsheet or other electronic program in lieu of a paper form.

4.1.3 Calculate the mean of the two trials $\bar{x}_i$ and the ranges between runs. The ranges R_i, are the absolute differences between run 1 and run 2 for the n tests. Calculate the average range $|\bar{R}|$ of the trials, for the n tests as follows:

$$\bar{R} = \frac{\sum |R_i|}{n} \qquad \text{Eqn. 1}$$

4.1.4 Estimate the standard deviation of the process s_p, based on the check standard volume on each of n occasions, as follows:

$$s_p = \sqrt{\frac{\sum \left(\bar{x}_i - \bar{\bar{x}}\right)^2}{(n-1)}} \qquad \text{Eqn. 2}$$

where:

$\bar{x}_i$	The mean value of each complete test.
$\bar{\bar{x}}$	The mean value of all averages made on n occasions

4.1.5 For a smaller number of measurements (less than 30) the standard deviation may be calculated using the average range as follows (obtain values for d_2^* from NISTIR 6969 Table 9.10 and see NISTIR 6969 Section 8.3 for additional notes):

$$s_p = \frac{\overline{R}}{d_2^*} \qquad \text{Eqn. 3}$$

Be sure that only absolute values are used in the determination of the range and average range!

4.2 Construction of Control Charts

Construct the following control charts using the data of section 4.1.

4.2.1 Construct an $\bar{x}$ control chart for a check standard with the following control limits:

Reference value (if available)	
Central Line =	$\bar{\bar{x}}$ (mean of the average values)
Lower warning limit (LWL) =	$\bar{\bar{x}} - 2s_p$
Lower control limit (LCL) =	$\bar{\bar{x}} - 3s_p$
Upper warning limit (UWL) =	$\bar{\bar{x}} + 2s_p$
Upper control limit (UCL) =	$\bar{\bar{x}} + 3s_p$

4.2.2 Construct an *R* (range chart) control chart for duplicate measurements having the following control (or action) limits. Note that *R* (the range) and |*d*| (absolute difference of duplicate measurements) are equivalent for duplicate measurements.

Central Line	=	$\overline{R}$ (average range)
LCL = LWL	=	0

(There should be no negative numbers recorded when using absolute values!)

UWL	=	$2.512\ \overline{R}$
UCL	=	$3.267\ \overline{R}$

These limits are *t* values for 95 % and 99.7 % confidence intervals for a sample size of 30.

4.3 Use of Control Charts

4.3.1 An appropriate QARF or check standard is calibrated each time the laboratory performs calibrations using the SOP. If the calibrations extend over several days, the check standard is calibrated daily. The values of $\bar{x}$ and *R* for each calibration of the check standard are plotted on the respective control charts, preferably in sequential order. The limits on the charts are such that 95 % of the values should fall within the warning limits and rarely should a value fall outside of the control limits, provided that the system is in a state of statistical control.

4.3.2 If the plotted value of $\bar{x}$ lies outside of the control limits and the corresponding value

on the *R* chart is within the control limits, a source of systematic error is suspected. Poor drainage is a possible source of bias for low values and changes of drainage technique should be considered as a cause for high values. Sources of error can result from the use of the volumetric standards as well as of the vessels being calibrated. Changes in criteria for reading the meniscus are also possible sources of error or difference.

4.3.3 If the values for the *R* chart fall outside of the warning limits but inside of the control limits, a decrease in precision is indicated. Cleanliness and procedural problems should be investigated.

4.3.4 No calibration data should be accepted when the system is out of control.

4.3.5 If the plotted values for either $\bar{x}$ or *R* are outside of the warning limits but inside of the control limits, a second set of duplicate calibrations should be made. If the new values are within the warning limits, the process may be considered to be in control. If they lie outside of the warning limits, lack of control is indicated. Corrective actions should be taken and attainment of control demonstrated before calibration measurements are considered to be acceptable.

4.3.6 Even while the system is in an apparent state of control, incipient troubles may be indicated when the control data show short- or long-term trends, shifts, or runs. The *t*-test and *F*-test may be used to assess the significance of such observations (see NIST IR 6969 Section 8.9, 8.10, and 8.11).

5 Interpretation of Control Chart Data

5.1 Demonstration of "in control" status indicates that the calibration process is consistent with the past experience of the laboratory. That is to say, there is no reason to believe that excessive systematic error or changes in precision have occurred.

5.2 To the extent appropriate, the precision of measurement of the QARF or check standard may be extended to the calibration of other glassware or small volume provers calibrated using the same SOP. This means that the process standard deviation, s_p, is transferable to measurements of similar nominal size made by the same measurement method.

5.3 Extension of the s_p for the QARF to other calibrations assumes that all aspects of its calibration correspond to those for the other calibration. If the volumes of the respective glassware are comparable as well as the sizes of necks and graduation lines, this may be justified. It may be necessary to have a series of QARF's or check standards with corresponding control charts to monitor the calibration process for a range of volumetric calibrations.

Appendix
Control Chart Data

QARF/Check Std ID _____ Nominal Capacity _____

Test Number	Date	Trial No. 1 V_{TD} X_1	Trial No. 2 V_{TD} X_2	V_{TDM} $(\bar{x})$	$\lvert d\rvert$ = $\lvert X_1 - X_2\rvert^*$	standard deviation***
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
13						
14						
15						
SUM						
				$\sum \bar{x}$	$\sum \lvert d\rvert$	pooled std dev:

n^{**} = _____ $\bar{\bar{x}} = \frac{\sum \bar{x}}{n} =$

$\bar{R} = \frac{\sum |R|}{n} =$ _____ UWL = $2.512\,\bar{R}$ =

$s = \sqrt{\frac{\sum \left(\bar{x} - \bar{\bar{x}}\right)^2}{(n-1)}}$ UCL = $3.267\,\bar{R}$ =

* This is the range, *R*, of the two trials and is actually the larger value minus the smaller value.
***n* is the number of tests used to calculate the control limits.
***Use of the standard deviation and pooled standard deviations are preferred when a standard artifact is maintained in the laboratory as a check standard.