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Acid number in petroleum products with thermometric titration

Industry sector

Chemical; petroleum & petrochemicals

Keywords

Titration; Thermoprobe; dThermoprobe; thermometric titration; TET; TAN; nonaqueous titration; total acid number; oil; crude oil; process oil; petroleum products; bitumen; high-wax samples; 6.01117.300; 6.9011.020; ASTM; D8045; S01; S010; S05; S050

Summary

Knowing the accurate acid number for crude oil is important for the setting the price of crude oil. Additionally, by monitoring the acidity of crude oil and its associated process oils, unexpected refinery shutdowns can be prevented, and thus expensive treatment chemicals preserved.

Thermometric titration is a reliable method for the analysis of the total acid number (TAN) in crude oils, bitumen, and high-wax samples. This Application Bulletin describes the determination of the acid number in crude oil and refinery process oil samples by catalytic thermometric titration as per ASTM D8045.

During thermometric titration, the enthalpy change of the reaction is monitored rather than the potential. The titration endpoint is revealed by an inflection in the temperature curve. In instances where enthalpy change is small (e.g., weak acids neutralized by strong bases), a catalytic indicator is used to make the titration endpoint apparent.

In comparison to ASTM D664, thermometric titration is much faster, requires fewer reagents, and requires only minimal sensor maintenance, making it much more cost-efficient.

Instruments and accessories

- Titrator with the mode TET
- Rod stirrer
- Buret(s)

Electrodes

dThermoprobe	6.01117.300
Thermoprobe	6.9011.020

Reagents

- Potassium hydroxide c(KOH) = 0.1 mol/L in 2-propanol
- 2-propanol, isopropanol, IPA, p.a.
- Xylenes, (mixture of isomers), p.a.
- Paraformaldehyde, >95% pure
- Benzoic acid, p.a.

Solutions

Titrant	KOH in IPA; c(KOH in IPA) = 0.1 mol/L; if possible this solution should be bought from a supplier
Solvent	250 mL isopropanol and 750 mL xylene are mixed in a volumetric flask.

Standard solution

Benzoic acid standard solution	Benzoic acid is dried in a desiccator overnight. Dried benzoic acid (0.61 g) is weighed into a 250 mL volumetric flask and dissolved in the solvent. After the complete dissolution the flask is filled up to the mark with solvent.

Sample preparation

Some samples may require slight warming or pre-dissolution in 10 mL of xylene prior to titration. It is possible to titrate warm samples (<60 °C) without a loss in resolution or precision.

In case of a pre-dissolution, this must be considered in the blank determination.

Analysis

Titer

A 30 mL aliquot of benzoic acid standard solution is pipetted into a titration vessel and 0.5 g paraformaldehyde is added. The solution is then titrated with c(KOH) = 0.1 mol/L to a single exothermic endpoint.

Blank

An appropriate amount of the sample is weighed into the titration vessel and 30 mL solvent and 0.5 g paraformaldehyde are added. The solution is stirred thoroughly for 30 s before titration with c(KOH) = 0.1 mol/L to a single exothermic endpoint.

Titrate at least four different aliquots of the sample in ascending sample weight. Use **Table 1** as a guideline for the sample weight.

Sample

An appropriate aliquot of the sample according to **Table 1** is weighed into the titration vessel and 30 mL solvent and 0.5 g paraformaldehyde are added. The solution is stirred thoroughly for 30 s before titration with c(KOH) = 0.1 mol/L to a single exothermic endpoint.

Table 1. Guideline for the sample size, dependent on the expected TAN.

Expected TAN in mg KOH/g sample	Sample weight in g
0.05–0.99	10–20
1.00–4.99	5
5.00–15.00	1

Parameters

Titer

Mode	TET
Stirring rate	15
Pause	60 s
Dosing rate	3.00 mL/min
Stop volume	10.00 mL
Stop slope mode	Off
Filtering factor	60
Damping until	0.10 mL
Evaluation start	0.20 mL
Sort equivalence points by	Volume (ascending)
Define EP conditions	
End point(s)	1
Reaction type	Exothermic
EP criterion	-300

Blank and sample

Mode	TET
Stirring rate	15
Pause	30 s
Dosing rate	3.00 mL/min
Stop volume	10.00 mL
Stop slope mode	Off
Filtering factor	50*
Damping until	0.50 mL
Evaluation start	0.20 mL
Sort equivalence points by	Volume (ascending)
Define EP conditions	
End point(s)	1
Reaction type	Exothermic
EP criterion	-50

* The filter factor depends on the sample and thus may vary. It is important that the same filter factor is used for the blank and sample determination.

Calculations

Titer

$$\text{Titer} = \frac{c_{BA} \times V_{BA}}{V_{EP1} \times c_{KOH}}$$

Titer: Titer of the selected titrant
c_{BA}: Exact concentration of the benzoic acid standard solution in mol/L
V_{BA}: Added volume of benzoic acid standard solution in mL
V_{EP1}: Titrant consumption until the first equivalence point in mL
c_{KOH}: Concentration of the selected titrant in mol/L; here c(KOH in IPA) = 0.1 mol/L

Blank

A linear regression of the different sizes of the sample (in g) against the volume of titrant consumed (in mL) is plotted automatically by OMNIS or *tiamo*™. The blank is defined as the intercept of the linear regression line with the y-axis.

Sample

$$\text{TAN} = \frac{(V_{EP1} - V_{blank}) \times c_{KOH} \times f \times M_A}{m_s}$$

TAN: Total acid number in mg KOH/g sample
V_{EP1}: Titrant consumption in mL to reach the first equivalence point
V_{blank}: Blank value consumption for the used quantity of solvent
c_{KOH}: Concentration of titrant in mol/L; here c(KOH in IPA) = 0.1 mol/L
f: Correction factor (titer), dimensionless
M_A: Molecular weight of KOH; here 56.106 g/mol
m_s: Sample weight in g

Example

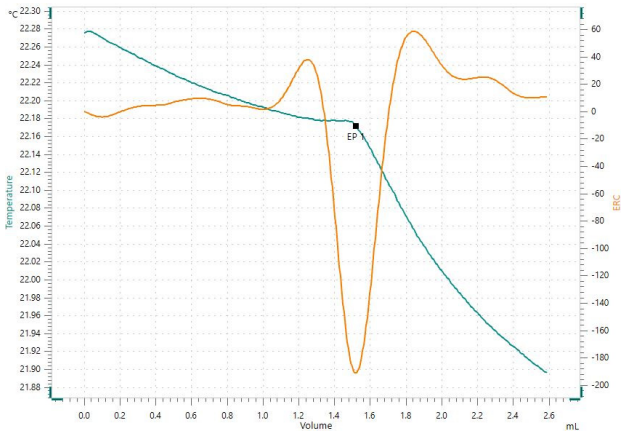

Figure 1. Thermometric titration curve for a raw crude oil sample (green = titration curve, orange = ERC).

Comments

The linear regression for the titer and the blank can be determined automatically from the results using appropriate software such as OMNIS or *tiamo*™.

For more information about the titer and blank determination using *tiamo*™, see Metrohm Application Note AN-H-131.

Various types of paraformaldehyde exist. Therefore, it is recommended to use the one mentioned under the Reagents section, as not every type of paraformaldehyde is suited for the catalysis of this reaction.

During the titration, the titrant reacts with the analyte in the sample either exothermically or endothermically. The Thermoprobe measures the temperature of the titrating solution. When all of the analyte in the sample has reacted with the titrant, the temperature of the solution changes, and the endpoint of the titration is indicated by an inflection in the temperature curve.

Catalytically enhanced titrations using paraformaldehyde as a catalyst are based on the endothermic hydrolysis of the paraformaldehyde in the presence of an excess of hydroxide ions.

The amount of analyte determined is not related to the change in temperature of the solution. Therefore, it is not necessary to use insulated titration vessels.

Thermometric titrations are conducted under conditions of constant titrant addition rate. In this respect, they differ from potentiometric titrations where the titrant addition rate may be varied during the titration according to the electrode response. In thermometric titrations, a constant addition rate of titrant equates to a constant amount of heat being emitted or absorbed, and hence a more or less constant temperature change up to the endpoint.

For the automation of the analysis, it is also possible to add the paraformaldehyde as a suspension with the solvent. Here, approximately 17 g paraformaldehyde is dissolved in 1 L of solvent, thus 30 mL solvent contains approximately 0.5 g paraformaldehyde. The suspension can then be added using pumps. To achieve the correct ratio of solvent and paraformaldehyde, the suspension must be stirred constantly during an analysis series.

As an alternative to the pumps, the paraformaldehyde-solvent-suspension can be added using a Dosino. The automated adding of a suspension is described in AN-T-095.

References

ASTM D8045
Standard Test Method for Acid Number of Crude Oils and Petroleum Products by Catalytic Thermometric Titration

AN-H-131
Determination of titer and method blank for thermometric titrations using *tiamo*™

AN-H-141
Determination of acid number in raw oil in accordance with ASTM D8045

AN-T-095
Automated mixing of a suspension and a solvent using a 50 mL dosing unit

Monograph: Practical thermometric titrimetry, 8.036.5003

Brochure: Thermometric Titration with OMNIS, 8.000.5446

Leaflet: Sensor dThermoprobe, 8.0109.8018

Leaflet: Thermoprobe, 8.109.8055

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