



Short communication

A green potentiometric method for the determination of the iodine number of biodiesel

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ABSTRACT

In this paper a green potentiometric method is proposed for the determination of the iodine number of biodiesel. The solvent used is simply a water–ethanol mixture (1:1 v/v) and the reagent is iodine. The analytical procedure can be performed even without a laboratory hood as no iodine vapors are released if the method is done as indicated. The analytical results obtained with this procedure were compared with those from Wijs' method. In order to strictly compare instrumental procedures potentiometry was also applied to the Wijs' procedure. Also for comparison purposes a green visual method was applied. Statistical comparison of the four methods, through the paired Student's *t* test and the *F* test of Snedecor showed excellent agreement among all of them.

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1. Introduction

Presently, high energy demand and increasing air pollution problems have led to the necessity of finding renewable sources of energy. Vegetable oils and animal fats, which are triglycerides, could be directly used as fuels. However, their performance is not satisfactory due to their relatively high viscosity, low volatility, incomplete combustion, production of acrolein, formation of deposits in engines, etc. [1–14].

The flash point of biodiesel is relatively high, varying from 100 to 130 °C, depending on national regulations. High flash point is always desirable, however biodiesel is mixed with conventional petrol diesel forming blends with relatively low contents of this biofuel (B5, B10, etc.). Considering that the flash point of these blends are low (the flash point of diesel is low), the use of biodiesel with high flash point is incoherent as it has a little influence on the final flash point of the blend [15].

The transesterification of triglycerides using a short chain alcohol, such as methanol or ethanol in the presence of a catalyst, furnishes a mixture of long chain fatty acid monoesters and also releases glycerin [5,16–19]. This mixture of monoesters is known as biodiesel as it presents similar properties to the diesel coming from petroleum [2,14,20–23]. Biodiesel can be directly used in diesel engines without the necessity of special adaptations [22]. It is biodegradable, it is produced from renewable sources and presents low levels of exhaust emissions [7,9,13,16,17,21].

The control of the quality of biodiesel is usually done according to standard procedures established, for example, by ASTM in the United States, by EN in the European Community and ABNT NBR in Brazil. Among the properties determined through these analyses, the iodine number reflects the stability of biodiesel to oxidation. It is also directly related to the number of double bonds present in the long chain fatty acid monoesters [18,3–25].

According to ASTM D1959 [26], the iodine number is not related to total unsaturation since double conjugated bonds as C18:3 (a minor constituent of biodiesel) do not react totally with iodine. To obtain the total iodine number of biodiesel samples ASTM D1541 [27] is used. However, conjugated double bonds are not present in significant amounts in fats and oils commonly used for the synthesis of biodiesel. Therefore, the iodine number reflects closely the tendency of biodiesel to oxidation. It is expressed in grams of iodine per 100.0 g of the sample. A high content of carbon double bonds in the fatty acid carbon chain will yield a high iodine number.

Biodiesel with high concentrations of unsaturated fatty acid chains, and therefore with high iodine numbers, is more susceptible to oxidative degradation [16,23,28–32]. Exposure to high temperatures, to light, to air and to moisture and the presence of certain contaminants increases biodiesel degradation [16,18,21–23,28–31,33–35]. Since at high temperatures highly unsaturated compounds can undergo polymerization leading to formation of gums and to the deterioration of lubrication in the injection nozzle and the combustion cylinder, it is important to pay attention to the degree of unsaturation of biodiesel [9,16,36].

Presently, norm EN-14111 [37] determines the use of the American Oil Chemists' Society Cd-1-25 method [38] for the

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determination of the iodine number of biodiesel. This procedure, originally used for the analysis of oils and fats, is currently known as Wijs' method. It is based on the reagent ICl, iodine monochloride, dissolved in glacial acetic acid (0.1 mol L⁻¹ solution). This reaction is shown in Scheme 1.

Wijs' method presents analytical excellence. However the reagent solution requires careful handling and it is relatively expensive. Therefore, safer and lower cost procedures are desirable. It is known that iodine number can also be calculated from the fatty acids composition as determined by gas chromatographic procedure [39], which can be correlated to the double bonds content (degree of unsaturation) and therefore to iodine number. However, several standard substances are necessary in order to obtain this information. The method proposed in the present communication and also the Wijs' procedure are absolute, i.e., they do not need a calibration curve (or standards) as, for example, is the case of GC analysis. The iodine number is directly related to C=C bonds present in the long chain alkyl esters. The obtained results are based on the stoichiometric correlation between unsaturation and consumed iodine in the reaction per 100 g of sample. This method does not require reference curves.

The oxidative stability of a biodiesel can be determined using the so-called Rancimat[®] instrument. This method expresses the oxidative stability of the tested material in terms of the time (Induction Period, IP) necessary for the beginning of the production of volatile organic acids, which are byproducts of fatty acid ester oxidative degradation with heat and oxygen. This method measures the IP in hours or days. Iodine number gives similar information but in terms of grams of iodine per 100 g of the sample. It is known that these two parameters, IP and iodine number, are closely related [40].

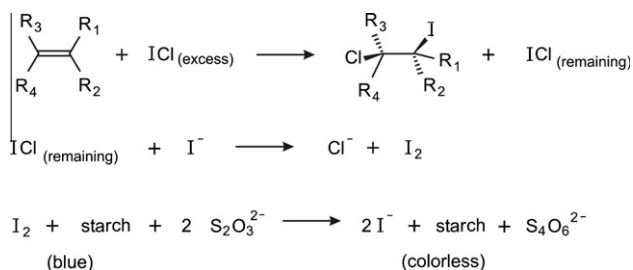
Recently a green and simple visual titrating method has been reported [41], where the sample is dissolved in ethanol–water solvent instead of carbon tetrachloride or chloroform. Also, the reagent was simply an iodine solution in ethanol replacing Wijs' solution.

In the present work a green potentiometric method for the determination of the iodine number of biodiesel is proposed. Similarly to the visual procedure the solvent used was a water–ethanol mixture (1:1 v/v) and the reagent was simply a solution of iodine in ethanol. The method has been applied not only to biodiesel but also to fatty material as vegetable oils etc. with success and hence this will be the subject of a future communication. Titration was done with a standard aqueous thiosulfate solution, as usual. This reaction is shown in Scheme 2.

In order to more strictly compare the results offered by the developed method, potentiometry was also applied to the Wijs' procedure. As far we know, such an instrumental extension of this method has been little reported in the literature [42].

2. Experimental

The Wijs' procedure was performed using chloroform instead of carbon tetrachloride due to the higher toxicity and price of the latter.



Scheme 1. Chemical reactions related with the Wijs method.

Biodiesels synthesized from several vegetable oils and from swine lard were analyzed using the Wijs' method and the method proposed in this work for comparison purposes.

2.1. Materials and methods

2.1.1. Instruments

The potentiometric titrations were performed using a Metrohm automatic titrator, model Titrand 808, operated through the TIA-MO[®] software. A Metrohm Pt Titrode[®] glass electrode was used.

The visual titrations were done using an electronic 50 mL digital burette (Biohit Digital Burette or a Brand Digital Burette III).

2.1.2. Chemicals and solutions

All chemicals used were of analytical grade except sodium methylate that was an industrial product (30% w/w). Water was obtained from a glass bidistillator. Vegetable oils and animal fats were obtained in the local market.

Iodine standard solution, 0.1 mol L⁻¹: prepared by dissolving 25.38 g of metallic iodine in 1000 mL of 96% ethyl alcohol in a volumetric flask. The solution was stored in a brown bottle and kept in a refrigerator.

Thiosulfate solution, 0.1 mol L⁻¹: prepared by dissolving 24.9 g of sodium thiosulfate pentahydrate (Na₂S₂O₃•5H₂O) in 1000 mL of boiled bidistilled water. The solution was standardized with a 0.02 mol L⁻¹ potassium permanganate standard solution and stored in a brown bottle.

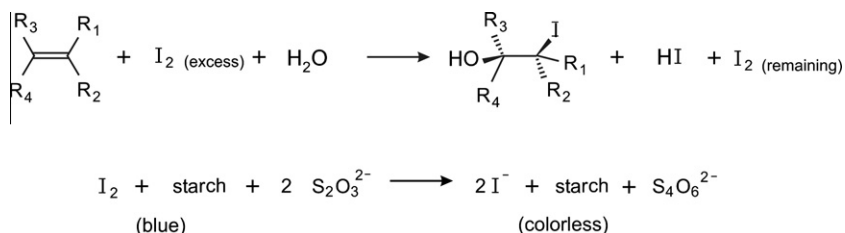
Potassium permanganate solution, 0.02 mol L⁻¹: prepared by dissolving about 3.2 g of potassium permanganate in 1000 mL of bidistilled water and then boiling for 1 h. This solution was filtered through glass wool directly into a brown storage bottle. Standardization was done with solid sodium oxalate.

Starch solution, 1% w/v: prepared by dissolving 10.0 g of starch in 1.5 L of bidistilled water. This solution was boiled until the volume was reduced to 1 L and then filtered. It was stored in a refrigerator.

Biodiesel preparation: Two transesterifications were performed in series in each case. The first reaction was done using 600 g of the fat, 120 g of methanol (20% w/w of the fat) and 3.36 g of sodium methylate (30% w/w methanolic solution). The mixture was heated for 1 h at 60 °C. The products obtained were decanted into a separation funnel to separate the glycerin. The supernatant was transferred to the reaction flask and again reacted with 0.84 g of the catalyst (30% w/w sodium methylate in methanol solution). Glycerin was removed from the final product as above and the esters obtained were washed with a series of five 100 mL portions of bidistilled water, in order to remove residual glycerin, methanol and any sodium hydroxide that was formed. The washed product was dried with anhydrous sodium sulfate (10% w/w) and filtered.

Iodine number: This was determined in the biodiesel samples synthesized in our laboratory. The Wijs' method [38], the Wijs' potentiometric method (this paper), the visual method [41] and the potentiometric method proposed in this paper were all applied.

EN-14111–2003 [38]: An aliquot of the sample was weighed according to the expected iodine number. It was dissolved in a 250 mL Erlenmeyer using 15 mL of chloroform and 25.0 mL of Wijs' solution. The Erlenmeyer was capped with a rubber stopper. This solution was allowed to rest for thirty minutes in the dark together with the blank sample prepared in the same manner. Then 20 mL of the 10% w/v potassium iodide solution and 100 mL of bidistilled water were added. Titration with standardized 0.1 mol L⁻¹ sodium thiosulfate solution, using a 50 mL electronic manual burette, was carried out until the solution was a pale yellow when 3 mL of the starch solution were added, forming the characteristic deep blue color. Titration continued until the disappearance of the blue color.



Scheme 2. Chemical reactions related with the proposed method.

Wijs' potentiometric method: An aliquot of the sample was weighed according to the expected iodine number. It was dissolved in a 250 mL beaker using 15 mL of chloroform and 25.0 mL of Wijs' solution. The beaker was capped with a plastic film. This solution was allowed to rest for thirty minutes in the dark together with the blank sample prepared in the same manner. Then 20 mL of the 10% w/v potassium iodide solution and 100 mL of bidistilled water were added. The solution was taken for titration in the Titrand 808 using the Pt Titrode glass electrode.

The visual method [41]: An aliquot (0.10–0.15 g) of the sample was weighed, transferred to a 400 mL erlenmeyer and dissolved with 15 mL 96% ethanol under vigorous magnetic stirring during five minutes. Stirring was stopped and 20.00 mL of the 0.1000 mol L⁻¹ ethanolic iodine solution was added. Magnetic stirring during five minutes was continued, when it was slowed down. 200 mL of bidistilled cold water (about 5 °C or colder) were added. If the ambient temperature is high (>25 °C) an ice bath can be used. The flask was kept covered and gently stirred magnetically during

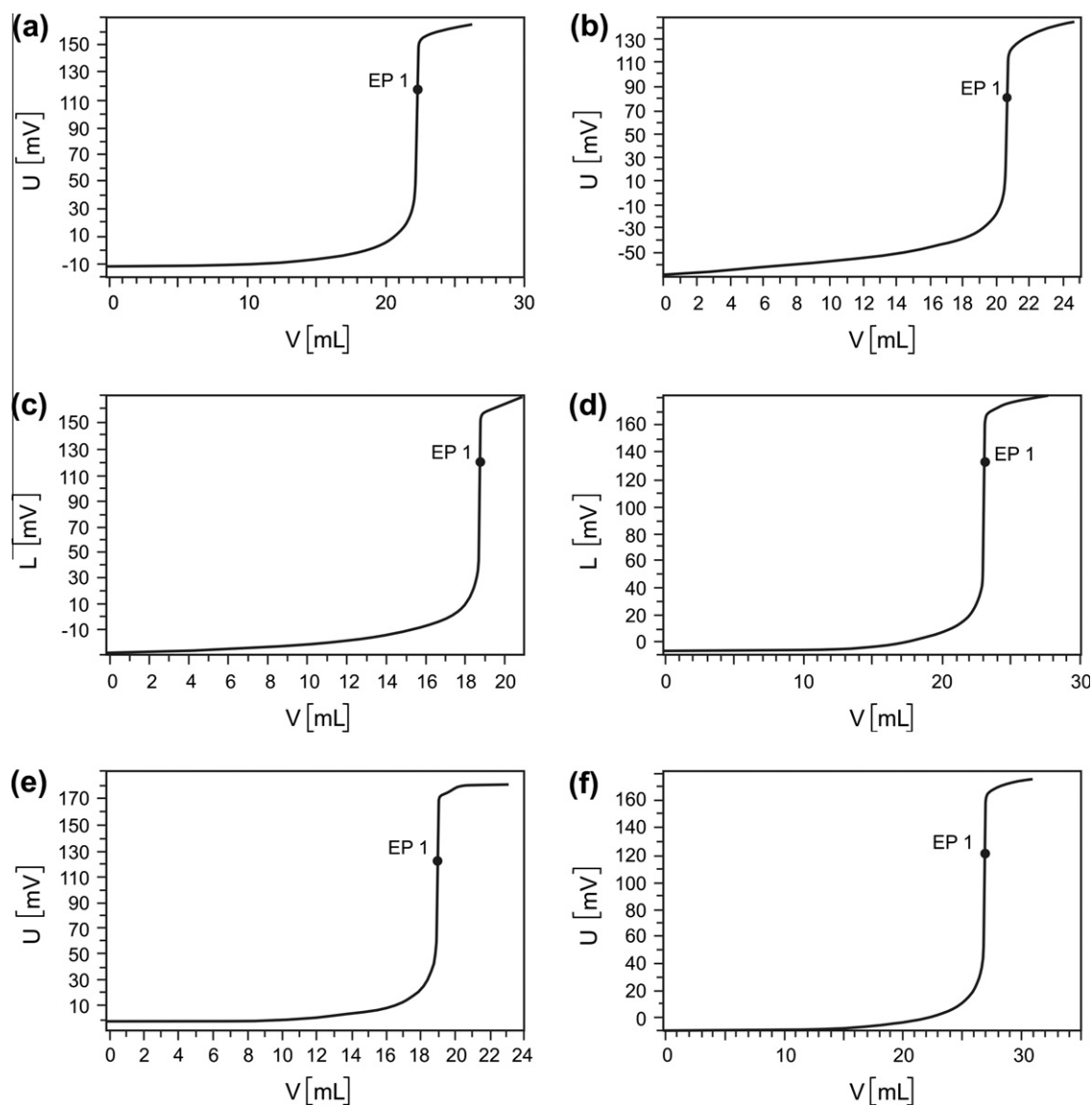


Fig. 1. Experimental potentiometric curves obtained with the Wijs' method for: (a) corn oil biodiesel; (b) soya oil biodiesel; (c) swine lard biodiesel; (d) canola oil biodiesel; (e) sunflower oil biodiesel; (f) castor oil biodiesel.

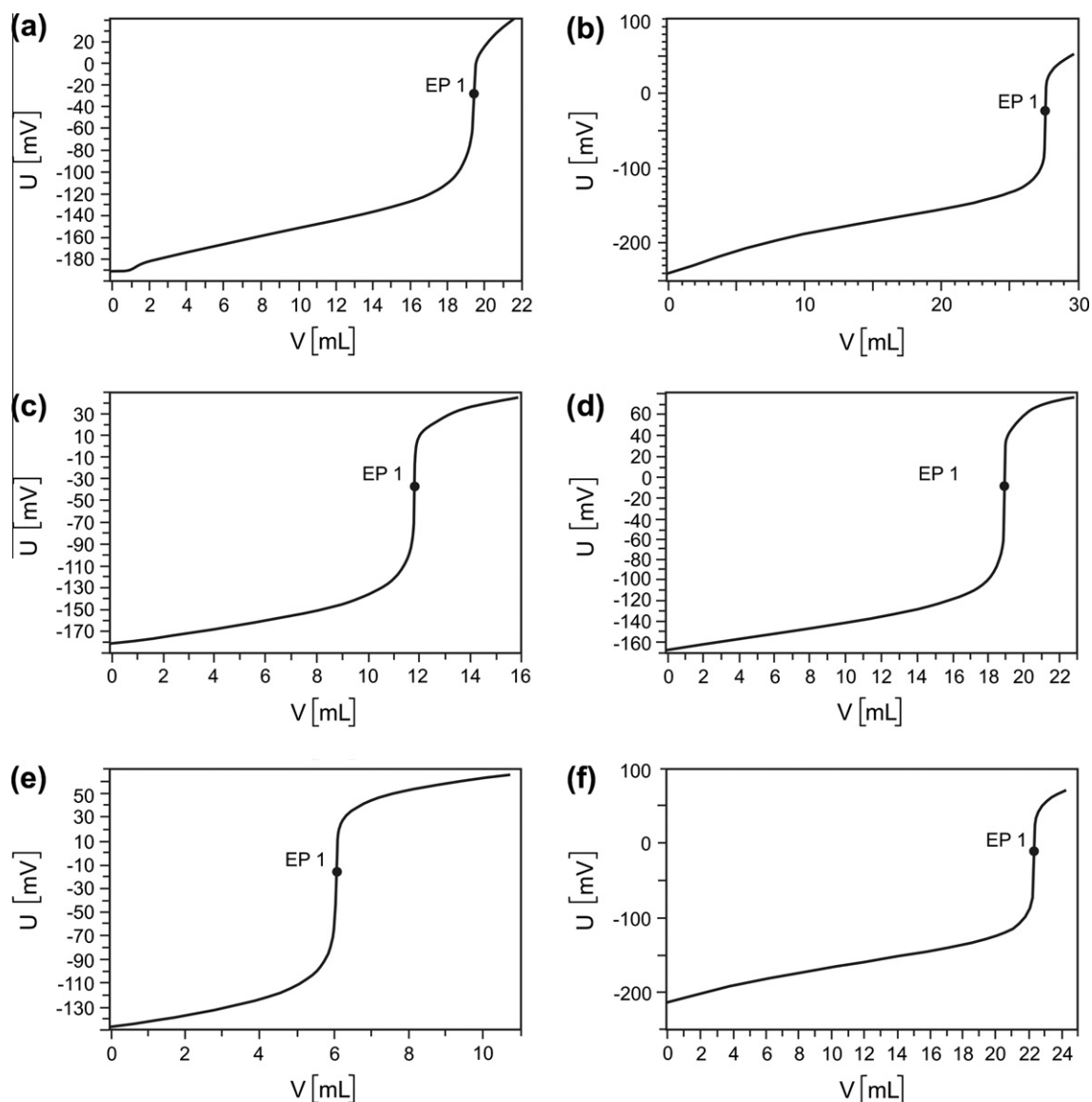


Fig. 2. Experimental potentiometric curves obtained with the green potentiometric method, for: (a) corn oil biodiesel; (b) soya oil biodiesel; (c) swine lard biodiesel; (d) canola oil biodiesel; (e) sunflower oil biodiesel; (f) castor oil biodiesel.

five minutes (attention to avoid loss of I_2). Titration with standard 0.1 mol L^{-1} sodium thiosulfate solution, using a 50 mL electronic manual burette, was carried out until the solution presents a pale yellow color, when 3.0 mL of the starch solution were added. The titration continued until the disappearance of the blue color, resulting in a milky solution.

Green potentiometric method: An aliquot (0.10–0.15 g) of the sample was weighed, transferred to a 400 mL beaker and dissolved with 15 mL 96% ethanol under vigorous magnetic stirring during five minutes. Stirring was stopped and 20.00 mL of the $0.1000 \text{ mol L}^{-1}$ ethanolic iodine solution were added, restarting vigorous magnetic stirring during five minutes. The stirring was slowed down and 200 mL of bidistilled cold water (about 5°C or colder) were added. The flask was kept covered and taken to gentle magnetic stirring during five minutes (attention to avoid loss of I_2). The solution was taken for titration in the Titrando 808 using the Pt Titrade glass electrode.

In the four methods the iodine number is calculated using Equation 1 where **B** is the sodium thiosulfate solution volume in mL used in the titration of the blank; **A** is the sodium thiosulfate

solution volume in mL used in the sample titration; **C** is the concentration of the sodium thiosulfate solution in mol L^{-1} ; **m** is the aliquot weight in grams.

$$\text{Iodine Number} = \frac{(\mathbf{B} - \mathbf{A}) \times \mathbf{C} \times 12.69}{\mathbf{m}} \quad (1)$$

3. Results and discussion

Fig. 1 shows the potentiometric titration curves obtained for biodiesel from corn, soy, canola, sunflower and castor oils and from swine lard, using the Wijs' potentiometric method.

The same samples were analyzed using the green potentiometric procedure proposed in this work. The experimental results are shown in Fig. 2.

In Table 1 are reported the iodine numbers obtained for the analyzed biodiesels whose potentiometric curves are shown in Figs. 1 and 2. Visual titrations were also performed using the Wijs' [38] procedure and the green visual method [41].

The iodine numbers obtained for the samples with the four methods were compared statistically through the paired *t* of Student's and the Snedecor's *F* test [43]. The results are shown in Tables 2 and 3.

According to the results shown in Table 2, the proposed methods are statistically equivalent to the Wijs' method at the 0.95 confidence level, with respect to accuracy. A small difference is observed between the Wijs' visual and the Wijs' potentiometric procedures and between Wijs' visual and the green potentiometric method, at this confidence level. However at 0.99 confidence level, complete concordance is observed.

Table 3 shows the statistical treatment performed between the results of the four analytical methods using the Snedecor *F* test.

Through the results observed in Table 3 it can be concluded that all the methods used in this work present equivalent precision at the 0.95 confidence level.

A possible criticism of the proposed potentiometric method is with respect to the loss of iodine by volatilization that might be expected to occur during the procedure. However, as can be observed from the experimental results, no significant difference among the methods was found that could imply the occurrence of this problem. This means that the cooled water added to the solution

in the titration flask is sufficient to avoid significant loss of iodine. However, if desired an ice bath can be used to guarantee a low enough temperature for the iodine solution.

As is known, Wijs' reagent is prepared using glacial acetic acid. Essentially it is a solution of ICl, iodine monochloride, in this acid. Concentrated acetic acid is quite corrosive and must be carefully handled since it can cause skin burns, permanent eye damage and irritation to the mucous membranes. ICl itself attacks the skin causing severe painful patches [44].

The green method proposed in this work can be considered a friendly procedure as only ethanol and water are used as solvents. Although exposure to iodine vapors can cause skin damage, if the method is performed according to the indicated procedure, no problems occur and the analysis can safely be carried out outside the laboratory hood. The procedure is rapid and the results are very reliable. The equipment used is very simple and easy to be operated. Considering the price of the necessary chemicals and of the equipment, the total cost of an analysis is fairly low.

Considering the results obtained with the proposed method in terms of safety, precision, accuracy and environmental aspects, it can be proposed for the determination of the iodine number in biodiesel.

Table 1
Iodine number (g of iodine per 100 g of the sample) of the analyzed biodiesels, using the visual and potentiometric Wijs' methods, the visual green method [41] and the potentiometric method proposed in this work. The number of determinations was 5 per sample.

Biodiesel sample	WV	RSD%	GMV	RDS%	WP	RDS%	GMP	RDS%
Corn	128.0 ± 1.2	0.9	127.0 ± 1.9	1.5	129.3 ± 1.0	0.8	128.3 ± 2.3	1.8
Soy	129.4 ± 0.7	0.4	128.5 ± 1.6	1.2	128.9 ± 1.0	0.8	127.8 ± 1.0	0.8
Canola	113.9 ± 1.3	1.1	114.5 ± 3.1	2.7	114.7 ± 1.3	1.1	114.0 ± 2.2	1.9
Sunflower	134.3 ± 2.0	1.5	135.3 ± 2.5	1.8	137.9 ± 1.2	0.9	135.6 ± 2.1	1.5
Castor	87.1 ± 1.5	1.7	87.5 ± 2.7	3.1	88.0 ± 2.3	2.6	87.3 ± 2.2	2.5
Swine lard	74.1 ± 2.3	3.1	74.3 ± 2.5	3.4	76.0 ± 2.5	3.3	74.0 ± 2.9	3.9
Mean RSD%		1.5		2.3		1.6		2.1

WV = Wijs' visual; GMV = green method, visual [38]; WP = Wijs' potentiometric; GMP = green method, potentiometric (proposed in this work).

Table 2
Statistical comparison of the iodine values obtained with the four methods, using the paired Student's *t* test. The number of determinations per sample was 5 (degree of freedom, $\nu = n_1 + n_2 - 2 = 8$).

Biodiesel sample	Student's <i>t</i> calculated values ^a					
	WV vs. GMV	WV vs. WP	WV vs. GMP	GMV vs. WP	GMV vs. GMP	WP vs. GMP
Corn	0.89	1.66	0.23	2.14	0.87	0.80
Soy	1.03	0.82	2.62	0.42	0.74	1.56
Canola	0.36	0.87	0.08	0.12	0.26	0.55
Sunflower	0.62	3.09	0.90	1.88	0.18	1.90
Castor	0.26	0.66	0.15	0.28	0.11	0.44
Swine lard	0.12	1.12	0.05	0.96	0.16	1.04
Mean calculated <i>t</i>	0.55	1.37	0.67	0.97	0.39	1.05

WV = Wijs' visual; GMV = green method, visual; WP = Wijs' potentiometric; GMP = green method, potentiometric (proposed in this work).

^a Tabled *t* is 2.30 for $\nu = 8$, and $\alpha = 0.05$; Tabled *t* is 3.36 for $\nu = 8$ and $\alpha = 0.01$ [43].

Table 3
Statistical treatment comparing the precision of the results of the four analytical methods, using the Snedecor *F* test. The number of determinations was 5 per sample (degree of freedom, $\nu = n - 1 = 4$).

Biodiesel sample	Calculated <i>F</i> values ^a					
	WV vs. GMV	WV vs. WP	WV vs. GMP	GMV vs. WP	GMV vs. GMP	WP vs. GMP
Corn	2.51	1.44	3.67	3.61	1.47	5.29
Soy	5.22	2.04	2.04	2.56	2.56	1.00
Canola	5.69	1.00	2.86	5.69	1.99	2.86
Sunflower	1.56	2.78	1.10	4.34	1.42	3.06
Castor	3.24	2.35	2.15	1.38	1.51	1.09
Swine lard	1.18	1.18	1.59	1.00	1.35	1.35
Mean calculated <i>F</i>	3.23	1.82	2.24	3.10	1.72	2.44

WV = Wijs' visual; GMV = green method, visual; WP = Wijs' potentiometric; GMP = green method, potentiometric (proposed in this work).

^a Tabled *F* is 6.40 for $\nu = 4$ and $\alpha = 0.05$; Tabled *F* is 16.0 for $\nu = 4$ and $\alpha = 0.1$ [43].

4. Conclusion

The green potentiometric method herein proposed is much greener than the Wijs' procedure, potentiometric or visual. If the price of solid iodine is compared with that of the Wijs solution and the price of ethanol is compared with that of carbon tetrachloride, the cost benefits and safety in terms of toxicity are quite favorable in the proposed method. Furthermore, the use of CCl_4 is banned in many countries.

An experimental comparison between the four methods clearly shows that all procedures provide statistically equivalent results. As a consequence, considering the equivalence of the analytical performance, the green methods are preferable as they present the environmentally amicable characteristics as an additional advantage. Moreover, the green potentiometric method provides a significant instrumental advantage over the visual ones enabling faster analyses.

Moreover, in this work it became clear that if the Wijs' method is chosen for the determination of the iodine number, the option of the automatic potentiometric titration, which reduces the presence of the operator near the instrument, offers the same results as the visual titration with the consequence decreasing of health risks.

Based on the results shown here and these considerations, the proposed green potentiometric procedure can be recommended for the determination of the iodine number in biodiesel as it gives reliable, accurate, and precise results and is simple to perform, of low cost, and provides a low level of toxicity and possible environmental contamination.

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