Practical Limitations in Determining Vegetable Oil Acid Values by a Novel pH-Metric Method

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ABSTRACT: A novel pH-metric method is described for the determination of acid values (AV) in vegetable oils without titration. The method is based on a reagent containing triethanolamine, isopropanol, and water to which an oil sample is added before measuring pH. Oil samples with AV in the range 0.006–0.107 mg KOH/g oil were prepared from commercial soybean oil by treatment with a strong-base anion exchanger in OH^- form and addition of oleic acid. Compared to the standard titrimetric method, significantly greater AV were obtained at less then 0.02 mg KOH/g oil. This was due to the influence of triethanolamine hydrolysis on the acid–base equilibrium in the mixture "oil-reagent." Thus, the AV 0.02 mg KOH/g oil is accepted as the limit of quantitation. Because refined oils usually have AV of 0.05 mg KOH/g oil or more, this method should be suitable for practical oil analyses.

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KEY WORDS: Acid value method, pH-metric, quantitation, vegetable oils.

A new method for pH-metric acid value (AV) determination in vegetable oils without using titration has been developed (1). The advantages in comparison to standard techniques (2) are the reduction of time and potential for automation. The new method is based on extraction of free fatty acids from an oil sample into a reagent containing triethanolamine (TEA), water, and isopropanol. The extraction is rapid (3–4 min) since TEA is a weak base and reacts easily with free fatty acids. The process involves mixing an oil sample with the reagent, measuring pH prior to (pH_1') and after addition of HCl (pH_2') using a commercial pH-meter with an aqueous reference electrode [version II of the method in (1)]. AV is calculated from the difference between pH_1' and pH_2':

$$AV = 56.11 N_{st} \bullet V_{st}/[(10^{\Delta pH} - 1)m], \text{ in mg KOH/g oil} \qquad [1]$$

where 56.11 is the molecular weight of KOH; N_{st} is the standard acid concentration (M); V_{st} is the volume of the standard acid added (mL), which is considerably less than the volume of the reagent; $\Delta pH = pH_1' - pH_2'$; and m is the weight of the oil (g).

The accuracy, reproducibility, and repeatability of this method satisfied AOAC requirements (3,4). The objective of this study was to determine the limit of quantitation (LOQ) for AV by the method. Since LOQ is the lowest level of analyte that can be accurately measured (5,6), AV_{LOQ} was determined with a bias (deviation from standard titrimetric results) not more than the expanded uncertainty of the method as calculated with a coverage factor 2 of 12–14% (7,8). The LOQ evaluation established the relevance of the method for commercial food oil analysis.

EXPERIMENTAL PROCEDURES

Chemicals. TEA, methyl isobutyl ketone, and oleic acid were obtained from Merck (Darmstadt, Germany); isopropanol and potassium hydroxide from Frutarom (Haifa, Israel); hydrochloric acid, phenolphthalein, and buffers from BDH (Poole, England); potassium nitrate from Baker (Phillipsburg, NY); and strong-base anion exchanger Amberlite IRA-400 (OH) from Supelco (Bellefonte, PA). Soybean oil was purchased from local suppliers.

Apparatus. The 632 Metrohm titroprocessor (Metrohm Ltd., Herisau, Switzerland) was used with a ±0.01 pH scale, a 6.0133.100 glass indicator electrode, and a 6.0726.110 aqueous reference electrode. The aqueous reference electrode consisted of Ag, AgCl, KCl, 3 M electrode, and a KNO_3 (sat.) electrolytic bridge. The 2-mL microburette (Bein, Z.M., Israel) had 0.01 mL divisions and a drop size reduced to 0.008 mL.

Sample preparation. Only a commercial soybean oil was used for LOQ evaluation since accuracy, reproducibility, and repeatability of the AV determination are not dependent on the oil matrices (3). The oil sample was treated with the anion exchanger in the OH^- form. The AV obtained after the treatment was $AV_0 = 0.0063$ mg KOH/g oil. This "blank oil" sample was used for preparation of two modified oil samples (models) by addition of oleic acid. The amount Q (g of oleic acid to be added) was calculated by the following formula:

$$Q = [(n - 1) \bullet AV_0 \bullet G]/[199 - (n - 1)\, AV_p] \qquad [2]$$

where G is the mass of the blank oil sample, g: AV_p is the planned acid value after oleic acid addition, and $n = AV_p/AV_0$ (model 1, $n \cong 2$, model 2, $n \cong 4$); $199 \cong 10^3 \bullet M_{KOH}/M_{OA}$, where M_{KOH} and M_{OA} are molecular masses of KOH and of oleic acid and 10^3 is the factor for conversion of g to mg.

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The AV in the commercial and prepared oil samples (blank oil and models) were determined by the standard titration method (2) using a microburette, 0.02 M KOH solution as titrant, phenolphthalein as indicator, and an oil test portion of 30–40 g.

The reagent volume used for the pH-metric determination was 50 mL. The mass of an oil test portion was ~40 g. AV were determined using additions of 0.5 M HCl (N_{st}). The acid volumes V_{st} were 25 μL for the blank oil and models and 100 μL for the commercial oil having the highest AV, in order to achieve a recommended ΔpH ~ 0.3 (8).

An average of 10 replicate determinations (or estimates) of the standard titration was accepted as the conventional "true" AV (9) and was designated AV_t. Average results with the new method, AV_n, were calculated from three replicates for the blank oil and model 1, and from 24 replicates for model 2 and the commercial oil. Corresponding standard deviations S_t and S_n were determined. The bias was calculated by the formula:

$$(|AV_t - AV_n|/AV_t) \bullet 100\% \qquad [3]$$

RESULTS AND DISCUSSION

As shown in Table 1, AV = 0.02 mg KOH/g oil was acceptable as the LOQ (AV_{LOQ}) since the bias is less than 12–14% (expanded uncertainty of the pH-metric method). For AV < AV_{LOQ}, greater systematic errors (bias values) were observed. This was due to the influence of TEA hydrolysis:

$$\mathrm{B} + \mathrm{H_2O} \leftrightarrow \mathrm{BH^+} + \mathrm{OH^-} \qquad [4]$$

where B is a base, in our case TEA. The hydrolysis produced the same acid (BH^+) as the analytical reaction of TEA with free fatty acids HAn_i:

$$\sum_1^m \mathrm{HAn}_i + m\mathrm{B} \leftrightarrow m\mathrm{BH}^+ + \sum_1^m \mathrm{An}_i^- \qquad [5]$$

For pH-metric AV determination, the equilibrium of the reaction in Equation 5 should be shifted to the right (1). At AV ≥ AV_{LOQ}, pH-metric results were approximately equal to titrimetric measurements (Table 1) since hydrolysis is insignificant, i.e., the sum of concentrations of the free fatty acids is much higher than the concentration of hydroxyl ions (mol/L):

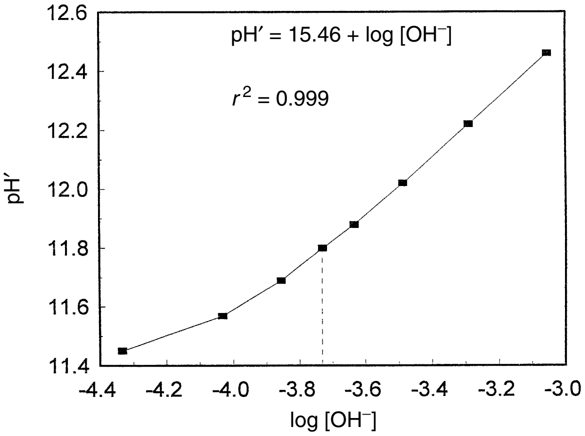

FIG. 1. Dependence of pH′ on log[OH⁻] for the reagent with pH_0' = 11.30. Values of [OH⁻] are accepted as the concentration of KOH added to the reagent. The linear range for the dependence (with the slope equal to one) used in the calculations is shown by dotted line.

TABLE 1
Results of the Experiment for Evaluation of the pH-Metric Limit of Quantitation[a]

	Standard titration method (mg KOH/g oil)		pH-Metric method (mg KOH/g oil)		
Sample	AV_t	S_t	AV_n	S_n	Bias (%)
Blank oil	0.0063	0.0005	0.0096	0.0007	52
Model 1	0.0143	0.0005	0.0173	0.0004	21
Model 2	0.0225	0.0004	0.0229	0.0008	2
Commercial oil	0.107	0.004	0.098	0.002	8

[a] Abbreviations: AV_t = standard titration method for acid value (AV); AV_n = pH-metric method for AV; S_t = standard deviation for AV_t; S_n = standard deviation for AV_n.

$$\sum_1^m [\mathrm{HAn}_i] >> [\mathrm{OH^-}] \qquad [6]$$

The [OH⁻] concentration may be evaluated by the equation

$$\mathrm{pH}' - \log[\mathrm{OH^-}] = k \qquad [7]$$

where k is a value dependent of the composition of the reagent and characteristics of the pH-sensor (1). This value equals the intercept of the linear part of the curve pH′ vs. log [OH⁻] which is plotted by measurements of pH′ after additions of KOH to the reagent. The intercept obtained for the reagent when initial pH_0' = 11.30 is 15.46 (Fig. 1). The nonlinear portion of the curve corresponded to a range of pH′ in which TEA hydrolysis is significant. Based on [OH⁻], the ratio $R = [\mathrm{OH^-}]/\Sigma_1^m[\mathrm{HAn}_i]$ may be calculated for evaluation of the influence of TEA hydrolysis on pH-metric AV determination and corresponding LOQ. The results of this calculation for the oil samples tested are shown in Table 2. As shown at AV ≥ 0.02 and corresponding pH difference ($pH_0' - pH'$) ≥ 0.66, the ratio R is not more than 0.05 (5% of the total concentration of free fatty acids) and hydrolysis of TEA is negligible. Therefore, results of pH-metric and titrimetric AV determinations presented in Table 1 were equivalent only for AV ≥ 0.02 which is the pH-metric AV_{LOQ}. This limit is less than the usual values for refined oils (0.05 mg KOH/g oil and more). So, estimation of LOQ is sufficient for practical purposes.

TABLE 2
Ratio of Concentration of Hydroxyl Ions and Free Fatty Acids

"True" acid value (mg KOH/g oil)	$\sum_{1}^{m}$ [HAn$_i$] (mol/L)	pH′	[OH$^-$] (mol/L)	Ratio (R)
0.0063	$8.5 \bullet 10^{-5}$	11.10	$4.4 \bullet 10^{-5}$	0.52
0.0143	$1.7 \bullet 10^{-4}$	10.81	$2.2 \bullet 10^{-5}$	0.13
0.0225	$3.0 \bullet 10^{-4}$	10.64	$1.5 \bullet 10^{-5}$	0.05
0.107	$1.5 \bullet 10^{-3}$	9.97	$3.2 \bullet 10^{-6}$	0.002

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