

## Acids Extraction from Vegetable Oils for Acid Value pH-metric Determination without Titration\*

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*Key words* Theoretical and experimental analysis of free fatty acids extraction from vegetable oils into a reagent containing triethanolamine for pH-metric acid value determination without titration was carried out. Practically complete extraction of the free fatty acids in the form of triethanol-ammonium salts was demonstrated. The obtained results allow to understand more possibilities of the pH-metric and other methods for acid value determination in different oils.

acid value  
vegetable oils  
palmitic and oleic acids  
dissociation constants  
extraction

### INTRODUCTION

The pH-metric method for acid value (AV) determination in vegetable oils without titration, developed in our laboratory,<sup>1–3</sup> is based on free fatty acids extraction into a special reagent and determination of the total acids concentration by pH measurements of the reagent. Although titration is not used here, AV is defined as the quantity of KOH (mg) needed to neutralize free fatty acids contained in 1g of oil. The reagent (designated as (I)) was of the following composition:<sup>1–3</sup> 0.2 mol dm<sup>-3</sup> triethanolamine + 0.02 mol dm<sup>-3</sup> KNO<sub>3</sub> in H<sub>2</sub>O + 2-PrOH (1:1) with the initial conditional pH value pH'<sub>0</sub> = 11.30 (see below).

High water concentration in the reagent leads during the analysis to formation of two-phase »oil-reagent« system. In such a system the free fatty acids contained in the oil are extracted into the reagent phase.

Unlike the waterless reagent<sup>4</sup> dissolving oils, reagent (I) has an important advantage consisting of stable

response of the glass pH-indicator electrode and of the aqueous reference electrode independently on the size of oil test portion.<sup>1–3,5</sup>

The stage limiting the accuracy of this method is acids extraction. The completeness of acids extraction into reagent (I) was assessed empirically for a number of oils by comparison of AV determination results obtained by the new pH-metric and those obtained by the standard titration methods. Since the results were found to be close (> 99 %), the extraction completeness was proved high. However, this empirically reached conclusion is relevant for the examined oils only.

The task of the present work is the theoretical and experimental study of the completeness of free fatty acids extraction from vegetable oils into water-containing reagent (I), with the purpose of expanding the possibilities of the pH-metric method for AV determination without titration.

\* Dedicated to professor Yu. A. Zolotov on occasion of his 70<sup>th</sup> birthday.

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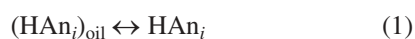
TABLE I. The main free fatty acids in vegetable oils (w/%, to total free fatty acids)

Acids	Oils		
	Canola <sup>(a)</sup>	Corn <sup>(b)</sup>	Soya <sup>(a)</sup>
Palmitic CH <sub>3</sub> (CH <sub>2</sub> ) <sub>14</sub> COOH	5.7	10.2	10.8
Stearic CH <sub>3</sub> (CH <sub>2</sub> ) <sub>16</sub> COOH	2.1	3.0	3.2
Oleic CH <sub>3</sub> (CH <sub>2</sub> ) <sub>7</sub> CH=CH(CH <sub>2</sub> ) <sub>7</sub> COOH	57.7	49.6	24.0
Linoleic CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> CH=CHCH <sub>2</sub> CH=CH(CH <sub>2</sub> ) <sub>7</sub> COOH	24.6	34.3	54.4
Linolenic CH <sub>3</sub> CH <sub>2</sub> CH=CHCH <sub>2</sub> CH=CHCH <sub>2</sub> CH=CH(CH <sub>2</sub> ) <sub>7</sub> COOH	7.9	–	6.8

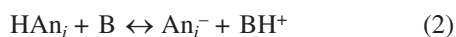
(a) Ref. 6., (b) Ref. 7.

## THEORETICAL

Extraction of free fatty acids (HAn<sub>*i*</sub>; *i* = 1, ..., *n*) from oil into reagent (I):



is stimulated by their reactions with triethanolamine (B) contained in this reagent:



For the extraction study, reagent (I) without B was used. This reagent is designated further as (II).

It is important, that the values of ionic strength of reagents (I) and (II) are close (*I* = 0.02) and remain practically constant even with small additions of acids or bases. All concentration equilibrium constants in the molar scale have the same values for both reagents (I) and (II) at the given temperature (25 °C).

Completeness of free fatty acids extraction in the form of the triethanolammonium salts is

$$\eta = \frac{[\text{BH}^+] \cdot V_r \cdot 56.11 \cdot 100}{AV \cdot m} / \%, \quad (3)$$

where [BH<sup>+</sup>] is equilibrium BH<sup>+</sup> concentration in reagent (I); *V<sub>r</sub>*/cm<sup>3</sup> is the volume of the reagent (I) interacted with an oil test portion; 56.11 is the molecular (formula) weight of KOH; *m*/g is the mass of the oil test portion.

Concentration [BH<sup>+</sup>] depends on equilibrium (2):

$$[\text{BH}^+] = \Sigma [\text{An}_i^-] = C_B - [\text{B}], \quad (4)$$

where *C<sub>B</sub>* is the triethanolamine analytical (initial) concentration, [B] is the equilibrium (residual) concentration of triethanolamine. To assess the [BH<sup>+</sup>] value and, hence, the *η* value, the following constants should be defined:

(i) the equilibrium constants of reaction (1)

$$K_i' = \frac{[\text{HAn}_i]}{[\text{HAn}_i]_{\text{oil}}}; \quad (5)$$

(ii) the equilibrium constants of reaction (2)

$$K_i'' = \frac{[\text{An}_i^-] \cdot [\text{BH}^+]}{[\text{HAn}_i] \cdot [\text{B}]} = \frac{K_{\text{HAn}_i}}{K_{\text{BH}^+}}; \quad (6)$$

(iii) the HAn<sub>*i*</sub> acid dissociation constants

$$K_{\text{HAn}_i} = \frac{[\text{H}^+] \cdot [\text{An}_i^-]}{[\text{HAn}_i]}; \quad (7)$$

(iv) and the BH<sup>+</sup> acid dissociation constant

$$K_{\text{BH}^+} = \frac{[\text{H}^+] \cdot [\text{B}]}{[\text{BH}^+]}. \quad (8)$$

Free fatty acids in vegetable oils have similar structures. Unsaturated bonds in these structures are separated from –COOH (acid group) by a large saturated carbon bridge –(CH<sub>2</sub>)<sub>*n*</sub>– (Table I). Therefore all *K<sub>i</sub>'* and all *K<sub>HAn<sub>i</sub>'</sub>*, respectively, are close (see Refs. 8, 9 and the experimental data below). Hence, Eqs. (5)–(7) for different acids can be summated into the following ones:

$$K_1 = \frac{\Sigma[\text{HAn}_i]}{\Sigma[\text{HAn}_i]_{\text{oil}}} = \frac{\Sigma C_{\text{HAn}_i} - \Sigma[\text{An}_i^-]}{\Sigma[\text{HAn}_i]_{\text{oil}}} \approx K_i', \quad (9)$$

where *ΣC<sub>HAn<sub>i</sub></sub>*

 is the total equilibrium concentration of the acids in reagent (II),

$$K_2 = \frac{(\Sigma[\text{An}_i^-]) \cdot [\text{BH}^+]}{(\Sigma[\text{HAn}_i]) \cdot [\text{B}]} = \frac{K_{\text{HAn}}}{K_{\text{BH}^+}} \approx K_i'' \quad (10)$$

$$K_{\text{HAn}} = \frac{[\text{H}^+] \cdot (\Sigma[\text{An}_i^-])}{\Sigma[\text{HAn}_i]} \approx K_{\text{HAn}_i} \quad (11)$$

For reagent (II), Eq. (11) has the following forms:

$$K_{\text{HAN}} = \frac{[\text{H}^+]^2}{\Sigma C_{\text{HAN}_i} - [\text{H}^+]} \approx K_{\text{HAN}_i} \quad (12)$$

or

$$K_{\text{HAN}} = \frac{\Sigma [\text{AN}_i^-]^2}{\Sigma C_{\text{HAN}_i} - \Sigma [\text{AN}_i^-]} \approx K_{\text{HAN}_i} \quad (13)$$

The material balance in oil-reagent (I) system can be described by the following equation:

$$\frac{\text{AV} \cdot m \cdot 10^{-3}}{56.11} = \frac{\Sigma [\text{HAN}_i]_{\text{oil}} \cdot m}{10^3 d} + \frac{\Sigma [\text{HAN}_i] \cdot V_r}{10^3} + \frac{\Sigma [\text{AN}_i^-] \cdot V_r}{10^3}, \quad (14)$$

where  $d$  is the oil density. Using Eqs. (3), (4), (9)–(11), the material balance expression (14) is transformed into the following one:

$$\left\{ \frac{1}{d \cdot K_1} + \frac{V_r}{m} - \frac{K_2 \cdot V_r}{m} \right\} \eta^2 + \left\{ \frac{\text{AV} \cdot m}{56.11} + V_r \cdot C_B \right\} \left\{ \frac{K_2 \cdot V_r \cdot 56.11 \cdot 100}{\text{AV} \cdot m^2} \right\} \cdot \eta - \left\{ \frac{K_2 \cdot C_B \cdot V_r^2 \cdot 56.11 \cdot 10^4}{\text{AV} \cdot m^2} \right\} = 0. \quad (15)$$

Thus, to determine the  $\eta$  value,  $K_1$  and  $K_2$  constants should be evaluated. For this purpose,  $K_{\text{HAN}}$  is assessed by Eq. (12) for several individual acids. Then  $K_1$  is calculated by Eq. (9) with the concentration  $\Sigma [\text{AN}_i^-]$  calculated from Eq. (13). For  $K_2$  calculation by Eq. (10), the  $K_{\text{BH}^+}$  values should be also assessed. They are calculated using the ionic production of the solvent in reagents (I) and (II):

$$K_s = [\text{H}^+] \cdot [\text{OH}^-] = K_B \cdot K_{\text{BH}^+}, \quad (16)$$

where  $K_B$  is the triethanolamine basic dissociation constant. At  $[\text{OH}^-] = [\text{BH}^+]$  the constant is

$$K_B = \frac{[\text{OH}^-]^2}{C_B - [\text{OH}^-]}. \quad (17)$$

The  $[\text{H}^+]$  and  $[\text{OH}^-]$  values are obtained from conditional pH ( $\text{pH}'$ ) measurements. The pH values are conditional here<sup>1</sup> since a glass electrode is calibrated in aqueous buffer solutions and then is used together with an aqueous reference electrode in the mixed (water-isopropanol) solvent of reagents (I) and (II). At the constant temperature and the ionic strength of the supporting electrolyte

(0.02 mol dm<sup>-3</sup> KNO<sub>3</sub>;  $[\text{H}^+] \ll 0.02$  mol dm<sup>-3</sup> and  $[\text{OH}^-] \ll 0.02$  mol dm<sup>-3</sup>), the conditional pH is:

$$\text{pH}' = A_H - \log [\text{H}^+]. \quad (18)$$

$A_H$  value depends on: (i) the difference between standard potentials of the glass electrode in water and in the mixed solvent; (ii) the difference between liquid junction potentials on boundaries of the aqueous reference electrode with water and of the same electrode with mixed solvent; and (iii) on the activity coefficient of H<sup>+</sup> ions in the mixed solvent.<sup>1,4</sup> At constant temperature and ionic strength all listed parameters (i)–(iii) are also constant, and hence  $A_H = \text{const.}$

Taking into account Eqs. (16) and (18) one can obtain

$$\text{pH}' = A_{\text{OH}} + \log [\text{OH}^-], \quad (19)$$

where  $A_{\text{OH}}$  is a constant also:

$$\log K_s = A_H - A_{\text{OH}}. \quad (20)$$

For  $A_H$  and  $A_{\text{OH}}$  determination, additions of HCl or KOH, respectively, into reagent (II) were made.

Thus, all the information necessary for calculation of  $\eta$  is accumulated by the procedure described.

## EXPERIMENTAL

### Apparatus

A pH/ion-meter PHM 95 (Radiometer, France, accuracy  $\pm 0.01$  pH) was used for pH measurements with a glass pH indicator electrode PHG 201 (Radiometer, France) and an aqueous Ag/AgCl 3 M KCl, 3 M KNO<sub>3</sub> reference electrode 6.0726.100 (Metrohm, Switzerland). A 2 mL micro-burette (Bein Z.M., Israel) with 0.01 mL divisions and drop size reduced to 0.008 mL was used for titrations.

### Reagents

Triethanolamine, potassium nitrate, potassium chloride, sulfuric acid, hydrochloric acid, potassium hydroxide, palmitic and oleic acids were purchased from Merck (Germany), isopropanol (2-PrOH) and diethyl ether from Frutarom (Israel), standard buffers and phenolphthalein from BDH (England). Vegetable oils for the analyses were purchased from local suppliers.

## RESULTS AND DISCUSSION

### Determination of Basic and Acid Dissociation Constants of Triethanolamine

The basic and acid dissociation constants of triethanolamine ( $K_B$  and  $K_{\text{BH}^+}$ , respectively) in reagents (I) and (II) were determined by the pH-metric method. For this pur-

TABLE II. Dependence of pH' on C<sub>HCl</sub> in reagent (II) + HCl, and the A<sub>H</sub> data at 25 °C

$\frac{C_{\text{HCl}} \times 10^5}{\text{mol dm}^{-3}}$	-log [H <sup>+</sup> ]	Replicates					
		1		2		3	
		pH'	A <sub>H</sub>	pH'	A <sub>H</sub>	pH'	A <sub>H</sub>
0.50	5.30	5.92	0.62	5.97	0.67	5.92	0.62
1.00	5.00	5.62	0.62	5.67	0.67	5.63	0.63
1.99	4.70	5.31	0.61	5.36	0.66	5.33	0.63
3.97	4.40	5.00	0.60	5.05	0.65	5.02	0.62

pose, the [H<sup>+</sup>] values were calculated by Eq. (16) using the pH' values and the average A<sub>H</sub> = 0.63 ± 0.02 (Table II). The [OH<sup>-</sup>] values were evaluated by Eq. (18), also using the pH' values and the average A<sub>OH</sub> = 15.44 ± 0.01 (Table III). From A<sub>H</sub> and A<sub>OH</sub> values obtained and Eq. (20), pK<sub>s</sub> = 14.81 ± 0.02 was calculated. Based on the Debye-Hückel limiting law,<sup>10</sup> the activity coefficients  $f_{\text{H}^+} = f_{\text{OH}^-} = 0.697$  were calculated at ionic strength  $I = 0.02$ ,  $T = 298$  K and relative permittivity for the studied solvent  $\epsilon = 46.8$ .<sup>11</sup> Hence, the thermodynamic value of K<sub>s</sub>, *i.e.* pK<sub>s</sub><sup>0</sup> = 15.12 was calculated. This value is close to pK<sub>s</sub><sup>0</sup> = 15.08 obtained in Ref. 12 by another technique. It should be noted also, that the value A<sub>OH</sub> = 15.46 in reagent (I), reported in Ref. 2, is close to the A<sub>OH</sub> values obtained in reagent (II) (Table III), *i.e.* the influence of the uncharged particles B on A<sub>OH</sub> is negligible.

To determine K<sub>B</sub> value, the data of [BH<sup>+</sup>] titration in reagent (I)<sup>1</sup> were applied. The initial BH<sup>+</sup> concentration was evaluated by a small HCl addition ( $C_{\text{HCl}} \ll C_{\text{B}}$ ). As a titrant KOH in reagent (I) was used. At the equivalence point of this titration [BH<sup>+</sup>] is equal to [OH<sup>-</sup>]. Since at this point pH' = 11.30 ± 0.02, (found from the differential titration curve), pK<sub>B</sub> = 7.58 ± 0.04 according to Eqs. (17) and (19).

Using the K<sub>B</sub> and K<sub>s</sub> values, pK<sub>BH<sup>+</sup></sub> = 7.23 ± 0.05 at 25 °C was obtained by Eq. (16).

#### Determination of Fatty Acids Dissociation Constants

The dissociation constants of palmitic acid (as an example of saturated acids) and oleic acid (as an example of unsaturated acids) were determined in reagent (II) by the pH-metric method. From the pH' values (Table IV) and the A<sub>H</sub> value, the [H<sup>+</sup>] values were obtained. Afterwards the K<sub>HAN</sub> values were calculated using Eq. (12), in which  $\Sigma C_{\text{HAN}_i}$  was replaced by C<sub>HAN</sub> for each individual acid in reagent (II) (Table IV).

As one can see from Table IV, K<sub>HAN</sub> values for palmitic and oleic acids are close. This closeness is supported also by the data<sup>8,9</sup> for high molecular fatty acids in the H<sub>2</sub>O + EtOH solvent. For further calculations, the average pK<sub>HAN</sub> = 5.95 ± 0.04 at higher acid concentration (1 · 10<sup>-3</sup> mol dm<sup>-3</sup>, Table IV) was used for both acids as a more reliable value.

TABLE III. Dependence of pH' on C<sub>KOH</sub> in reagent (II) + KOH, and the A<sub>OH</sub> data at 25 °C

$\frac{C_{\text{KOH}} \times 10^5}{\text{mol dm}^{-3}}$	-log [OH <sup>-</sup> ]	Replicates					
		1		2		3	
		pH'	A <sub>OH</sub>	pH'	A <sub>OH</sub>	pH'	A <sub>OH</sub>
39.8	3.40	12.05	15.45	12.02	15.42	12.03	15.43
79.4	3.10	12.36	15.46	12.33	15.43	12.33	15.43
158	2.80	12.65	15.45	12.62	15.42	12.64	15.44
310	2.51	12.96	15.47	12.93	15.44	12.93	15.44

TABLE IV. Data for determination of dissociation constants of free fatty acids in reagent (II) at 25 °C

Palmitic acid			Oleic acid		
$\frac{C_{\text{HAN}} \times 10^5}{\text{mol dm}^{-3}}$	pH'	pK <sub>HAN</sub>	$\frac{C_{\text{HAN}} \times 10^5}{\text{mol dm}^{-3}}$	pH'	pK <sub>HAN</sub>
9.54	5.63	5.93	9.91	5.68	6.06
104	5.11	5.96	108	5.09	5.94

#### Determination of the Equilibrium Constant of Reaction (1)

The following procedure was used to obtain the equilibrium constant of reaction (1) K<sub>1</sub>. The exact weight of an oil test portion ( $m \approx 50$  g, Table V) and 50 mL of reagent (II) were put into a separatory funnel and shaken over 2–3 hours to achieve an equilibrium distribution of acids HAN<sub>i</sub> in the oil-reagent (II) system. After separation of the phases, 25 mL of reagent (II) phase were put into a flask for titration. Isopropanol ~ 25 mL was added and the acids were titrated against KOH with the phenolphthalein indicator to determine the total concentration  $\Sigma C_{\text{HAN}_i}$  of acids extracted in reagent (II) at equilibrium (Table V).

The total concentration of acids in oils at equilibrium ( $\Sigma[\text{HAN}_i]_{\text{oil}}$ ) shown in Table V were calculated from AV values, density values of oils and C<sub>HAN</sub> values. The AV values were obtained by the standard titration.<sup>13</sup> The density values were found by the gravimetric method.

K<sub>1</sub> was calculated by Eq. (9) using  $\Sigma[\text{HAN}_i]_{\text{oil}}$ , C<sub>HAN</sub> and  $\Sigma[\text{AN}_i^-]$ . The latter was found from K<sub>HAN</sub> value and Eq. (13). As one can see from Table V, the K<sub>1</sub> values are close for different oils with different contents of free fatty acids shown in Table I. The average value is K<sub>1</sub> = 0.14 ± 0.01.

Unlike slow acids extraction from an oil test portion into reagent (II), both equilibrium (1) and (2) in reagent (I) are achieved rapidly (2–3 min) due to the acids' reaction with triethanolamine. The latter is highly important for AV determination by the pH-metric method.<sup>1–3</sup>

TABLE V. Data for determination of the equilibrium constant of reaction (1) at 25 °C

Oil $d$ g cm <sup>-3</sup>	Replicates	$m$ / g	AV <sup>(a)</sup>	$(\Sigma[\text{HAn}_i])_{\text{oil}}$ mol dm <sup>-3</sup>	$\Sigma C_{\text{HAn}_i}$ mol dm <sup>-3</sup>	$\Sigma[\text{An}_i^-]$ mol dm <sup>-3</sup>	$K_1$
Canola 0.904	1	53.12	0.049	$6.90 \cdot 10^{-4}$	$1.17 \cdot 10^{-4}$	$1.09 \cdot 10^{-5}$	0.15
	2	50.37	0.049	$6.96 \cdot 10^{-4}$	$1.09 \cdot 10^{-4}$	$1.05 \cdot 10^{-5}$	0.14
	3	49.67	0.048	$6.89 \cdot 10^{-4}$	$1.05 \cdot 10^{-4}$	$1.09 \cdot 10^{-5}$	0.14
Corn 0.901	1	49.19	0.24	$3.40 \cdot 10^{-3}$	$4.85 \cdot 10^{-4}$	$2.28 \cdot 10^{-5}$	0.14
	2	49.33	0.24	$3.48 \cdot 10^{-3}$	$4.93 \cdot 10^{-4}$	$2.29 \cdot 10^{-5}$	0.14
	3	49.53	0.23	$3.33 \cdot 10^{-3}$	$4.77 \cdot 10^{-4}$	$2.26 \cdot 10^{-5}$	0.14
Soya 0.902	1	48.39	0.66	$9.40 \cdot 10^{-3}$	$1.30 \cdot 10^{-3}$	$3.82 \cdot 10^{-5}$	0.13
	2	50.01	0.67	$9.52 \cdot 10^{-3}$	$1.38 \cdot 10^{-3}$	$3.93 \cdot 10^{-5}$	0.14
	3	50.15	0.67	$9.60 \cdot 10^{-3}$	$1.34 \cdot 10^{-3}$	$3.82 \cdot 10^{-5}$	0.14

<sup>(a)</sup> The quantity of KOH (mg) needed to neutralize free fatty acids contained in 1 g of oil.

TABLE VI. Completeness of acids extraction at 25 °C

AV <sup>(a)</sup>	0.02	0.1	0.1	1.0	1.0	4.0	4.0	15
$m$ / g	40	40	12	12	3	3	0.6	0.6
$\eta$ / %	100.0	99.7	100.0	99.6	100.0	99.9	100.0	99.9

<sup>(a)</sup> See footnote to Table V.

#### Determination of the Equilibrium Constant of Reaction (2)

Using  $K_{\text{HAN}} = 1.12 \times 10^{-6}$  and  $K_{\text{BH}^+} = 5.89 \times 10^{-8}$ , the equilibrium constant of reaction (2) was calculated by Eq. (10):  $K_2 = 19.0 \pm 1.2$  at 25 °C.

#### Calculation of the Completeness of Acids Extraction

To determine the completeness of acids extraction from the oils into reagent (I) by Eq. (15), the following values were used: AV and  $m$  from Table VI,  $V_r = 50 \text{ cm}^3$ ,  $d = 0.90 \text{ g cm}^{-3}$  (Table V),  $C_B = 0.2 \text{ mol dm}^{-3}$ ,  $K_1 = 0.14$  and  $K_2 = 19.0$ . The initial concentration of triethanolamine in reagent (I)  $C_B = 0.2 \text{ mol dm}^{-3}$  was used for the calculation, since triethanolamine extraction from reagent (I) into oil is negligible.

Results of  $\eta$  calculations, found to be practically the same for canola, corn and soya at the optimal masses of the test portions,<sup>3</sup> are presented in Table VI. Since  $\eta \geq 99.6 \%$ , a complete extraction of free fatty acids from oils into reagent (I) in the form of triethanolammonium salts takes place for a wide range of acid values and masses of an oil test portion. It explains the satisfactory metrological parameters of the developed pH-metric method<sup>1-3</sup> for acid value determination in vegetable oils without titration. The proposed methodology for the evaluation of the completeness of extraction allows one

to choose the optimum conditions for acid value determination in other oils by other methods such as pH-metry,<sup>1-3</sup> voltammetry,<sup>14</sup> and titration.<sup>15</sup>

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**SAŽETAK****Ekstrakcija kiselina iz biljnih ulja za određivanje njihovih  
pH-metrijskih vrijednosti bez titriranja****Elena Kardash-Strochkova, Yakov I. Tur'yan, Avi Shenhar i Ilya Kuselman**

Provedena je teorijska i eksperimentalna analiza slobodnih masnih kiselina ekstrahiranih iz biljnih ulja u reagens koji sadrži trietanolamin za određivanje kiselinskih pH-metrijskih vrijednosti bez titriranja. Demonstrirana je praktički potpuna ekstrakcija masnih kiselina u obliku trietanolamonijevih soli. Dobiveni rezultati ukazuju na mogućnost šire primjene prikazane pH-metrijske metode i njoj srodnih metoda.