

Thermo. Titr. Application Note No. H-072

Title: Determination of Low Levels of Free Fatty Acids in Edible Fats and Oils

Scope: Determination of Free Fatty Acid (FFA) values in edible fats and oils to levels below 0.1mg KOH/g sample, or 0.05% w/w oleic acid equivalent.

Principle: Dissolve oil sample in mixture of toluene and 2-propanol, add paraformaldehyde and titrate with 0.1M KOH in 2-propanol. The endpoint is indicated by an endothermic response caused by the base-catalyzed de-polymerization of paraformaldehyde.

Reference:

1. M. J. D. Carneiro, M. A. Feres Júnior, and O. E. S. Godinho. Determination of the acidity of oils using paraformaldehyde as a thermometric end-point indicator. *J. Braz. Chem. Soc.* **13** (5) 692-694 (2002)

Reagents: 0.01 mol/L KOH in 2-propanol. Prepare by 1:10 dilution of standardized 0.1 mol/L KOH in 2-propanol with 2-propanol. Protect the titrant from atmospheric CO₂ contamination with a soda-lime guard tube on the Dosino.

Paraformaldehyde (eg, Sigma-Aldrich cat. no. 158127)

75% A.R. toluene:25% A.R. 2-propanol

Method: Basic Experimental Parameters:

Titration delivery rate (mL/min.) 10

No. of exothermic endpoints 1

Data smoothing factor 75

Stirring speed (802 stirrer) 15

Delay before start (secs.) 30

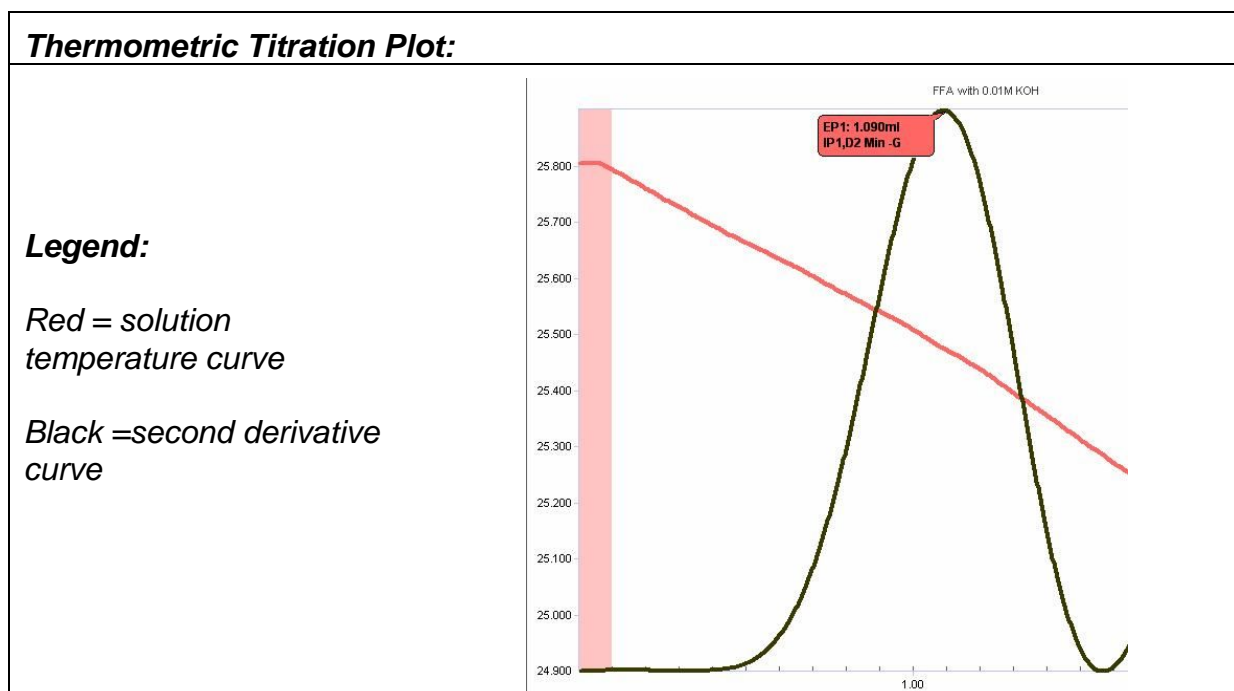
Weigh accurately approximately 5 g of warm melted fat or oil in a clean dry 150mL titration beaker. Add 30mL of toluene/2-propanol mixture. Add ~0.5-0.6g paraformaldehyde (a level metric 1/8th kitchen teaspoon measure is ~0.5g). Titrate to an inflection characterized by a reduction in the rate of temperature increase or decrease.

Results: (results expressed as commonly used fatty acids and as TAN)

All samples were solid fats, melted in a microwave oven immediately before weighing.	Sample no.	% w/w oleic acid	% w/w palmitic acid	% w/w lauric acid	mg KOH/g sample (TAN)
	1 (n=7)	0.062 ± 0.0014	0.057 ± 0.0013	0.044 ± 0.0010	0.124 ± 0.0028
	2 (n=6)	0.040 ± 0.0010	0.036 ± 0.0009	0.028 ± 0.0007	0.079 ± 0.0020
	4 (n=7)	0.042 ± 0.0013	0.038 ± 0.0012	0.029 ± 0.0009	0.083 ± 0.0026
	5 (n=7)	0.038 ± 0.0006	0.035 ± 0.0006	0.027 ± 0.0005	0.076 ± 0.0013

Calculations:

$$\% FFA = \frac{((mL \text{ titre} - mL \text{ blank}) \times M \text{ KOH} \times FW \text{ acid} \times 100)}{(sample \text{ mass}, g \times 1000)}$$

$$TAN = \frac{(mL \text{ titre} - mL \text{ blank}) \times M \text{ KOH} \times FW \text{ KOH}}{(sample \text{ mass}, g)}$$


Blank determination:

The blank value to be subtracted from the endpoint volume is determined by titrating a range of masses (say between 2 and 7g) of a sample with a typically low level FFA content. The blank value is obtained from regression analysis of the data as the y-intercept value. The relatively large blank value is due to the weak titrant, and the need for a small but finite amount of base to trigger the endothermic depolymerization of the paraformaldehyde indicator.

