

Surface tension measurements – A comparative study

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ABSTRACT

The lack of intercomparisons in surface tension measurements, and the need to establish the degree of equivalence of such measurements, lead to a comparative study on this subject carried out by 3 National Metrology Institutes (from Poland, Portugal, and Turkey), within the scope of the Project 17RPT02-rhoLiq. For this purpose, the surface tension of 6 liquids, was determined at 20 °C, using force tensiometers, with 2 different measuring probes (Du Noüy ring and Wilhelmy plate), and by applying different correction factors. The results of this work allowed to conclude on the degree of equivalence of surface tension measurement results, obtained by each NMI, by using different probes and measurement models.

Section: RESEARCH PAPER

Keywords: Surface tension; comparative study; Du Noüy ring; Wilhelmy plate; corrections

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1. INTRODUCTION

Surface tension, which is due to intermolecular forces, is a characteristic of fluids interfaces, either between fluids (gas-liquid or liquid-liquid) or between fluids and solids (solid-gas or solid-liquid). The interaction between the molecules of two immiscible liquids, or of a liquid and a gas, results in the formation of an interface or surface. Pragmatically, surface tension is defined as the force acting on the surface per length of the area perpendicular to the force.

Different methods can be used to measure surface tension, namely: capillary rise method; stalagmometric method; drop weight method; Wilhelmy plate or Du Noüy ring method; maximum bulk pressure method; by shape analysis of the hanging liquid drop or gas bubble method and dynamic methods. One of the most common methods to measure the surface/interfacial tension is the Wilhelmy plate method and the Du Noüy ring method.

A Wilhelmy plate is a thin, generally rectangular plate, made of metal platinum (with an extremely high surface free energy and therefore also the required excellent wetting properties) with

a few centimetres in length and height. In this method, the plate is oriented perpendicular to the interface, at the surface of the liquid and the force exerted on it is measured.

On the other hand, the ring method uses the interaction of a platinum ring with the surface of the liquid. The platinum-iridium metal alloy made ring is submerged below the interface by moving a platform where the liquid container is placed. After ring immersion, this platform is gradually lowered, and the ring pulls up the meniscus of the liquid. Eventually, this meniscus tears from the ring. Before this event, the volume (and thus the exerted force) of the meniscus passes through a maximum value and begins to drop before the tearing event.

The purpose of the work presented in this communication is to compare results of surface tension measurements of 6 liquids, performed at 20 °C, by means of force tensiometers with the use of different probe types (corresponding to Du Noüy ring and Wilhelmy plate), with different reference liquids, by 3 National Metrological Institutes (NMIs), namely GUM, from Poland, IPQ, from Portugal, and TUBITAK-UME, from Turkey. Beside the knowledge of the degree of equivalence of such measurement results, this study displays an opportunity to share knowledge

and experiences in this field, between these NMIs. Furthermore, the determination of the liquids' surface tension aimed at gathering information to the rhoLiq project's robustness studies, regarding the influence of the liquid surface tension (between 20 mN/m and 72 mN/m) on accuracy and uncertainty of density measurements performed by hydrostatic weighing method. Indeed, in this method, one of the major measurement uncertainty components is the one associated to the additional mass of the liquid arisen in the suspension wire, due to surface tension and adhesion forces. This effect occurs, even when using different methods to reduce it, such as a small wire diameter or rising and lowering the liquid level under test before each measurement. Consequently, a better knowledge in surface tension uncertainty may be helpful for more accurate liquid surface tension measurements. This work is also an important step to the mutual recognition of surface tension measurement results by NMIs different measurement procedures.

2. DESCRIPTION OF THE WORK

2.1. Methods and materials

This comparative study involved a set of measurements performed with 3 commercial tensiometers, K100, MK2 and K11HRX models, from Krüss, by 3 NMIs (GUM, Poland; IPQ, Portugal; and TUBITAK-UME, Turkey). 6 reference liquids were prepared and distributed for the density diagnostic and consolidation comparisons and for the robustness studies, organized within the scope of the EURAMET Project 17RPT02-rhoLiq [1].

The nominal surface tension values σ_n , at 20 °C and ambient pressure, and the codification of the test liquids, namely one heavy water sample with a deuterium volume fraction $X_{V_{D_2O}}$ of 1.5 cL, n-Dodecane, Tetrachlorethylene (TCE) and 3 different oil samples (EF168, 1000B and 2000A) are given in Table 1.

Each participant followed their own measuring procedures: GUM used 2 different Du Noüy ring probes and the Harkins-Jordan corrections [2]; IPQ used Du Noüy ring method with 2 different corrections (Fox & Chrisman [3] for TCE and Harkins-Jordan [2] for the remaining samples) and Wilhelmy plate method for all samples; TUBITAK UME used both Du Noüy ring with Huh & Mason corrections [4] and Wilhelmy plate method.

The metrological traceability of surface tension measurement results of each participant is considered independent. All the measurements were performed at 20 °C and at ambient pressure.

To access how the different laboratories, handle the correction of surface tension measurement, the assessment of a reference value $\overline{\sigma_W}$, and respective expanded uncertainty $U_{\overline{\sigma_W}}$, will be presented and discussed [5], [6].

Table 1. Codification of the test liquids (L#) and nominal surface tension values σ_n , at 20 °C and ambient pressure.

L#	Liquid	σ_n / (mN / m)
L1	Deuterated water ($X_{V_{D_2O}} = 1.5$ cl/L)	72
L2	n-Dodecane	25
L3	Tetrachlorethylene (TCE)	27
L4	Viscosity oil O EF168	30
L5	Viscosity oil 1000B	31
L6	Viscosity oil 2000A	31

2.2. Results assessment

As there is no internationally-recognized Calibration and Measurement Capabilities (CMCs) in surface tension field published at BIPM key comparison database (KCDB – BIPM) [7], initially, the reference surface tension value of each liquid was assumed to be the weighted mean of the surface tension values $\overline{\sigma_W}$ calculated by equation (1), and respective standard uncertainty $u_{\overline{\sigma_W}}$, equation (2).

$$\overline{\sigma_W} = \frac{\sigma_1/u^2(\sigma_1) + \dots + \sigma_N/u^2(\sigma_N)}{1/u^2(\sigma_1) + \dots + 1/u^2(\sigma_N)}, \quad (1)$$

$$1/u^2(\overline{\sigma_W}) = 1/u^2(\sigma_1) + \dots + 1/u^2(\sigma_N). \quad (2)$$

These values were calculated taking in account the consistency check described by Cox [8]. The viscous samples measurement results passed the consistency test, but not the non-viscous ones.

It was then considered to evaluate a consensus value from the participant results, calculating a reference value $\overline{\sigma_W}$, and respective expanded uncertainty $U_{\overline{\sigma_W}}$, by robust analysis according to ISO13528:2015 [5].

As each laboratory has its own measurement traceability chain, the expanded uncertainties of the weighted mean surface tension values, $U_{\overline{\sigma_W}}$, were computed without any correlation. Furthermore, the resulting uncertainty does not include the contribution of the uncertainty due to the heterogeneity and drift of the samples, as it was not possible to estimate these uncertainty components.

In the robust analysis it was used the Algorithm A [9] to estimate the mean and standard deviation of the data, where the robust average is given by the median, x^* , of x_i , equation (3) and the robust standard deviation, s^* , according to equation (4):

$$\overline{\sigma_W} = x^* = \text{median of } x_i \quad (i = 1, 2, \dots, p), \quad (3)$$

$$s^* = 1.483 \cdot \text{MAD} \{\text{of lab deviations}\}, \quad (4)$$

where MAD is the Median Absolute Deviation of laboratory deviations, median of $|x_i - x^*|$ with $(i = 1, 2, \dots, p)$.

The values of x^* and s^* were update calculating δ , and using the following equations:

$$\delta = 1.5 s^*, \quad (5)$$

$$\text{for each } x_i, \quad x^* = \begin{cases} x^* - \delta & \text{when } x_i < x^* - \delta \\ x^* + \delta & \text{when } x_i > x^* + \delta \\ x_i & \text{otherwise} \end{cases}, \quad (6)$$

$$x^* = \frac{\sum_{i=1}^p x_i^*}{p}, \quad (7)$$

$$s^* = 1.134 \sqrt{\frac{\sum_{i=1}^p (x_i^* - x^*)^2}{(p-1)}}. \quad (8)$$

The robust estimates of x^* and s^* are derived by an iterative calculation, i.e. by updating the values several time using equations (5) to (8) until the process converges. Convergence was assumed when there was no change from one iteration to the next in the third significant figure of the robust mean and standard deviation. [5]

When the reference value is determined by robust analysis, the standard uncertainty of the assigned value may be estimated as:

$$u(x_{pt}) = 1.25 \cdot \frac{s^*}{\sqrt{p}} \quad (9)$$

The degree of equivalence, d_{σ_i} , of the NMI, labelled by the letter i , for surface tension measurement results against the reference surface tension values $\overline{\sigma_W}$, was given by:

$$d_{\sigma_i} = \sigma_i - \overline{\sigma_W} \quad (10)$$

and the associated expanded uncertainties, $U_{d_{\sigma_i}}$, (for $k = 2$) was determined according to the following equations when the reference values were determined by consistency or robust analysis, respectively:

$$U_{d_{\sigma_i}} = \sqrt{U_{\sigma_i}^2 - U_{\overline{\sigma_W}}^2}, \quad (11)$$

$$U_{d_{\sigma_i}} = \sqrt{U_{\sigma_i}^2 + U_{\overline{\sigma_W}}^2}. \quad (12)$$

For each test liquid, the surface tension values obtained by each NMI were then compared by a statistical evaluation through the normalized error, E_n , [5] according to:

$$E_n = \left| \frac{d_{\sigma_i}}{U_{d_{\sigma_i}}} \right|. \quad (13)$$

2.3. General measurement procedure

A test liquid is filled into a glass vessel of approximately 50 mm to 70 mm diameter, placed in a thermoregulated vessel of the tensiometer and a sensor placed in the liquid for temperature measurement and left for about one hour to reach thermal equilibrium. The density of each sample was measured prior to surface tension measurement by means of oscillating-type density meters. The density of air was calculated with CIPM-2007 formula [9] based on pressure, temperature, and humidity measurements results.

For each sample, surface tension was measured 5 to 10 times (meaning that the sensor was cleaned between each measurement, by first appropriate solvent followed by flame). Before starting the measurements, the force sensor adjustment was realized with internal mass standard. The validation of the device was realized by 0.2 g, 0.5 g and 1 g according to the manual of Calibration Set CP14 for tensiometers [10].

2.4. Measurement uncertainties

The surface tension measurement standard uncertainties values are obtained by combining the individual standard uncertainties from Type A and Type B evaluations, within the GUM framework [6]. The balance of the uncertainty evaluations included the contributions of all influencing sources (for instance, instrumental measurement uncertainty arising from the force sensor) and input quantities (such as: temperature of the liquid, cubic thermal expansion of liquid, dimension of the probes, applied corrections, among others), their values, and associated standard uncertainties, together with their degrees of freedom, leading to the combined standard uncertainty, as well as the effective degrees of freedom.

The uncertainty budget for all the participating NMIs was expressed with not also the standard deviation of the tension or force and the temperature (including the liquid thermal

coefficient) measurement readings and instrument resolutions but also the accuracy of Harkins & Jordan correction factor. GUM considered the ring irregularities. TUBITAK used a mathematical model to estimate the uncertainty contributions, whereas IPQ uncertainty budget also took into account the ring or plate dimensions.

The declared uncertainties are quite similar for IPQ and TUBITAK, were GUM estimated an uncertainty about five times lower for the ring method. Differences are also observed in the declared uncertainty for the plate method were IPQ declared about two times lower than TUBITAK.

Thanks to its more than 50 years practice in surface tension measurements GUM measurement uncertainty were expected to be lower than the on the other NMIs.

3. RESULTS

In this section, the surface tension measurement results obtained by Du Noüy ring and by Wilhelmy plate methods are presented and compared. For the sake of simplicity, surface tension measurement values obtained with Du Noüy ring method are denoted with σ_R (with associated uncertainty U_{σ_R}), surface tension measurement values obtained with Wilhelmy plate method are denoted with σ_P (with associated uncertainty U_{σ_P}). The uncertainties values, U , are presented as expanded uncertainty with a $k = 2$ coverage factor for a 95 % level of confidence, based on a normal distribution, from the standard uncertainties.

3.1. Du Noüy ring method surface tension measurement results

Table 2 shows the resume of surface tension measurement results, σ_R and respective expanded uncertainty, U_{σ_R} , obtained with Du Noüy ring method at 20 °C, by IPQ, TUBITAK and GUM. TUBITAK was not able to measure L3 sample.

As above mentioned, the reference values of the samples surface tensions were determined using the weighted mean $\overline{\sigma_W}$ of the obtained surface tension values according to Cox's test [8] or by robust mean [6]. For L1 to L3 samples, the reported surface tension values reported did not pass the consistency test [8]. The surface tension reference values $\overline{\sigma_{W,R}}$ are showed in Table 3 together with the associated expanded uncertainty $U_{\overline{\sigma_{W,R}}}$, for $k = 2$.

For a better measurement results analysis, the samples were grouped according to some similar physical characteristic, in this case, according to their viscosity values.

It can be notice that the reference value practically coincides with that of the GUM laboratory, when the reference value is considered to be the weighing mean, i.e. when results are consistent.

Table 2. Resume of surface tension measurement results, σ_R and respective expanded uncertainty, U_{σ_R} , obtained with Du Noüy ring (R) method at 20 °C, by IPQ, TUBITAK and GUM.

Samples	IPQ		TUBITAK		GUM	
	σ_R	U_{σ_R}	σ_R	U_{σ_R}	σ_R	U_{σ_R}
/ (mN / m)						
L1	71.81	0.45	72.58	0.61	72.36	0.16
L2	24.62	0.45	24.76	0.61	25.21	0.11
L3	26.76	0.45	Not measured		28.24	0.54
L4	29.58	0.45	29.68	0.61	29.66	0.11
L5	30.73	0.45	30.87	0.61	30.79	0.11
L6	30.71	0.45	30.98	0.61	30.71	0.12

Table 3. Reference surface tension values obtained by robust mean (L1 to L3) and by weighted mean (L4 to L6), $\overline{\sigma_{w,R}}$ and the associated expanded uncertainty, $U_{\overline{\sigma_{w,R}}}$, obtained with Du Noüy ring (R) method at 20 °C.

Samples	$\overline{\sigma_{w,R}}$ / (mN / m)	$U_{\overline{\sigma_{w,R}}}$ / (mN / m)
L1	72.27	0.30
L2	24.82	0.19
L3	27.50	0.85
L4	29.66	0.11
L5	30.79	0.11
L6	30.72	0.11

Table 4. Resume of surface tension results, $\sigma_R \pm U_{\sigma_R}$, degree of equivalence, d_{σ_R} , and associated expanded uncertainty, U_{d_i} and normalized error, $E_{n,R}$, of high viscosity samples (L4-L6), obtained by Du Noüy ring (R) method results, at 20 °C.

Laboratory / Samples	σ_R	U_{σ_R}	d_{σ_R}	$U_{d_{\sigma_R}}$	$E_{n,R}$
	/ (mN / m)				
Viscosity oil O EF168 (L4)					
IPQ	29.58	0.45	-0.08	0.44	0.2
TUBITAK	29.68	0.61	0.02	0.60	0.0
GUM	29.66	0.11	0.00	0.02	0.1
Viscosity oil 1000B (L5)					
IPQ	30.73	0.45	-0.06	0.44	0.1
TUBITAK	30.87	0.61	0.08	0.60	0.1
GUM	30.79	0.11	0.00	0.03	0.0
Viscosity oil 2000A (L6)					
IPQ	30.71	0.45	-0.01	0.44	0.0
TUBITAK	30.98	0.61	0.26	0.60	0.4
GUM	30.71	0.12	-0.01	0.04	0.2

Table 5. Resume of surface tension results, $\sigma_R \pm U_{\sigma_R}$, degree of equivalence, d_{σ_R} , and associated expanded uncertainty, U_{d_i} and normalized error, $E_{n,R}$, of low viscosity samples (L1-L3), obtained by Du Noüy ring method results, at 20 °C.

NMI / Samples	σ_R	U_{σ_R}	d_{σ_R}	$U_{d_{\sigma_R}}$	$E_{n,R}$
	/ (mN / m)				
Water (D ₂ O 1.5 cL/L) (L1)					
IPQ	71.81	0.45	-0.46	0.54	0.9
TUBITAK	72.58	0.61	0.31	0.68	0.5
GUM	72.36	0.16	0.09	0.34	0.3
n-Dodecane (L2)					
IPQ	24.62	0.45	-0.20	0.49	0.4
TUBITAK	24.76	0.61	-0.06	0.64	0.1
GUM	25.21	0.11	0.39	0.22	1.8
Tetrachlorethylene (TCE) (L3)					
IPQ	26.76	0.45	-0.74	0.97	0.76
TUBITAK	-	-	-	-	-
GUM	28.24	0.54	0.74	1.01	0.73

Table 6. Comparison of surface tension results, $\sigma_R \pm U_{\sigma_R}$, degree of equivalence, d_{σ_R} , and associated expanded uncertainty, U_{d_i} and normalized error, $E_{n,R}$, of sample L3, obtained by Du Noüy ring method results, at 20 °C.

NMI / Samples	σ_R	U_{σ_R}	d_{σ_R}	$U_{d_{\sigma_R}}$	$E_{n,R}$
	/ (mN / m)				
Tetrachlorethylene (TCE) (L3)					
IPQ	26.76	0.45			
GUM	28.24	0.54	1.48	0.70	2.1

When measuring the surface tension of viscous samples, the effect of adhesive forces may affect the probes and consequently lead to errors that cannot be corrected. However, it seems that, for the viscous samples (L4, L5 and L6) used in the comparison, all participants showed satisfactory results, i.e. $E_{n,R} < 1$ (Table 4). One can postulate that even with adhesive forces, that are not considered, all partners measurements were subject to a systematic error of the same magnitude leading to compatible results.

On the other hand, for low viscous samples, other physical properties, such as vapour pressure, gas content, hygroscopic capacity, among others, may have great influence in the stability of gas-liquid interface leading to random errors that are not easily corrected. These effects may explain the results showed in Table 5. Nevertheless, most participants showed satisfactory results, i.e. $E_{n,R} < 1$.

For sample L3 (TCE), TUBITAK was not able to measure it, and IPQ and GUM results did not pass consistency test according to Cox [8], having the higher difference to the reference value. If we compare the two declared results, as showed in Table 6, we can assume that these results may be due to the great instability of such compound.

Furthermore, it should be noted that these samples were previously used in the hydrostatic weighing comparison organized within rhoLiq project framework. This means that their composition could have changed due their previous manipulation.

In Figure 1, a summary of the degrees of equivalence, d_{σ_R} , observed for all samples and for all NMIs is presented.

3.2. Wilhelmy plate method surface tension measurement results

The plate method was only used by two of the partners (TUBITAK and IPQ). For this reason, two different measurement results assessments were considered. In the first one, the results evaluation was made by direct comparison between the surface tension measurement results obtained by each NMI ($\sigma_{P,TUBITAK}$ and $\sigma_{P,IPQ}$):

$$\Delta_{\sigma_P} = \sigma_{P,TUBITAK} - \sigma_{P,IPQ} \quad (14)$$

and associated expanded uncertainties, $U_{\Delta_{\sigma_P}}$ were determined according to:

$$U_{\Delta_{\sigma_P}} = \sqrt{U_{\sigma_{P,TUBITAK}}^2 + U_{\sigma_{P,IPQ}}^2} \quad (15)$$

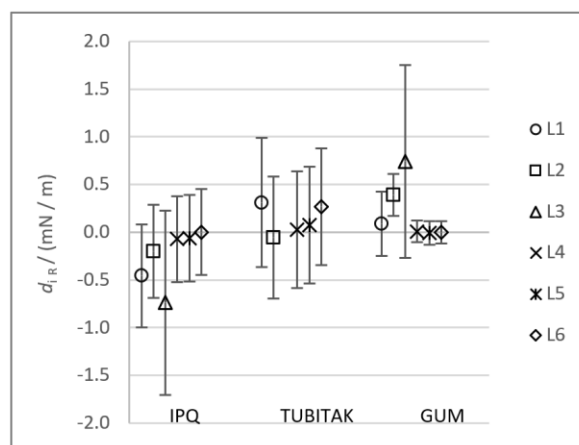


Figure 1. Summary of the degree of equivalence, d_{σ_R} , for all samples and all NMI are presented, obtained by Du Noüy ring method results, at 20 °C.

In this situation, normalized error $E_{n,PP}$ was calculated as:

$$E_{n,PP} = \left| \frac{\Delta\sigma_P}{U_{\Delta\sigma_P}} \right|. \quad (16)$$

According to this first assessment, around 67 % of the results failed the consistency test introduced by Cox [8], therefore presenting a $E_{n,PP} > 1$ (Table 7). They are not consistent results corresponding to the high viscosity samples (L4 to L6) and to dodecane (L2) sample. The first maybe due to viscous drag and the time set for the experiments, and the second maybe due to sample contamination, as the density values of TUBITAK and IPQ samples already detected that difference [1].

As some authors [2], [11] mentioned that the ring method may be considered an accurate method for the determination of surface tension, in this second assessment, the evaluation of the results was made by direct comparison between the surface tension measurement results obtained by the NMI with Wilhelmy plate (P) against the reference surface tension value (obtained with Du Noüy ring), $\overline{\sigma_{W,R}}$ presented in Table 3. In this case the deviation of surface tension measurements results

obtained by each NMI, $\Delta\sigma_{PW,R}$ against the reference surface tension values $\overline{\sigma_{W,R}}$, is given by:

$$\Delta\sigma_{PW,R} = \sigma_P - \overline{\sigma_{W,R}} \quad (17)$$

and associated expanded uncertainties, $U_{\Delta\sigma_P}$ were determined according to equation (18):

$$U_{\Delta\sigma_{PR}} = \sqrt{U_{\sigma_P}^2 + U_{\overline{\sigma_{W,R}}}^2}. \quad (18)$$

In this situation normalized error $E_{n,PR}$ was calculated as:

$$E_{n,PR} = \left| \frac{\Delta\sigma_{PW,R}}{U_{\Delta\sigma_{PR}}} \right|. \quad (19)$$

As shown in Table 8 and Table 9, part of the results obtained by TUBITAK and IPQ did demonstrate metrological compatibility, i.e., $E_{n,PW,R} < 1$, between the two methods of surface tension determination (ring and plate). Both NMIs obtained a better agreement in low viscous samples (L1 to L3), but IPQ seems to have some problems for L1 sample values by the ring method where a smaller value was obtained when compared with the overall reported values.

The differences obtained in high viscosity samples (L4 to L6) may be due to viscous drag and the time set for the experiments as referred before.

Table 10 and Table 11 display the results of the evaluation made by direct comparison between the surface tension measurement results obtained with Wilhelmy plate (P) against the reference surface tension value (obtained with Du Noüy ring), $\overline{\sigma_{W,R}}$ presented in Table 3. Both NMIs obtained good agreement in low viscous samples (L1 to L3). For sample L3, TCE, corresponding to the liquid with higher density tested, interestingly both NMIs obtained satisfactory results, i.e., $E_{n,PW,R} < 1$, as in the ring method the results obtained show a

Table 7. Resume of surface tension measurement results σ_P and respective expanded uncertainty U_{σ_P} , and difference between TUBITAK and IPQ values $\Delta\sigma_{PP}$ and associated expanded uncertainty $U_{\Delta\sigma_{PP}}$, and normalized error $E_{n,PP}$, obtained by TUBITAK and IPQ, with Wilhelmy plate method, at 20 °C.

Samples	TUBITAK		IPQ		$\Delta\sigma_{PP}$	$U_{\Delta\sigma_{PP}}$	$E_{n,PP}$
	σ_P	U_{σ_P}	σ_P	U_{σ_P}			
	/ (mN / m)						
L1	72.80	0.64	72.56	0.36	0.24	0.73	0.32
L2	24.17	0.64	25.02	0.36	-0.85	0.73	1.16
L3	27.28	0.64	27.26	0.36	0.02	0.73	0.02
L4	30.99	0.64	30.17	0.36	0.82	0.73	1.11
L5	32.25	0.64	31.14	0.36	1.11	0.73	1.51
L6	31.88	0.64	30.70	0.36	1.18	0.73	1.61

Table 8. Surface tension deviation, $\Delta\sigma_{P,R}$, respective uncertainty, $U_{\Delta\sigma_{PR}}$ and normalized error, $E_{n,PR}$ between TUBITAK reported values for surface tension determined by Du Noüy ring and Wilhelmy plate method at 20 °C.

Samples	$\Delta\sigma_{PWR}$ / (mN / m)	$U_{\Delta\sigma_{PR}TUBITAK}$ / (mN / m)	$E_{n,PR}TUBITAK$
L1	0.22	0.88	0.25
L2	-0.59	0.88	-0.67
L3	-	-	-
L4	1.31	0.88	1.48
L5	1.38	0.88	1.56
L6	0.90	0.88	1.02

Table 9. Surface tension deviation, $\Delta\sigma_{P,R}$, respective uncertainty, $U_{\Delta\sigma_{PR}}$ and normalized error, $E_{n,PR}$ between IPQ reported values for surface tension determined by Du Noüy ring and Wilhelmy plate method at 20 °C.

Samples	$\Delta\sigma_{PWR}$ / (mN / m)	$U_{\Delta\sigma_{PR}IPQ}$ / (mN / m)	$E_{n,PR}IPQ$
L1	0.75	0.58	1.30
L2	0.41	0.58	0.70
L3	0.50	0.58	0.87
L4	0.59	0.58	1.03
L5	0.41	0.58	0.71
L6	-0.01	0.58	-0.03

Table 10. Surface tension deviation, $\Delta\sigma_{PW,R}$ respective uncertainty, $U_{\Delta\sigma_{PR}}$ and normalized error, $E_{n,PR}$ between reference values for surface tension determined by weighted mean for Du Noüy ring and TUBITAK reported values for surface tension by Wilhelmy plate method at 20 °C.

Samples	$\Delta\sigma_{PWR}$ / (mN / m)	$U_{\Delta\sigma_{PR}TUBITAK}$ / (mN / m)	$E_{n,PR}TUBITAK$
L1	0.53	0.71	0.75
L2	-0.65	0.67	-0.97
L3	-0.22	1.07	-0.21
L4	1.34	0.64	2.09
L5	1.45	0.64	2.26
L6	1.17	0.64	1.83

Table 11. Surface tension deviation, $\Delta\sigma_{PW,R}$ respective uncertainty, $U_{\Delta\sigma_{PR}}$ and normalized error, $E_{n,PR}$ between reference values for surface tension determined by weighted mean for Du Noüy ring method at 20 °C and IPQ reported values for surface tension by Wilhelmy plate method at 20 °C.

Samples	$\Delta\sigma_{PWR}$ / (mN / m)	$U_{\Delta\sigma_{PR}IPQ}$ / (mN / m)	$E_{n,PR}IPQ$
L1	0.29	0.47	0.63
L2	0.21	0.41	0.51
L3	-0.24	0.93	-0.26
L4	0.52	0.36	1.45
L5	0.34	0.36	0.94
L6	-0.01	0.36	-0.04

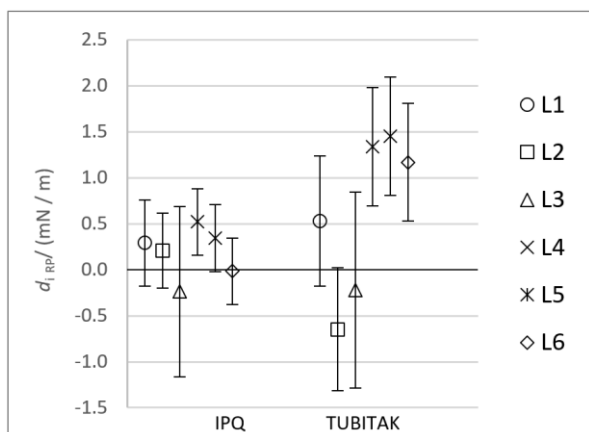


Figure 2. Summary of the degree of equivalence, $d_{\sigma_{PR}}$ for all samples and all NMI are presented, obtained by Wilhelmy Plate method results, at 20 °C.

higher difference and TUBITAK do not reported surface tension results for the ring method. For the high viscosity samples (L4 to L6), around 33 % of the results were found satisfactory, suggesting that both NMIs have room to improve their measurement methodology, and as referred earlier, the differences obtained may be due to the viscosity values of these liquids.

In Figure 2, a summary of the degrees of equivalence, $d_{\sigma_{PRW}}$ observed for all samples and for TUBITAK and IPQ is presented.

4. CONCLUSIONS

The results of this comparison showed a good degree of equivalence of surface tension measurement results of GUM, IPQ and TUBITAK, by using the Du Noüy ring method (by using correction factor based on Harkins & Jordan [2] and Huh & Mason [4]) both for low and high viscosity samples.

It seems that even with inherent corrections, the surface tension values obtained by Du Noüy ring method permitted to compare and evaluate results. The relative expanded uncertainties reported by NMIs are equivalent to 0.2 % to 2.5 % of the report value for surface tension with GUM reporting the smaller uncertainty budget due to longer experience in this field.

It was also possible to conclude about the degree of equivalence for TUBITAK and IPQ between the two methods of surface tension determination and for each NMI their metrological compatibility between these two methods (plate and ring). It was a good start to validate the method and re-evaluate the uncertainty budget. It is also possible to observe that the surface tension values obtained with the plate are almost always higher than the ones obtained with the ring method, for both NMI. In most cases, these differences are higher than the

uncertainty declared, meaning that it will be interesting to work upon this situation to understand the reasons behind these significant differences.

Also, this work, shows how important knowledge and experimental transfer is between NMIs.

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