Uncertainty due to Meniscus Reading on Conical Graduated Volumetric Instruments

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ABSTRACT A method to determine the uncertainty in reading the location of a concave meniscus in conical graduated volumetric instruments (CGVI) is presented. To estimate the meniscus uncertainty contribution in a volumetric instrument, the cross-section area of the meniscus location is required. Although data for the internal diameter of several volumetric instruments are available in international standards, all of them have cylindrical bodies. Hence, just one internal diameter value is reported for all the readings that can be made on the same apparatus. This work addresses the determination of meniscus reading uncertainty in CGVI through some internal diameters measurements made with an optical comparator. The measurements were used to generate cubic splines to interpolate all the other internal diameters required. With the internal diameter data, proposed formulae allow the computation of the meniscus reading contribution, which had a two percent error at most.

INDEX TERMS Centrifuge tube, Imhoff cone, meniscus reading, volume measurement.

I. INTRODUCTION

THE measurement of a liquid volume with an instrument is a frequent laboratory task in many sciences like chemistry or biology [1]. However, many other fields, including (bio)fuels, medicine, soil analysis, or oil industries, also require the maximum attainable accuracy in volume measurements of liquids [2]–[4]. The volumetric instruments usually are made of glass, plastic, or metal, with several capacities, accuracy, and shapes to meet their specific application requirements [1].

Most volumetric instruments have cylindrical bodies, so they only have to meet one specification in terms of their internal diameter; this is the case of burettes [5], pipettes [6], [7], one-mark volumetric flasks [8], or graduated measuring cylinders [9]. However, in soil analysis or crude oil analysis, for example, the use of conical graduated volumetric instruments (CGVI), such as Imhoff cones or centrifuge tubes, is also widespread [10] and metrologically relevant [11]. These type of volumetric instruments have their graduation lines in cone-shaped bodies and, because of this, they usually have a different internal diameter value for each graduation line [12], [13].

The most popular management systems standards require that the measurement instruments be calibrated or verified, especially if the measurements are involved in the customer value stream [14], [15]. Even when there are alternative methods for the calibration of volumetric instruments and vessels, the gravimetric method is the standard method used by accredited laboratories [16]–[18]. Procedures for the calibration by the gravimetric method is available in several international standards and other publications [19]–[21].

The mathematical model for the gravimetric calibration method has been established and reported elsewhere [19], [20]. The difference when calibrating CGVI compared to the calibration of cylindrical instruments is the contribution of meniscus position reading, which is usually the most significant source of uncertainty in volume determination [4], [17], [19]. All other sources of uncertainty, like weighing, water density, water temperature, thermal expansion, or air density, could be treated the same way.

On the other hand, setting the meniscus depends on the technical skills of the operator, the visual aids available, and the internal diameter of the volumetric instrument. For cylindrical volumetric instruments, how to address the un-
uncertainty due to meniscus reading has been stated for both graduated scale or one-mark volumetric apparatus [20]. In both cases, assuming there is only one internal diameter value for the entire instrument, which is valid for the cylindrical instruments whose values are included in the corresponding standards cited above. So the internal diameter specifications can be used during the calculation of the meniscus reading uncertainty.

However, the CGVI do not meet the assumptions of either of the two cases addressed in [20] because the CGVI do not have a constant volume between graduation lines along the scale of the volumetric apparatus, nor are they one-mark instruments. Moreover, they have several different internal diameter values along a graduated scale. So they can not be treated as constant internal diameter graduated instruments nor as instruments with a single graduation mark.

This paper is an extension of work initially presented in the XXII World Congress of the International Measurement Confederation (IMEKO 2018) and published [22]. While the same starting point is taken, the problem is addressed more comprehensively here. The original conference proceeding was oriented more to show how to use a nomogram (without showing how to build it) that contained the contributions due to the adjustment of the meniscus for just one instrument. On the other hand, in this work, how to address the meniscus reading uncertainty in any CGVI is shown. For a CGVI, some internal diameter measurements were done with an optical comparator, following a validated proposed method. With that measurements, cubic splines were used to generate interpolation polynomials for all other possible calibration points. Once having a way to know the internal diameter of the CGVI at any graduation line, the calculation of the uncertainty in the meniscus reading is straight-forward, as shown.

II. MATERIALS AND METHODS
For the internal diameter measurements of the CGVI, an optical comparator was used. A Vernier caliper is not an advisable option because the small inside jaws are not long enough to reach even the first graduation mark from top to bottom in an Imhoff cone. An alternative approach could be to measure the external diameters with the Vernier caliper and then discount twice the wall thickness of the volumetric instrument, assuming it is possible to measure the wall thickness. Doing so assumes that the wall thickness of the volumetric instrument remains constant at all graduation marks, which is not valid for the glassware (see Fig. 1), and glass is the most used material for laboratory apparatus [23].

A. EXPERIMENTAL SETUP
An optical comparator yields better accuracy than a Vernier caliper, even when it is more expensive and more complex equipment by far. Another advantage is that the internal diameter measurement is direct for any CGVI, provided the method suggested below is followed. In this work, an optical comparator with measurement intervals from (0 to 250) mm on the X-axis and (0 to 150) mm on the Y-axis, a 0.001 mm display resolution, and a 20X lens was used.

FIGURE 1: Close-up on the tip of a CGVI (an Imhoff cone). Notice how uneven the wall thickness is towards the tip.
C. OPTICAL COMPARATOR MEASUREMENT UNCERTAINTY

Table 1 shows the uncertainty analysis of the internal diameters with the optical comparator. There are only three significant contributors to the uncertainty: the optical comparator calibration, the display resolution, and the repeatability. The expanded uncertainty using a coverage factor of $k = 2$ to reach a 95.45% confidence level is also included. Values ranging from 0.004% to 0.055% were obtained as relative uncertainties to the average value of five measurements for all the internal diameter determinations made in this work. The values referred in Table 1 correspond to the highest value of nominal volume included in this work, i.e., the 1 000 mL volume of the Imhoff cone listed in Table 2.

D. MEASUREMENT METHOD ASSESSMENT

The measurements of the internal diameters of the CGVI were evaluated by comparing the results obtained with the proposed method in Section II-B against the internal diameter specifications given in international standards for the constructional requirements of glassware. Single-volume pipettes [6] and one-mark volumetric flask [8] of several glassware commercial brands were used for the evaluation. The results of the comparison are shown in Fig. 4 for volumetric glassware with several nominal values. As could be expected with a valid measurement method, the internal diameters of recognized glassware trademarks met the specification limits of international standards, and the expanded measurement uncertainty, $U_D(k = 2)$, is adequate for the intended use.

E. INTERNAL DIAMETER DATA CURVE FITTING

An Imhoff cone has more than 80 graduation lines [24], and a conical centrifuge tube has more than 40 [12]. Measuring the internal diameters of all of those graduation lines following the proposed method in Section II-B would be impractical, time-consuming, and hence, expensive. Therefore, as will be show in Section III-A, less than a half of the total required internal diameter values could be enough to adjust a mathematical model for the internal diameter of the CGVI as a function of its nominal volume at each graduation line. The fraction suggested of points actually measured must be distributed between the span of the calibration points required including the extreme values. Also, it is advisable to include more measured points in the zones with wall thickness variations.

1) Cubic splines approach

For mathematical modeling in this case, the best approach is to fit a series of curves that pass through each of the data points measured to get interpolation models [25]. Even when

| Parameter                          | Uncertainty /mm |
|-----------------------------------|-----------------|
| Calibration of comparator         | 8.38E-04        |
| Resolution                        | 2.887E-04       |
| Repeatability                     | 23.66E-04       |
| Combined standard uncertainty     | 0.002 527       |
| Expanded uncertainty ($k = 2$)    | 0.005 1         |

### FIGURE 2: Leveling and Imhoff cone on its stand with aid of a spirit level.

### FIGURE 3: Internal diameter measurement of a centrifuge tube with an optical comparator.
the nominal volume in a cone is just a quadratic function of its diameter, a second-order polynomial curve adjusting the whole set of measurements is not advisable because of the irregularities in the CGVI wall thickness (Fig. 1). Here we use cubic splines to get the equations for every interval of measured internal diameter data [25].

The cubic splines aims to develop a third-order polynomial for each interval between internal diameter measurements. Therefore, \( n + 1 \) internal diameter measurements yields \( n \) intervals and \( n - 1 \) interior knots. When writing (1) for each one of these interior measurements, \( n - 1 \) simultaneous equations arise, with the second derivatives of the corresponding interior nominal volumes as unknowns

\[
(V_i - V_{i-1})f''(V_{i-1}) + 2(V_{i+1} - V_i)f''(V_i) + (V_{i+1} - V_i)f''(V_{i+1}) = \frac{6}{V_{i+1} - V_i}(D_{i+1} - D_i) + \frac{6}{V_i - V_{i-1}}(D_{i-1} - D_i).
\]  

(1)

Once solved the \( n - 1 \) simultaneous (1), all the second derivatives of the interpolation knots are known, providing the end knots could be assumed to have second derivatives equal to zero [25]. Then, for each interval of two nominal volumes, \( V_{i-1} \) and \( V_i \), with measured internal diameters, \( D_{i-1} \) and \( D_i \), there will be a cubic equation like the following interval.

2) Cubic splines computing

The cubic splines were implemented in \( \mathbb{R} \) language for statistical computing [26] as follows:

1) Create a vector with the ordered values of the internal diameter measurements made with the optical comparator. For example:

\[
> D <- c(5.530, 7.979, 10.372, \ldots)
\]

2) Create a vector with the ordered values of the nominal volume that corresponds to each of the internal diameter measurement data. For example:

\[
> V <- c(0.1, 0.5, 1, \ldots)
\]

3) Get the cubic splines interpolation coefficients for each segment determined by two adjacent values of internal diameters and the corresponding nominal volumes.

\[
> \text{splines::interpSpline}(V,D) \text{coeff}
\]

F. UNCERTAINTY IN READING THE POSITION OF THE MENISCUS

When all required internal diameter values are known, the calculation of the uncertainty in reading the position of the meniscus must be done. For that purpose, an equation for the volume of a cylinder (not necessarily circular) is suggested [20]:

\[
 u_{\text{meniscus}} = (u_{\text{position}})(A), \tag{3}
\]

where, \( u_{\text{meniscus}} \), is the uncertainty due to setting the meniscus, \( u_{\text{position}} \), is the uncertainty in the location of the lowest point of a concave meniscus, and \( A \), is the cross-section of the volumetric instrument at the meniscus location. A value of \( u_{\text{position}} = 0.05 \) mm is easily achieved using simple optical aids [20], and the cross-section calculation is straightforward once the internal diameter has been measured or interpolated as described above.

In the CGVI, the uncertainty in the volume due to setting the meniscus should be calculated as the volume of a cone
frustum, whose height is \( u_{\text{position}} \). However, the use of (3) remains advisable because the relationship between any of the two diameters of the cone frustum and its height is at least two orders of magnitude greater than the relationship between the larger diameter to the smaller one.

### III. RESULTS

Internal diameters of some CGVI were measured using the method described in Section II-B. Table 2 shows the results for an Imhoff cone with nominal capacity of 1 L, while Table 3 contains the data for a centrifuge tube with nominal capacity equals 100 mL. For the Imhoff cone measurements, a stand was used (Fig. 2), while for the centrifuge tube, a base plate and tweezers were needed (Fig. 3).

It is worthy to note that the centrifuge tubes have a conical section followed by a cylindrical section [12], where the internal diameter value remains constant, so the values in Table 3 are reported up to the graduation mark where the internal diameter value remains constant. On the other hand, the uncertainties of the internal diameter measurements have been stated in Section II-C of this paper.

| TABLE 2: Measurement results for an Imhoff cone using the optical comparator proposed method. |
|---------------------------------------------------------------|
| Nominal volume /mL | Internal diameter /mm |
|-------------------|-----------------------|
| 0.1               | 5.530                 |
| 0.5               | 7.979                 |
| 1                 | 10.372                |
| 2                 | 13.309                |
| 5                 | 16.657                |
| 10                | 19.775                |
| 15                | 22.426                |
| 20                | 24.528                |
| 25                | 26.390                |
| 50                | 33.516                |
| 100               | 42.535                |
| 500               | 74.026                |
| 1 000             | 96.184                |

| TABLE 3: Measurements results for a centrifuge tube using the optical comparator proposed method. |
|---------------------------------------------------------------|
| Nominal volume /mL | Internal diameter /mm |
|-------------------|-----------------------|
| 0.05              | 5.892                 |
| 0.1               | 6.309                 |
| 0.2               | 6.969                 |
| 0.5               | 9.072                 |
| 1                 | 11.051                |
| 3                 | 15.625                |
| 5                 | 18.359                |
| 9                 | 22.405                |
| 20                | 29.143                |
| 30                | 33.033                |

### A. INTERNAL DIAMETER DATA INTERPOLATION

Table 4 shows the coefficients of the cubic splines obtained with the ten different values of measurements in Table 3 when executing the procedure described in Section II-B.

The `splines::interpSpline(V,D)$coef` output in \( \mathbb{R} \) are the coefficients of the cubic polynomial adjusted between one value of the internal diameter, \( D_{i-1} \), and the next one, \( D_i \), in an ordered fashion. In that way, the values under the Cubic column of Table 4 are the coefficients of \((V_x - V_{i-1})^3\), where \( V_x \) is any volume value between the interval limited by \( V_{i-1} \) and \( V_i \). Similarly, values under the Quadratic column are the coefficients of \((V_x - V_{i-1})^2\), and so on, until the values under the Constant column are reached, which are just the corresponding \( D_{i-1} \) values.

For example, the cubic polynomial that allows interpolation between nominal volumes in the (3.0 to 5.0) mL range is:

\[
D_x = 15.6252 + 1.7709(V_x - 3.0) - 0.2877(V_x - 3.0)^2 + 0.0430(V_x - 3.0)^3.
\]

Where \( V_x \) is any nominal volume between \( V_{i-1} = 3.0 \) mL and \( V_i = 5.0 \) mL, and \( D_x \) is its corresponding interpolated internal diameter, which will fall between \( D_{i-1} = 15.625 \) mm and \( D_i = 18.360 \) mm. With the cubic splines defined in Table 4, eleven additional values of the internal diameter of the centrifuge tube were interpolated. The results are shown in Table 5 and were evaluated against their actual measurements following the method proposed in this work.

The comparison between the interpolated and the measured internal diameter values yields absolute errors of one percent at most for this CGVI.

### B. MENISCUS READING UNCERTAINTY RESULTS

Finally, Table 6 shows the contribution due to meniscus reading, \( u_{\text{meniscus}} \), for all of the 21 graduation lines of the centrifuge tube. A value of \( u_{\text{position}} = 0.05 \) mm was assumed when using (3), and the computation of \( A \) follows the formula for a circle area. The third column of Table 6 exhibits the uncertainty of the meniscus reading calculated with the interpolated internal diameter value, and the last
proposed method that was validated through the information for a couple of CGVI with an optical comparator using a dressed. Several internal diameter values have been measured for the concave meniscus in a CGVI has been successfully added. Applying the proposed interpolation stated in Table 5.

Finally, the computation of the meniscus reading uncertainty in the centrifuge tube was exemplified. Absolute errors of two percent at most were achieved when internal diameters were interpolated instead of measured. Applying the proposed approach will deal with the uncertainty in reading the position of the concave meniscus during the calibration of CGVI.

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### TABLE 5: Performance assessment of the cubic splines interpolation with eleven additional internal diameters of the centrifuge tube.

| Nominal volume /mL | Interpolated diameter /mm | Measured diameter /mm | % relative error |
|--------------------|----------------------------|------------------------|------------------|
| 0.15               | 6.655 3                    | 6.640 4                | 0.22             |
| 0.25               | 7.302 5                    | 7.301 8                | 0.01             |
| 1.5                | 12.371 6                   | 12.496 4               | 1.00             |
| 3.5                | 16.444 1                   | 16.303 8               | 0.86             |
| 4.0                | 17.151 4                   | 17.018 6               | 0.78             |
| 4.5                | 17.779 2                   | 17.682 2               | 0.55             |
| 6                  | 19.465 1                   | 19.322 2               | 0.74             |
| 7                  | 20.508 8                   | 20.377 8               | 0.64             |
| 8                  | 21.489 3                   | 21.376 0               | 0.53             |
| 15                 | 26.675 7                   | 26.934 6               | 0.96             |
| 25                 | 31.179 2                   | 30.991 6               | 0.61             |

### TABLE 6: Meniscus reading uncertainty contribution of the centrifuge tube.

| Nominal volume /mL | $u_{meniscus}$ /mL | $D_i$ measured | $D_i$ interpolated | % relative error |
|--------------------|--------------------|-----------------|-------------------|------------------|
| 0.05               | 0.013 6            |                 |                   |                  |
| 0.10               | 0.015 6            |                 |                   |                  |
| 0.15               | 0.017 3            | 0.017 4         | 0.45              |
| 0.20               | 0.019 1            |                 |                   |                  |
| 0.25               | 0.020 9            | 0.020 9         | 0.02              |
| 0.50               | 0.032 3            |                 |                   |                  |
| 1.0                | 0.048 0            |                 |                   |                  |
| 1.5                | 0.061 3            | 0.060 1         | 1.99              |
| 3.0                | 0.095 9            |                 |                   |                  |
| 3.5                | 0.104 4            | 0.106 2         | 1.73              |
| 4.0                | 0.113 7            | 0.115 5         | 1.57              |
| 4.5                | 0.122 8            | 0.124 1         | 1.10              |
| 5.0                | 0.132 4            |                 |                   |                  |
| 6.0                | 0.146 6            | 0.148 8         | 1.48              |
| 7.0                | 0.163 1            | 0.165 2         | 1.29              |
| 8.0                | 0.179 4            | 0.181 3         | 1.06              |
| 9.0                | 0.197 1            |                 |                   |                  |
| 15.0               | 0.284 9            | 0.279 4         | 1.91              |
| 20.0               | 0.333 5            |                 |                   |                  |
| 25.0               | 0.377 2            | 0.381 8         | 1.21              |
| 30.0               | 0.428 5            |                 |                   |                  |

column contains the relative error of the contribution of the meniscus reading with interpolated diameters versus measured diameters (in the second column). As can be seen, the absolute error doubles their values regarding the error of interpolation stated in Table 5.

### IV. CONCLUSION

Determination of the uncertainty contribution for reading the concave meniscus in a CGVI has been successfully addressed. Several internal diameter values have been measured for a couple of CGVI with an optical comparator using a proposed method that was validated through the information of standardized glassware. Also, a procedure to make cubic splines interpolation for the non-measured internal diameters was exposed and exemplified with one CGVI case: a centrifuge tube. Optical comparator relative measurements uncertainties ranged between 0.004 % to 0.05 %, whereas the internal diameter interpolation error was one percent at most. Finally, the computation of the meniscus reading uncertainty in the centrifuge tube was exemplified. Absolute errors of two percent at most were achieved when internal diameters were interpolated instead of measured. Applying the proposed approach will deal with the uncertainty in reading the position of the concave meniscus during the calibration of CGVI.
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