Determination of low-level total acid number in mineral oils and biodiesel and low-level free fatty acid content in edible fats and oils

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Titration

Introduction

The reduction of the greenhouse gas emissions and the assessment of renewable energy sources are among mankind`s most urgent challenges. In this context biodiesel is a promising renewable energy source. In a so-called trans-esterification reaction that is catalyzed by a base, acid or enzyme, biodiesel is produced by chemically reacting a vegetable oil or fat with methanol to yield fatty acid methyl esters. Depending on production and storage conditions, biodiesel can contain small amounts of detrimental free fatty acids (FFA) that cause corrosion and deposits in the engine. The FFA content, defined as the percent by mass of oleic acid in the sample, and the total acid number (TAN), expressed in mg KOH required to neutralize 1 g of FAME, are used as reliable monitoring tools. Both determinations are non-aqueous acid-base titrations using a strong base dissolved in alcohol. Endpoint recognition, unlike that applied in EN 14104 and ASTM D 664, is performed thermometrically using a very sensitive temperature sensor.

By means of a straightforward thermometric titration procedure using a catalytically enhanced indication reaction, several solid palm oil and biodiesel samples are analyzed in terms of FFA content and TAN, respectively.

Drawbacks of current titration procedures

a) Manual titration with phenolphthalein indicator according to EN 14104

- Slow
- Endpoint can be difficult to detect, especially with colored solutions and using weak titrants

b) Potentiometric titration according to ASTM D 664

- Non-aqueous environment – glass membrane becomes rapidly dehydrated and therefore requires frequent regeneration
- Poor electrical conductivity of titrating medium can lead to imprecise endpoints, particularly with low FFA content or TAN

The solution

Thermometric titration with catalytically-indicated endpoint.

Thermometric titration

Each chemical reaction is associated with a change in enthalpy that causes a temperature change, which, when plotted versus volume of titrant, can be used to monitor the course of the reaction and thus to detect the titration endpoint. For a simple reaction this means that the increase (exothermic reaction) or reduction (endothermic reaction) in temperature depends on the amount of substance converted.

In a thermometric titration, reagent solution (titrant) is added to the sample at a constant rate until the endpoint is reached. The latter can be recognized by a break in the titration curve obtained by plotting the amount of titrant added to the sample versus the temperature. Since the temperature sensor has a response time of 0.3 s and a resolution of 10^{-5} K, even small enthalpy changes are reliably monitored.

How it's done

- Weigh sample and dissolve it in hydrocarbon/alcohol solvent mixture (e.g. toluene/2-propanol)
- Add catalytic indicator (paraformaldehyde)
- Carry out thermometric titration with 0.01 mol/L KOH in 2-propanol
- Endpoint indicated by reduction in solution temperature (first trace of excess hydroxyl ions catalyzes endothermic depolymerization of paraformaldehyde)

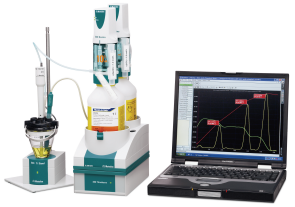
Advantages

- Fast – titrations take from approximately 10…60 seconds to complete
- Reliable – Thermoprobe always ready to go – stored dry, it never needs regenerating, never needs recalibrating
- Works with highly colored and turbid samples
- Carried out in normal titration vessels
- Can be automated with sample processor – automatic addition of solvent, programmed sample dissolution

What we used

a) Instrumentation

859 Titrotherm
800 Dosinos
804 Ti Stand and 802 Stirrer



b) Reagents

Titrant: 0.01 mol/L KOH in 2-propanol
Sample solvents: 3:1 toluene/2-propanol (for solid fats)
2-propanol (for biodiesel)
Paraformaldehyde 95%
Titer determination with: 0.01 mol/L AR benzoic acid in 2-propanol

c) Hardware

Metrohm 859 Titrotherm thermometric titration interface module
Metrohm 6.9011.020 Thermoprobe thermometric sensor
Metrohm 802 Stirrer with 804 Titration Stand
Metrohm 6.1415.220 titration vessel made of glass

d) Software:

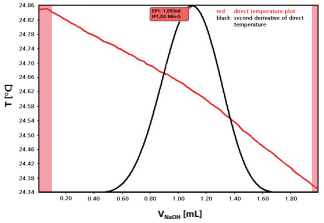
Metrohm Titrotherm software 2.0

Samples

Free fatty acids: solid palm oil products
Total acid number: biodiesel manufactured from mixed tallow and vegetable oil feedstocks

Analytical precision

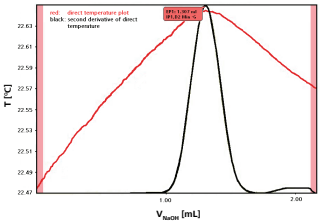
a) Free fatty acid content



Sample	Free fatty acid content [%]*	Number of determinations n
P-1	0.062 ± 0.001	7
P-2	0.040 ± 0.001	6
P-3	0.042 ± 0.001	7
P-4	0.038 ± 0.001	7

*(w/w) as oleic acid

b) TAN



Sample	Total acid number [mg KOH/g sample]	Number of determinations n
B-1	0.064 ± 0.001	5
B-2	0.062 ± 0.001	5
B-3	0.073 ± 0.001	5

*(w/w) as oleic acid

Summary

The determination of the total acid number (TAN) in mineral oils and the free fatty acid (FFA) content in edible fats and oils both involve the titration of weakly acidic species in non-aqueous media with a dilute solution of a strong base in alcohol as the titrant. A new thermometric titration procedure overcomes inherent problems with the current manual and potentiometric methods.

References

(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 endpoint indicator. J. Braz. Chem. Soc. **13** (5), 692-694 (2002).
(2) Metrohm Application Note AN-H-072, Determination of low levels of free fatty acids in edible oils and fats, http://products.metrohm.com (search for AN-H-072).
(3) S. Mahajan, S.K. Konar and D.G.B. Boocock, Determining the acid number of biodiesel, JAOCS, **83** (6), 567-570 (2006).

Download a copy of this poster from http://products.metrohm.com (search for 8.000.6050EN).

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