UFSM

CIÊNCIA e NATURA

ISSN 2179-460X
OPEN ACCESS

Ci. e Nat., Santa Maria, e85536, v. 48, 2026 • https://doi.org/10.5902/2179460X85536
Submitted: 10/26/2023 • Approved: 06/24/2025 • Published: 07/17/2026

Chemistry

Reproducibility and repeatability in tensiometry

Reprodutibilidade e repetibilidade em tensiometria

Felipe de Orquiza Milhomem[I], Bruna de Oliveira Gomes[II], José Aurélio Medeiros da Luz[III], Higor Vinícius Lopes Guedes[IV]

[I] Universidade Federal de Mato Grosso, Cuiabá, MT, Brasil
[II] Universidade Federal de Catalão, Catalão, GO, Brasil
[III] Universidade Federal de Ouro Preto, Ouro Preto, MG, Brasil
[IV] Vale S.A., Nova Lima, MG, Brasil

ABSTRACT

Flotation is a physical-chemical process in which there is selective hydrophobization of particles and subsequent capture of these hydrophobic particles by bubbles. Critical micelle concentration (*cmc*) is an important parameter in this process, as its value supports the selection of the appropriate concentration of reagents. One of the apparatuses for such measurement is the Du Noüy ring tensiometer. In this work, the repeatability and statistical reproducibility (***R&R***) parameter for tensiometry of saponified solutions of vegetable oils used as anionic collectors in mineral flotation was analyzed. The mean value-amplitude method was used, with two operators and three oils studied. The *cmc* results for both operators showed very close values, with mango and palm oils showing approximately 35 mN/m, while copaiba oil resulted in an approximate *cmc* value of 46 mN/m. These values resulted in an ***R&R***% of 5.07 % and number of distinct categories (*ndc*) of 27.8, indicating reliability in the measurements. Given the simplicity of the method, it can be directed towards a wide range of studies.

Keywords: Critical micelle concentration; Ring tensiometer; Tensiometry; Vegetable oils; Statistical analysis

RESUMO

A flotação é um processo físico-químico no qual há hidrofobização seletiva de partículas e subsequente captura dessas partículas hidrofóbicas por bolhas. A concentração micelar crítica (*cmc*) é parâmetro de importância nesse processo, pois seu valor subsidia a seleção da adequada concentração dos reagentes. Um dos aparatos para tal medição é o tensiômetro de anel de Du Noüy. Neste trabalho analisou-se o parâmetro de repetibilidade e reprodutibilidade estatística (***R&R***) de tensiometria de soluções saponificadas de óleos vegetais utilizados como coletores aniônicos em flotação de minerais. Foi utilizado o método das médias e amplitudes, com dois operadores e três óleos estudados. Os

resultados da *cmc* para ambos os operadores apresentaram valores muito próximos, sendo os óleos de manga e de palma acusaram aproximadamente 35 mN/m, ao passo que o óleo de copaíba resultou valor aproximado de *cmc* de 46 mN/m. Tais valores resultaram em um ***R&R***% de 5,07 % e número de categorias distintas (*ndc*) de 27,8 indicando confiabilidade nas medidas. Dada à simplicidade do método, o mesmo pode ser direcionado aos mais variados estudos.

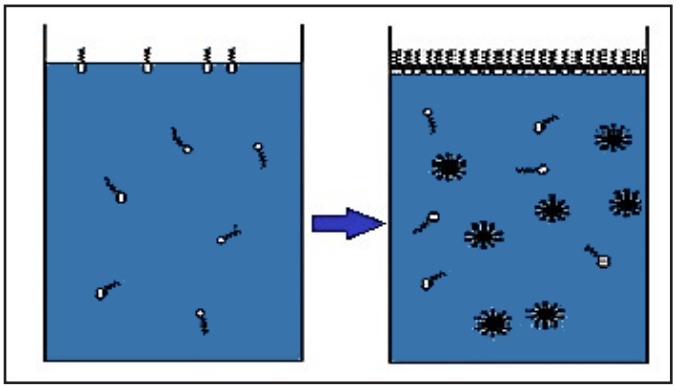
Palavras-chave: Concentração micelar crítica; Tensiômetro de anel; Tensiometria; Óleos vegetais; Análise estatística

1 INTRODUÇÃO

Surface tension is a physicochemical parameter present in many natural processes, such as the fact that some insects walk on water (Hu, Chan & Bush, 2003), the formation of spherical drops (Luz & Lima, 2007), capillary phenomena (liquid flow through narrow conduits) (Benedetto, Zolotucho & Prado, 2015), among others. It is also very important in industry, such as in the preparation of detergents, paints and pharmaceutical components or in processes in which the addition of a reagent cannot exceed certain concentration limits (Rabóczkay, 2016).

When the concentration of a surfactant (*i.e.*, an amphipathic reagent capable of modifying the interfacial tension) exceeds a certain level, the critical micellar concentration (*cmc*) is reached when additional introduction of the surfactant into the system leads to the formation of micelles (Figure 1).

Figure 1 – Emergence of micelles due to excessive addition of surfactant



Source: Authors (2023)

Micelles are usually globular bodies in which the hydrophobic portion is excluded from the medium (in the case of aqueous systems), isolating itself within the micelle and reducing the effectiveness of the surfactant (Butt, Graf & Kappl, 2003). An example of micelle formation can be seen in Figure 1.

Froth flotation is an industrial operation in which such surface phenomena are of paramount importance. In this process, the surfactants act on the surface of the particles of a given mineral (or chemical species), selectively hydrophobizing them and ensuring their separation, in an aqueous medium (due to their adhesion to air bubbles, with subsequent transport), from other non-hydrophobized particles, which remain in suspension. In this process, the knowledge of the *cmc* is important as excessive reagent dosage can be harmful to flotation performance (Rao & Leja, 2004; Braga; Souza Pinto; Matai & Leal Filho, 2015; Luz, 2015).

Therefore, knowledge of the critical micelle concentration is an important parameter, for example, in mineral processes and in choosing the dosage of reagents. There are several apparatuses for measuring surface tension (and consequently *cmc*), with the force tensiometer using the Du Noüy ring being one of the most known and widely used industrially (Rao & Leja 2004; Rabóczkay, 2016). It uses the elevation of a platinum ring, previously immersed in the liquid that is being studied, until the liquid film is completely detached, which adheres via surface tension to its perimeter. The moment of rupture indicates the value of the surface tension of the liquid.

Among other methods used to estimate surface tension, the following methods are commonly used: measuring the elevation (or descent) of liquid in a capillary tube, determining the average weight of drops slowly dripping from a capillary tube; determining radii of curvature in the drop contour (via image analysis and application of the Young-Laplace equation), and determining the maximum bubble pressure immersed in the liquid and the Wilhelmy plate method. Details of these methods can be found in textbooks on interfacial physical chemistry, or in Luz and Lima (Luz & Lima, 2007; Rabóczkay, 2016).

Despite the variety of methods, measurement techniques can be challenging in static methods due to droplet ricochet or requiring a long time to perform, such as the droplet method. Therefore, it is desirable to have a simple device that is easy to handle and has sufficient precision (Du Noüy, 1919).

Although the Du Noüy ring method is widely used, certain precautions must be taken when measuring surface tension (Harkins & Jordan, 1930; Masutani & Stenstrom, 1984): leaving the ring in a horizontal plane, as well as the container with the liquid; there must be no disturbances in the container; the ring must not be deformed; there must be no evaporation or freezing of the liquid; the diameter of the container must not be so small that there are wall effects influencing the liquid rising next to the ring; the movement of pulling the ring must be done very slowly.

Even though the technique is convenient for routine work, one disadvantage noted by Macy (1935) is the loss of time needed to familiarize oneself with the method. Therefore, the operator's sensitivity factor can make a big difference to the results, especially when twisting the equipment's lifting bolt.

An extensive experimental campaign should be carried out when analyzing the use of new reagents in flotation, ranging from their characterization to in-depth laboratory and/or industrial performance studies. Studies on the *cmc* of new reagents are important in the context of fundamental research, and as demonstrated, the technique of using the Du Noüy ring is simple and widespread. However, it can present many errors if not carried out correctly. The aim of this article was therefore to study the reproducibility and repeatability of a ring tensiometer using measurement system analysis (MSA).

2 THEORETICAL BACKGROUND

There is, roughly speaking, a barrier separating the phases, in this case, the surface of the water. This region of separation is not continuous but is formed by the components of each phase (liquid and gas molecules). Inside the liquid, the short-

range forces of attraction between atoms and molecules, resulting from the London–van der Waals forces, cause the molecules to be equally attracted from all sides. On the surface, however, there will be a resultant towards the inside of the liquid phase, forcing the surface to contract spontaneously. This is why small liquid drops or air bubbles take on a spherical shape (Shaw, 1992; Luz & Lima, 2007; Rabóczkay, 2016).

This behavior also makes the surface behave like a film or a thin membrane, whose resistance allows, for example, some animals, such as water strider and other insects, to land or walk on water. Surface tension is the ability to resist rupture of the film, or according to Rabóczkay (2016): surface tension is the work required to increase the surface area of a unit, in an isothermal and reversible process (at fluid interfaces). It is expressed as energy over area (J/m^2), which is equivalent to force per displacement (N/m), although the term interfacial tension (g) is more commonly used (Lima & Luz, 2007).

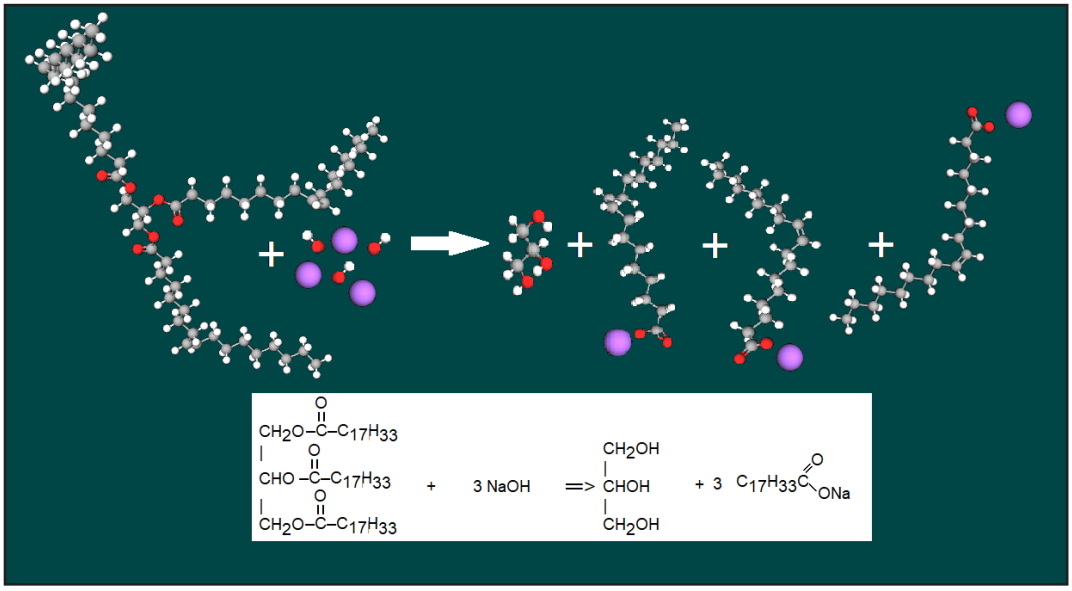
Surfactants are responsible for reducing the surface tension and can interact with polar and nonpolar substances, *i.e.,* substances that have or do not have an electric dipole in their molecules (Rocha, 2001). This property of surfactants is due to their amphipathic nature: with one (or more) polar "head" and a nonpolar "tail". Certain surfaces have natural hydrophobicity, and the presence of these reagents makes it possible to wet them (or vice versa), as can be seen in Figure 2.

Figure 2 – Effect of surfactants on the wettability of a surface: on the left, a drop of water mixed with detergent and on the right, a drop of water alone

Source: Authors (2023)

Several types of reagents can be used in flotation systems. The so-called collectors act on the surface of the mineral, hydrophobizing it so that it can be captured by rising bubbles and collected at the top of the equipment. In the case of iron ore flotation, the common practice in Brazil is to carry out reverse cation flotation, in which a cationic reagent (amines) is used to collect the quartz at the top of the equipment and the hematite (iron source mineral) at the bottom (Araújo; Peres; Viana & Oliveira, 2013). New studies have been carried out in recent years to perform direct anionic flotation, in which the collecting reagent acts directly on the surface of the hematite rather than the quartz. In this case, hydroxamates, sulfonates or fatty acids can be used as collectors. In the case of the latter, they must be saponified before they can be used (Figure 3 illustrates formation of three carboxylates and glycerol from triacylglycerol and sodium hydroxide).

Figure 3 – Triacylglycerol saponification (R_1, R_2 and R_3 are hydrocarbon chains, usually with cis unsaturation — in this example $R_1 = R_2 = R_3 = C_{18}O_2H_{33}$)



Source: Authors (2023)

Vegetable oils are primarily (over 95 %) a mixture of triacylglycerols (with an ester structure), which can be hydrolyzed by bases such as NaOH or KOH, producing glycerol and strongly ionizable carboxylic acid salts, generating anionic surfactant

species made up of hydrocarbon chains terminated by polar heads. These are the classic soaps. The saponification reaction can be simplified as shown in Figure 3, according to the literature (Rao & Leja, 2004).

According to Borsato, Moreira & Galão (2004), the saturation of fatty acids depends on the presence of double bonds in the carbon chain: when all the carbon atoms are linked to at least two carbon atoms, the fatty acid is saturated and if there are one or more double bonds generating carbons linked to a single hydrogen atom, they are unsaturated. Several references show the main saturated and unsaturated fatty acids and their composition. Table 1 shows the fatty acid composition of some vegetable oils.

Table 1 – Fatty acid composition of some vegetable oils

Fatty acid	Oil composition					
	Mango[1]	Copaíba[2]	Palm[3]	Soy[4]	Corn[5]	Sunflower[5]
Palmitic	7,32	24,9	44	11,8	14,03	8,36
Stearic	39,97	-	4,1	3	3,33	5,03
Oleic	43,71	35,3	39,3	23	35,08	27,65
Linoleic	9	35,7	10	57	44,44	56,3
Others	0	4,1	2,6	5,2	3,12	2,66

Source: 1) Vieira et al. (2009); 2) Soares Maia et al. (1978); 3) Erhan (2005); 4) Caires & Brandão (1992); 5) Fonseca & Gutierrez (1974)

In the specific case of anionic flotation, vegetable oil soaps are widely used as collectors, selectively lending the particles a hydrophobic character, due to the directional adsorption of the hydrophobic chains (with anchoring of the polar heads on the particle substrate). Usually, to ensure selective separation, agents that depress the particles (usually minerals) that are to be hydrophilic must be added to the system. Because surfactants lower the surface tension (they are called surfactants), these carboxylates are also used as foaming agents in many flotation systems. This lowering of surface tension is described by the classic Gibbs equation of adsorption (Lima & Luz, 2007), which gives the variation in interfacial tension with the variation in chemical potential (*i.e.*, concentration) of the *n* chemical species present (usually the solute). This very important equation is expressed in diffusive systems by Equation (1):

$$d\gamma = -\sum_{i=1}^{n} \frac{n_i}{A} d\mu_i = -\sum_{i=1}^{n} \Gamma_i d\mu_i \quad (1)$$

Where:
γ — interfacial tension (for liquid-gas interfaces, called surface tension) [J/m², or N/m];
n_i — number of moles of solute (generic), ***i*** [mol/L];
A — interface area [m²];
μ — chemical potential of the solute in the system [J/mol];
$\Gamma = n_i/A$ — adsorption (or interfacial concentration) [mol/m²].

The physical significance of the negative sign in the second member of the Gibbs adsorption equation is that an increase in the concentration of the solute (surfactant) at the interface leads to a decrease in the surface tension of the system.

In terms of quantifying this decrease with concentration, Szyszkowski (1908) established an equation for the surface tension of surfactant solutions, which involves two constants, one of which (a) depends sensitively on the system in question (Meissner & Michaels, 1949). This equation can be expressed as Equation (2):

$$\gamma = \gamma_0 \times \left[1 - 0{,}178495 \times \ln\left(1 + \frac{c}{a}\right)\right] \quad (2)$$

Where:
γ — surface tension of the solution [J/m²];
γ_0 — surface tension of pure water [J/m²];
c — molar concentration of the surfactant [mol/L];
a — experimental parameter [mol/L].

Note that, as the concentrations are usually small, you can use molar fractions (***x***) as the argument (correspondingly changing the value of the parameter ***a***, to suit the unit).

Guay & Bisaillon (1983) studied the interfacial properties of the soybean oil/water system. Their results suggest that the best model to describe surface tension is the logarithmic one originally proposed by von Szyszkowski.

The longer the hydrocarbon chain of the surfactant (the nonpolar, hydrophobic part), the greater the rate of decrease in surface tension (in other words, the lower the

parameter a of the Szyszkowski equation). Traube's (approximate) rule, formulated in 1891 (*apud* Rao & Leja, 2004), states that, for a particular homologous series of surfactants, the concentration required for an equal reduction in surface tension in dilute solution decreases by a factor of around 3.0 for each additional CH_2 group in the chain.

In the context of anionic flotation, however, if there is an excess of this type of collector (soaps, especially long-chain soaps), micelles (sometimes referred to in this context as hemimicelles) will form on the substrate to be hydrophobized (*i.e.*, mineral particles). These micellar agglomerates have a double-lamellar configuration, in which the hydrocarbon chains interpenetrate, resulting in polar heads anchoring the surface of the particles, on the one hand, and — on the other hand — polar heads directed towards the aqueous medium, which also has a polar character, due to the strong electrical asymmetry of the water molecules (Luz, 2015).

In case of micelle formation, the particles, which should be hydrophobic due to the adsorption of the collector, return to their natural hydrophilicity, collapsing the selectivity of flotation.

Overall, in the case of flotation using substances with hydrocarbon chains of considerable size (such as fatty acid or carboxylic acid soaps from vegetable oils), care should be taken with the appropriate dosage, and studies should be carried out to find out the *cmc* of these reagents (and therefore the maximum recommended dosage). In the case of soaps, knowledge of the *cmc* is important due to their effects on detergency and solubilization processes (Chupa, Misner & Smith, 2012).

Gibbs' law and this occurrence of micelles explain the concavity of the concentration versus surface tension curves (see results below), with a decrease in the modulus of the derivative (tangent) of the surface tension curve until it reaches a plateau, which occurs when the critical micellar concentration (*cmc*) is reached, since — when this concentration is exceeded — additions of surfactant will increase the number of micelles in solution, without their contribution to the interface (since there is no longer a decrease in surface tension in this region of the graph).

The following table (Table 2) illustrates literature values for sodium soaps of six saturated and one unsaturated carboxylic acid (oleate), from the original data by Mukerjee & Mysels (1971), including average values calculated by Rao & Leja (2004) and Bulatovic (2007).

Table 2 – Some *cmc* values for carboxylic acid soaps

Number of carbons	Nomenclature IUPAC	Common name	Mol [kg]	*cmc* [mol/L]
8	Sodium octanoate: CH3(CH2)6COOH	sodium caprylate	0.16620	3.50E-01
10	Sodium decanoate: CH3(CH2)8COOH	sodium caprylate	0.19425	9.40E-02
12	Sodium dodecanoate: CH3(CH2)10COOH	sodium laurate	0.22230	2.60E-02
14	Sodium tetradecanoate: CH3(CH2)12COOH	sodium myristate	0.25036	6.90E-03
16	Sodium hexadecanoate: CH3(CH2)14COOH	sodium palmitate	0.27841	2.10E-03
18	Sodium octadecanoate: CH3(CH2)16COOH	sodium stearate	0.30647	1.80E-03
18	Sodium octadecenoate: CH3(CH2)16COOH	sodium oleate	0.30445	2.09E-02

Source: Authors (2023)

Determining the *cmc* is usually done by constructing graphs of the physicochemical properties as a function of the concentration of the surfactant solution. Some of these physicochemical properties are: surface tension, viscosity, osmotic pressure and conductivity for ionic surfactants (Maniasso, 2001; Santos, 2014). Sharma and colleagues (Sharma, Saxena & Sharma, 2018), for example, used viscosimetry to determine the *cmc* of cupric soaps from the saponification of edible oils.

Surface tension can be measured using various techniques, such as capillarity, the Wilhelmy plate method, the hanging drop, methods based on the weight and volume of the drop, Du Noüy's ring and the oscillating jet method (Shaw, 1992).

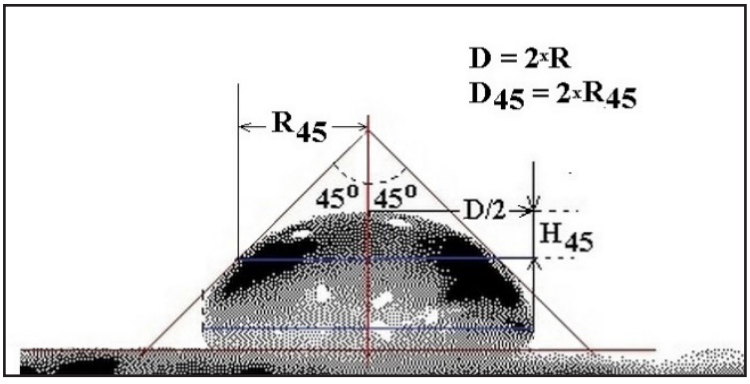
Just to give an example of two simple methods, we will first mention the work of Román, Faro & Velasco (2001), who used an expeditious method to determine the surface tension of a soap solution, based on measuring the internal pressure of the films (bubbles) using a sensitive manometer, with the application of the Young—Laplace equation, given by Equation (3), shown below:

$$\Delta p = p_{int} - p_{ext} = 2 \times \gamma \times \left(\frac{1}{r_1} + \frac{1}{r_2}\right) \quad (3)$$

The previous equation (in its classic form, for an interface with principal radii of curvature r_1 and r_2) has been multiplied by two because a soap bubble in air is made up of two films (two interfaces). With a bubble small enough to be considered spherical (of radius r — where we have: $r_1 = r_2 = r$) and knowing the internal pressure (p_{in}) and the external pressure (p_{ext}, usually atmospheric pressure), the only unknown will be the surface tension of the soap solution (γ).

An alternative method exemplified here, based on simple image analysis of an axisymmetric drop of the liquid under study, is the Dorsey method (Zhao et al., 2018). The parameters used can be seen in Figure 4, showing the equatorial diameter (D), the radius of the parallel (R_{45}) which contains the two points of tangency of the lines who form an angle of 45° with the axis of symmetry, as well as the height of the cap (H_{45}) generated by the plane of the parallel of radius R_{45}.

Figure 4 – Processed image of a drop of water on a paraffin-covered surface (the explanation of the geometric parameters is in the text)



Source: Authors (2023)

The surface tension can be calculated directly using Equation (4), shown below, as a function of the parameters mentioned:

$$\gamma = \frac{g \times \rho \times D^2}{4}\left\{0{,}048 \times \left[\frac{2 \times (R_{45} - H_{45})}{D} - 0{,}4142\right] - 0{,}1227 + \frac{0{,}052}{\left[\frac{2 \times (R_{45} - H_{45})}{D} - 0{,}4142\right]}\right\} \quad (4)$$

The Du Noüy ring tensiometer makes it possible to check the *cmc* of liquids or solutions by taking measurements with increasing concentrations of reagents. Reis, Araújo & Rodrigues (2017) confirmed the applicability of the method for dodecylamine solution comparing to reference values. The surface tension can be calculated by Equation (5) (Freud & Freud, 1930; Harkins & Jordan, 1930):

$$\gamma = \frac{m \times \mathrm{g}}{4 \times \pi \times \mathrm{r}} \quad (5)$$

In this case, ***m*** represents the mass of water displaced when the ring ruptures. In some equipment, however, the surface tension value is already given directly. Although the equipment is relatively simple to use, it is subject to errors. In addition, special care should be taken when several operators are taking measurements of the same liquid, since the force applied to lift the ring can be a source of error.

A repeatability and reproducibility (***R&R***) study allows the evaluation of equipment performance. Repeatability is the accuracy of the various measurements of a material/part by a single operator and reproducibility is the accuracy of the measurements of a material/part with a variation of operators (Mandel, 1972; Sullivan et al., 2015; Action, 2020).

Andrade et al. (2011) used an ***R&R*** study to evaluate the uncertainty in the granulometric analysis of two soils, a latosoil and an argisoil, and found that the former had an uncertainty in the analysis of 3 % and the latter 2 %. Chui, Barros & da Silva (2009) used the ***R&R*** parameters to verify protocols between twelve laboratories in the quality control of metallurgical silicon. According to them, the values obtained indicate the existence of problems, but the study is still valid to reduce variability between laboratories. Feng et al. (2015) analyzed the measurement

of porous body characteristics. According to them, the characteristic heterogeneity of such materials leads to problems in reproducibility, however, if good repeatability is achieved in the measurements, such results can be reliable. Wrzochal & Adamczak (2019) evaluated the production of bearings with three different production systems in a factory. According to them, the methodology clearly demonstrated the accuracy of the systems. In addition, it allows a given process to be evaluated even without having reference values from other factories, for example. Thus, ***R&R*** analysis can demonstrate the performance of a method. Furthermore, this methodology can be adopted in various industrial or laboratory practices.

3 EXPERIMENTAL PROCEDURE

This work was one of the stages in the fundamental characterization of new reagents for use in iron ore flotation, specifically direct anionic flotation. Three vegetable oils were chosen for the tests to measure surface tension and determine *cmc*: mango, palm oil and copaiba. Given the oils' immiscibility in water, they were subjected to a saponification process, *i.e*., alkaline hydrolysis (Oliveira, Luz & Ferreira, 2006), making them soluble for the preparation of solutions with various concentrations.

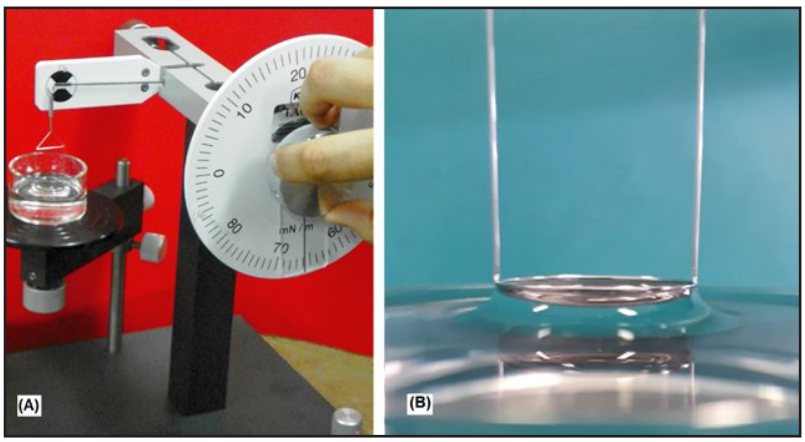
Saponification in an alcoholic medium was used. The process was carried out as follows: 1 g of the sample was weighed into a 1.000 L volumetric flask and then 15 mL of a 2 % NaOH alcohol solution was added. The volumetric flask was placed on a hot plate and stirred for 20 minutes. Then 80 mL of distilled water was added and the mixture was left on the hotplate for another hour, still stirring and using a reflux condenser to prevent the loss of alcohol through evaporation. After this period, and once the oil had been solubilized, the condenser was removed, and the volumetric flask was heated for another half an hour to allow the rest of the alcohol to evaporate. After this, the volumetric flask was allowed to cool and then its volume was topped up with distilled water. This produced a stock solution with a mass concentration of 0.1 %.

With the stock solutions prepared based on the saponified oils, we proceeded to prepare solutions with different concentrations to study the critical micellar concentration in the tensiometer. Solutions of the saponified oils were analyzed at concentrations of 1, 2, 5, 10, 15, 20, 50, 100, 150, 200, 250, 300, and 350 mg/L.

Surface tension measurements were carried out on the Krüss K6 analog force tensiometer (measuring range from 0 to 90 mN/m), which uses the Du Noüy ring method. The ring is made of platinum-iridium with a circumference of 19 mm (circular cross-section wire with a diameter of 0.5 mm), whose composition is due to its high hardness and stability, as well as ease of cleaning (Reis et al., 2017). Figure 5 shows the tensiometer and the elevation of the water film with the ring.

The solution with the desired concentration was placed in a truncated glass container (diameter 67 mm at the base and 72 mm at the top), which was placed on a platform with height adjustment. The ring was immersed in the solution so that it was horizontal and practically at the liquid/air interface, with the applied force indicator pointer set to the original position (0.0 mN/m). The indicator is then turned very slowly clockwise to gradually suspend the ring. The rupture of the liquid film adhered to the ring indicates the value of the surface tension, which can be read on the equipment's display (Figure 5).

Figure 5 – *A)* Ring tensiometer and *B*) elevation of the water film, before it breaks, next to the platinum-iridium ring (the scale values are in mN/m, equivalent to mJ/m²)



Source: Authors (2023)

It is worth noting that care was taken to ensure that the equipment was not tilted and that the ring was cleaned with distilled water, dried and quickly passed through the oxidation zone of an alcohol lamp flame before and after each measurement. In addition, the process of twisting the lifting screw was carried out very slowly, since if done abruptly, it causes variations of around 50 % (Luz & Soares Júnior, 2012).

Two operators have taken measurements on the equipment separately, on different days and at different times. The temperature in the laboratory was controlled at 296.1 K (23 °C).

Evaluation by ***R&R*** can be done in two ways: i) the method of averages and amplitudes and ii) the ANOVA method - analysis of variance (Melo, Pinheiro & Barbosa, 2017). There is also the method of averages, which does not break down the variability of the measurement into repeatability and reproducibility and serves only as a quick check of the system.

Both ANOVA and mean and range methods generate similar results, which is why the latter was chosen, as it is more practical. The general average and amplitude of the surface tension measurements obtained by each evaluator were calculated, considering the three oil soaps. Then the overall averages and amplitudes were calculated.

As mentioned, the study was carried out with two operators and three saponified oils. At the three highest concentrations (250, 300 and 350 mg/L), the values took on an asymptotic behavior, indicating that the *cmc* had been reached. The triplicate measurements of each of these concentrations were used in the ***R&R*** calculations.

The averages of each test (***i***) were calculated for each evaluator (***k***). Next, the same was done with the mean and range of each oil (***j***). After this, the overall average and overall amplitude were also calculated for each operator. Table 3 shows an example of the procedures carried out.

Table 3 – Statistical parameters

Operator	Test	Oil 1	Oil 2	Oil 3	Average of each test for each operator
k	1	R11k	R12k	R13k	X_{1jk}
	2	R21k	R22k	R23k	X_{2jk}
	3	R31k	R32k	R33k	X_{3jk}
Average of each oil for each operator		X_{i1k}	X_{i2k}	X_{i3k}	Overall average for each operator X_{ijk}
Amplitude of each oil for each operator		Ri1k	Ri2k	Ri3k	General amplitude for each operator R_{ijk}

Source: Authors (2023)

After obtaining the general average and amplitude for each operator, the average ($\overline{\boldsymbol{X}}$) and average amplitude ($\overline{\boldsymbol{R}}$) between the operators were found. In addition, the amplitude between the averages of each oil ($\boldsymbol{R_o}$) was found, according to Equation (6) below:

$$\mathrm{R_o} = \overline{\mathrm{X_{óleo}}}_{\mathrm{MÁX}} - \overline{\mathrm{X_{óleo}}}_{\mathrm{MÍN}}\ \mathrm{R_o} = \overline{\mathrm{X_{óleo}}}_{\mathrm{MÁX}} - \overline{\mathrm{X_{óleo}}}_{\mathrm{MÍN}} \quad (6)$$

With all these values, the parameters needed for the ***R&R*** calculation were found. The calculations used are shown in Equations (7) to (11) below:

$$VE = \overline{R} \times k_1 \quad (7)$$

$$VA = \sqrt{\left(\overline{X} \times k_2\right)^2 - \left(\frac{VE^2}{n \times r}\right)} \quad (8)$$

$$R\&R = \sqrt{VE^2 + VA^2} \quad (9)$$

$$VO = R_o \times k_3 \quad (10)$$

$$VT = \sqrt{R\&R^2 + VO^2} \quad (11)$$

Where:
VE — equipment variation, or repeatability;
VA — evaluator variation, or reproducibility;
R&R — repeatability and reproducibility;

VO — variation in measurements between the different oils;
VT — total variation; **R** — average range between operators; R_o — range of oils (or parts); ***X*** — overall average; **n** and ***r*** — number of evaluations (oils tested) and tests, respectively; k_1, k_2 and k_3 — parameters that will depend on the number of tests, evaluators and parts, respectively, given in Tables 4, 5 and 6;

Table 4 – k_1 values according to number of tests

Tests	2	0.8862
k_1	3	0.5908

Source: Authors (2023)

Table 5 – k_2 values according to number of assessors

Evaluators	**2**	**3**
k_2	0.707	0.5231

Source: Authors (2023)

Table 6 – k_3 values according to number of parts

Parts	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
k_3	0.7071	0.5231	0.4467	0.403	0.3742	0.3534	0.3375	0.3249	0.3146

Source: Authors (2023)

Once this data is available, the ***ndc*** or *number of distinct categories* is calculated, which indicates the measurement system's ability to discriminate between categories (MSA, 2010; Pedott & Fogliatto, 2012). It is calculated using Equation (12) and its value must be greater than or equal to 5 to validate the measurement system.

$$ndc = 1.41 \times \frac{VO}{R\&R} \tag{12}$$

In addition to the ***ndc***, the ***R&R*** itself is a validation parameter. To find out whether it is significant or not, the ratio of the ***R&R*** to the total variation is used to obtain the %***R&R***, the classification of which is shown in Table 7 (MSA, 2010; Melo et al., 2017).

Table 7 – Acceptance criteria for the system analyzed

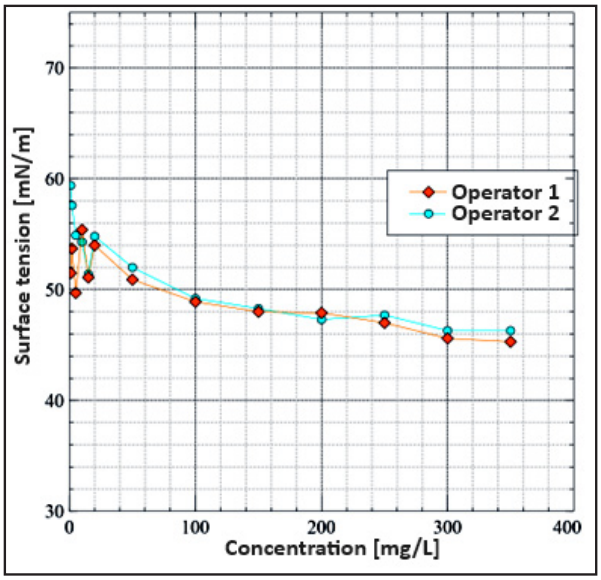
%R&R	Notes
Less than 10 %	System considered acceptable
Between 10 and 30%	System can be accepted, depending on its importance in the process
Above 30 %	Failed system

Source: Authors (2023)

4 RESULTS

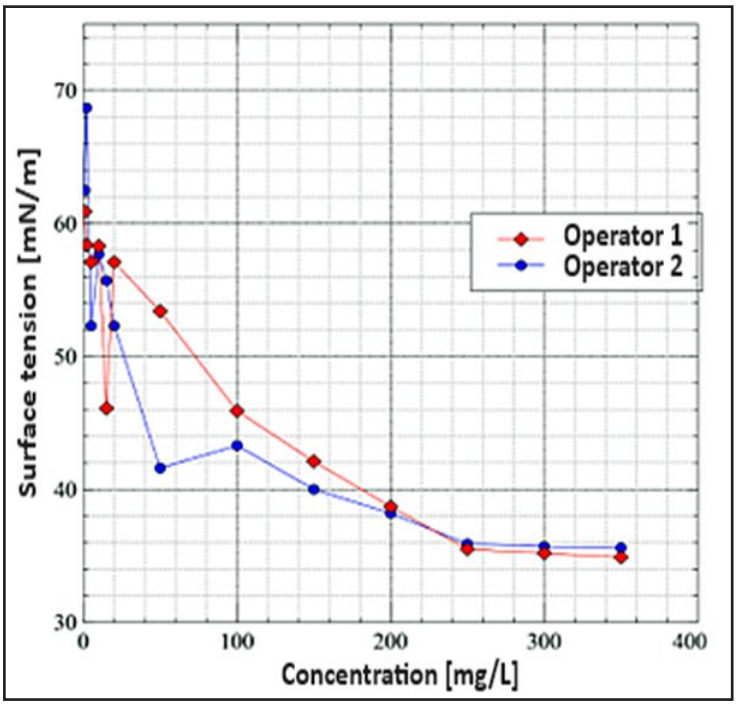
Figures 6, 7 and 8 show the results of the measurements for the solutions of the three oils with the two operators. Although in the case of mango and palm oils, the operators found slightly divergent values in the case of lower concentrations, the tendency was for the values to converge as the concentration of the solution increased and approached the *cmc* value. As for the *cmc* value, mango oil reached a concentration of approximately 300 mg/L, palm oil reached 225 mg/L and copaiba oil reached a *cmc* value of 115 mg/L. As for the surface tension values, mango and palm oils reached similar values of approximately 35 mN/m, while copaiba oil had an average value of 46 mN/m. These values are shown in Table 8, which considers the last three measurements, at concentrations of 250, 300 and 350 mg/L, due to the asymptotic trend of the values obtained.

Figure 6 – Surface tension values for different concentrations of saponified copaiba oil solution for the two operators



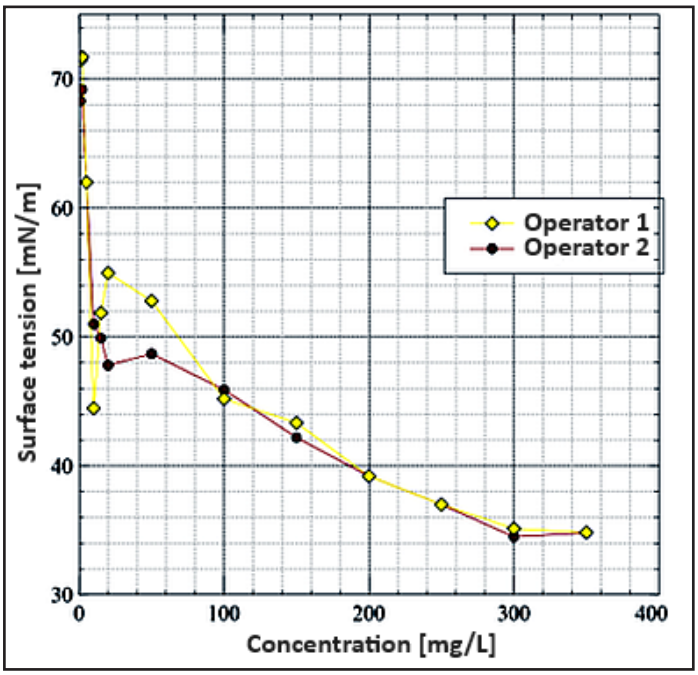
Source: Authors (2023)

Figure 7 – Surface tension values for different concentrations of saponified palm oil solution for the two operators



Source: Authors (2023)

Figure 8 – Surface tension values for different concentrations of saponified mango oil solution for the two operators



Source: Authors (2023)

The use of the last three concentrations is due to the very large difference in surface tension values between the lowest and highest concentrations. If all the values were taken, the variability of the oil measurements — Equation (10) — would be very high, leading to errors in the measurements.

Table 8 – Values of the surface tension measurements of the last three concentrations, considering the stability obtained in the measurements

Operator	Test	Mango	Oil Palm	Copaiba	Overall value
1	1	35.73	35.27	45.93	
	2	35.57	35.07	45.90	
	3	35.67	35.23	46.10	
	Average	35.66	35.19	45.98	38.94
	Range	0.17	0.20	0.20	0.19
2	1	35.80	35.87	46.70	
	2	35.17	35.60	46.87	
	3	35.40	35.73	46.73	
	Average	35.46	35.73	46.77	39.32
	Range	0.63	0.27	0.17	0.36

Source: Authors (2023)

Once the data in Table 10 was available, the repeatability and reproducibility analyses were carried out. As mentioned, the methodology used here was that of averages and amplitudes. Table 9 shows the calculations made. The right-hand column represents the variation in relation to the total variation and the ***ndc*** is calculated using Equation (12).

Table 9 – Variation results obtained from measurements

Source of variation	VE	VA	VO	*R&R*	VT
	0.16	0.26	6.06	0.31	6.01
Total variation	**%VE**	**%VA**	**%VO**	***%R&R***	***ndc***
	2.65	4.32	99.87	5.07	27.8

Source: Authors (2023)

The variation in measurements between the oils (%VO) was high, but this is because three different types of oil were used instead of three analyses with the same oil. The %***R&R*** value was 5.7 % while the ***ndc*** value was 27.8. Both parameters are considered

satisfactory (MSA, 2010; Pedott & Fogliatto, 2012; Melo et al., 2017), demonstrating the good applicability of the equipment—even when operated by different users—provided they are properly trained and attention is given to potential sources of measurement error.

5 CONCLUSIONS

Although the Du Noüy ring tensiometer is widely used, as it is relatively simple to use, it requires a lot of care in its handling. Measurement system concepts were applied, specifically the ***R&R*** parameter (repeatability and reproducibility) and the ***ndc*** (number of distinct categories), for the tensiometer measurements, using two operators and three reagents (vegetable oil soaps). The methodology used was that of averages and amplitudes, which is relatively simple and equally useful compared to the analysis of variance method, and it is possible to carry out this type of analysis in various methodologies in the most varied fields of study.

The critical micellar concentration values found by the two operators were similar, with mango and palm oils approximately in the 35 mN/m surface tension range and copaiba oil around 46 mN/m.

Results of 5.07 % were found for ***R&R*** and 27.8 for ***ndc***. These values indicate that the Du Noüy ring method shows good reliability, if the correct guidelines for its use are followed and is suitable for evaluating the *cmc* of vegetable oil soap solutions, or even for determining the surface tension of other substances. In addition, this study demonstrated the feasibility of using the method of averages and amplitudes, which can be used in various fields of study.

ACKNOWLEDGEMENTS

The Authors would like to thank the Federal University of Ouro Preto (UFOP), CAPES, CNPq and Fapemig for supporting this research.

REFERENCES

Action, P. *Repetitividade e reprodutibilidade*. (2020, 20 de março). Recuperado de: http://www.portalaction.com.br/analise-dos-sistemas-de-medicao/24-repetitividade-e-reprodutibilidade

Andrade, H. M., Viana, J. H. M., Donagemma, G. K., Paz, L. F., & de Melo, B. M. (2011). Avaliação da repetitividade e reprodutibilidade para cálculo de incerteza na análise granulométrica. *Anais do XXXIII Congresso Brasileiro de Ciência Do Solo Biologia Do Solo,* Uberlândia, MG.

Araújo, A. C., Peres, A. E. C., Viana, P. R. M., & Oliveira, J. F. (2013). Flotação de minérios de ferro. In A. P. Chaves (Ed.), *Teoria e prática do tratamento de minérios: a flotação no brasil* (Volume 4, 3a ed., pp. 354–367). Oficina de Textos.

Benedetto, F. E., Zolotucho, H., & Prado, M. O. (2015). Critical assessment of the surface tension determined by the maximum pressure bubble method. *Materials Research*, 18(1), 9-14. https://doi.org/10.1590/1516-1439.232513

Borsato, D., Moreira, I., & Galão, O. F. (2004). *Detergentes naturais e sintéticos: um guia técnico* (2a ed.). Editora da Universidade Estadual de Londrina: EDUEL.

Braga, A. S., Souza Pinto, T. C., Matai, P. H. L. S., & Leal Filho, L. S. (2015). Determinação da concentração micelar crítica e a de coalescência de reagentes de flotação. *Anais do XXVI Encontro nacional de tratamento de minérios e metalurgia extrativa,* Poços de Caldas-MG.

Bulatovic, S. M. (2007). *Handbook of flotation reagents: chemistry, theory and practice (vol. 1: flotation of sulfide ores*). Elsevier.

Butt, H. J., Graf, K., & Kappl, M. (2003). *Physics and chemistry of interfaces*. Wiley-VCH.

Caires, L. G., & Brandão, P. R. G. (1992). Óleos vegetais saponificados na flotação de um minério fosfático. *Associação Brasileira de Tecnologia Mineral*, 1, 65–81.

Chui, Q. S. H., Barros, C. B. de, & Silva, T. D. da. (2009). Parâmetros R e R obtidos de programa interlaboratorial - como usá-los. *Química Nova*, 32(8), 2209–2213. https://doi.org/10.1590/S0100-40422009000800037

Chupa, J., Misner, S., & G. A. Smith. (2012). Soap, fatty acids, and synthetic detergents. In J. A. Kent (ed.), *Handbook of industrial chemistry and biotechnology* (12th ed., pp. 1098–1140). Springer Science & Business Media.

Du Noüy, P. L. (1919). A new apparatus for measuring surface tension. *The Journal of General Physiology*, 1(5), 521–524. https://doi.org/10.1085/jgp.1.5.521

Erhan, S. Z. (2005). *Industrial uses of vegetable oil*. AOCS publishing.

Feng, C., Janssen, H., Feng, Y., & Meng, Q. (2015). Hygric properties of porous building materials: Analysis of measurement repeatability and reproducibility. *Building and Environment*, 85, 160–172. https://doi.org/10.1016/j.buildenv.2014.11.036

Fonseca, H., & Gutierrez, L. E. (1974). Composição em ácidos graxos de óleos vegetais e gorduras animais. *Anais da Escola Superior de Agricultura Luiz de Queiroz*, 31, 485–490. https://doi.org/10.1590/S0071-12761974000100038

Freud, B. B., & Freud, H. Z. (1930). A theory of the ring method for the determination of surface tension. *Journal of the American Chemical Society*, 52(5), 1772–1782.

Guay, F., & Bisaillon, S. (1983). Validation of a mathematical model using the computer for the evaluation of different parameters related to interfaces of air/water and soyabean oil/water systems. *Journal of Colloid and Interface Science*, 93(1), 25–32. https://doi.org/10.1016/0021-9797(83)90380-6

Harkins, W. D., & Jordan, H. F. (1930). A method for the determination of surface and interfacial tension from the maximum pull on a ring. *Journal of the American Chemical Society*, 52(5), 1751–1772.

Hu, D. L., Chan, B., & Bush, J. W. M. (2003). The hydrodynamics of water strider locomotion. *Nature*, 424(6949), 663–666.

Lima, R. M. F., & Luz, J. A. M. (2007). Mobilidade eletroforética. In J. A. Sampaio, S. C. A. França, & P. F. A. Braga (Eds.), *Tratamento de minérios: práticas laboratoriais* (pp. 505-530). CETEM/MCT.

Luz, J. A. M. (2015) Flotation of iron ore. In G. E. Totten, & R. Colas. (Org.), *Encyclopedia of iron, steel, and their alloys* (v. 2, p. 1249-1288). Taylor & Francis Group.

Luz, J. A. M., & Lima, R. M. F. (2007). Medida da tensão superficial. In J. A. Sampaio, S. C. A. França, & P. F. A. Braga (Eds.), *Tratamento de Minérios: práticas laboratoriais* (pp. 473–488). CETEM/MCT.

Luz, J. A. M., & Soares Júnior, A. Interfacial tension from profile of the pendant drop versus Du Noüy's Method. (2012). In *Proceedings of XIIIth International Mineral Processing Symposium*, (pp. 297–303).

Macy, R. (1935). Surface tension by the ring method. Applicability of the du Nouy apparatus. *Journal of Chemical Education*, 12(12), 573-576.

Mandel, J. Repeatability and reproducibility. (1972). *Journal of Quality Technology*, 4(2), 74–85. https://doi.org/10.1080/00224065.1972.11980520

Maniasso, N. Ambientes micelares em química analítica. (2001) *Química Nova*, 24, 87-93. https://doi.org/10.1590/S0100-40422001000100015

Masutani, G., & Stenstrom, M. K. (1984). A Review of surface tension measuring techniques, surfactants, and their implications for oxygen transfer in waste water treatment plants. *Water Research Program, School of Engineering and Applied Science, University of California: Los Angeles, CA, USA*.

Meissner, H. P., & Michaels, A. S. (1949). Surface tension of pure liquids and liquid mixtures. *Industrial Engineering Chemistry*, 41(12), 2782–2787.

Melo, J. C. S., Pinheiro, B. C. A., & Barbosa, E. C. (2017). O parâmetro R&R e suas formas de obtenção: uma revisão de literatura. *Sigmae*, 5, 12–26.

MSA. (2010). *Measurement System Analysis - Reference manual* (4th ed.).

Mukerjee, P. & Mysels, K. J. (2021, 10 de março). *Critical micelle Concentration of Aqueous Surfactant Systems*. National Bureau of Standard (NSRDS□NBS 36), Washington, 1971. 227 p. Recuperado de: https://srd.nist.gov/NSRDS/NSRDS-NBS361.pdf

Oliveira, J. A., Luz, J. A. M. Da, & Ferreira, E. E. (2006). Grau de saponificação de óleos vegetais na flotação seletiva de apatita de minério carbonatítico. *Rem: Revista Escola de Minas*, 59(4), 385–390. https://doi.org/10.1590/S0370-44672006000400006

Pedott, A. H., & Fogliatto, F. S. (2012). Estudos de repetitividade e reprodutividade para dados funcionais. *Produção*, 23(3), 548–560. https://doi.org/10.1590/S0103-65132012005000087

Rabóczkay, T. (2016). *Físico-química de interfases*. Edusp.

Rao, S. R. & Leja, J. (2004). *Surface chemistry of froth flotation (volume I)*. Kluwer Academic.

Reis, J. L. M., Araújo, A. C. A., & Rodrigues, O. M. S. (2017). Aplicabilidade do método do anel de Du Noüy para realização de medidas de tensão superficial de soluções do surfactante dodecilamina. Anais do *XXVII Encontro Nacional de Tratamento de Minérios e Metalurgia Extrativa*, Belém-PA.

Rocha, W. R. (2001). Interações intermoleculares. *Cadernos Temáticos de Química Nova na Escola*, 4, *31*-36.

Román, F. L., Faro, J., & Velasco, S. (2001). A simple experiment for measuring the surface tension of soap solutions. *American Journal of Physics*, 69(8), 920–921.

Santos, M. S. (2014). *Teoria de micelização: propriedades de soluções de surfactantes via minimização da energia livre de Gibbs* (Tese de Doutorado). COPPE/UFRJ, Rio de Janeiro, Brasil.

Sharma, A. K., Saxena, M., & Sharma, R. (2018). Surface active properties and micellar features of copper soaps derived from various edible oils. *Open Chemistry Journal*, 5, 119-133. http://dx.doi.org/10.2174/1874842201805010119

Shaw, D. J. (1992). *Introduction to colloid & surface chemistry* (4th ed.). Butterworth Heinemann.

Soares Maia, J. G., Varejão, M. J. C., Filho, W. W., Mourão, A. P., Craveiro, A. A., & Alencar, J. W. (1978). Composição e oxidação do óleo de uma espécie de Copaifera. *Acta Amazonica*, 8(4), 705.

Sullivan, D. C., Obuchowski, N. A., Kessler, L. G., Raunig, D. L., Gatsonis, C., Huang, E. P., Kondratovich, M., Mcshane, L. M., Reeves, A. P., Barboriak, D. P., Guimaraes, A. R., & Wahl, R. L. (2015). Metrology standards for quantitative imaging biomarkers. *Radiology*, 277(3), 813–825. https://doi.org/10.1148/radiol.2015142202

Szyszkowski, B. V. (1908). Experimentelle Studien über kapillare Eigenschaften der wässerigen Lösungen von Fettsäuren. *Zeitschrift für physikalische Chemie*, *64*(1), 385-414.

Vieira, P. A. F., Queiroz, J. H., Vieira, B. C., Mendes, F. Q., Barbosa, A. A., Muller, E. S., Sant'ana, R. C. O., & Moraes, G. H. K. (2009). Caracterização química do resíduo do processamento agroindustrial da manga (Mangifera indica L.) var. Ubá. *Alimentos e Nutrição*, 20(4), 617–623.

Wrzochal, M., & Adamczak, S. (2019). Application of a gage R&R study in evaluation of rolling bearing measurement system accuracy. *Transportation Research Procedia*, 40, 934–939. https://doi.org/10.1016/j.trpro.2019.07.131

Zhao, X., Xie, F., Fan, J., Liu, D., Huang, J., & Chen, S. (2018). Evaluation on Dorsey method in surface tension measurement of solder liquids containing surfactants. *International Journal of Thermophysics*, *39*(6), 76.

Authorship contributions

1 – Felipe de Orquiza Milhomem

Associate professor at the Department of Mining Engineering at the UFMT.
https://orcid.org/0000-0002-9830-8374 • felipemilhomem6@gmail.com
Contribution: Conceptualization, Data curation, Formal Analysis, Methodology, Project administration, Software, Supervision, Validation, Writing – original draft, Writing – review & editing.

2 – Bruna de Oliveira Gomes

PhD student at the Postgraduate Program in Sciences and Materials Engineering in the UFCAT.
https://orcid.org/0000-0003-0627-5542 • bruna.ogomes@hotmail.com
Contribution: Data curation, Investigation, Methodology, Project administration, Software, Supervision, Validation, Writing – original draft, Writing – review & editing

3 – José Aurélio Medeiros da Luz

Full professor at the Department of Mining Engineering, in UFOP.
http://orcid.org/0000-0002-7952-2439 • jaurelio@ufop.edu.br
Contribution: Formal Analysis, Funding acquisition, Methodology, Resources, Software, Validation, Writing – original draft, Writing – review & editing

4 – Higor Vinícius Lopes Guedes

Senior mine operations engineer at Vale S. A.
https://orcid.org/0000-0003-4664-5560 • guedeshigor5@gmail.com
Contribution: Investigation, Software

How to quote this article

Milhomem, F. O., Gomes, B. O., Luz, J. A. M., Guedes, H. V. L. (2026). Reproducibility and repeatability in tensiometry. *Ciência e Natura,* Santa Maria, 48, e85536.DOI 10.5902/2179460X85536. Disponível em: https://doi.org/10.5902/2179460X85536.