Metrohm

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Acidity in crude oils and petroleum products by thermometric titration according to ASTM D8045

Branch

Petrochemistry

Keywords

TAN; titration; crude oil; process oil; thermometric titration; 859; Titrotherm; Thermoprobe; branch 5; D8045; ASTM; 6.9011.050; bitumen; high wax samples

Summary

The reliable knowledge of the accurate acid number for crude oil is important for the determination of the price of crude oil. Additionally, by monitoring the acidity of crude oil and the associated process oils unexpected shutdowns can be prevented and thus expensive treatment chemicals preserved.

Thermometric titration is a reliable method for the analysis of the acid number 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.

In thermometric titration, enthalpy change of the reaction is monitored rather than potential. The titration endpoint is revealed by an inflection in the temperature curve. In the instance 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 less reagents and only minimum sensor maintenance making it much more cost efficient.

Instruments

- Thermometric titrator
- Rod stirrer for intensive stirring
- Buret 20 mL for the titration
- Buret 50 mL for the addition of solvent

Electrodes

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, Sigma-Aldrich, 158127
- Benzoic acid, p.a.

Solutions

Titrant	c(KOH) = 0.1 mol/L in IPA 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

Benzoic acid standard solution	Benzoic acid is dried in a desiccator over-night. 0.61 g dried benzoic acid 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 of resolution or precision.

In case of a pre-dissolution this has to be considered in the blank determination.

Analysis

Titer

30 mL 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 aliquot 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 4 different aliquots of the sample in an ascending order. Use the table below as a guideline for the sample weight.

Sample

An appropriate aliquot of the sample (see table below) 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.

Guideline for the sample size in dependency of the expected TAN

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

Parameters

Titer

Pause	60 s
Stirring rate	15
Dosing rate	4 mL/min
Filter factor	60
Damping until	1 mL
Stop slope	off
Added volume after stop	0.5 mL
Evaluation start	1 mL
End points	ex (exothermic)
EP criterion	-10

Blank and Sample

Pause	30 s
Stirring rate	15
Dosing rate	2 mL/min
Filter factor	50 – 75*
Damping until	0.2 mL
Stop slope	off
Added volume after stop	0.5 mL
Evaluation start	0 mL
End points	ex (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.

Calculation

Titer

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

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
c_{KOH}:	Concentration of titrant in mol/L
V_{EP1}:	Titrant consumption in mL to reach the first equivalence point.

Blank

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

For further explanation on the titer calculation please have a look at AN-H-131.

Sample

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

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

Example determination

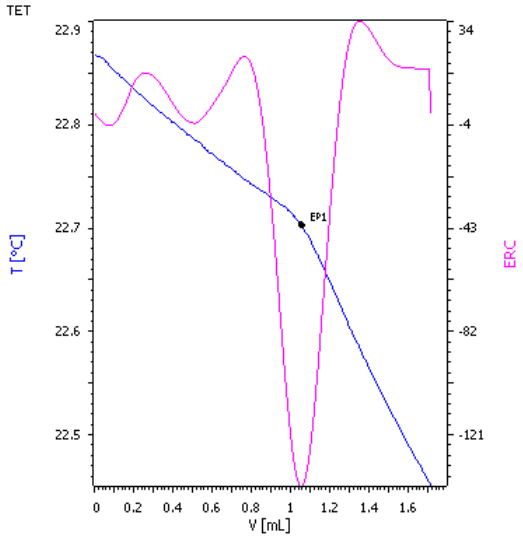

Fig. 1: Thermometric titration curve for a raw crude oil sample (blue = titration curve, pink = ERC)

Comments

- The linear regression for the blank can be determined automatically from the results using appropriate software such as ***tiamo***™.
- For more information about the blank determination using ***tiamo***™, see also Metrohm Application Note AN-H-131.
- Various types of paraformaldehyde are existing. Therefore, it is recommended to use the one mentioned under reagents, as not every paraformaldehyde is suited for the catalysis of this reaction.
- In a titration, the titrant reacts with the analyte in the sample either exothermically or endothermically. The thermoprobe measures the temperature of the solution during the titration. When all of the analyte in the sample has reacted with the titrant, the rate of the temperature change will alter, and the endpoint of the titration is indicated by an inflection in the temperature curve.
- Catalytically enhanced titrations using paraformaldehyde as 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 released or consumed, 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 suspension with the solvent. Therefore approx. 17 g paraformaldehyde is dissolved in 1 L of solvent, thus 30 mL solvent contain approx. 0.5 g paraformaldehyde. The suspension can then be added using pumps.
  For correct ratio of solvent and paraformaldehyde the suspension must be stirred all the time 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-T-095
  Automated mixing of a suspension and a solvent using a 50 mL dosing unit

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