

UDC 543.635.35

<https://doi.org/10.15407/kataliz2021.31.069>

The simple method of vegetable oils and oleochemical products acid value determination

S.O. Zubenko

V.P. Kukhar Institute of Bioorganic Chemistry and Petrochemistry NAS of Ukraine
1, Murmanska str., 02660 Kyiv, Ukraine., tel./fax: (044) 559-98-00, S.O.Zubenko@ukr.net

Acid value is one of the key technical characteristic of vegetable oils and oleochemicals, obtaining on its basis. The existing standard methods of acid value measurement are relatively complicated and have some disadvantages. There are including utilization of the significant amounts of solvents, throwing out as wastes, and necessity in special equipment for determination. Also, a special issue is visual indication of the equivalence point of indicator transfer from acid to alkali form for intensive colored oils' samples. Visual indication of the color transfer of phenol-phthalein as indicator (from colorless to pink) is quite difficult. The color transfer of thymolphthalein (from yellow to green) in such condition is not determined. Using of alkali blue 6B is complicated by the necessity of use ethanol and aromatic compounds mixture.

*In current work the rapid and simple method of acid value determination was proposed. It consists in alkali-acid titration of the sample by sodium butoxide solution in *n*-butanol with bromothymol blue, *n*-butanol is also using as solvent. The method was tested on 3 series of the mixtures of the refined sunflower oil and free fatty acids (distilled fatty acids of sunflower and rapeseed oils and chemical grade oleic acid). The fatty acid content in tested mixtures was in range 1-50 % wt. Some disadvantages of traditional methods, such as the necessity of mixed solvents' and relatively complicated laboratory equipment use, titration in a hot state, effect of temperature changes in the laboratory and difficulties with visual indication of color transfer, were overcome. Proposed method requires only the simplest laboratory glassware (conic flasks, non-calibrated pipettes, hermetically sealed glass vessels for titrant) and technical laboratory scales (weighting accuracy ± 0.01 g). The method allows to determine the acid value in wide range of samples, including the samples with intense coloration. The relatively high accuracy of acid value determination was shown. The method sensitivity is 0.02-0.10 mg KOH/g. The time for analyze is enough short (about 5-15 minutes).*

Key words: acid value, vegetable oils, biodiesel, titration, *n*-butanol

Introduction

Acid value, or free fatty acids (FFA) content is one of the key technical characteristic of vegetable oils as the raw materials for the production of fatty acid alkyl esters (biodiesel) or another oleochemical purposes. Raw materials used for fatty acids esters production is often characterized by significant FFA content due to partial oil degradation or different other causes. In biodiesel production it is desirable to use non-food grade raw material [1]. The latter includes oils of technical cultures or oils, which not corresponds quality requirements for food grade products (wasted frying oils, oils with expired term of use, technological wastes etc.). One of the main parameters, determining the unsuitability for use as edible oils is fatty acids content, which is displayed as acid value. The latter usually must be lower than 0.3% (counted as oleic acid) [2].

Moreover, commercial biodiesel must correspond to requirements of free fatty acids content (lower than 0.25 % count as oleic acid) [3, 4]. Also, acid value is main parameter, controlling in the course of the reaction of fatty acids esterification with alcohols over acid

catalysts, which is main route for synthesis of fatty acids esters from raw materials with significant content of FFA.

Therefore, in biodiesel fuel manufacturing and in quality control of obtained intermediate products and final products the acid value determination is very necessary.

The methods of acid value determination

Acid value is amount of alkali (potassium hydroxide), which is needed to spend for neutralization of acids in 1 g of mixture subjected to analysis. In case of oils and fatty acids esters, acid value reflects the amount of fatty acids. The products of the fatty acids neutralization with alkali are soaps. Formed soaps in water media hydrolyze and form acids and alkali, which leads to alkali reaction in water solution. Therefore, the titration of FFA by alkali water solutions leads to understatement of resulted acid value.

For overcoming the hydrolysis variety of methods was developed. One of them is utilization of saturated water solution of sodium chloride, which used in mixture with sample analyzed. Obtained mixture is

titrated by alkali water solution with phenol-phthalein as indicator [5].

Using of supporting co-solvents such as chloroform or diethyl ether with ethyl alcohol leads to formation of large amounts of organic wastes, which difficult to separate or regenerate for reuse. In this method phenol-phthalein is used as indicator. For colored samples thymolphthalein is recommended to use as indicator. In the latter case, titration is carried out using special flask with external glass branch pipe to observe the color transfer of the mixture from yellow to green [5].

Another method of acid value determination consists in titration of hot solution of the oil sample in ethanol by alkali ethanol solution, using phenolphthalein or thymolphthalein as indicators [5].

Analysis may be carried out without heating of the mixture using isopropyl alcohol as solvent and, alkali ethanol solution as titrant and phenol-phthalein or thymolphthalein as indicators [6].

The method of acid value determination of colored petrol products, including diesel fuels, is based on using of ethanol-aromatic (benzene, toluene or xylene) solution of indicator alkali blue 6B as co-solvent. The sample is dissolved in the latter and then titration by alkali ethanol solution is performed, observing the color transfer from blue to red [7].

In another method [8, 9] *iso*-propanol/toluene mixture as solvent, KOH solution in *iso*-propanol as titrant and *p*-naphtholbenzein as indicator (color transfer from orange to green) are used. In method [10], which is relies on potentiometric titration, the same solvent and titrant are used.

Listed methods have a number of disadvantages, including utilization of the significant amounts of solvents, throwing out as wastes, and necessity in special equipment for determination.

Also, a special issue is visual indication of the equivalence point of indicator transfer from acid to alkali form. First of all, these applies the acid value determination of the reaction mixtures during acid-catalyzed esterification of fatty acids and in case of the intensive colored oils' samples, such as not refined oils of technical cultures, wasted cooking oils etc. The latter may have color from mild-brown to almost black. Visual indication of the color transfer of phenol-phthalein as indicator (from colorless to pink) is quite difficult. The color transfer of thymolphthalein (from yellow to green) in such condition is not determined. Using of alkali blue 6B is complicated by the necessity of use ethanol and aromatic compounds mixture. Also, the significant amount of such a mixture of solvents is needed to fully dissolve the analyzed oil sample.

Moreover, titration by alkali ethanol or *iso*-propanol solutions is related with practical difficulties. At-first, alkali solutions can't be kept for a long time. At-second, alkali alcohol solutions can dissolve rubber parts of burette or jamming of glass tap due to carbonate

formation. At-third, such alkali solutions leach the surface of the glass vessel, in which it is stored. This also results in the contamination of titrant. At-fourth, high volatility of both ethyl and *iso*-propyl alcohols leads to distortion of results of analysis, especially at high room temperature in summer. At-fifth, determination of alkali molar concentration in mol/dm³ is not comfortably, because of the possible deviation of temperature in laboratory from 20 °C. The concentration in this case may change significantly, which leads to distortion of the determination results too.

This article deals with developing of the simple alternative method of vegetable oils' and oleochemical products' acid number determination, which is able to overcome most of the listed disadvantages. The method consists in the titration of the oils by sodium butoxide solution in butanol in the medium of *n*-butyl alcohol.

Materials and methods

Chemicals

Analytical grade NaOH (China; for preparation of sodium butoxide); chemical grade *n*-butyl alcohol (Czech; for preparation of sodium butylate), technical grade *n*-butyl alcohol (Turkey; as solvent in titration); food grade H₃PO₄ (for preparation of fatty acids from vegetable oils); technical grade KOH (China; for preparation of fatty acids from vegetable oils), technical grade EtOH (Ukraine, for preparation of fatty acids from vegetable oils); commercial refined sunflower oil (Ukraine; as base oil for preparation of oil/fatty acids mixtures for titration); not refined rapeseed oil (Ukraine; as raw material for preparation fatty acids); not refined sunflower oil (Ukraine; as raw material for preparation of fatty acids); chemical grade oleic acid (Czech; for preparation of oil/fatty acids mixtures for titration), analytical grade HCl (Ukraine; 14 % solution in water), chemical grade bromothymol blue (indicator).

Alkali titrant solution preparation

Sodium butoxides solution, used in current study as titrant solution, was prepared from *n*-butanol and sodium hydroxide according to well-known method [11] using Dean-Stark trap. Obtained solution was diluted by *n*-butyl alcohol to the concentration of alkali around 1 %wt. (calculated in terms of initial NaOH). The exact concentration was determined by means of titration by 0.1 N HCl in water.

Potassium butoxide solution also can be used for titration. But its preparation is complicated by higher moisture content in reactive KOH of the same class of purity (about 14-16 %). As result, its production of potassium butoxide is significantly longer.

Fatty acid preparation

Fatty acids of rapeseed or sunflower oil were prepared by saponification of the corresponding oil triglycerides followed by transformation of obtained potassium soaps to fatty acids by means of treatment with H₃PO₄.

For this purpose, to the round bottom flask equipped with Liebig condenser was loaded with 100 g

rapeseed of oil and 33 g of KOH dissolved in 140 g rectified ethyl alcohol (94.6 %wt.). Mixture was heated by oil bath (120 °C) throughout 3 hours and then 900 cm³ of distilled water was added. Obtained products were fully dissolved in water, which gives evidence the high oil saponification level. Then about 300 cm³ of water-ethanol mixture was separated by distillation. The residue mixture was poured to separation funnel, followed by addition of H₃PO₄ and shaking. After that, the formation of two layers was observed. The top layer was the fatty acids. It was treated by phosphoric acid in the same way one more time and thoroughly washed by water using separation funnel. Obtained cloudy fatty acids were dried several days over calcined sodium sulfate until clear liquid was formed. The last one was filtered through paper filter. Brown colored dried and filtered fatty acids was distilled under vacuum. As result light-yellow clear distillate was obtained light-yellow distillates.

Preparation of the fatty acids/oil mixtures

The solutions of fatty acids in refined sunflower oil (approximately 1, 2, 5, 10, 15, 20 and 50 %wt.) were prepared using distilled fatty acids of rapeseed and refined sunflower (marked as FA-1 and FA-2 series correspondingly), as well as commercial oleic acid (marked as FA-3 series). Approximately 100 g of each solution was prepared by mixing of fatty acids with oil in conic flask with magnetic stirrer (1 h, ambient temperature). Components were weighted on technical scales (accuracy ± 0.01 g), the exact concentration of fatty acids were calculated using the weighting data.

Methodology of titration

The sample (10-15 g) was put into pre-weighed flask and weighted on technical scales with accuracy ± 0.01 g. Then, 15-20 g of *n*-butanol (technical or higher purity grade) and 5-10 drops of 0.5 % bromothymol blue solution in *n*-butanol were added as solvent and indicator respectively. Before analysis *n*-butanol (solvent) was also titrated in order to determine its acidity for the accounting in the calculating of fatty acids content in sample analyzed. Obtained mixture after addition of the solvent and indicator was weighted, its color was brown. Then the titration by sodium butoxide solution in butanol (about 1 % of alkali in terms of NaOH), using non-calibrated pipette, was carried out until the changing of the mixture color to deep blue. The color transfer in equivalent point occurs at several drops of solution, thus operator should be carefully. After that mass of the obtained mixture was measured and FFA content was calculated. Titration of each mixture was repeated three times and the confidence interval of fatty acid content ($p = 0.95$) was calculated. The results of the analyses can be expressed as acid value (mg KOH/g) or as the fatty acid concentration itself. The latter may be counted as oleic acid or, if the fatty acid composition of the sample is known, as the mass concentration of all presented acids.

Results and discussions

The results of the titration of prepared series of fatty acids/oil mixtures are given in Table below. First of all, it should be emphasized the quite narrow confidence interval ($p = 0.95$, 3 parallel analyses). This indicates a good reproducibility of the titration results. However, noticeable deviation from the actual concentration of FFA in prepared mixtures, changing linearly with its concentration, was observed (see Fig.). There are some insignificant overestimation at low FFA contents (in case of series FA-1 and FA-2) and more significant underestimation at higher FFA contents, growing linearly with its concentration. The underestimation reaches about 0.6-1.4 % for different mixtures' series at the maximum FFA content. The deviation values are higher, than the confidence interval wide, thus they can't be explained by the scattering of the titration results. In addition, the reason of the deviation can't be result of the expression of FFA content as oleic acid. The difference between the latter and real FFA content, calculated on the basis average molecular weight of fatty acid, taking into account the fatty acid composition of fatty acids (not shown in article), is insignificant or even negligible (see Table). The linear growth of absolute error with FFA content, in our opinion, can be explained by the partial formation of fatty acid salts associated with free fatty acids. In such case it may be assumed, that using the lower mass of the sample and/or higher amount of the solvent (*n*-butanol) will minimize such a systematic error of proposed method.

The proposed method is applicable for acid value determination of the wide variety of the samples' types, including refined and not refined oils and fats from different sources, wasted frying oils, fatty acids alkyl esters, fatty acids, products of fatty acids' esterification by different alcohols, etc. Even in case of titration of the samples, having intense dark-brown and almost black color, the color transfer is easily indicated visually.

Another advantage of the method is using of *n*-butanol as solvent. It is able to efficiently dissolve petrol products, vegetable oils, fats, monoalkyl esters, fatty acids, soaps and another alcohols. Due to the low toxicity and the possibility of the *n*-butanol production by biotechnological fermentation of various sugar-containing raw-stuff, it is considered as green solvent. Moreover, *n*-butanol can be easily recovered by distillation and reused in analyses repeatedly.

When the titration is holding by the operator, the method sensitivity is 0.01-0.05 % of free fatty acids (depending on sample amount and titrant concentration), which equivalent of acid value about 0.02-0.10 mg KOH/g. The time for analyze is enough short (about 5-15 minutes).

The proposed method is also able to overcome some disadvantages of the standard methods of acid value determination.

Table. Results of titration

FFA content in mixture, % wt.	FFA content by titration, % wt.		Confidence interval of FFA content, ±%
	Counted as oleic acid	Counted for real fatty acids' composition	
FA-1 (fatty acids of rapeseed oil)			
1.08	1.17	1.17	0.01
2.14	2.24	2.23	0.05
5.23	5.21	5.19	0.01
10.11	10.00	9.97	0.07
14.97	14.70	14.65	0.04
20.17	19.80	19.73	0.04
50.07	48.85	48.68	0.31
FA-2 (fatty acids of sunflower oil)			
1.07	1.17	1.16	0.03
2.07	2.16	2.15	0.03
5.04	5.10	5.07	0.06
10.05	10.03	9.97	0.08
15.04	14.88	14.80	0.09
19.99	19.74	19.63	0.11
50.00	49.18	48.90	0.70
FA-3 (reagent grade oleic acid, Czech)			
1.03	1.04	1.03	0.01
2.11	2.06	2.05	0.01
5.06	4.92	4.89	0.07
10.09	9.80	9.73	0.11
15.06	14.65	14.55	0.08
19.94	19.47	19.33	0.36
49.81	48.35	48.01	0.78

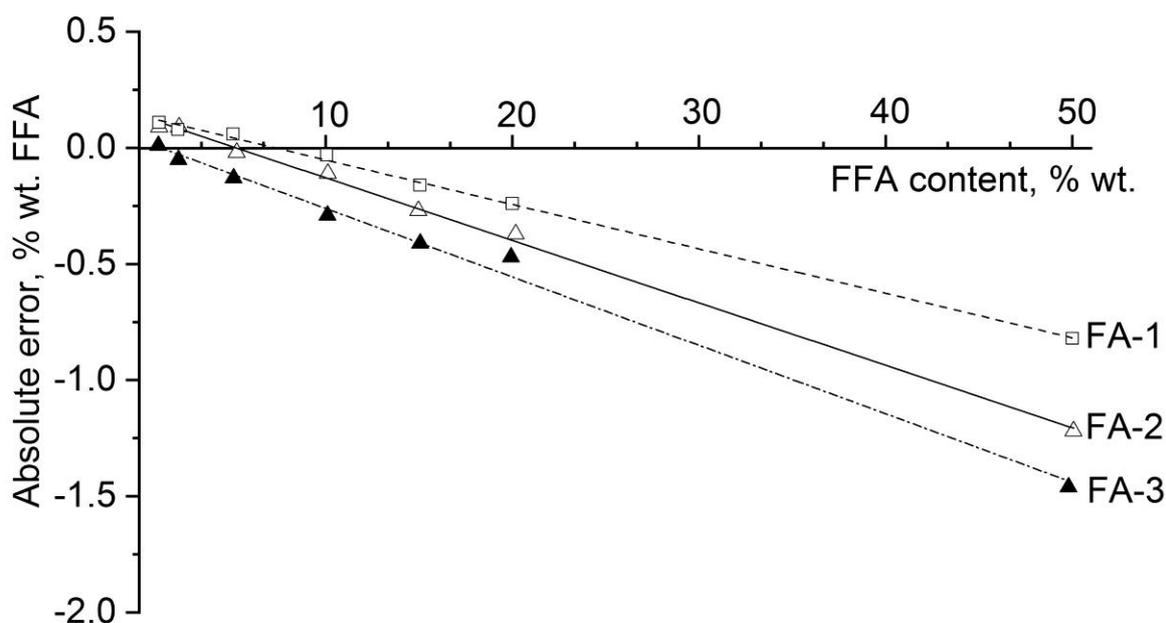


Fig. The absolute error of the FFA content determination.

Titration (sodium butoxide solution in butanol) in case of its storing in tightly closed bottle can be used with the same efficiency after the year or longer, as the concentration of the alkali doesn't change. Also, the long-term storing of the titrant anhydrous alkali solution doesn't result in any leaching of the glass tare even in case of not chemical resistant glass. Proposed method requires only the simplest laboratory glassware (conic flasks, non-calibrated pipettes, hermetically sealed glass vessels for titrant) and technical laboratory scales (weighting accuracy ± 0.01 g). Used glassware can be easily washed with only water. The dosage of the sample and titrant not by volume, but by mass is easy and rapid. It also eliminates the distortion of the results due to the titrant volume change with temperature in laboratory. Additionally, the relatively low volatility of the *n*-butanol (117 °C boiling temperature) excludes the meaningful evaporation during the analysis, and therefore minimizes the error of determination.

Practical application of the method

This method of acid value determining was tested on a number of refined and unrefined natural oils (including strongly colored mustard oil), waste edible oils, as well as on technical fats with high acidity (chicken fat, beef fat, etc.). (More than 80 samples).

Also, this method has been successfully used to control the process during the esterification of fatty acids derived from natural oils and oils with high acidity (unrefined mustard oil, waste cooking oil, etc.) on acid heterogeneous and homogeneous catalysts with methyl, ethyl, *iso*-propyl, *n*-propyl, *iso*-butyl, *n*-butyl, heptyl, decyl and cetyl alcohols. It should be noted that the products of acid synthesis have an intense dark brown color. (More than 150 definitions).

In addition, this method has been successfully used to determine the acid value of purified fatty acid esters (methyl, ethyl, *iso*-propyl, *n*-propyl, *iso*-butyl, *n*-butyl, *n*-amyl and *n*-heptyl), as well as intermediate determinations during the purification process. (More than 300 samples).

Conclusions

The rapid and simple method of acid value determination using alkali-acid titration by butoxide solution and butyl alcohol as solvent was developed. The method allows to determine the acid value in wide range of samples, including the samples with intense coloration. The relatively high accuracy of acid value determination was shown. Some disadvantages of traditional methods of acid value determination were overcome.

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Надійшла до редакції 14.05.2021 р.

Простий метод визначення кислотного числа рослинних олій та олеохімічних продуктів

С.О. Зубенко

*Інститут біоорганічної хімії та нафтохімії ім. В.П. Кухаря НАН України, Україна,
02660 Київ, вул. Мурманська, 1, тел./факс: (044) 559-98-00, S.O.Zubenko@ukr.net*

Кислотне число – це одна з ключових технічних характеристик рослинних олій та олеохімікатів, одержаних на цій основі. Існуючі стандартні методи визначення кислотного числа відносно складні та мають деякі недоліки. В даній роботі було запропоновано швидкий та простий метод визначення кислотного числа. Він полягає у кислотно-лужному титруванні зразка бутанольним розчином бутилату натрію з використанням бромтимолового синього, а також використання *n*-бутанолу в ролі розчинника. Метод тестувався на трьох серіях сумішей рафінованої соняшникової олії та вільних жирних кислот (дистильованих жирних кислот соняшникової та ріпакової олій та хімічно чистої олеїнової кислоти). Вміст жирних кислот в тестових сумішах був у межах 1-50 % мас. Метод дозволяє визначати кислотне число у широкому асортименті зразків, який включає зразки з інтенсивним забарвленням. Було показано порівняно високу точність визначення кислотного числа. Деякі недоліки традиційних методів, такі як необхідність використання змішаних розчинників та порівняно складне використання лабораторного обладнання, титрування в гарячому стані, вплив температурних змін у лабораторії та труднощі з візуальною індикацією передачі кольору, були подолані.

Ключові слова: кислотне число, рослинні олії, біодизель, титрування, *n*-бутанол