Determination of the total acid number (TAN) using thermometric titration

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Titration

Introduction

As manifested by numerous international standard procedures, the determination of the total acid number (TAN) is crucial for quality control in the oil industry. The TAN provides invaluable information regarding petroleum degradation (oil aging) and corrosion enhancement properties. It is commonly determined by a non-aqueous titration with strong bases and defined as mg of potassium hydroxide consumed in neutralizing weakly acidic substances per gram of mineral oil. The sample is dissolved in a nonaqueous solvent, often a mixture of a nonpolar hydrocarbon and an alcohol. The titrant, a strong base such as potassium hydroxide, is dissolved in an alcohol. In standard methods, endpoint detection is performed either manually using the color change of an indicator (e.g., ASTM D 974) or instrumentally using a pH electrode (e.g., ASTM D 664). Whereas manual methods suffer from the challenge of observing a faint, fading endpoint in a frequently highly colored solution, instrumental methods using a glass-membrane pH electrode suffer from the difficulty of working in a water-free environment.

A new thermometric titration procedure overcomes the above mentioned shortcomings. The procedure is very fast, robust, and reliable. The new method involves the titration of weakly acidic species in nonaqueous media with a solution of sodium hydroxide or tetrabutylammonium hydroxide (TBAH) in an alcohol mixture.

This work describes the determination of the TAN in petroleum products via thermometric titration using catalytically enhanced endpoint recognition with a very sensitive temperature sensor.

Drawbacks of ASTM D 664

- Glass membrane easily gets fouled resulting in decreasing performance
- Nonaqueous environment – glass membrane becomes rapidly dehydrated and therefore requires frequent regeneration
- Poor electrical conductivity of titrating medium can lead to imprecise end-points, particularly with low TAN

The solution

TAN determination using thermometric titration with catalytically-indicated endpoint recognition

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. The titrant is added to the sample at a constant rate until the endpoint is reached. The endpoint is recognized by the inflection of the titration curve.

The temperature sensor has a response time of 0.3 s and a resolution of 10^{-5} K: therefore, even smallest enthalpy changes can be monitored.

How it`s done

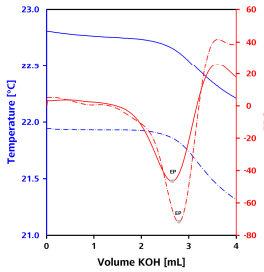
- Weigh sample and dissolve it in a suitable hydrocarbon/alcohol solvent mixture (e.g., toluene/isopropanol)
- Add paraformaldehyde as catalytic indicator
- Carry out thermometric titration with 0.1 mol/L KOH (or TBAH) in isopropanol
- The endpoint is indicated by a temperature drop and reflects the onset of the endothermic depolymerization of paraformaldehyde caused by the first trace of excess of hydroxyl ions (catalyzed endpoint thermometric titrimetry). The endpoint is identified by the second derivative.

Instrumentation

- 859 Titrotherm
- 815 Robotic Sample Processor XL
- 800 Dosinos
- 772 Pump Unit
- ***tiamo***™ 2.2

TAN reference standard

The verification standard «TAN030» from Paragon Scientific Ltd. (Birkenhead, UK) is used for validation of thermometric titration. The certified TAN is 2.93 mg KOH/g and was determined according to ASTM D 664 and IP 1777. The second derivative (red) of the volume-temperature curve (blue) yields the corresponding endpoint.



TAN [mg KOH/g]

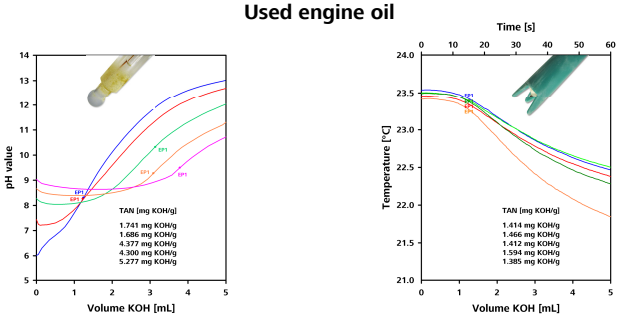
Thermometric titration:	**2.87**
Certified value:	**2.93**

The TAN obtained by thermometric titration is in good agreement with the certified value and shows the applicability of the method presented.

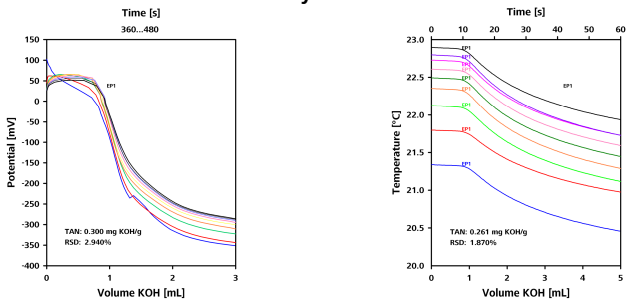
Potentiometric versus thermometric titration

Potentiometric titration according to ASTM D 664		Thermometric titration
toluene : isopropanol : water 495 : 500 : 5	**solvent mixture**	toluene : isopropanol 1 : 1
Solvotrode easyClean	**electrode**	Thermoprobe
LiCl in ethanol	**reference electrolyte**	–
50 mL	**solvent volume**	35 mL
–	**addition of paraformaldehyde**	yes
c(KOH) = 0.1 mol/L in isopropanol	**titrant**	c(KOH) = 0.1 mol/L in isopropanol
a) isopropanol b) solvent mixture c) water d) isopropanol	**cleaning procedure of electrode**	a) isopropanol b) solvent mixture c) dry storage

Used engine oil



Fresh hydraulic fluid



Summary

The thermometric titration method presented here permits a simple and direct determination of the total acid number (TAN) in petroleum products. It is an invaluable alternative to current manual and potentiometric methods. Thermometric titration uses a maintenance-free temperature sensor that does not require rehydration and is free of fouling and matrix effects. The procedure requires minimal sample preparation. Results agree closely with those from the potentiometric titrimetric procedure according to ASTM D 664, but the thermometric titration method is far superior in terms of reproducibility and speed of analysis, with determinations being complete in approximately one minute.

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