pH-Metric Determination of Acid Values in Vegetable Oils Without Titration

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ABSTRACT: A new method for determining acid values in vegetable oils has been developed for a nontitration pH-metric technique with a reagent consisting of 0.20 M triethanolamine in a 1:1 solution of water and isopropanol. The emulsive properties of this reagent provide rapid (within a minute) and quantitative extraction of free fatty acids from an oil into the solvent phase. Acid values were determined by measuring conditional pH of the emulsified reagent in a pH-meter with an aqueous reference electrode. Three different applications of this technique are discussed.

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KEY WORDS: Acid value, conditional pH, isopropanol, pH-metry, titration, triethanolamine, vegetable oils.

The majority of national and international standards for acid value (AV) determination in oils (1–3) is based on the acid-base titration techniques in nonaqueous systems. These techniques are time- and labor-consuming and automated with difficulty, particularly on industrial lines. They use toxic solvents, such as diethylether and methyl-isobutyl ketone, as well as nonaqueous alkaline titrants, which are sensitive to carbon dioxide contamination from the atmosphere.

A number of techniques for AV determination in oils without titration have been suggested. These include a pH-metric technique in the presence of a special reagent (4), chromatographic techniques (5–7), and spectroscopic techniques with (8) and without solvent (9,10). This issue was considered in more detail in our review (11).

We consider the pH-metric technique with a special reagent to be the most efficient technique without titration because of its simplicity, rapidity, low-cost instruments, and facility for automation.

The pH-metric technique is based on the use of a reagent in the form of a weak base in a suitable solvent (4,12,13). We consider the solvent to be a component of the reagent, taking into account the large influence of the solvent on the completeness of the acid-base analytical reaction. This reaction between the sum of free fatty acids (ΣHAn) in an oil sample and the weak base (B) in the reagent may be expressed by:

$$\Sigma HAn + B \rightleftarrows \Sigma An^- + BH^+ \qquad [1]$$

For pH-metric determination of AV, the following conditions (4) are necessary: (i) equilibrium (Equation 1) must be shifted to the right side; and (ii) the weak base (B) in the reagent must be at high excess compared to the sum of free fatty acids.

In accordance with these conditions, the following theoretical equation was obtained (13) for aqueous solutions of the reagent with acid addition:

$$pH = -\log \frac{K_w^\circ f_{BH^+}}{K_B^\circ C_B} - \log N_a \qquad [2]$$

where K_w° is the thermodynamic autoprotolysis constant for water; f_{BH^+} is the activity coefficient ($f_B \approx 1$); K_B° is the thermodynamic constant for the basic dissociation of the weak base in water; C_B is the total concentration of the weak base in the reactive mixture; and N_a is the concentration of the sum of acids in the reactive mixture, M.

As has been shown (4) for nonaqueous or mixed solvents, under the previously mentioned conditions, the theoretical dependence pH vs. N_a remains equal to that for aqueous solutions. Hence, in Equation 2, the parameters K_w°, K_B°, and f_{BH^+} may be substituted for the corresponding values for a given nonaqueous or mixed solvent.

Because the measurements of true pH values are known to be complicated for many nonaqueous and mixed solvents, the corresponding calibration buffer solutions are not developed. Therefore, measuring conditional pH values (pH′) in a pH-meter with an aqueous reference electrode [Ag, AgCl, KCl (sat.)], calibrated by regular aqueous buffer solutions, was suggested (4,12).

If the difference between pH′ and pH is assumed to be A_s°, Equation 2 becomes (4):

$$pH' = A_s^\circ - \log \frac{K_s^\circ f_{BH^+}}{K_B^\circ C_B} - \log N_a \qquad [3]$$

where K_s° is the thermodynamic autoprotolysis constant for a given solvent. A_s° depends on the standard potential of the glass electrode in a given solvent and also on the value of the interfacial potential on the boundary with the aqueous reference electrode. For example, for the reagent (4) of 0.15–0.20 M triethanolamine (TEA) in the solvent of 80% di-

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ethyl ether + 19% C_2H_5OH + 1% H_2O (% vol), the values of the parameters are $K_s^\circ = 22.80$, $K_B^\circ = 11.50$, and $f_{BH^+} = 0.1$ (the ionic strength = $5 \cdot 10^{-3}$). For the indicated reagent, as well as for the reagent where chloroform is used instead of diethyl ether (12), it was shown (4,12) that the dependence of pH′ vs. log N_a is linear with a slope equal to 1 in the range of $N_a = 3 \cdot 10^{-5} - 1 \cdot 10^{-2}$ M. This fact was explained (4) by the constancy of A_s° in Equation 3. Therefore, Equation 3 acquires the form:

$$pH' = A - \log N_a \qquad [4]$$

where

$$A = A_s^\circ - \log \frac{K_s^\circ f_{BH^+}}{K_B^\circ C_B} = \text{constant} \qquad [5]$$

Equation 4 is the basis for pH-metric determination of AV for both aqueous (13) ($pH' = pH$, $A_s^\circ = 0$, $K_s^\circ = K_w^\circ$) and nonaqueous (4) systems. The drawbacks of the indicated reagents (4,12) are as follows: (i) the reagents are toxic; (ii) low water concentration in the reagents causes insufficient stability of the pH-metric sensor with a glass indicator electrode and an aqueous reference electrode, and it slows down the glass electrode response (14); (iii) the base reagents with low water concentrations are sensitive to carbon dioxide contamination from the atmosphere due to the insolubility of carbonates being formed, which may affect the pH′ value, particularly at high pH′.

Our work was aimed at eliminating the indicated drawbacks and improving the capacities of the pH-metric technique for AV determination in vegetable oils.

EXPERIMENTAL PROCEDURES

Chemicals. TEA was obtained from Fluka (Buchs, Switzerland); methyl-isobutyl ketone and oleic acid from Merck (Darmstadt, Germany); isopropanol and potassium hydroxide from Frutarom (Haifa, Israel); hydrochloric acid and buffers from BDH (Poole, England); and potassium nitrate from Baker (Philippsburg, NY). The vegetable oils (olive, corn, soy) were 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.

Procedure. Because the investigated commercial liquid oils had a relatively small interval of AV values (0.2–4.0 mg KOH/g oil), we prepared the models in a wide range of AV: from 0.15 to 22 mg KOH/g oil. Oleic acid was dissolved in refined soy oil to prepare the models.

The AV value in the oil samples were determined by the standard potentiometric titration (2) with use of the titroprocessor. A weighed oil sample was added to methyl-isobutyl ketone, and this solution was titrated with the standardized KOH solution in isopropanol. The results were assumed to be the correct AV values.

The same oil samples and the same titroprocessor were used for development of the pH-metric technique without titration. In this case, the titroprocessor was applied for direct pH measurements. The pH-sensor was dipped in the reagent or in the mixture of the reagent with the sample (in the form of an emulsion, see next section) while being stirred. In all experiments with mixed solvents (water + isopropanol), the conditional pH (pH′) was measured. A regular, less expensive pH-meter with the uncertainty not exceeding ±0.01 pH may be used for this purpose as well.

Because the investigated oils were liquids, all the operations for AV determinations were carried out at room temperature.

RESULTS AND DISCUSSION

Development of the reagent. The development of the new reagent was based on the emulsive property of the TEA–water–isopropanol system to form a milklike emulsion with an oil. This property and the presence of TEA provide rapid (within a minute) and quantitative extraction of free fatty acids from an oil into the TEA–water–isopropanol phase. Room temperature fluctuations (17–25°C) do not influence the completeness of extraction. It should be noted that the water–isopropanol system without TEA at a water content ≤25% still extracts free fatty acids from oils sufficiently for technological purposes (15).

We have found that a water concentration above 50% (vol) in the TEA–water–isopropanol system leads to incomplete extraction of acids from oil. At the same time, to provide a stable performance of the pH-metric sensor and lower sensitivity of the reagent to carbon dioxide contamination from the atmosphere, the reagent should contain a maximum of water in the solvent. Therefore, the solvent composition of 50% water + 50% isopropanol (% vol) was chosen.

A TEA concentration of 0.20 M ensures an excess of the weak base, sufficient in comparison with the sum of the acids under determination. The condition of constant ionic strength was reached by adding an indifferent salt (0.02 M KNO_3) to the reagent. Thus, the proposed reagent consists of: 0.20M TEA + 0.02M KNO_3 in the solvent of 50% water + 50% isopropanol (% vol) (16). This reagent does not practically dissolve a vegetable oil, and AV determination is carried out in the formed oil-reagent emulsion. This reagent's high ability to extract acids from oil allows one to use the volumetric ratio of an oil sample to the reagent up to 1.1. In this case, the acids' extraction remains complete. It permits one to increase the weight of the oil sample up to 45 g at 50 mL of the reagent, and to decrease the AV detection limit accordingly.

Another important characteristic of the reagent is its conditional pH in the initial state (pH'_0). The correct choice of the pH'_0 allows the decrease of the $(N_a)_{min}$ value and, hence, the extension of the linear range of the pH′ vs. log N_a dependence (Eq. 4). It was shown (12,13) that the optimum pH'_0 value is equal to pH′ of the pure weak base in a given solvent. A pH'_0 value lower than the optimum may be a cause for a positive error in AV determination. At pH'_0 larger than the optimum, the concentration of the strong base (OH^-) increases, which may lead to a negative error.

For optimum pH'_0 determination, the potentiometric titration of the acid admixtures that are usually present in the reagent was suggested (12). The pH′ value of the titration equivalence point is assumed to be equal to the optimum pH'_0. However, the low concentration of acid admixtures makes this technique insufficiently reliable (compare Refs. 4 and 12). Therefore, we carried out the potentiometric titration after addition of aqueous HCl solution to the reagent. The concentration of HCl in the reagent is sufficiently low (0.01 M), and the TEA concentration C_B, as well as the solvent composition, remains practically unchanged. The titrant is KOH in the same reagent (without HCl). The curve of the potentiometric titration allows for reliable determination of the optimum pH'_0 as pH′ for the titration equivalence point, i.e., for the bend point in the titration curve (Fig. 1). For the reagent we developed, pH'_0 was 11.30 ± 0.05.

Usually, the prepared reagent has a pH′ lower than pH'_0 due to acid contamination. Thus, it is necessary to increase the pH of the reagent up to pH'_0 by traces of the KOH aqueous solution.

An important peculiarity of the reagent we developed is a high water content. It brings about the following advantages: (i) reducing the sensitivity to carbon dioxide contamination from the atmosphere (pH′ drift after sample introduction into the reagent was practically absent); (ii) a rapid response (within a minute); (iii) long (over a year) steady work of the pH glass indicator electrode and aqueous reference electrode, which is essential for automatic control on-line.

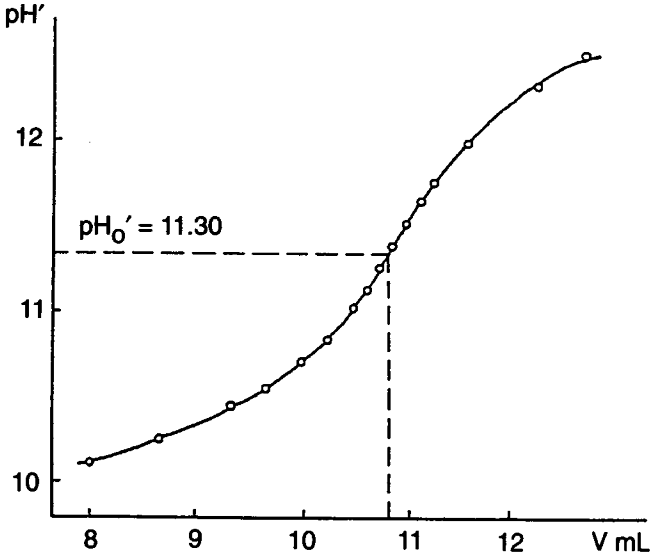


FIG. 1. The curve of titration for 50 mL HCl ($N_{HCl} = 7.70 \cdot 10^{-3}$ M) in the reagent of 0.20 M triethanolamine + 0.02 M KNO_3 in the solvent of 50% water + 50% isopropanol (% vol). The titrant is $3.52 \cdot 10^{-2}$ M KOH in the same reagent; pH, conditional pH; pH_0, conditional pH in the initial state.

Dependence of pH′ vs. log N_a. The dependence of pH′ vs. log N_a (Fig. 2) was found by means of pH′ measurements for solutions prepared by additions of aqueous HCl to 50 mL of the reagent with $pH'_0 = 11.30 \pm 0.05$. The C_B value and the solvent composition remained practically unchanged in these pH′ measurements.

For the proposed reagent, the dependence of pH′ vs. log N_a (N_a is the HCl concentration in the reagent here) is linear in a wide interval of N_a (Fig. 2), conforms to Equation 4. The slope of the straight line in Figure 2 is equal to 1.003 (the squared correlation coefficient is 0.999). An analogous dependence is observed in the presence of an oil added to the reagent, i.e., in the "reagent-oil" emulsion. Thus, it is important to emphasize that neither the nature of the studied oils nor the quantity of an oil sample has any influence on the character of pH' vs. log N_a dependence (Fig. 2) at volumetric ratios of sample to reagent up to 1.1.

For the linear range of dependence for pH′ vs. log N_a, the upper boundary of N_a is $(N_a)_{max} = 1.0 \cdot 10^{-2}$ M (Fig. 2). C_B = 0.20 M was sufficiently large in relation to $(N_a)_{max}$. This excess of TEA allows Equation 4 to be applicable up to $(N_a)_{max}$. From $(N_a)_{max}$, we calculated the upper boundary for AV (AV_{max}) by the equation:

$$AV = 56.11 \frac{50\,N_a}{m} \qquad [6]$$

where m is the weight of an oil sample; 50 mL is the volume of the reagent; and 56.11 is the molecular weight of KOH. For m = 0.5 to 1.0 g and $(N_a)_{max} = 1.0 \cdot 10^{-2}$ M, we calculated by (with Eq. 6) that AV_{max} = 28 to 56 mg KOH/g oil.

The lower boundary of N_a for the linear interval for the dependence of pH′ vs. log N_a in Figure 2 is $(N_a)_{min} = 5.0 \cdot 10^{-4}$ M ($pH'_{max} = 10.63$).

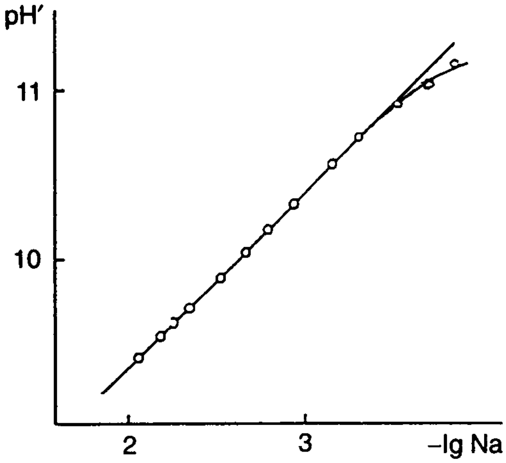


FIG. 2. Dependence of pH′ vs. HCl concentration (N_a, M) in the reagent of 0.20 M triethanolamine + 0.02 M KNO_3 in the solvent of 50% water and 50% isopropanol, % vol ($pH'_0 = 11.30 \pm 0.05$); N_a, M, concentration of the sum of acids in the reactive mixture. See Figure 1 for other abbreviations.

From $(N_a)_{min} = 5.0 \cdot 10^{-4}$ M by Equation 6, the lower boundary for AV (AV_{min}) at m = 40 to 45 g of oil sample and 50 mL of the reagent was determined to be $AV_{min} = 3 \cdot 10^{-2}$ mg KOH/g oil.

The deviation from linear dependence for pH′ vs. log N_a in the area of low N_a values (Fig. 2) is due to the dominant influence of the product of weak base (B) hydrolysis or solvolysis. This product and the product of Equation 1 (BH′) are the same, which increases the N_a value and causes the deviation from a linear pH′ vs log N_a dependence (Fig. 2). This effect may be neglected at the following condition (4,13):

$$N_a \geq (N_a)_{min} = 10\, N_a^{\circ} \qquad [7]$$

where N_a° is the concentration of the product of hydrolysis or solvolysis in the pure reagent solution. At Equation 7, the concentration of BH^+ due to B hydrolysis or solvolysis is not larger than 1% of N_a (4,13).

From Equation 7 and the equation for the constant of the B basic dissociation at the condition $C_B \gg N_a$ we have:

$$pH'_{max} = pH'_o - 1 \qquad [8]$$

On the basis of Equation 8 at $pH'_o = 11.30$, we calculated $pH'_{max} = 10.30$. The experimental value of pH'_{max} is 10.63 (Fig. 2), i.e., close to the calculated value. A certain extension of the linear range of the pH′ vs. log N_a curve under experimental conditions may be caused by noncompensation of the opposite effects of B hydrolysis or solvolysis and the OH concentration rise (4).

pH-Metric technique. We applied three versions of the pH-metric technique for AV determination without titration. These are shown schematically in Figure 3 and are described below.

In Version I (Scheme I in Fig. 3), we used the experimental curve of pH′ vs. log N_a in the linear range (17). We improved the technique (17) in the following way from the experimental curve of pH′ vs. log N_a in the linear range; the calibration table (for example, Table 1) was calculated for values pH′ vs. G, where G is the number of mg KOH equivalent to the sum of acids introduced into the given volume of the reagent. Because G is the numerator in Equation 6 (i.e., G = 56.11 50 N_a), the acid value may be expressed as:

$$AV = \frac{G}{m}\left(\frac{\text{mg KOH}}{\text{g oil}}\right) \qquad [9]$$

The pH′ measurement in the reagent-oil system enables us to obtain G from the calibration table (Table 1) and then to calculate AV by Equation 9 in accordance with the mass (m) of the sample.

In Version II (Scheme II in Fig. 3), we used the standard addition method, where standard acid is added after oil sample introduction into the reagent (4,18). First pH'_1 for the reagent-oil system was measured, and then pH'_2 was measured after the standard acid was added to the system. The equation for AV calculation may be transformed here from Equations 4 and 5 into the following:

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

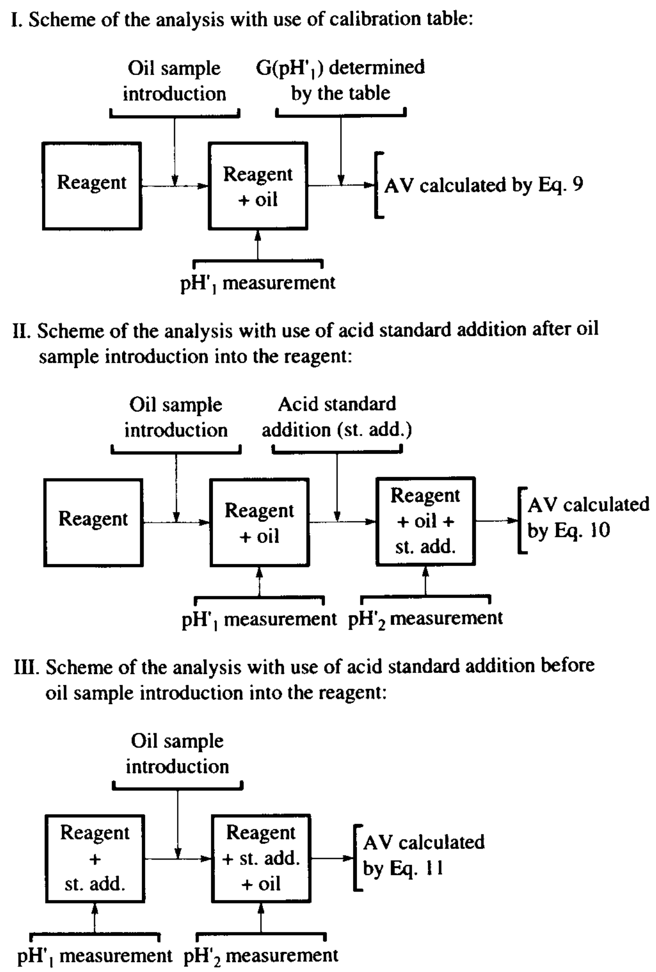
where N_{st} is the standard acid concentration (M); V_{st} is the standard addition volume (mL), which is considerably less than volume, V_r (mL), of the reagent; $\Delta pH' = pH'_1 - pH'_2$.

For Version III of the technique (Scheme III in Fig. 3), we transformed the standard addition method. The standard acid was added first, and only then an oil sample was added. It is important that the mixture of the reagent with the standard acid addition is prepared just before the analysis. At the be-

TABLE 1
Calibration Table: pH′ vs. G for Different Acid Content Equal to G mg KOH in 50 mL of the Reagent (pH'_0 = 11.30)[a]

pH′	G, mg KOH	pH′	G, mg KOH	pH′	G, mg KOH	pH′	G, mg KOH	pH′	G, mg KOH	pH′	G, mg KOH	pH′	G, mg KOH	pH′	G, mg KOH
9.22	35.05	9.40	23.24	9.58	15.41	9.76	10.21	9.94	6.77	10.12	4.49	10.30	2.98	10.48	1.97
9.23	34.26	9.41	22.71	9.59	15.06	9.77	9.98	9.95	6.62	10.13	4.39	10.31	2.91	10.49	1.93
9.24	33.49	9.42	22.20	9.60	14.72	9.78	9.76	9.96	6.47	10.14	4.29	10.32	2.84	10.50	1.89
9.25	32.73	9.43	21.70	9.61	14.39	9.79	9.54	9.97	6.32	10.15	4.19	10.33	2.78	10.51	1.84
9.26	31.99	9.44	21.21	9.62	14.06	9.80	9.32	9.98	6.18	10.16	4.10	10.34	2.72	10.52	1.80
9.27	31.27	9.45	20.73	9.63	13.74	9.81	9.11	9.98	6.04	10.17	4.01	10.35	2.66	10.53	1.76
9.28	30.56	9.46	20.26	9.64	13.43	9.82	8.91	10.00	5.90	10.18	3.91	10.36	2.60	10.54	1.72
9.29	29.87	9.47	19.81	9.65	13.13	9.83	8.71	10.01	5.77	10.19	3.83	10.37	2.54	10.55	1.68
9.30	29.20	9.48	19.36	9.66	12.83	9.84	8.51	10.02	5.64	10.20	3.74	10.38	2.48	10.56	1.64
9.31	28.54	9.49	18.92	9.67	12.54	9.85	8.32	10.03	5.51	10.21	3.66	10.39	2.42	10.57	1.61
9.32	27.90	9.50	18.49	9.68	12.26	9.86	8.13	10.04	5.39	10.22	3.57	10.40	2.37	10.58	1.57
9.33	27.27	9.51	18.08	9.69	11.98	9.87	7.95	10.05	5.27	10.23	3.49	10.41	2.32	10.59	1.53
9.34	26.65	9.52	17.67	9.70	11.71	9.88	7.77	10.06	5.15	10.24	3.41	10.42	2.26	10.60	1.50
9.35	26.05	9.53	17.27	9.71	11.45	9.89	7.59	10.07	5.03	10.25	3.34	10.43	2.21	10.61	1.47
9.36	25.46	9.54	16.88	9.72	11.19	9.90	7.42	10.08	4.92	10.26	3.26	10.44	2.16	10.62	1.43
9.37	24.89	9.55	16.50	9.73	10.94	9.91	7.25	10.09	4.81	10.27	3.19	10.45	2.11	10.63	1.40
9.38	24.33	9.56	16.13	9.74	10.69	9.92	7.09	10.10	4.70	10.28	3.12	10.46	2.07		
9.39	23.78	9.57	15.76	9.75	10.45	9.93	6.93	19.11	4.59	10.29	3.05	10.47	2.02		

[a] Underlined numbers allow to assign every ten pH values for simplification of the table use; G = 56.11 50 N_a; pH, conditional pH value; pH_o, conditional pH in the initial stats.



I. Scheme of the analysis with use of calibration table:

II. Scheme of the analysis with use of acid standard addition after oil sample introduction into the reagent:

III. Scheme of the analysis with use of acid standard addition before oil sample introduction into the reagent:

FIG. 3. Schemes of the analysis; AV calc., acid value calculation; st. add., standard addition.

ginning, pH'_1 was measured in the mixture of the reagent with the standard acid. Then, an oil sample was introduced into the mixture, and pH'_2 was measured. From these measurements, AV is calculated on the basis of Equations 4 and 5 by the formula:

$$AV = 56.11\,N^r_{st}\,\frac{V_r\left(10^{\Delta pH'}-1\right)}{m}\left(\frac{\text{mg KOH}}{\text{g oil}}\right) \qquad [11]$$

where N^r_{st} is the standard acid concentration in the reagent.

We used an aqueous HCl solution as a standard acid. Concentrations of HCl in the reagent were $N^r_{st} = 5 \cdot 10^{-4}$ to $5 \cdot 10^{-3}$ M. The volume of the reagent was $V_r = 50$ mL. The weight of the oil sample was m = 0.5 to 32 g. Examples of AV determinations by the different versions of the proposed technique are shown in Table 2.

Comparing the versions of the technique, we can see that the advantage of Version I (usage of the calibration table) is its simplicity. However, the calibration table is to be corrected whenever temperature or pH-sensor characteristics are changed. Such changes can occur, for example, due to the difference between the values of the interfacial potential on the boundary with the aqueous reference electrode (in measurements for the calibration table calculation and measurements for the analysis). Versions II and III of the technique are free from this drawback because neither temperature nor pH-sensor characteristics are changed during the measurements of pH'_1 and pH'_2. Therefore, temperature control is not necessary here, but Versions II and III are relatively more complicated than Version I. Another advantage of Version III is the use of the acidified reagent, which makes it less sensitive to carbon dioxide contamination from the atmosphere. Furthermore, Equations 10 and 11, used in Versions II and III, do not differ essentially from the corresponding equations of the standard addition method in ionometric techniques. Therefore, the AV calculation can be executed automatically with any modern pH-meter/ionometer. The analysis time for the technique in all versions is 1–3 min. Comparison of Versions I–III shows that none of them has any essential advantages.

Evaluation of precision and accuracy of the results. Precision and accuracy of the results of AV determination with the proposed reagent are similar or higher than those for the precursor technique (4) and slightly lower than those for the standard titration technique (2) at the condition of uncertainty of pH measurements not exceeding ±0.01.

TABLE 2
Examples of Acid Value (AV) Determination by the Versions[a] of the Proposed Technique

No.	Oil	Version	m (g)	pH'_1	pH'_2	G (mg KOH)	V_{st} (mL)	N_{st} (M)	V_r (mL)	N^r_{st} (mM)	AV (mg KOH/g)
1	Olive	II	2.439	9.62	9.27	—	0.2	1.0	—	—	3.71
2	Soy (model 1)	III	1.510	9.66	9.05	—	—	—	50	4.0	22.8
3	Soy (model 2)	III	26.965	10.20	9.80	—	—	—	50	1.0	0.156
4	Corn	I	31.647	10.24	—	3.41	—	—	—	—	0.108

[a] See Figure 3; m, weight of the oil sample; pH'_1, pH'_2, conditional pH values; G = 56.11 50 N_a; V_{st}, standard addition volume; N_{st}, standard acid concentration (M); V_r, volume of the reagent; N^r_{st}, standard acid concentration.

Table 3 presents the average results obtained by standard titration (2), $\overline{AV}_s$, and the proposed technique (for versions, see Table 2), $\overline{AV}_p$, from 5 replicates per technique; deviations for these replicates are S_s and S_p, respectively, and:

$$F = \frac{S_p^2}{S_s^2} \quad \text{and} \quad t = \frac{\left|\overline{AV}_s - \overline{AV}_p\right|}{\left(\dfrac{S_s^2 + S_p^2}{5}\right)^{0.5}} \qquad [12]$$

The critical value for the F-ratio ($\alpha = 0.05$, degree of freedom = 4 for both the numerator and the denominator) is 6.39. For the t-ratio, the critical value is 2.31 ($\alpha = 0.05$, degree of freedom = 8). From comparison of the F-data with the critical value, it follows that the differences between precision of results obtained by standard titration and those by the proposed technique are insignificant (all F are less than 6.39). The accuracy for both techniques is approximately the same, because the deviations of the average AV results obtained by the proposed technique and those obtained by the standard titration technique are insignificant in comparison with random errors (all t are less than 2.31). The precision and accuracy obtained by the proposed pH-metric technique are sufficient for quality control in industry.

In conclusion, the proposed method is intended for evaluation of a vegetable oil's quality during production, in trade, and during food preparation. Its advantages are (i) reduction of time and labor consumption in comparison with standard techniques (1–3), as well as with gel techniques (9,10); (ii) use of cheaper instruments in comparison with chromatographic (5–7) and infrared spectroscopic (8) methods; and (iii) easy automation.

Metrological characteristics of the proposed method (including influence of oil contamination on AV determination) will be studied more carefully in a wide range of AV values during method validation for all vegetable oils significant for trade. Automation of AV on-line determinations and the applicability of the method for analysis of animal fats are the subjects for future work.

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TABLE 3
Comparison of Acid Value (AV) Determination Results Obtained by the Standard Titration Technique with Those Obtained by the Proposed Technique[a]

		Standard titration		Proposed technique			
No.	Oil	$\overline{AV}_s$	S_s	$\overline{AV}_p$	S_p	F	t
1	Olive	3.69	0.05	3.68	0.09	3.24	0.22
2	Soy (model 1)	22.32	0.27	22.40	0.49	3.29	0.32
3	Soy (model 2)	0.153	0.003	0.151	0.006	4.00	0.67
4	Corn	0.104	0.004	0.106	0.007	3.06	0.55

[a] AV_s, average results obtained by standard titration; AV_p, average results obtained by the proposed technique, from 5 replicates per technique; deviations for these replicates are S_s and S_p, respectively; F, F-ratio is 6.39; t, critical value for t-ratio is 2.31.

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