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COMPARISON BETWEEN THE WILHELMY SURFACE TENSION MEASUREMENT METHOD AND THE PENDANT DROP SHAPE ANALYSIS METHOD

Estela Cristina Cavalcante de Farias,
Ricardo Kropf Santos Fermam*,
Amsterdam de J. Souza Marques de Mendonça

National Institute of Metrology, Quality and Technology (INMETRO), Av. Nossa Senhora das Graças 50, Xerém, Duque de Caxias, 25250-020 Rio de Janeiro, Brazil

* corresponding author: rkfermam@inmetro.gov.br

Abstract. Surface tension plays an essential role in various laboratory and industrial processes. The Fluid Metrology Laboratory (Laflu) of the National Institute of Metrology, Quality and Technology (Inmetro) uses the Wilhelmy and DuNoüy methods and has a tensiometer for determining surface tension by the drop shape analysis method in use. One way to ensure the reliability of surface tension measurement results is to compare the methods used. A comparison was made between the Wilhelmy method and the drop shape analysis method. The comparison involved measurements of the surface tension of these liquids: bidistilled water, n-dodecane, and Perfluorocarbon (FC-40), and used the calculation of the Normalized Error (EN), presenting results according to acompatible criterion. Analysing the uncertainties involved, the contribution of the uncertainty of the regression used in the correction of the tensiometer indication was the most relevant.

Keywords: Surface tension, Wilhelmy method, drop shape analysis method.

1. Introduction

Surface tension, as an inherent characteristic of the liquid-air interface, plays a significant role in various segments of industry, science, and technology through wettability, capillarity, atomisation, jetting, and the dynamics of liquid surfaces [1]. These phenomena are intensely present in production and industrial processes [2], such as the manufacturing of chemicals, semiconductor manufacturing, steel production, galvanisation processes, and the exploration and refining of oil, in addition to a variety of applications relevant to health, the economy, and the environment, such as the manufacturing of automotive components, electronic devices, food, beverages, and pharmaceuticals [3].

For the measurement of the surface tension of liquids, the most commonly used methods are the Wilhelmy method, also called the plate method, which is based on the force that prevents the removal of the plate from the surface of the liquid [4], the DuNoüy method, also called the ring method, which is based on the force required to remove a metal ring from the surface of a liquid [5], and the pendant drop shape analysis method, in which the surface tension is calculated from known parameters, theoretical images are generated and compared with experimental images [6]. The last one has only become more accurate and faster with the advance of computer image analysis [7].

The DuNoüy and Wilhelmy methods are commonly used for the determination of surface tension in various sectors of industry, calibration laboratories, and research institutes. However, an increase in the use of the pendant drop shape analysis method has been observed.

The Fluid Metrology Laboratory (Laflu) at the National Institute of Metrology, Quality, and Technology (INMETRO), in addition to conducting research in the field of fluid property measurement [8–11], is responsible for maintaining metrological traceability and disseminating the magnitude of surface tension in Brazil [9], using the Wilhelmy and DuNoüy methods and a tensiometer for determining the surface tension by the pendant drop shape analysis method in use. Laflu provides calibration services for surface tension instruments using the Wilhelmy and DuNoüy methods, having expertise in the use of these methods.

2. Materials and methods

One way to ensure the reliability of surface tension measurements using the pendant drop shape analysis method is through method comparison [12]. A comparison was made between the Wilhelmy measurement method and the pendant drop shape analysis method with measurement uncertainty analysis. The ring method was not used because the Wilhelmy method is the most used method in the Laflu, but it may be used in future studies to complement the analyses.This comparison involved surface tension measurements of these liquids: bidistilled water, n-dodecane, and perfluorocarbon (FC-40), these liquids were chosen to cover a wide range of surface tension with stability [8], allowing for a more comprehensive evaluation of the

Influence quantities	Unit	Estimate	Distribution	Divisor	Sensitivity coefficient	Contributions
Indicated temperature	°C	0.012	Normal	2.000	1.000	10.4 %
Correction of the apparent tension	$\mathrm{mN\,m^{-1}}$	0.037	Normal	2.000	1.000	31.8 %
Regression deviation	$\mathrm{mN\,m^{-1}}$	0.033	Rectangular	3.464	1.000	91.2 %
Resolution	$\mathrm{mN\,m^{-1}}$	5×10^{-4}	Rectangular	3.464	1.000	1.3 %
Mass	g	12×10^{-6}	Normal	2.000	243.2	7.1 %
Acceleration of gravity	$\mathrm{m\,s^{-2}}$	5×10^{-5}	Normal	2.000	2.898×10^{-4}	0.0 %
Wetted perimeter	m	2×10^{-2}	Normal	2.000	-7.046×10^{5}	0.4 %
Regression deviation	$\mathrm{mN\,m^{-1}}$	0.163	Triangular	1.732	1.000	57.7 %

Table 1. Contributions considered in the estimation of uncertainty of the measurement of the correction regression determined in the surface calibration of the tensiometer by the Wilhelmy method.

methods used.The temperatures of 20 °C and 25 °C were chosen because they are the most requested temperatures for calibration at Laflu by clients, thus ensuring the practical relevance of the results obtained. The Kruss K100 model tensiometer was used for the Wilhelmy method, and the Kruss DSA100 model for the pendant drop shape analysis method.

To perform the comparison of the results, the Normalized Error (E_N) comparison parameter was used, where the results are considered satisfactory if E_N is less than or equal to 1 [13].

3. Measurement of surface tension by the Wilhelmy method

The calibration certificate provides a regression for obtaining surface tension by the Wilhelmy method in $\mathrm{mN\,m^{-1}}$ (Equation (1)), for measurements of liquids in the surface tension range of $15\,\mathrm{mN\,m^{-1}}$ to $75\,\mathrm{mN\,m^{-1}}$, in the temperature range of 15 °C to 40 °C, with an expanded uncertainty of $0.077\,\mathrm{mN\,m^{-1}}$, and a coverage factor of 2.000:

$$\gamma_c = C_0 + C_1 \cdot \gamma_i + C_2 \cdot (T_R - T_L), \qquad (1)$$

where γ_c is the corrected surface tension, in $\mathrm{mN\,m^{-1}}$; γ_i is the indicated surface tension, in $\mathrm{mN\,m^{-1}}$; C_0, C_1, and C_2 are the parameters of the regression equation; T_R is the reference temperature, in °C; and T_L is the measurement temperature, in °C. The apparent surface tension was calculated according to Equation (2), being the surface tension that the tensiometer should indicate as a function of the applied force and the perimeter of the plate:

$$\gamma_a = \frac{m \cdot g}{L_w \cdot \cos\theta}, \qquad (2)$$

where γ_a is the apparent surface tension, in $\mathrm{mN\,m^{-1}}$; m is the mass of the calibrated standard weights, applied on the tensiometer, in grams; g is the local gravity acceleration, in $\mathrm{m\,s^{-2}}$; L_w is the wetted perimeter of the plate, in m, and θ is the contact angle between the liquid and the plate.

Figure 1. Plate used in the Wilhelmy method measurements [14].

The regression uncertainty provided by the calibration certificate of the tensiometer for the Wilhelmy method considers the uncertainties of temperature, the regression deviation, and the correction of the apparent surface tension (which is also given by a regression). The apparent surface tension is the verification of the tensiometer's response with the application of a known force, and considers the uncertainties of the tensiometer's resolution, the standard masses used, the acceleration of gravity, the wet perimeter of the plate, and the regression deviation. Table 1 presents the contributions of the correction regression uncertainty provided in the calibration certificate of the tensiometer considered in the calculation; the shaded part in italics are the contributions to the uncertainty of the apparent surface tension.

The plate used in the measurements (Figure 1) is of the Pt-Ir (platinum-iridium) type, with a support rod, 19.912 mm long and 0.212 mm thick.

The flask with the liquid was placed in the thermostatic bath adjusted to the measurement temperature, and a temperature sensor was inserted into the liquid inside the flask to monitor the liquid's temperature. The plate was attached to the tensiometer, and the tensiometer software parameters were entered, such as plate or ring dimensions, reference temperature, air density, liquid to be measured, number of measurements, etc. Once the temperature of the liquid has stabilised, which takes an hour and a half on average to reach 20 °C, and two hours to reach 25 °C, an aliquot of the fluid was transferred to a glass crucible (the volume should be slightly above half of the crucible, usually around 50 mL). The tank supporting the crucible is connected to a thermostatic bath via hoses to ensure the solution inside the crucible remains at the measurement temperature. Subsequently, the tank with the crucible was brought close to the plate without touching the liquid's surface, and a sequence of twenty measurements was initiated, with the first five discarded. Thus, the liquid measurements were performed using the Wilhelmy method at temperatures of 20 °C and 25 °C, ensuring rigorous cleaning of the plate between measurements and using a clean crucible for each liquid.

4. Surface tension measurement by the pendant drop shape analysis method

The calibration data include the regression for obtaining the surface tension in $\mathrm{mN\,m^{-1}}$ in the temperature range from 18 °C to 30 °C and the surface tension measurement range was from $16\,\mathrm{mN\,m^{-1}}$ to $73\,\mathrm{mN\,m^{-1}}$ with an expanded uncertainty of $0.28\,\mathrm{mN\,m^{-1}}$ and a coverage factor $k = 2.00$, according to:

$$\gamma_c = C_0 + C_1 \cdot T_L + C_2 \cdot \gamma_i, \tag{3}$$

where γ_c is the corrected surface tension, in $\mathrm{mN\,m^{-1}}$; γ_i is the indicated surface tension, in $\mathrm{mN\,m^{-1}}$; C_0, C_1 and C_2 are the parameters of the regression equation, and T_L is the measurement temperature, in °C.

The correction regression (Equation (3)), used to correct the tensiometer reading by the pendant drop shape analysis method, considers the contributions from the standard tensiometer uncertainties (23 %), tensiometer resolution (2 %); liquid temperature (7 %) and regression deviation (69 %) in the calculation of measurement uncertainty. The uncertainty in this method is influenced by the repeatability in the drop formation process, which becomes more sensitive to changes in surface tension as the measured liquid has a lower surface tension [15]. Additionally, the resolution in the pendant drop shape method ($0.01\,\mathrm{mN\,m^{-1}}$) is higher than the resolution of the Wilhelmy method ($0.001\,\mathrm{mN\,m^{-1}}$).

A thermostatic bath was used to stabilise the temperature of the measurement liquid. This bath was connected to the measurement chamber via hoses (Figure 2). The chamber, which has a double glass wall, allows the circulation of water from the thermostatic bath, keeping the measurement environment, where the drop forms, more stable. An aliquot (5 mL) of the liquid was taken with a syringe after the stabilisation to the bath's temperature (approximately one and a half hours on average to reach 20 °C and two hours to reach 25 °C), and the syringe was fixed in the holder of the tensiometer. The adjustment was made to visualise the drop on the computer screen and to start the program for forming and visualising the pendant drop (Figure 3).

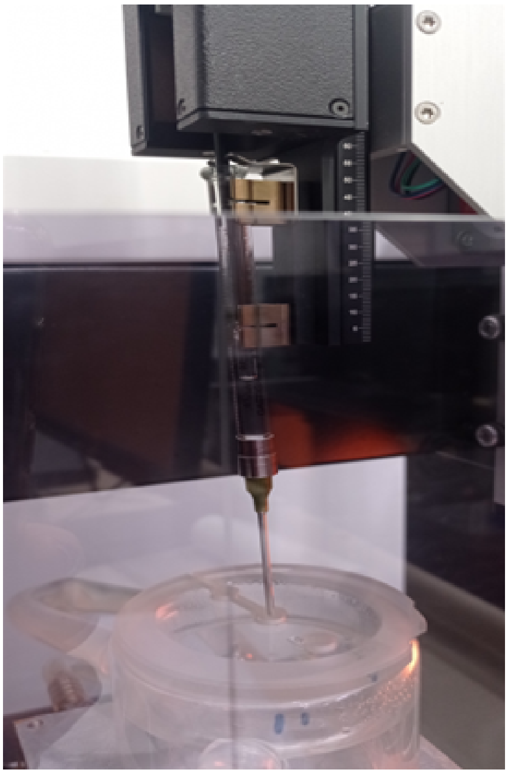

Figure 2. Syringe connected to the tensiometer positioner [14].

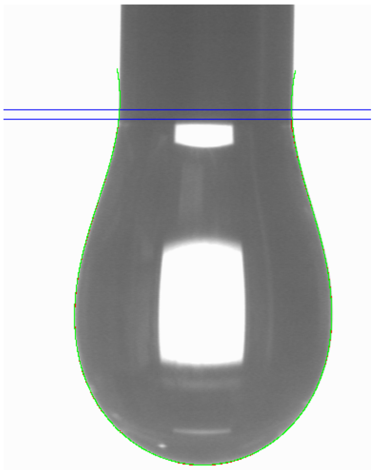

Figure 3. Captured images of the formation of the pendant drop.

Liquid	Wilhelmy		Drop shape analysis method	
	γ	U_γ	γ	U_γ
FC-40	16.820	0.077	16.36	0.51
n-dodecane	25.743	0.077	25.77	0.25
Water	72.970	0.078	72.76	0.24

TABLE 2. Measurement results for the temperature of 20 °C.

Liquid	Wilhelmy		Drop shape analysis method	
	γ	U_γ	γ	U_γ
FC-40	16.502	0.078	16.16	0.68
n-dodecane	25.435	0.077	25.32	0.28
Water	71.382	0.077	72.27	0.26

TABLE 3. Measurement results for the temperature of 25 °C.

The tensiometer software uses the Young-Laplace equation [7] (Equation (4)) to determine the curve that provides the best fit to the contour of the formed drop (Figure 3):

$$\Delta P = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right), \tag{4}$$

where γ is the surface tension, in $\mathrm{mN\,m^{-1}}$; R_1 and R_2 are the two principal radii of the curvature; ΔP is the pressure difference at the interface, given by:

$$\Delta P = \Delta P_0 + (\Delta \rho) g z, \tag{5}$$

where ΔP_0 is the pressure difference at a reference plane; $\Delta \rho$ is the density difference between the two phases; g is the acceleration due to gravity; and z is the vertical height of the given point on the drop surface, measured from the reference level.

With the known parameters, the software calculates the theoretical images and compares them with the experimental images.

5. Results and discussions

The results of the corrected surface tension of the liquids (γ), according to the equation provided in the calibration certificate and the measurement uncertainty calculated according to GUM [16] (U_γ), are provided in Tables 2 and 3.

In the measurement uncertainty of the results by the Wilhelmy method, approximately 88 % of the contribution to the uncertainty comes from the correction regression, while the remaining 12 % are attributed to repeatability. In the measurements performed by the pendant drop shape analysis method, the contributions to the measurement uncertainty were approximately 77.3 % from the standard used in the calibration, 0.1 % from the temperature, 0.1 % from the temperature variation, and 22.5 % from repeatability.

In the Wilhelmy method, the correction of the apparent surface tension was one of the main contributions to the measurement uncertainty in the tensiometer calibration. For the tensiometer used in this work, it is the second largest contribution. The largest contribution was from the regression deviation that corrects the indication and adjusts it to the reference temperature. In this regard, the pendant drop shape analysis method presents an advantage, as there is no need for an apparent tension correction in the calibration. The pendant drop shape analysis method is more suitable for small sample volumes. In this work, 5 mL was used for each liquid measurement, while for the Wilhelmy method, approximately 50 mL of each liquid was used.

In a temperature-controlled environment, as in the measurements conducted in this study, the impact of temperature on the uncertainty calculations is minimal. The liquids were stabilised at measurement temperatures in a bath, and the measurement tank of the tensiometer has a jacket that circulates the bath water, ensuring better temperature stabilisation during measurements. Some tensiometer models do not have temperature stabilisation features, requiring an understanding of how the surface tension of the liquid changes with temperature. It is essential to conduct measurements close to the desired temperature to apply tension corrections accurately. This is particularly important when the tensiometer's reference temperature differs from the measured temperature.

Table 4 presents the results of the calculation of the normalised error (E_N) between the measurement results obtained by the Wilhelmy method and the pendant drop shape analysis method according to:

$$|E_N| = \frac{V_p - V_R}{\sqrt{{U_p}^2 + {U_R}^2}}, \tag{6}$$

where V_p is the measured value, V_R is the reference value, U_p is the measurement uncertainty of the mea-

Liquid	EN (20 °C)	EN (25 °C)
FC-40	0.90	0.57
n-dodecane	0.11	0.38
Water	0.82	0.41

Table 4. Normalised error.

sured value, and U_R is the measurement uncertainty of the reference value.

Comparing the EN results of liquid measurements between methods using the normalised error criterion, the results are compatible. The result for water at 20 °C was the closest to the failure limit. The measurement of water is more susceptible to variations due to the characteristics of its molecular interactions. It is important to note that the measurement uncertainty for the FC-40 results was higher compared to the other liquids measured, as there was a greater variation in the measurement. With lower surface tension, the drop shape becomes more sensitive to changes in surface tension, as was the case here, as FC-40 has the lowest surface tension of the liquids measured.

6. Conclusion

The results of the comparison between the methods were compatible, which ensures the reliability of measurements with the pendant drop shape analysis method. The tensiometers used have a regression in their calibration certificate to correct the indicated surface tension values. An advantage is the ease of correcting the instrument indication across the calibrated range. However, the disadvantage is the increase in the measurement uncertainty due to the regression deviation, which, as shown in the results, is the largest contribution. In the case of the pendant drop shape analysis tensiometer, which has a resolution of $0.01\,\mathrm{mN\,m^{-1}}$, the uncertainty was about $0.25\,\mathrm{mN\,m^{-1}}$ in the best case, which was the measurement of dodecane. Regression can be an alternative for cases where the measured values are intermediate to the calibration points. Recalibrating the tensiometers, providing the measured results as an alternative to the adjustment regression, can be a viable option to improve the measurement uncertainty. Each method has peculiarities, with inherent advantages and disadvantages. The choice of the appropriate method is influenced by the specific characteristics of the liquid to be measured and the experimental conditions.

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