Estimation of meniscus reading uncertainty in volume calibration of conical volumetric instruments

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Abstract. One of the major uncertainty sources during gravimetric volume calibration of laboratory glassware is the meniscus reading. To estimate this uncertainty, the internal diameter of the volumetric instrument at the calibration point must be known. Data for internal diameters are available from international standards for several volumetric instruments with cylindrical meniscus reading section. However, there are another kind of volumetric instruments with conical meniscus reading section, like Imhoff cones, whose internal diameter values are not available. This work aims to show how to overcome this problem through the measurement of the internal diameters with an optical comparator. The calculated correction due to the meniscus setting was also put in nomograms, which allow reading directly the value of the uncertainty contribution and illustrates the changes in the meniscus reading uncertainty contribution as the calibration point changes, unlike what happens with cylindrical laboratory volume instruments.

1. Introduction

In the volume calibration of volumetric instruments by the gravimetric method, one of the influence quantities for the uncertainty budget is the correction due to the meniscus setting. This contribution depends on the error of meniscus reading and the cross-section area of the instrument at the graduation line [1, 2]. Typical values of the error of meniscus reading are reported elsewhere [1]. This error depends strongly on the skill of the operator and the visual aids the laboratory has available for the meniscus reading. Moreover, there are international standards that include specification of the internal diameter of the volumetric instruments (single-volume pipettes [3], one-mark volumetric flasks [4], etc.), and the calculation of the meniscus setting uncertainty contribution is straight [1, 2]. However, it is common for a calibration laboratory be prompted to the volume calibration of another kind of laboratory volumetric instruments, which has a conical shape in the meniscus reading zone (Imhoff cones, centrifuge tubes, etc.) Here, there is no internal diameter data available for every graduation line.

In this work, internal diameter measurements of conical laboratory glassware were made with an optical comparator according to an accredited measurement procedure [5]. The measurement system was validated with the measurements obtained for cylindrical volumetric instruments, whose internal diameters requirements are reported in [3, 4]. Then, the correction due to meniscus resolution was calculated for various combinations of instruments and values of the error in the meniscus reading. Provided the point of calibration and the value of the error in the adjustment of the meniscus are known, as suggested in [1, 2], nomograms for the correction illustrate the changes in the contribution due to a change in the calibration point, unlike what happens with the cylindrical volumetric instruments.
2. Materials and Methods

2.1. Measuring the internal diameter of volumetric laboratory glassware
An optical comparator with a 20X lens was used for all the measurements of internal diameters. The measurement intervals are (0 to 250) mm on the X axis and (0-150) mm on the Y-axis, with a display resolution of 0.001 mm. The measurement procedure was carried out in an accredited laboratory according to the standard [5] and implies to place the volumetric instrument vertically using a fixture. A bubble level is used to ensure that the container is leveled and then the image is adjusted to find the internal walls of the container and take the reading of the internal diameter (figure 1).

![Centrifuge tube internal diameter measurement with an optical comparator.](image)

Figure 1. Centrifuge tube internal diameter measurement with an optical comparator. Experimental setup.

2.2. Uncertainty of the internal diameter measurement with an optical comparator
The uncertainty of the internal diameter measurement is a Type B evaluation one and accounts for the following contributions: repeatability, $u(\text{rep}_{oc})$; resolution, $u(d_{oc})$; and optical comparator standard, $u(Std_{oc})$. Combining these contributions allows estimating the uncertainty of measurement of the internal diameter through the following equation:

$$u_{D_i} = [u(\text{rep}_{oc})^2 + u(d_{oc})^2 + u(Std_{oc})^2]^{1/2}$$

The expanded uncertainty of the internal diameter measurement is calculated with a coverage factor $k = 2$. Values from 0.004 % to 0.045 % relative to the average value of the measurements were obtained.

2.3. Measurement method validation through normalized laboratory volumetric instruments
The results obtained when applying the proposed measuring methodology for internal diameters of standard volumetric containers are shown in table 1. One-mark volumetric flasks and single-volume pipettes of several commercial brands were used to validate the agreement between the values reported on the standards and the results of the measurement method.

| Volumetric instrument | Standard | Internal diameter (standard) / mm | Internal diameter (measurement) / mm | Uncertainty (k = 2) / mm |
|-----------------------|----------|---------------------------------|-------------------------------------|------------------------|
| Single-volume pipette Pyrex 10 ml | [3] | ≤ 5 | 4.783 | 0.001 9 |
| Single-volume pipette Assistant 5 ml | [3] | ≤ 4.5 | 3.324 | 0.001 7 |
| Volumetric flask Pyrex 100 ml | [4] | 13 ± 1 | 13.743 | 0.003 9 |
| Volumetric flask Marienfeld 100 ml | [4] | 13 ± 1 | 12.373 | 0.002 5 |

Note: Pyrex, Assistant, and Marienfeld are trademarks.
2.4. Meniscus setting uncertainty
As shown in [1] for a cylindrical volumetric container, computing the meniscus setting uncertainty involves the following formula.

\[ C_{res} = \pi D_i^2 h / 4 \]  \hspace{1cm} (2)

Where, \( C_{res} \) is the correction for adjusting the meniscus, cm\(^3\); \( D_i \) is the internal diameter of the volumetric instrument in the meniscus lowest point, cm; and \( h \) is the error in the observation of the meniscus position, cm. Moreover, the relationship between the volume contained in a conical volumetric measurement and the inner diameter, at a certain calibration point may be suitably modeled as:

\[ D_i = KA^p \]  \hspace{1cm} (3)

Where, \( A \) is the nominal volume at the calibration point, cm\(^3\); and \( K \) and \( p \) are the constants of a power regression model. Constants \( K \) and \( p \) for each of the conical volumetric instruments mentioned in the results section were obtained. The coefficients of determination \( (R^2) \) obtained, ranging from 0.979 4 to 0.999 4, indicating a good performance of statistical models to predict the measured values.

2.5. Nomograms
Nomograms (the Greek nomos: law) are graphical representations of relationships or mathematical laws [6]. Nomograms survive computers because of its versatility to display the solution of complex nonlinear equations, as well as its training appeal. Although there are many types of nomograms, the most common is the parallel scales, which generally consists of three linear or curved scales, two for the independent variables, and another for the dependent one. Its use is simple: the values of the independent variables are in their respective scales, then a straight line joining both locations is traced. The intersection of the drawn line with the third line represents the value of the dependent variable. Nomograms of parallel scales showing the simultaneous solution of equations (2) and (3) are shown in figure 2.

3. Results and Discussion
Figure 2 shows the nomogram for a centrifuge tube. The independent variables are the volume at the calibration point, \( A \), and the error in the position of the meniscus, \( h \), while the dependent variable is the uncertainty contribution due to the meniscus setting, \( C_{res} \). For example, suppose you want to know the value of the uncertainty contribution of the meniscus reading, \( C_{res} \), for the centrifuge tube whose data are depicted in figure 2. The calibration point is at 2 cm\(^3\), and the reached error in the setting of the meniscus, \( h \), equals 0.01 cm. The use of the nomogram is as follows:

1. On the left scale, the volume value of the calibration point is located: \( A = 2 \) cm\(^3\);
2. On the center scale (without line), the point corresponding to the \( h \) value is located: \( h = 0.01 \) cm;
3. A straight line (dotted in figure 2), from the \( A \) point, crossing the \( h \) point, until reaching the right scale, where \( C_{res} \) value could be read: \( C_{res} = 0.015 \) cm\(^3\).

Only one nomogram is shown for the sake of saving space and not sacrifice ease of reading and clarity by inserting many very small nomograms in the document. Besides, the choice of the cylindrical volumetric instrument (a centrifuge tube) is based on information from the accredited laboratory of the institution of affiliation of most of the authors. That information shows that the centrifuge tubes comprise nearly 40% of conical volumetric instruments to which the laboratory is asked to calibrate.

4. Conclusions
Without information on internal diameters of conical volumetric instruments, the laboratories do not have the conditions to correctly estimate the uncertainty due to the correction for the meniscus reading during calibration of such containers, which use is considerable in the industry.

Measurements of the internal diameter of cylindrical volumetric instruments were conducted using a reliable and validated system, with values of relative uncertainty in the measurement under 0.5%. How
to construct a nomogram starting with the experimental information has been shown. The nomogram allows to read directly on it the uncertainty contribution due to the meniscus setting and serves as a tool to illustrate the gradient of the contribution because of the change in the point of calibration.

![Nomogram for a LK® centrifuge tube, model ASTM®](image)

**Figure 2.** Nomogram for a LK® centrifuge tube, model ASTM®.

**References**

[1] ISO 4787:2010 (E) *Laboratory glassware – Volumetric instruments – Methods for testing of capacity and for use* (Geneva: ISO).

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