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METROLOGICAL EVALUATION OF TITRATION TECHNIQUES FOR THE DETERMINATION OF THE IODINE VALUE IN BIODIESEL

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Abstract: Based on international standard procedures, the degree of unsaturation on biodiesel was evaluated, called iodine value. Two titration techniques were used to determine the iodine value: colorimetric and potentiometric techniques. The uncertainty of measurement was used to evaluate the quality of the results.

The potentiometric technique showed better quality in the determination of the iodine value because of its accuracy as well as lower uncertainty result of the measurements, with values between 0,613 g I_2 / 100 g and 1,438 g I_2 / 100 g), compared to the results from the colorimetric technique, with values between 1,61 g I_2 / 100 g and 3,30 g I_2 / 100 g.

1. INTRODUCTION

The specification of biodiesel (B100) establishes the degree of unsaturation which is present in its composition, or its iodine value, which is related to factors in the quality of the biodiesel fuel, such as polymerization, stability and viscosity. The unsaturated fatty acids are susceptible to the oxidation reactions, which can be accelerated by the exposition to oxygen and high temperatures. Thus, they are able to result in polymeric composites and gum formation, influencing in the performance of the engine for the increase of viscosity and acidity, capable of generating corrosive processes [1]

The standard procedures use colorimetric titration, with a starch indicator, as the main method for iodine value measurement. Some of them also mention potentiometric titration as an alternative.

Related to the accurate measurement of the biodiesel quality parameter, the National Institute of Metrology – Inmetro has been developing research activities aiming at the production of certified reference materials for biodiesel. Therefore, Inmetro needs to use adequate methods of measurement to be adopted in the analyses, providing guarantee and reliabity to the results.

2. PURPOSE

Based on the standard procedures, a comparison of the techniques was developed to determine the end point of titration, either potentiometric or colorimetric. The experiments were conducted varying the solvent for dissolution of the biodiesel, either carbon tetrachloride or cyclohexane / glacial acetic acid (1:1) and the temperature of reaction, either 25 °C or 37 °C. The experiments were performed on a biodiesel matrix from palm oil. The quality of the measurements was evaluated through the uncertainty of each result in accordance with the described method in Eurachem Guide [2].

3. METHODS

The experiments were carried out by using biodiesel B100 of the palm oil produced from the esterification process of fatty acid. All reagents were of analytical degree. The water used in the preparation of the solutions was deionized water by Milli-Q® system.

The potenciometric titrations were carried out by using platinum ring electrode, model 6.0431.100 Pt Tirode (Metrohm), connected to an automatic titrator, model Titrino 756 (Metrohm) with the use of software Tinet 2.5. The colorimetric titrations were carried out in burette of 10 mL, with 0,02 mL as the value of each division.

The methodology had its starting point in the assessment of the techniques of titration in national and international standards for measuring the iodine value.

The potentiometric titrations, whose end point was determined by changes in the electrode potential, were performed using a combined electrode of platinum ring coupled to an automatic titrator with burette of 20 mL and resolution of 0.0001 mL. The colorimetric titrations were performed using burette glass of 10 mL, with value of each

division equal to 0.02 mL and starch as an indicator to identify the end point of the titration

For the iodine value determination, a particular case of titration, called iodometry, is used which is an indirect titration method where the species to be determinated is the iodine (I_2) through a reducing agent as a standardized solution of sodium thiosulphate. The solution of sodium thiosulphate must be prepared from the pentahydrate salt ($Na_2S_2O_3 \bullet 5H_2O$). For the standardization, the principle of equivalence is applied between the sodium thiosulphate and potassium dichromate as described in Equation 1, where n_{eqg} is the number of equivalent-gram.

$$n_{eqg} Na_2S_2O_3 = n_{eqg} K_2Cr_2O_7 \quad (1)$$

Resulting from Equation 2, which determines the concentration of sodium thiosulphate solution, where C_t = sodium thiosulphate solution concentration (N); V_t = volume of sodium thiosulphate solution, necessary to titrate potassium dichromate (mL); m_d = mass of potassium dichromate (g); 20,394 = factor proceeding from the reason between the k = number of transferred electrons and M_d = molar mass of potassium dichromate values.

$$C_t = \frac{20,394 \cdot m_d}{V_t} \quad (2)$$

In the same way, the principle of equivalence for the obtainance of the iodine value is applied between the sodium thiosulphate and iodine, as described in Equation 3, where n_{eqg} is the number of equivalent-gram.

$$n_{eqg} Na_2S_2O_3 = n_{eqg} I_2 \quad (3)$$

And finally the Equation 4 for iodine value determination, where: $I.V$ = iodine value (g I_2 / 100 g); V_t = volume of sodium thiosulphate solution, necessary to titrate the sample (mL); V_b = volume of sodium thiosulphate solution, necessary to titrate the blank (mL); C_t = concentration of sodium thiosulphate solution (N); m_a = mass of biodiesel sample (g); 12,69 = factor proceeding from the reason between the k = number of transferred electrons and M_I = molar mass of iodine values.

$$I.V = \frac{12,69 \cdot (V_b - V_t) \cdot C_t}{m_a} \quad (4)$$

The uncertainties of the measurements, considering the methodology for estimating uncertainty of the measurement described in the Eurachem Guide [2] were first estimated by the results concerning the standardization of sodium thiosulfate, using both techniques of titration: colorimetric and potentiometric. The results in triplicate were considered to estimate the uncertainties concerning the iodine value.

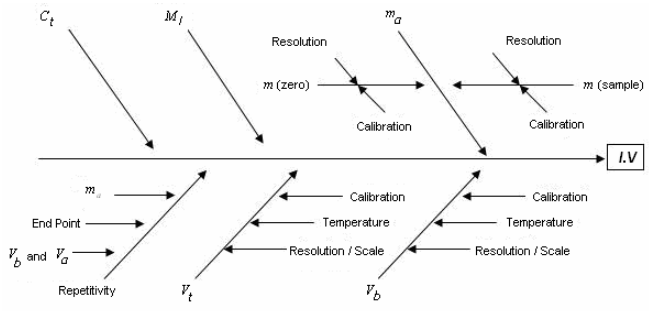
The calculation used in the determination of sodium thiosulphate concentration, according to Equation 2, was modified to become easier to identify the uncertainty sources, resulting in Equation 5, where C_t = sodium thiosulphate solution oncentration (N); V_t = volume of sodium thiosulphate solution (mL); m_d = mass of potassium dichromate (g); P_d = purity of potassium dichromate; M_d = molar mass of potassium dichromate; k = number of transferred electron

$$C_t = \frac{1000 \times m_d \times P_d \times k}{V_t \times M_d} \quad (5)$$

Therefore, the calculation used in the iodine value determination, according to Equation 4, was modified to become easier to identify the uncertainty sources, resulting in Equation 6, where $I.V$ = Iodine value (g I_2 / 100 g amostra); V_t = volume of sodium thiosulphate solution for the sample (mL); V_b = volume of sodium thiosulphate solution for the blank (mL); C_t = sodium thiosulphate solution oncentration (N); m_a = mass of the biodiesel sample (g); M_I = molar mass of iodine; k = number of transferred electrons.

$$I.V = \frac{M_I \cdot (V_b - V_t) \cdot C_t}{k \cdot m_a} \quad (6)$$

The sources of uncertainty considered for the calculation concerning the standardization of sodium thiosulfate were: purity, molar mass and the mass of potassium dichromate; volume of potassium thiosulphate solution. Furthermore, the sources of uncertainty to determine the iodine value were: concentration of sodium thiosulphate, the mass of biodiesel, the volumes of sodium thiosulphate solution used to determine the sample of biodiesel and to determine with blank, and molar mass of iodine. The Ishikawa diagram illustrates the identified contributions of uncertainty.



The values obtained from each measurement and their respective standard uncertainties were in accordance with the Kragten method [3], described in Eurachem Guide [2].

4. RESULTS

All the evaluated standard procedures [4-10] showed the colorimetric titration as the main methodology for iodine

value measurement. Only two of these standards [4][8] mention the potentiometric titration. Thus, Table 1 was built, listing the standard with the method of titration.

Table 1. Relation between the standards and techniques of titration.

STANDARD	METHOD OF TITRATION
ISO 3961	*Colorimetric (Potentiometric is mentioned)*
ABNT MB 77	*Colorimetric*
ASTM 5554	*Colorimetric*
EN ISO 14111	*Colorimetric (Potentiometric is mentioned)*
DIN 53241-1	*Colorimetric*
AOCS Tg 1a-64	*Colorimetric*
AOCS Cd 1b-87	*Colorimetric*

ISO – International Standard Organization; ABNT – Associação Brasileira de Normas Técnicas; ASTM – American Society for Testing and Materials; EN – European Normalization; DIN – Deutsches Institut für Normung; AOCS – American Oil Chemists' Society.

The potentiometric technique showed better quality in the determination of the iodine value because of its accuracy as well as lower uncertainty result of the measurements, with values between 0,613 g I_2 / 100 g and 1,438 g I_2 / 100 g), compared with the results from the colorimetric technique, with values between 1,61 g I_2 / 100 g and 3,30 g I_2 / 100 g, considering the expanded uncertainty result k = 4,3 with 95 % of confidence as shown in Table 2.

Table 2. Results and uncertainty of iodine value

SOLVENT / REACTION TEMPERATURE	IODINE VALUE (g I_2 / 100 g Biodiesel)	
	Colorimetric	Potentiometric
Carbon Tetrachloride / 26°C	61.97 ± 3.30	63.264 ± 0.613
Carbon Tetrachloride / 37°C	63.88 ± 3.18	62.838 ± 1.407
Ciclohexane + Acetic Acid (1:1) / 26 °C	61.48 ± 3.14	61.706 ± 1.438
Ciclohexane + Acetic Acid (1:1) / 37 °C	62.12 ± 1.61	63.244 ± 1.296

5. DISCUSSION

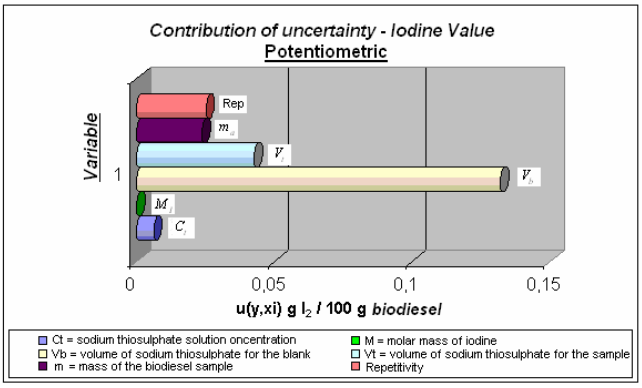
The potentiometric technique was shown to be more accurate, since the results are presented with the highest number of significant figures. This difference is due to the use of automatic burette, which provides results with larger numbers of decimal places.

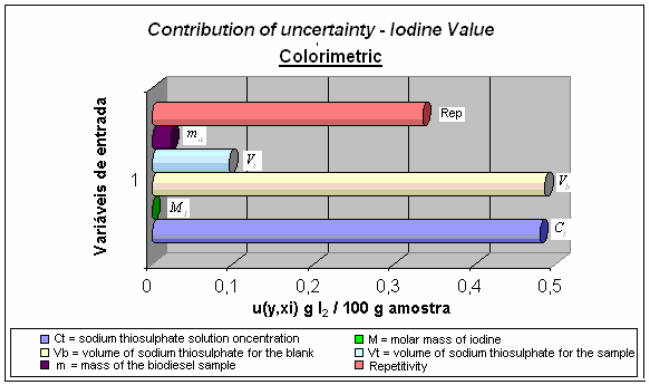
Taking all the results into account, it should be noted that all uncertainties concerning the potentiometric measurements showed lower values compared with colorimetric measurements. It could be similarly seen by comparing measurements made under the same conditions of solvent and reaction temperature, for example, when used the solvent carbon tetrachloride and temperature of 37 ° C, the value of the uncertainty was 3.30 for the colorimetric technique and 0.613 for the potentiometric.

Among the sources of uncertainties estimated, the most representative ones for these results were: the concentration of sodium thiosulphate, whose uncertainty was estimated using variables from the process of standardization; the repeatability, determined experimentally by means of standard deviations; and the volume of sodium thiosulphate used in titration, especially with the blank determination, which required a greater volume to detect the end point.

The measured volume was the one that presented more uncertainties associated; however, they can be minimized with some measures of control, such as: the temperature of the measurement being close to the calibration of the burette as possible, the volume of the burette to be coherent with the volume expense of titrant and the technique of end point detention been the most accurate as possible.

Comparing the contributions of uncertainty, through histogram, between the colorimetric and potentiometric techniques, for example, the condition of analysis with tetrachloride of carbon and 26ºC of reaction temperature, a significant difference in the repetitivity and the standardization of the sodium thiosulphate solution can be noted.





6. CONCLUSIONS

It was verified in all analyzed standards that the unit of concentration used for the standardization of the sodium thiosulphate solution is the normality (N), which is defined by the reason between the number of equivalent gram of solute dissolved and the volume of solution in liters; however, this unit is becoming obsolete and it is not the

concentration unit in accordance with the International System of Units (SI) [11].

The colorimetric technique showed some disadvantages, limitations and difficulties in relation to the potentimetric technique, such as: the starch is always subject to degradation due to environmental factors such as the temperature, thus having less validate; the determination of the end point through the color change was subject to errors for detection due to intense coloration coming from iodine in solution; the glass burette with centesimal scale showed very fragile and less practical. On the other hand, the potentiometric method showed to be more practical due to addition of the titrant, as well as the detection of the end point, which was carried out by automatic form, still presenting a higher optimization of the time spent with the assays. Therefore the insertion of the appropriate parameters of titration in the software resulted in faster analyses.

The potentiometric technique showed higher accuracy of results, with greater number of significant figures (eg 63.264), while the colorimetric technique showed two decimal places (eg 61.97). Better accuracy was also attributed to potentiometric technique, which could be verified through the calculation of standard deviations, finding a range of 0.04% to 0.32%, while those obtained by technical colorimetric, from 0.25% to 1.03%.

The analysis of uncertainty in measurements of iodine value showed that the potentiometric technique presented better quality of results, since they obtained the lowest uncertainties (between 0.613 g I_2/ 100 g and 1.438 g I_2/ 100 g), compared with the results by colorimetric technique (between 1.61 g I_2/ 100 g and 3.30 g I_2/ 100 g).

Therefore, it could be assigned greater quality of the measurements of the iodine value obtained by potentiometric technique, because they have better accuracy and less uncertainty in all conditions of variables. Thus, the potentiometric titration technique could be considered not only as an alternative but also the main technique to be used

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