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

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.

Reagents
- Potassium hydroxide c(KOH) = 0.1 mol/L in 2-propanol
- 2-propanol, isopropanol, IPA, p.a.
- Paraformaldehyde, >95% pure, Sigma-Aldrich, 158127
- Benzoic acid, p.a.

Solutions

<table>
<thead>
<tr>
<th>Titrant</th>
<th>c(KOH) = 0.1 mol/L in IPA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>If possible this solution should be bought from a supplier.</td>
</tr>
</tbody>
</table>

| Solvent         | 250 mL isopropanol and 750 mL xyylene are mixed in a volumetric flask. |

Standard

| Benzoic acid   | Benzoic acid is dried in a desiccator over-night. |

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
50 – 100 mg dried benzoic acid is weighed into a titration vessel and 30 mL solvent and 0.5 g paraformaldehyde are added. The solution is stirred thoroughly for 60 s to dissolve the benzoic acid and then titrated with c(KOH) = 0.1 mol/L to a single exothermic endpoint.

Titrator at least 4 different amounts of benzoic acid in an ascending order.
**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.

Titrater 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**

<table>
<thead>
<tr>
<th>Expected TAN / [mg KOH/g sample]</th>
<th>Sample weight / [g] ± 10%</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05 – 0.99</td>
<td>10 – 20</td>
</tr>
<tr>
<td>1.00 – 4.99</td>
<td>5</td>
</tr>
<tr>
<td>5.00 – 15.00</td>
<td>1</td>
</tr>
</tbody>
</table>

**Parameters**

**Titer**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pause</td>
<td>60 s</td>
</tr>
<tr>
<td>Stirring rate</td>
<td>15</td>
</tr>
<tr>
<td>Dosing rate</td>
<td>4 mL/min</td>
</tr>
<tr>
<td>Filter factor</td>
<td>60</td>
</tr>
<tr>
<td>Damping until</td>
<td>1 mL</td>
</tr>
<tr>
<td>Stop slope</td>
<td>off</td>
</tr>
<tr>
<td>Added volume after stop</td>
<td>0.5 mL</td>
</tr>
<tr>
<td>Evaluation start</td>
<td>1 mL</td>
</tr>
<tr>
<td>End points</td>
<td>ex (exothermic)</td>
</tr>
<tr>
<td>EP criterion</td>
<td>-10</td>
</tr>
</tbody>
</table>

**Calculation**

**Titer**

A linear regression of the mL of titrant consumed versus the different sample sizes of the standard in mg is plotted automatically by tiamo™. The titer is then calculated from the slope.

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

\[
\text{Titer} = \frac{1}{a \times c_{\text{KOH}} \times M_A}
\]

- **Titer**: Titer of the selected titrant
- **a**: Slope of the linear regression
- **c_{\text{KOH}}**: Concentration of titrant in mol/L
- **M_A**: Molecular weight of the standard; here 122.12 g/mol

**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

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

- **TAN**: Total acid number in mg KOH / g sample
- **\(V_{\text{EP1}}\)**: Titrant consumption in mL to reach the first equivalence point.
- **Blank**: Blank value; consumption for the used quantity of solvent
- **\(c_{\text{KOH}}\)**: 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

![Thermometric titration curve for a raw crude oil sample](image)

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

Comments

- The linear regression for the titer and the blank can be determined automatically from the results using appropriate software such as tiamo™.
- For more information about the titer and 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 either be added using pumps or with a Dosino. For correct ratio of solvent and paraformaldehyde the suspension must be stirred all the time during an analysis series. 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

Author

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