

## Thermo. Titr. Application Note No. H-073

**Title:** Determination of Total Acid Number in Biodiesel

**Scope:** Determination of Total Acid Number (TAN) values in biodiesel to <0.05 mg KOH/g sample.

**Principle:** Dissolve biodiesel sample in 2-propanol, add paraformaldehyde catalyst and titrate with 0.01M 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 CO<sub>2</sub> contamination with a soda-lime guard tube on the Dosino.

Paraformaldehyde (eg, Sigma-Aldrich cat. no. 158127)  
2-propanol, A.R.

**Method:** Basic Experimental Parameters:

Titration delivery rate (mL/min.)	5
No. of exothermic endpoints	1
Data smoothing factor	55
Stirring speed (802 stirrer)	15
Delay before start (secs.)	10

Weigh accurately approximately 5 – 10mL biodiesel in a clean dry 150mL titration beaker. Add 30mL of 2-propanol mixture. Add ~0.5-0.6g paraformaldehyde (*a level metric 1/8<sup>th</sup> kitchen teaspoon measure is ~0.5g*). Titrate to an inflection characterized by a reduction in the rate of temperature increase or decrease.

**Results:**

<p>Samples of biodiesel from company "A" were made from used cooking oil and tallow; biodiesel from company "B" was produced from palm oil</p>	Sample	mg KOH/g sample
	A – batch 62 06-04-08	0.064±0.0009 (n=5)
	A – batch 72 13-05-08	0.062±0.0005 (n=5)
	A – batch 74 03-06-08	0.073±0.0013 (n=5)
	B - 23-04-08	0.421±0.0045 (n=5)

**Calculations:**

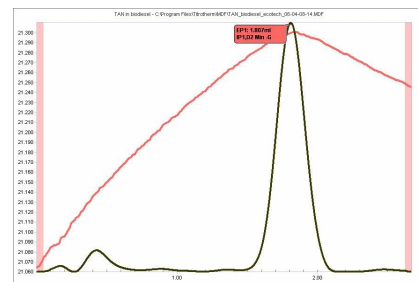
$$TAN = \frac{(mL\ titre - mL\ blank) \times M\ KOH \times FW\ KOH}{(sample\ mass,\ g)}$$

**Thermometric Titration Plots:**

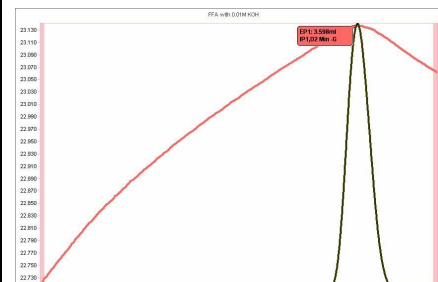
**Legend:**

Red = solution temperature curve

Black = second derivative curve



Biodiesel company "A"



Biodiesel company "B"

**Blank determination:**

The blank value to be subtracted from the endpoint volume is determined by titrating a range of masses (say between 4 and 12g) of a sample with a typically low level TAN 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.

