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LETTER TO THE EDITOR

pH-Metric Determination of Free Fatty Acids in Oils and Fats During Frying in the Absence of a Chemical Laboratory

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Sir:

Numerous small food businesses, i.e., restaurants, snack producers etc, that use oils and fats for frying do not have chemical laboratories available for controlling free fatty acids (FFA) in oils and fats by means of the standard titration methods [1, 2]. At the same time, FFA content is one of the major parameters for the regulation of frying oils and fats [3]. Any excess FFA above the permissible FFA content would make the products unacceptable to the consumers (Table 1, where %FFA as %oleic acid) [3].

The most suitable methods for FFA determination in oils and fats during frying in the absence of a chemical laboratory is the pH-metric method [4]. The main goal of this work is to simplify and speed up the pH-metric method on the basis of the experimental data [4]. The magnetic stirrer, reagent package and pH-metric cell were the same as in [4].

The pH-metric method [4] is based on a rapid and complete extraction of FFA from an oil or fat test sample into the reagent: 0.2 M triethanolamine + 0.02 M KNO_3 in 50% H_2O + 50% i-PrOH (%V). Theoretically and experimentally it was shown [4], that:

$$\mathrm{pH} = A - \log N_a, \quad (1)$$

where: N_a is the FFA concentration (mol/L) in the reagent and A is the constant value for the given reagent and temperature ($A = 7.322$ at 20 ± 2 °C). On the basis of Eq. 1 we have developed Table 2 (%FFA as %of oleic acid, MW = 282.5) for 20 ± 2 °C, the reagent volume of 50 mL, the test sample volume of 5 mL, the density of oils and fats of 0.910 ± 0.008 g/cm^3 [5–7] at 20 °C (for liquid samples at room temperature) and at 45 °C (for semi-liquid and solid samples at room temperature). Upon mixing 50 mL reagent (20 °C) and 5 mL test sample (45 °C), the final temperature of the system equals 24 °C [5–7] i.e., close to room temperature. Thus, using of Table 2 eliminates the weighing of the sample [4] that is important in the absence of chemical laboratory.

The proposed pH-metric method possesses high accuracy, repeatability, reproducibility and sensitivity. For all FFA, percentage range (Table 2) values of the replicate relative standard deviation during the day (RSD_1, number of replicates equals 4) and values of the daily relative standard deviation (RSD_2, between 5 days) were determined. The values found for RSD_1 and RSD_2 satisfy Horwits's criterion [RSD_1 and RSD_2 were between (1.4–4.72)% and (0.76–4.20)%, respectively]. Therefore, repeatability and reproducibility are satisfactory. The limit of quantitation was found to equal 0.01% confirming high sensitivity of the method [8]. The recoveries found are satisfactory to requirements of the AOAC Peer-Verified Methods Program. Differences between results obtained by

Table 1 Permissible FFA content for controlling regulation of oils and fats used in frying

Country	%FFA
Germany	≤1.0
Austria	≤1.2
Finland	≤1.2
Japan	≤1.2
USA	≤2.0
Netherlands	≤2.2
Belgium	≤2.5

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Table 2 Dependence "pH versus %FFA" at room temperature (20 ± 2 °C)

pH	%FFA	pH	%FFA	pH	%FFA	pH	%FFA	pH	%FFA	pH	%FFA	pH	%FFA	pH	%FFA
9.22	3.93	9.40	2.59	9.58	1.71	9.76	1.13	9.94	0.75	10.12	0.49	10.30	0.33	10.48	0.22
9.23	3.84	9.41	2.54	9.59	1.67	9.77	1.11	9.95	0.73	10.13	0.48	10.31	0.32	10.49	0.21
9.24	3.74	9.42	2.48	9.60	1.64	9.78	1.08	9.96	0.71	10.14	0.47	10.32	0.31	10.50	0.21
9.25	3.66	9.43	2.42	9.61	1.60	9.79	1.06	9.97	0.70	10.15	0.46	10.33	0.30	10.51	0.20
9.26	3.58	9.44	2.37	9.62	1.56	9.80	1.03	9.98	0.68	10.16	0.45	10.34	0.30	10.52	0.20
9.27	3.50	9.45	2.31	9.63	1.53	9.81	1.01	9.99	0.67	10.17	0.44	10.35	0.29	10.53	0.19
9.28	3.42	9.46	2.26	9.64	1.49	9.82	0.99	10.00	0.65	10.18	0.43	10.36	0.28	10.54	0.19
9.29	3.34	9.47	2.21	9.65	1.46	9.83	0.96	10.01	0.64	10.19	0.42	10.37	0.28	10.55	0.18
9.30	3.26	9.48	2.16	9.66	1.42	9.84	0.94	10.02	0.62	10.20	0.41	10.38	0.27	10.56	0.18
9.31	3.19	9.49	2.11	9.67	1.39	9.85	0.92	10.03	0.61	10.21	0.40	10.39	0.26	10.57	0.18
9.32	3.18	9.50	2.06	9.68	1.36	9.86	0.90	10.04	0.59	10.22	0.39	10.40	0.26	10.58	0.17
9.33	3.05	9.51	2.01	9.69	1.33	9.87	0.88	10.05	0.58	10.23	0.38	10.41	0.25	10.59	0.17
9.34	2.98	9.52	1.97	9.70	1.30	9.88	0.86	10.06	0.57	10.24	0.38	10.42	0.25	10.60	0.16
9.35	2.91	9.53	1.93	9.71	1.27	9.89	0.84	10.07	0.55	10.25	0.37	10.43	0.24	10.61	0.16
9.36	2.84	9.54	1.88	9.72	1.24	9.90	0.82	10.08	0.54	10.26	0.36	10.44	0.24	10.62	0.16
9.37	2.78	9.55	1.84	9.73	1.21	9.91	0.80	10.09	0.53	10.27	0.35	10.45	0.23	10.63	0.15
9.38	2.72	9.56	1.79	9.74	1.19	9.92	0.78	10.10	0.52	10.28	0.34	10.46	0.23		
9.39	2.65	9.57	1.75	9.75	1.16	9.93	0.76	10.11	0.51	10.29	0.33	10.47	0.22		

Underlined numbers allow one to assign values to every 0.1 pH for simplication of the table use

the standard titration method and by the pH-metric method are insignificant, and method accuracy is satisfactory.

Analysis of oils and fats that are liquid at room temperature (20 ± 2 °C) is carried out at room temperature; 50 mL of the reagent from the disposable package kept at room temperature are put into the pH-metric cell. A magnetic stirrer is turned on; 5 mL of the test sample is added with the pipette to the reagent. The pH value is measured after approximately 3 min, and the %FFA is found using Table 2. The test takes approximately 5 min.

For oils and fats that are semi-liquid or solid at room temperature, the test samples are melted by heating up to 45 ± 2 °C. Afterwards, 5 mL of the test sample is added to 50 mL of the reagent in the pH-metric cell at room temperature (20 ± 2 °C). Slight cooling down to 20 ± 2 °C of the reagent-test sample mixture is carried out, either by water from the water pipe connected to the cell shirt, or by adding not more than half of tea spoon of crumbled ice into the mixture. After approximately 5 min, pH is measured, and %FFA is found using Table 2. The test takes approximately 10 min.

Thus, the developed modification of pH-metric method allows it to be used for FFA determination in oils and fats during frying in the absence of a chemical laboratory.

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