Introduction

For the determination of acidic constituents in petroleum products and lubricants by potentiometric titration. The total acid number TAN is the quantity of base, expressed in milligrams of potassium hydroxide, that is required to neutralize all acidic constituents present in 1 g of sample.

Apparatus

- TitroLine® 7000 or higher
- Magnetic stirrer (TM 235)
- 10 or 5 mL Exchange unit WA 10/WA 5, with amber glass bottle for the titrant, TZ 1643 titration tip

Electrode and Electrolyte

- Electrode: N 6480 eth with cable L 1 A
- Electrolyte: L 503 4 (LiCl/Ethanol)

Reagents

- Solvent: Toluene/isopropyl alcohol/water (500/495/5)
- Standardization: Potassium hydrogen phthalate standard
- Titrant: KOH 0.1 mol/L in isopropyl alcohol
**Procedure**

**Preparation and standardization of the alcoholic KOH solution**

Add 6 g of KOH to approximately 1 L of anhydrous isopropyl alcohol. Boil gently for 10 min to effect solution. Allow the solution to stand for 2 days and then filter through a fine sentered-glass funnel. Store the solution in a chemical resistant bottle and protect the solution for CO₂ with a guard tube containing soda lime. Standardize with exact weighed quantities of 0.2 g of potassium hydrogen phthalate. Add 80 ml CO₂ free water. **Ready to use solutions are recommended.** Use the method Titer KOH.

Repeat the standardization three times. The average value is stored automatically in the exchangeable unit.

**Blank value of the solvent mixture**

Add 125 mL of the titration solvent into the beaker. Place the beaker on the magnetic stirrer and start the titration method. After titration rinse the electrode and burette tip with solvent, then with water, then again with solvent in a beaker for approximately 1 minute each. Use method **BLANK TAN.**

Repeat the blank titration one time. The average value can be stored in a global memory e.g. M01 (TAN blank) which must be created before running the blanks.

**Titration of sample**

Weigh the sample in a 250 mL beaker and add 125 mL of the titration solution to the sample. The sample weight should be calculated and selected so that the titration amount is not more than 4 ml because of the long titration time.

Place the beaker on the magnetic stirrer and start the titration method (TAN). After the titration, rinse the electrode and burette tip with solvent, then with water (5 min), then again with solvent (1 min).

**Maintenance of Electrodes**

If you use a combination electrode like N 6480, store the electrode in the LiCl/Ethanol electrolyte. If you use a separate pH glass electrode and reference electrode, then store the glass electrode in water or KCl solution and the reference electrode in LiCl/Ethanol electrolyte.
Results

Standardization (Page 1)

GLP documentation

Titration graph

Method data
Method name: Titer KOH
End date: 21.09.12
Titration duration: 3 m 31 s
End time: 15:13:54

Titration data
Sample ID: KHPthalat
Start mV: 167.9 mV
End mV: -167.2 mV
EQ: 5.739 ml / -92.0 mV

Calculation formula
Titer: (W*F2)/(EQ1-B)*M*F1) -> M103
Mol (M): 204.22000

Weight (W): man
Blank value (B): 0.0000 ml
Statistics: Off

Titer: 0.1032 mol/l

5.74 ml
-92.0 mV
### Method data overall view

- **Method name:** Titer KOH
- **Created at:** 09/19/12 17:05:06
- **Method type:** Automatic titration
- **Last modification:** 09/19/12 17:32:02
- **Measured value:** mV
- **Damping settings:** None
- **Titration mode:** Dynamic
- **Documentation:** GLP

### Dynamic

- **Dynamic:** Steep

### Measuring speed / drift

- **Normal:**
  - minimum holding time: 02 s
  - maximum holding time: 15 s
  - Measuring time: 02 s
  - Drift: 20 mV/min

### Initial waiting time: 0 s

### Titration direction: Decrease

### Pretitration: Off

### End value: Off

### EQ: On (1)

### Slope value: Steep

#### Value

- **700**

### Dosing parameter

- **Dosing speed:** 100 %
- **Filling speed:** 30 s
- **Maximum dosing volume:** 50.00 ml

### Unit values

- **Unit size:** 10 ml
- **Unit ID:** 00072696
- **Reagent:** TBA Hydroxid
- **Batch ID:** 1.0265
- **Concentration [mol/l]:** 0.10365
- **Determined at:** 09/20/12 0:57:27
- **Expire date:** 04/12/12
- **Opened/compounded:** 10/19/11
- **Test according ISO 8655:** 12/01/10
- **Last modification:** 09/21/12 15:06:50
GLP documentation

Titration graph

Method data
Method name: Blank TAN-TBN
End date: 21.09/12
Titration duration: 3 m 1 s
End time: 16:27:20

Titration data
Sample ID: BW Solvent
Start mV: 82.7 mV
End mV: -29.1 mV
EQ: 0.070 ml / 13.0 mV
Blank: 0.070 ml

Calculation formula
Blank: EQ1 -> M01
Mol (M): 1.00000
Statistics: Off

0.07 ml
13.0 mV
**Method data overall view**

<table>
<thead>
<tr>
<th>Method name</th>
<th>Blank TAN-TBN</th>
<th>Created at:</th>
<th>09/21/12 15:29:51</th>
</tr>
</thead>
<tbody>
<tr>
<td>Method type</td>
<td>Automatic titration</td>
<td>Last modification:</td>
<td>09/21/12 16:22:36</td>
</tr>
<tr>
<td>Measured value</td>
<td>mV</td>
<td>Damping settings:</td>
<td>strong</td>
</tr>
<tr>
<td>Titration mode</td>
<td>Linear</td>
<td>Documentation:</td>
<td>GLP</td>
</tr>
<tr>
<td>Linear steps</td>
<td>0.010 ml</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Measuring speed / drift**

- Measuring speed / drift: 15 s

**Initial waiting time**

- Initial waiting time: 10 s

**Titration direction**

- Titration direction: Decrease

**Pretitration**

- Pretitration: Off

**End value**

- End value: Off

**EQ**

- EQ: On (1)

**Slope value**

- Slope value: Flat

**Dosing parameter**

<table>
<thead>
<tr>
<th>Dosing speed</th>
<th>100 %</th>
<th>Filling speed</th>
<th>30 s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum dosing volume</td>
<td>0.20 ml</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Unit values**

<table>
<thead>
<tr>
<th>Unit size</th>
<th>10 ml</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unit ID</td>
<td>00072696</td>
</tr>
<tr>
<td>Reagent</td>
<td>TBA Hydroxid</td>
</tr>
<tr>
<td>Batch ID</td>
<td>1.0265</td>
</tr>
<tr>
<td>Concentration [mol/l]</td>
<td>0.10350</td>
</tr>
<tr>
<td>Determined at</td>
<td>09/21/12 22:27:50</td>
</tr>
<tr>
<td>Expire date</td>
<td>04/12/12</td>
</tr>
<tr>
<td>Opened/compounded</td>
<td>10/19/11</td>
</tr>
<tr>
<td>Test according ISO 8655</td>
<td>12/01/10</td>
</tr>
<tr>
<td>Last modification</td>
<td>09/21/12 15:28:02</td>
</tr>
</tbody>
</table>
Sample Titration (Page 1): Example with high or normal TAN value >1

GLP documentation

Titration graph

Method data
Method name: TAN ASTM 664
Titration duration: 10 m 9 s
End date: 21.09.12
End time: 16:48:29

Titration data
Sample ID: Mineral Oil
Weight: 4.0225 g
Start mV: 161.9 mV
End mV: -39.4 mV
EQ: 3.496 ml / -18.9 mV
TAN mg KOH/g: 4.95

Calculation formula
TAN mg KOH/g: (EQ-B)*T*M*F1/(W*F2)
Mol (M): 56.10000
Blank value (B): 0.0700 ml (M01)
Factor 1 (F1): 1.0000
Factor 2 (F2): 1.0000
Titre (T): 0.10350000 (a)
Weight (W): man
Statistics: Off
## Method data

### Method data overall view
- **Method name:** TAN ASTM 664
- **Method type:** Automatic titration
- **Measured value:** mV
- **Titration mode:** Linear
- **Linear steps:** 0.050 ml
- **Created at:** 09/19/12 16:27:55
- **Last modification:** 09/21/12 16:31:53
- **Damping settings:** strong
- **Documentation:** GLP

### Measuring speed / drift
- **User-defined:**
  - minimum holding time: 07 s
  - maximum holding time: 20 s
  - Measuring time: 04 s
  - Drift: 20 mV/min

### Initial waiting time: 10 s
- **Titration direction:** Decrease
- **Pretitration:** Off
- **End value:** Off
- **EQ:** On (1)
- **Slope value:** Flat

### Dosing parameter
- **Dosing speed:** 100 %
- **Filling speed:** 30 s
- **Maximum dosing volume:** 5.00 ml

### Unit values
- **Unit size:** 10 ml
- **Unit ID:** 00072696
- **Reagent:** TBA Hydroxid
- **Batch ID:** 1.0265
- **Concentration [mol/l]:** 0.10350
- **Determined at:** 09/21/12 22:27:50
- **Expire date:** 04/12/12
- **Opened/compounded:** 10/19/11
- **Test according ISO 8655:** 12/01/10
- **Last modification:** 09/21/12 15:28:02
Sample Titration (Page 1): Example with low TAN value <1

GLP documentation

Titration graph

Method data
Method name: TAN ASTM 664
End date: 12.10.12
Titration duration: 2 m 49 s

End time: 10:01:49

Titration data
Sample ID: Gt 1R
Start mV: 49.6 mV
Weight: 19.1539 g
End mV: -135.0 mV

EQ: 0.103 ml / -83.2 mV
TAN mg KOH/g: 0.009

Calculation formula
TAN mg KOH/g: \((\text{EQ1-B})\times\text{T}\times\text{M}\times\text{F1}/(\text{W}\times\text{F2})\)
Mol (M): 56.10000
Blank value (B): 0.0740 ml (M01)
Titre (T): 0.10580000 (a)
Factor 1 (F1): 1.0000
Weight (W): man
Factor 2 (F2): 1.0000
Statistics: Off
**Sample Titration (Page 2): Example with low TAN value <1**

### Method data

<table>
<thead>
<tr>
<th>Method data overall view</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Method name:</td>
<td>TAN ASTM 664</td>
<td>Created at:</td>
<td>10/12/12 9:56:06</td>
</tr>
<tr>
<td>Method type:</td>
<td>Automatic titration</td>
<td>Last modification:</td>
<td>10/12/12 9:58:13</td>
</tr>
<tr>
<td>Measured value:</td>
<td>mV</td>
<td>Damping settings:</td>
<td>strong</td>
</tr>
<tr>
<td>Titration mode:</td>
<td>Linear</td>
<td>Documentation:</td>
<td>GLP</td>
</tr>
<tr>
<td>Linear steps:</td>
<td>0.020 ml</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Measuring speed / drift</th>
<th>User-defined:</th>
<th>minimum holding time:</th>
<th>07 s</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>maximum holding time:</td>
<td>20 s</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Measuring time:</td>
<td>04 s</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Drift:</td>
<td>20 mV/min</td>
</tr>
</tbody>
</table>

| Initial waiting time:          | 10 s |         |         |
| Titration direction:           | Decrease |         |         |
| Pretitration:                  | Off |         |         |
| End value:                     | Off |         |         |
| EQ:                            | On (1) |         |         |
| Slope value:                   | Flat | Value: | 120 |

**Dosing parameter**

| Dosing speed:                  | 100 % | Filling speed | 30 s |
| Maximum dosing volume:         | 1.00 ml |         |       |

**Unit values**

| Unit size:                     | 10 ml |         |       |
| Unit ID:                       | 10035468 |         |       |
| Reagent:                       | KOH 0.1 mol/L |         |       |
| Batch ID:                      | no entry |         |       |
| Concentration [mol/l]:         | 0.10580 |         |       |
| Determined at:                 | 10/12/12 16:16:25 |         |       |
| Expire date:                   | --- |         |       |
| Opened/compounded:             | --- |         |       |
| Test according ISO 8655:       | --- |         |       |
| Last modification              | 10/12/12 9:44:44 |         |       |
Literature

ASTM 664