STATISTICAL ANALYSIS

Interlaboratory System to Ensure and Improve the Quality of Glassware Calibration and Use in a Large Laboratory

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This paper describes the implementation and methodology of an interlaboratory system that ensures the quality of glassware calibration and use in a large laboratory. The interlaboratory system involves periodic comparisons between laboratories with evaluations and improvements made over time. Two similar items are calibrated in each exercise according to a detailed calibration procedure. The reference value is traceable to the international system supplied by a metrology laboratory. The results are evaluated as normalized errors and analyzed by Youden graphs. The calibration procedure is presented. An interlaboratory experiment is described in which 7 participating laboratories performed calibrations of 2 volumetric flasks. The reported results, the interlaboratory evaluation, and the actions taken are presented.

A good analytical method is necessary to obtain reliable results. However, that is not enough; additional requirements must be met to obtain acceptable results. Consequently, most laboratories have implemented a quality assurance system, for example, by following ISO 17025 guidelines (1).

The Technological Laboratory of Uruguay is certified according to ISO 9001 (2). Approximately 250 tests and calibrations are accredited by ISO 17025, which has a Quality Management System that ensures the quality of our results and complies with legal, technical, and formal requirements.

ISO 9001, section 7.6, and ISO 17025, section 5.6, have established the need to use calibrated equipment during a test procedure.

Because we are describing a large laboratory that includes different specialized departments, a large volume of glassware is used. In the past, all glassware used in the laboratory was calibrated by an internal department specializing in metrological measurements, the Scientific Metrology Department. To improve the management of our laboratory resources and the quality of our analytical results, we implemented a policy requiring calibration of glassware by the personnel of the department using it. The advantages of this policy include (*1*) assurance that the glassware is used by the same personnel under the same conditions as those used for calibration, (*2*) glassware is readily available when needed, and (*3*) the possibility of decreasing calibration costs.

One way to ensure the quality of the test process is to maintain the quality of each subprocess involved in the test. When glassware is used in a test, we can assume that the test includes the subprocess "use of glassware." Therefore, it is important to use both calibrated glassware during the test and the "use of glassware" subprocess to ensure the quality of the test process. We must consider that issues detected in glassware calibration reflect problems in its use, including all processes that involve glassware.

To evaluate the performance of glassware "use" and "calibration" processes, an internal interlaboratory system was implemented.

The main objectives of an interlaboratory comparison are to provide a strong tool for laboratories to evaluate the competency of personnel, the calibration of equipment, quality control, the applicability of the method, and the tendencies of the results obtained over time.

Description

Summary

The interlaboratory system consists of periodic internal comparisons, obtained by using a detailed calibration procedure based on ISO standards, which also define how all the involved equipment is calibrated and traceable to the International System.

The interlaboratory reference value is supplied by the Scientific Metrology Department. These volume measurements are traceable to the International System; because the Quality System is based on ISO 17025, good results are obtained in Sistema Interamericano de Metrologia (SIM) intercomparisons. Mass and temperature capacities are declared in °C in the appendix of the agreement of the International Committee for Weights and Measures (CIPM); the mass and temperature calibrations are accredited by an International Laboratory Accreditation Cooperation (ILAC) signatory organization.

Interlaboratory System

The interlaboratory system consists of periodic intercomparisons with evaluation and improvement

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Table 1. Results reported by participants for flask 1

	Lab No.						
Parameter	1	2	3	4	5	6	7
V_{20}, cm^3	100.008	100.077	100.057	100.094	100.069	100.089	100.071
U_{DEPT}	0.009	0.018	0.013	0.030	0.012	0.037	0.018
E	–0.086	–0.017	–0.037	0.000	–0.025	–0.005	–0.023
E_n	–3.24	–0.54	–1.30	0.01	–0.89	–0.11	–0.74

undertaken over time. Periodic interlaboratory exercises are organized through an internal Chemical Metrology Program, in which different types and capacities of glassware are selected to evaluate calibration performance.

In each interlaboratory exercise, 2 items of the same nominal value are selected and calibrated by the Scientific Metrology Department to assign the reference value. These items are calibrated by the participant departments in a planned round, with a sequence agreed to by all participants. Calibrations are performed, and results (calibration data with the associated uncertainty) are sent to the organizer, who processes the data, evaluates the results, and prepares the final report.

A meeting takes place after each interlaboratory exercise to discuss the results and assign the causes of tendencies and deviations. Corrections and corrective and preventive actions to be implemented are discussed. Improvements in procedures and organizations are agreed upon for implementation.

Calibration of Interlaboratory Results

The reported participant results are evaluated as normalized error, E_n, and calculated as follows:

$$E_n = \frac{E}{\sqrt{\left(U^2_{REF} + U^2_{DEPT}\right)}} = \frac{E_{DEPT} - E_{REF}}{\sqrt{\left(U^2_{REF} + U^2_{DEPT}\right)}}$$

where E is the error value in cm^3, E_{DEPT} is the participant value in cm^3, E_{REF} is the reference value in cm^3, U_{DEPT} is the participant value uncertainty in cm^3, and U_{REF} is the reference value uncertainty in cm^3. Calibration performance is considered good if normalized errors are ≤1.

Interlaboratory Final Report

Error graphs with uncertainty bars and Youden graphs are given in the final report to make the interpretation of results and the evaluation easier. Systematic and random deviations are analyzed.

An Interlaboratory Exercise

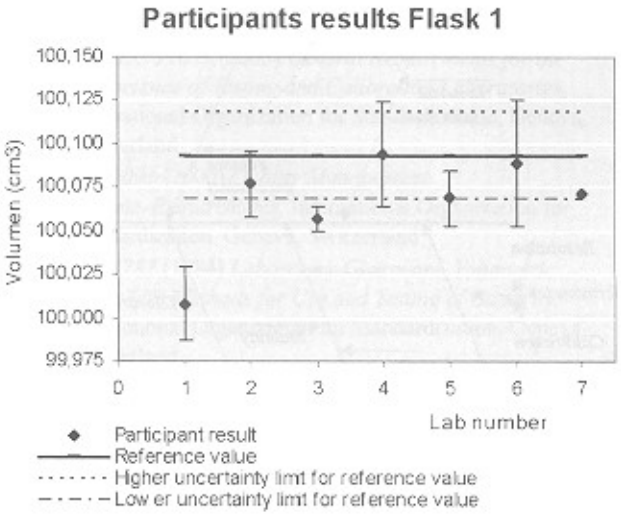
The items calibrated in this interlaboratory exercise were 2 type A volumetric flasks with a nominal capacity of 100 cm^3. Seven participating departments were involved in this exercise. The participant-reported results, the error results, and the normalized errors are shown in Tables 1 and 2 for flasks 1 and 2, respectively. The results of the participants and the Youden graph are shown in Figures 1 and 2, respectively.

The analyses of the normalized errors show good performance of participants 2, 4, 6, and 7. Participant 1 shows normalized errors of >1 for both flasks, and participants 3 and 5 show normalized errors of >1 for one of the items. The Youden graph shows a preeminence of systematic errors for participants 1 and 3–7, and participant 2 has a preeminence of random errors. The main possible causes for systematic errors are "setting the meniscus," "temperature measurements," and the "quality of distilled water" used.

At the final evaluation meeting where a glassware calibration expert explained the main goals of glassware calibration, training was implemented as a corrective action. The participants who did not have good performance in the intercomparison study repeated the calibrations until the results were accepted. Additional precautionary notes were included in the calibration procedure to improve performance.

Table 2. Results reported by participants for flask 2

	Lab No.						
Parameter	1	2	3	4	5	6	7
V_{20}, cm^3	99.948	100.072	100.046	100.055	100.007	100.050	100.059
U_{DEPT}	0.021	0.019	0.007	0.030	0.016	0.036	0.021
E	–0.111	0.013	–0.013	–0.004	–0.052	–0.009	–0.003
E_n	–3.32	0.40	–0.48	–0.10	–1.70	–0.20	–0.09



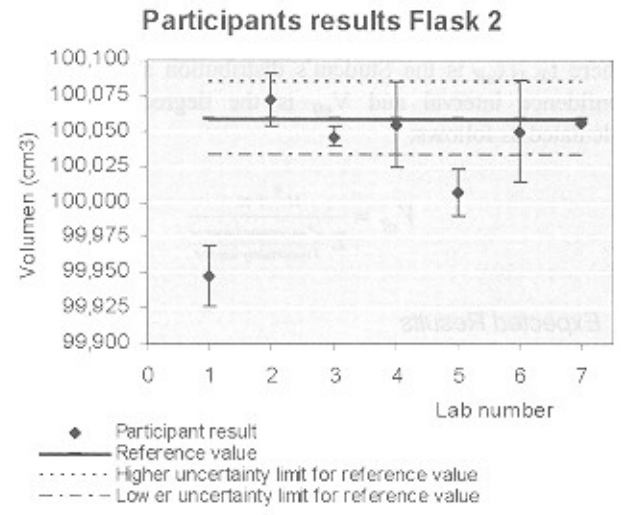


Figure 1. Participants' results.

Summary of the Calibration Procedure

(a) *Scope.*—The calibration procedure is applicable to glassware (volumetric pipets, flasks, and burets) with a capacity of 0.1–2000 cm^3.

(b) *Equipment and materials.*—Distilled or deionized water suitable for general laboratory purposes must be used. All equipment must be traceable to the International System and includes a laboratory balance with sufficient capacity to weigh the load vessel (in the case of pipets and burets) or the flask with an uncertainty of ≤1/10 of the tolerance of the glassware class to be calibrated, as stated in the corresponding ISO standard, and a thermometer to measure water temperature with an uncertainty of <0.1°C.

(c) *Environmental conditions.*—All calibrations must be carried out at constant room temperature (drift must be <1°C/h).

(d) *Calibration method.*—The method is based on ISO 4787 (3), which can be summarized as follows:

During the calibration, measure the average temperature of the water. All calibrations must be made at least in triplicate. (*1*) *For calibration of volumetric flasks.*—Weigh the dry flask. Fill the flask with water to a distance of a few millimeters under the graduation line by running water down the vessel wall of the neck. Dry the neck above the graduation line and set the volume. Weigh the flask again. (*2*) *For calibration of pipets and burets.*—Weigh a vessel. Clamp the pipet in a vertical position, and fill it above the graduation mark; dry the end of the pipet, set the volume, and deliver the water in the vessel. Weigh the vessel again.

(e) *Volume calculation.*—Use the following equation:

$$V_{20} = (M_2 - M_1) * \left(\frac{1}{\rho_w - \rho_a}\right) * \left(1 - \left(\frac{\rho_a}{\rho_b}\right) * (1 - \gamma(t - 20))\right)$$

where V_{20} is the volume at the reference temperature of 20°C in cm^3, t is the average calibration temperature of the water in °C, $M_2 - M_1$ is the conventional mass of water at t in g, ρ_w is the water density in g/cm^3, ρ_a is the density of the air in g/cm^3 (we assume normal local conditions, i.e., 0.0012 g/cm^3 with a tolerance of 0.0001 g/cm^3), ρ_b is the conventional weight density in g/cm^3, and γ is the volumetric thermal expansion coefficient of the glass in $°C^{-1}$.

Conformity with the tolerance of the glassware class is evaluated by comparing the results with the requirement established in ISO 648 (4), ISO 385 (5), and ISO 1042 (6) standards.

(f) *Uncertainty estimation.*—Estimation of uncertainty is based on the *Guide to the Expression of Uncertainty in Measurement* (7). To estimate the total uncertainty, it may be necessary to identify the major sources of uncertainty and evaluate the contribution of each source. The relevant sources of uncertainty are shown in Figure 3.

Each uncertainty component associated with each potential source is quantified as follows:

Uncertainty $(M_2 - M_1)$:

$$u_{m2-m1\text{-}balance\text{-}uncertainty} = \frac{u_{balance\text{-}calibration}}{k_{balance\text{-}calibration}}$$

Uncertainty (t):

$$u_{t,\,termometer\text{-}resolution} = \frac{termometer \cdot resolution}{\sqrt{12}}$$

$$u_{t,\,termometer\text{-}calibration} = \frac{u_{termometer\text{-}calibration}}{k_{termometer\text{-}calibration}}$$

$$u_{t,\,stability} = \frac{temperature \cdot drift}{\sqrt{12}}$$

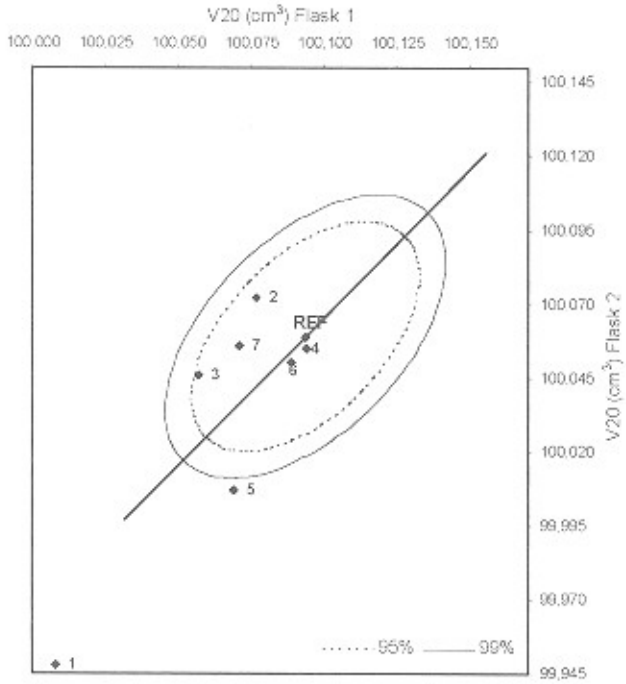


Figure 2. Youden graph of participants' results for flasks 1 and 2.

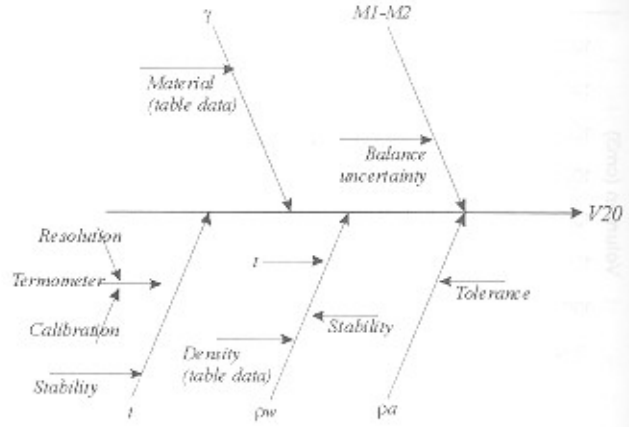


Figure 3. Cause-effect diagram showing the major sources of uncertainty.

Uncertainty (ρw):

$$u_{\rho w\ data\ table} = \frac{U_{experimental}\ (table\ data)}{k(table\ data)}$$

Uncertainty (ρa):

$$u_{\rho a\ tolerance} = \frac{tolerance}{\sqrt{3}}$$

Uncertainty (γ):

$$u_{\gamma data\ table} = \frac{U_{experimental}\left(table\ data\right)}{k\left(table\ data\right)}$$

Combined uncertainty is calculated as follows:

$$u_{cV20} = \sqrt{\left(c\cdot u\right)^2_{M2} + \left(c\cdot u\right)^2_{M1} + \left(c\cdot u\right)^2_{\rho a} + \left(c\cdot u\right)^2_{\rho w} + \left(c\cdot u\right)^2_{t}}$$

where u is the standard uncertainty of the subscripted source and c is the sensitivity coefficient of the subscripted source quantified as follows:

$$c_i = \frac{\partial V_{20}}{\partial Uncertainty\cdot source\cdot i}$$

Finally, expanded uncertainty is quantified as follows:

$$U = u_{cV20}\cdot t_{95.45;Veff}$$

where $t_{95.45;Veff}$ is the Student's distribution at the 95.45% confidence interval and V_{eff} is the degree of freedom calculated as follows:

$$V_{eff} = \frac{u^4_{cV20}}{\sum \frac{u^4_{uncertainty\ source}}{Vuncertainty\ source}}$$

Expected Results

Results expected as a consequence of this interlaboratory system over time are shown below:

(a) *Measurement traceability.*—International System traceability of volumetric measurements assigned through the Metrology Department.

(b) *Procedure improvement.*—Improvement of the calibration procedure in a synergic way as a result of personnel feedback shared in discussions that take place after each exercise.

(c) *Lower uncertainties.*—Lower uncertainties achieved over time as a result of improvements in the procedure and analyst competence.

(d) *Unified glassware list.*—Implementation of a unified glassware list where all departments can find information related to the uncertainty and accuracy of each glassware item allowing the use of alternative glassware when required.

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