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Acid Value Determination in Vegetable Oils by Indirect Titration in Aqueous-alcohol Media

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A new method of acid value determination in vegetable oils has been developed. The method is based on (a) simple, rapid and complete extraction of acids from an oil test portion into reagent (0.05 mol dm^{-3} triethanolamine (B) in the mixture of 50 % H_2O + 50 % 2-PrOH) and (b) indirect titration of acids in BH^+ form against aqueous alkali in the presence of a phenolphthalein indicator. Suitable metrological parameters of acid value determination have been obtained. The advantages of the method are (i) absence of a toxic solvent, (ii) extraction and titration of acids at room temperature, and (iii) no need for preliminary neutralization of acid admixtures in a solvent.

INTRODUCTION

Acid value (AV) is an important indicator of vegetable oil quality. AV is expressed as the amount of KOH (in milligrams) necessary to neutralize free fatty acids contained in 1 g of oil.[1,2]

The majority of national and international standards for AV determination in vegetable oils are based on the acid-base titration techniques in non-aqueous solvents.[1,2] These techniques have a number of drawbacks:

(i) Currently used non-aqueous solvents are toxic, *e.g.*, ethanol or isopropanol heated up to 60 °C or higher (exact temperature is not indicated),[1] or diethyl ether–ethanol solvent (1:1 vol. ratio).[2]

(ii) Incomplete solubility of a test oil portion in alcohol (even under heating)[1] caused by the formation of a dispersed system.[3]

(iii) Conditions for accurate acid-base titration in hot amphoteric solvents might deteriorate due to the increase of the solvolysis constant for anion titrable weak acids with an increase in temperature. This conclusion follows from the fact that the solvent auto-protolysis constant increases, and the acid dissociation constant decreases with increased temperature.[4]

(iv) Need to previously neutralize solvents.[1,2]

The objective of the present work was to develop a new technique of AV determination in vegetable oils, free from the above listed drawbacks.

The proposed technique is based on indirect acid-base titration using a special reagent. The reagent is similar to the reagent for pH-metric AV determination in vegetable oils.[5] The reagent does not dissolve the test portion oil due to the high content of water (50 %; vol. fraction, ϕ). On the other hand, the presence of triethanolamine (B) causes rapid (within 1 min) and full extraction of free fatty acids (HAn_i, $i = 1,…,n$) from the test oil portion into the reagent:[5]

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$$(\mathrm{HAn}_i)_{\mathrm{oil}} \leftrightarrow (\mathrm{HAn}_i)_{\mathrm{r}} \qquad (1)$$

$$(\mathrm{HAn}_i)_{\mathrm{r}} + (\mathrm{B})_{\mathrm{r}} \leftrightarrow (\mathrm{An}^-)_{\mathrm{r}} + (\mathrm{BH}^+)_{\mathrm{r}} \qquad (2)$$

Full acids extraction in BH^+ form into the reagent was initially shown indirectly by the results of pH-metric AV determination in vegetable oils.[5] A similar result was recently obtained in our study by direct investigations of acids extraction.[6]

The technique proposed in the present study involves rapid and full acids extraction both during a preliminary short exposure (1 min) and during subsequent indirect titration of acids in BH^+ form against an aqueous alkali with a color indicator:

$$(\mathrm{BH}^+)_{\mathrm{r}} + \mathrm{OH}^- \rightarrow (\mathrm{B})_{\mathrm{r}} + \mathrm{H_2O} \qquad (3)$$

This titration allows AV determination in vegetable oils. In our previous study, indirect titration of this type was used to determine the acid number in motor oil.[7] In that case, the standard titration technique with a color indicator was not applicable because the presence of metallic dispersion affected the accuracy of the results.

THEORETICAL

Optimum Composition of the Reagent

The composition of the reagent for the pH-metric technique of AV determination in vegetable oils, proposed elsewhere,[5] namely, 0.2 mol dm^{-3} triethanolamine (B) + 0.02 mol dm^{-3} KNO_3 in the mixture of 50 % H_2O + 50 % 2-PrOH (ϕ), was slightly changed for indirect titration. The high B concentration in this reagent increases the error of indirect titration occurring in reaction (3), which is considered in detail below. Besides, KNO_3 in this reagent is not required for our purpose, since the condition of ionic strength constancy during titration is excessive. Thus, development of the optimum reagent composition for indirect titration included a decrease of B concentration (C_B) in order to retain the conditions for rapid and full extraction of acids from the test oil portion into the reagent. Another change was elimination of KNO_3 from the reagent.

To choose the optimum C_B value, calculation of the completeness of acids extraction was carried out by a previously developed method.[6] Completeness of acids extraction (η) is described by the following equation:

$$\eta \,/\, \% = \frac{[\mathrm{BH}^+]_{\mathrm{r}} \cdot V_{\mathrm{r}} \cdot 56.11 \cdot 100}{\mathrm{AV} \cdot m} \qquad (4)$$

where $[BH^+]_r$ / mol dm^{-3} is the equilibrium BH^+ concentration in the reagent, V_r / cm^3 is the reagent volume, 56.11 is the molecular (formula) weight of KOH, m / g is the mass of the oil test portion.

The η value was calculated by Eq. (5):[6]

$$\left(\frac{1}{d \cdot K_1} + \frac{V_{\mathrm{r}}}{m} - \frac{K_2 \cdot V_{\mathrm{r}}}{m}\right) \cdot \eta^2 + \left(\frac{\mathrm{AV} \cdot m}{56.11} + V_{\mathrm{r}} \cdot C_{\mathrm{B}}\right) \cdot \frac{K_2 \cdot V_{\mathrm{r}} \cdot 56.11 \cdot 100}{\mathrm{AV} \cdot m^2} \cdot \eta - \frac{K_2 \cdot C_{\mathrm{B}} \cdot V_{\mathrm{r}}^2 \cdot 56.11 \cdot 10^4}{\mathrm{AV} \cdot m^2} = 0 \qquad (5)$$

where d is oil density, (d = 0.90 g cm^{-3}),[6] K_1 and K_2 are the equilibrium constants for Eqs. (1) and (2), respectively. For different acids in vegetable oils, K_1 and K_2 values are close.[6] At low ionic strength (I) its influence on K_1 can be negligible, so for 25 °C and $I \leq 0.02$ K_1 is equal to:[6]

$$K_1 = \frac{\sum [\mathrm{HAn}_i]_{\mathrm{r}}}{\sum [\mathrm{HAn}_i]_{oil}} = 0.14 \qquad (6)$$

and K_2 for I = 0.02 is equal to:[6]

$$K_2 = \frac{(\sum [\mathrm{An}_i^-]_{\mathrm{r}})[\mathrm{BH}^+]_{\mathrm{r}}}{(\sum [\mathrm{HAn}_i]_{\mathrm{r}})[\mathrm{B}]_{\mathrm{r}}} = 19.0 \qquad (7)$$

The following equation, based on the Debye-Hückel limiting law,[4] was used for K_2 recalculation for indirect titration of solutions with $I < 0.02$:

$$(K_2)_{\mathrm{recal}} = K_2 \, \frac{((f_{z=1})_{I=0.02})^2}{((f_{z=1})_I)^2} \qquad (8)$$

where $f_{z=1}$ is the activity coefficient for one-charge ion, $(f_{z=1})_{I=0.02} = 0.697$.[6] The $(f_{z=1})_I$ values (Table I) were calculated by the Debye-Hückel limiting law.[4] The values of I (Table I) were assumed to be suitable for full acids extraction, which was later confirmed by calculation. The relative permittivity ε_r equals 46.8 for 50 % H_2O + 50 % 2-PrOH mixture (ϕ) at 25 °C.[8] The results of $(K_2)_{recal}$ calculation are shown in Table I.

The V_r value was increased up to 100 cm^3, and the maximum mass value was decreased up to 30 g compared to the pH-metric method[5] in order to decrease the C_B value as much as possible and provide full acids extraction. It is shown by Eq. (5) that under these conditions, in the wide range of AV, a decrease of C_B to 0.05 mol dm^{-3} provides almost 100 % completeness of acids extraction (Table I). Compared to the pH-metric AV determination,[5] the time of preliminary acids extraction from the test oil portion into the reagent, occurring while stirring the mixture, was reduced to 1 min, since the extraction continued during titration. This additional acids extraction during titration, which was not taken into account while calculating the extraction completeness (Table I), increases the completeness.

TABLE I. Calculations of the completeness of free acids extraction (η) from the oil test portion and the theoretical relative errors (P) for indirect titration of acids[(a)]

Expected AV / (mg KOH / 1 g of oil)	0.05	0.15	0.15	0.6	0.6	2.5	2.5	10
Sample mass, m / g	30	30	10	10	4	4	1	1
$(C_{\mathrm{BH^+}} = I) \times 10^4$ / mol dm^{-3}	2.67	8.02	2.67	10.7	4.28	17.8	4.46	17.8
$(f_{z=1})_I$	0.959	0.930	0.959	0.920	0.949	0.898	0.946	0.898
$(K_2)_{\mathrm{recal}}$	10.04	10.68	10.04	10.91	10.26	11.45	10.28	11.45
η / %	99.8	99.5	99.9	99.6	99.9	99.6	99.9	99.7
$\pm P$ / %	9.1	3.1	_	2.4	_	1.5	_	1.5

[(a)] Reagent volume = 100 dm^3, C_{B} = 0.05 mol dm^{-3}.

The phenolphthalein indicator added to 100 cm^3 of the reagent causes pink coloring, which corresponds to the pH range in which the indicator color is changed, taking into account natural neutralization of acid admixtures by the reagent.

Thus, the optimum composition of the reagent for indirect titration is 0.05 mol dm^{-3} triethanolamine (B) in 50 % H_2O + 50 % 2-PrOH mixture (vol. fractions). The optimum reagent volume for indirect titration is 100 cm^3, and the maximum oil test portion is 30 g.

Theoretical Analysis of Indirect Titration Errors

Indirect titration of HAn_i in the form of the other weak acid $\mathrm{BH^+}$ in excess of the product titration (B) by reaction (3) has not been studied enough, and thus requires theoretical analysis.

Thermodynamic ionic production of the solvent in the reagent is $\mathrm{p}K^0_{\mathrm{S}} = 15.12$,[6] and the thermodynamic acid dissociation constant of $\mathrm{BH^+}$ is $\mathrm{p}K^0_{\mathrm{BH^+}} = 7.23$,[6] which allows calculating the thermodynamic basic dissociation constant of B as $\mathrm{p}K^0_{\mathrm{B}} = \mathrm{p}K^0_{\mathrm{S}} - \mathrm{p}K^0_{\mathrm{BH^+}} = 7.89$. Using, $\mathrm{p}K^0_{\mathrm{S}}$, $\mathrm{p}K^0_{\mathrm{B}}$ and the condition for the equivalent point in indirect titration by reaction (3):

$$[\mathrm{B}] \cong C_{\mathrm{B}} = 0.05 \text{ mol dm}^{-3} \tag{9}$$

$$a_{\mathrm{BH^+}} \cong a_{\mathrm{OH^-}}, \tag{10}$$

(a is activity), it is possible to calculate pH of the equivalent point ($\mathrm{pH_e}$):

$$\mathrm{pH_e} = \mathrm{p}K^0_{\mathrm{S}} - \frac{1}{2}(\mathrm{p}K^0_{\mathrm{B}} + \mathrm{p}C_{\mathrm{B}}) = 10.52\,. \tag{11}$$

It should be noted that $\mathrm{pH_e}$ is the true pH, which differs from the experimentally found conditional value[5] $\mathrm{pH}^1_{\mathrm{e}} = 11.30$ for $C_{\mathrm{B}} = 0.2$ mol dm^{-3} (recalculation $\mathrm{pH}^1_{\mathrm{e}}$ for $C_{\mathrm{B}} = 0.05$ mol dm^{-3} yields $\mathrm{pH}^1_{\mathrm{e}} = 11.00$).

The theoretical relative error of titration with a color indicator, provided that dilution of the solution by reagent is neglected, is described by the following equation:[9]

$$P\,/\,\% = \pm\left(\frac{\partial X}{\partial \mathrm{pH}}\right)_{X=1} \cdot \delta(\mathrm{pH}) \cdot 100, \tag{12}$$

where X is the titrable share.

$$X = \frac{[\mathrm{K_t}^+]}{C_{\mathrm{BH^+}}} \tag{13}$$

where $[\mathrm{K_t^+}]$ is the concentration of the alkali cation added to the reagent during the titration process; $C_{\mathrm{BH^+}}$ is the initial concentration of $\mathrm{BH^+}$; $C_{\mathrm{BH^+}} = \mathrm{I}$ (Table I); $\delta(\mathrm{pH})$ is the maximum error of visual pH measurement with a color indicator ($\delta(\mathrm{pH}) = \pm\, 0.2$).[9]

The condition of electroneutrality in the reagent during titration has been used to determine the $(\partial X/\partial \mathrm{pH})_{X=1}$ value:

$$[\mathrm{K_t^+}] + [\mathrm{H^+}] + [\mathrm{BH^+}] = [\mathrm{OH^-}] + \sum[\mathrm{An}_i^{\,-}] \tag{14}$$

Taking into account that $\mathrm{p}K^0_{\mathrm{BH^+}} = 7.23$,[6] $\mathrm{p}K^0_{\mathrm{S}} = 15.12$,[6] $C_{\mathrm{B}} = 0.05$ mol dm^{-3}, $C_{\mathrm{BH^+}} = (2.67 \div 17.8) \times 10^{-4}$ mol dm^{-3} (Table I) and the range of X values is close to 1 ($\mathrm{pH_e} = 10.52$), the following relationships have been obtained:

$$\sum[\mathrm{An}_i^{\,-}] = C_{\mathrm{BH^+}} \tag{15}$$

$$C_{\mathrm{B}} \gg C_{\mathrm{BH^+}}, \tag{16}$$

$$[\mathrm{B}] \cong C_{\mathrm{B}}, \tag{17}$$

$$[\mathrm{H^+}] \ll [\mathrm{OH^-}] \tag{18}$$

From these relationships and Eq. (14), the following equation was derived:

$$\mathrm{pH} = -\lg\left\{\frac{(f_{z=1})_I \cdot K^0_{\mathrm{BH^+}} \cdot (X-1) \cdot C_{\mathrm{BH^+}}}{2C_{\mathrm{B}}} + (f_{z=1})_I \cdot \left(\left[\frac{K^0_{\mathrm{BH^+}} \cdot (x-1) \cdot C_{\mathrm{BH^+}}}{2C_{\mathrm{B}}}\right]^2 + \frac{K^0_{\mathrm{S}} \cdot K^0_{\mathrm{BH^+}}}{((f_{z=1})_I)^2 \cdot C_{\mathrm{B}}}\right)^{0.5}\right\}. \tag{19}$$

The $(\partial X/\partial \mathrm{pH})_{X=1}$ value was obtained from Eq. (19), and by means of Eq. (12) the equation for calculating the relative error of indirect titration with a color indicator in the presence of titration product (B) in excess (reaction (3), was obtained:

$$P\,/\,\% = \pm\frac{4.6}{C_{\mathrm{BH^+}}(f_{z=1})_I}\sqrt{\frac{K_\mathrm{S}^0\cdot C_\mathrm{B}}{K_{\mathrm{BH^+}}^0}}\,\delta(\mathrm{pH})\cdot 100 \quad (20)$$

Results of P calculation by Eq. (20) for different conditions of indirect titration of free acids in the test oil portion are presented in Table I.

It is interesting to compare Eq. (20) with Eq. (21) for P calculation of direct titration of a weak acid including BH$^+$ performed without B addition using a color indicator as well. Eq. (21) was considered[9] for the same conditions (except for condition (16)), which we accepted for Eq. (20). For simple comparison with Eq. (20), the equation for direct titration of BH$^+$ [9] is presented in the following form:

$$P_\mathrm{dt}\,/\,\% = \pm\frac{4.6}{C_{\mathrm{BH^+}}\cdot(f_{z=1})_I}\cdot\sqrt{\frac{K_\mathrm{S}^0\cdot C_{\mathrm{BH^+}}}{K_{\mathrm{BH^+}}^0}}\cdot\delta(\mathrm{pH})\cdot 100 \quad (21)$$

Comparison of Eqs. (20) and (21) shows that if condition (16) ($C_\mathrm{B} >> C_{\mathrm{BH+}}$) for Eq. (20) is fulfilled, the relative error of indirect titration is larger than the error of direct titration. At the same time, as indicated above, the conditions for accurate direct titration of weak acids in hot, practically non-aqueous, alcohol are worse than those in indirect titration; hence, the obtained errors of this titration[1] were larger than found in the present paper. In the latter case, the obtained errors were lower (Table I) than those reported for direct titration.[1] Decreasing the error of AV determination in vegetable oils by indirect titration (Eq. 20) through decreasing the C_B value (lower than 0.05 mol dm^{-3}) is not efficient because it deteriorates the conditions of free fatty acids extraction from the test oil portion.

EXPERIMENTAL

Apparatus

A 2 ml microburette (Bein Z.M, Israel) with 0.01 ml divisions and the drop size reduced to 0.008 ml.

Reagents

Triethanolamine, sodium hydroxide, hydrochloric acid and oleic acid from Merck (Germany), isopropanol (2-PrOH), ethanol and diethyl ether from Frutarom (Israel), phenolphthalein from BDH (England). Vegetable oils for analyses were purchased from local suppliers.

Procedure

To prepare the titration reagent, (≈ 1 L), mix 500 cm^3 deionized water, 500 cm^3 2-PrOH and 7 cm^3 triethanolamine. Place about 100 cm^3 of the reagent into a conical flask on a magnetic mixer, add 0.5 cm^3 of phenolphthalein solution[2] to obtain pink color of the reagent. Add an oil test portion of the mass according to Table I, accuracy ± 0.2 %, to the reagent. Mix the reagent on the stirrer until colorless for about 1 min, and then, keeping on stirring, begin titration with 0.1 M NaOH (or KOH) aqueous solution. The titration is finished at the appearance of the first permanent pink color of the same intensity as before adding the sample. The color is supposed to persist for 10 s.

RESULTS AND DISCUSSION

Precision and Accuracy of the Results

Three different vegetable oils and one model (Canola + oleic acid) were investigated (Table II). Evaluation of the precision and accuracy of the results of AV determination by indirect titration was carried out according to Ref. 10.

Table II shows the average results of AV determination obtained by standard titration[2] and by the proposed novel indirect titration from $n = 5$ replications for each sample (marked AV$_\mathrm{s}$ and AV$_\mathrm{p}$, respectively); standard deviations for these replications, marked S_s and S_p, respectively; $F = S_\mathrm{p}^2\,/\,S_\mathrm{s}^2$, and $t = [\mathrm{AV_s} - \mathrm{AV_p}]\,/\,[(S_\mathrm{s}^2 + S_\mathrm{p}^2)\,/\,5]^{0.5}$. The chosen standard method[2] is the most reliable one due to high solubility of vegetable oils in the diethyl ether + ethanol solvent used in this method.

The critical value for F-ratio is 6.39 at a 95 % level of confidence, and the number of degrees of freedom $n - 1 = 4$. For t-ratio, the critical value is 2.31 at a 95 % level of confidence, and the number of degrees of freedom $2\cdot(n - 1) = 8$. From the comparison of F-data with the critical value (Table II), it follows that the differences

TABLE II. Comparison of the results of AV determination by the standard titration method (AV$_\mathrm{S}$) with those obtained by the proposed novel titration method (AV$_\mathrm{P}$)

No.	Oil sample	AV$_\mathrm{s}$	S_s	AV$_\mathrm{p}$	S_p	F	t
1	Canola	0.071	0.002	0.073	0.001	0.50	1.71
2	Maize	0.223	0.004	0.224	0.007	2.38	0.30
3	Soya	0.60	0.017	0.61	0.011	0.41	0.62
4	Canola + oleic acid	5.95	0.09	6.00	0.11	1.54	0.78

in precision of the results obtained by the standard titration and those obtained by the proposed titration technique are insignificant (all *F*-values are less than 6.39). The accuracy of these techniques is approximately the same; deviations of the average AV_p, obtained by the proposed method, from the average results, obtained by the standard technique, are insignificant compared to random errors (all *t*-values are less than 2.31).

Hence, the precision and accuracy obtained by the proposed indirect titration for AV determination in vegetable oils are adequate for quality control of oils. It is important to note that this conclusion applies to a wide range of AV values (Table II).

Advantages of the Proposed Indirect Titration

No toxic solvent is used in the proposed method and the procedure is carried out at room temperature. No preliminary neutralization of acid admixtures is required.

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SAŽETAK

Određivanje kiselinskih vrijednosti u biljnim uljima indirektnom titracijom u smjesi alkohola i vode

Elena Kardash i Yakov I. Tur'yan

Razvijena je nova metoda za određivanje kiselinskih vrijednosti u biljnim uljima. Metoda se temelji na: (a) jednostavnoj, brzoj i potpunoj ekstrakciji kiselina u uzorku pomoću reagensa (0,05 mol dm^{-3} trietanolamina (B) u smjesi 50 % H_2O + 50 % 2-PrOH (vol. udjeli)) i (b) indirektna titracija kiselina u BH^+ obliku u alkalnom mediju uz fenolftalein. Prednost te metode je u (i) ne rabi se toksično otapalo; (ii) ekstrakcija i titracija kiseline izvode se kod sobne temperature i (iii) nije potrebna prethodna neutralizacija kiseline u otapalu.