Total Acid Number (TAN) (ASTM D664)

DOC316.52.93095

Potentiometric titration
Application: Petrochemical oils

1. Introduction

This working procedure deals with the titration of Total Acid Number (TAN) in oil.

2. Principle

The working procedure determines the sum of all acid compounds present in petrochemical samples by an acid-base titration using KOH as titrant. TAN is expressed in mg of KOH per g of sample.

Since samples are non-aqueous, they are diluted in a mix of chloroform and isopropyl alcohol. The solvent for KOH is isopropyl alcohol.

3. Electrode and reagents

Electrodes: Glass pH electrode, PHG201-8

Ag/AgCl reference electrode, REF361: the reference electrode has a sleeve junction with important diffusion in order to prevent clogging from oily samples. The REF361 is delivered filled with aqueous KCl solution. Empty this solution, rinse the electrode with deionized water then with isopropyl alcohol and fill it with a 1M LiCl alcoholic solution

Legacy adapter: the working electrode PHG201-8 is connected to the BNC socket, and the reference electrode REF361 is connected using a BNC-to-banana connector

Titrant: KOH 0.1 eq/L in isopropyl alcohol. It is recommended to buy a commercial 0.1 N alcoholic potassium hydroxide solution. Titer is not stable so a titrant calibration is recommended before use

Solvent: Mix 5 mL of water with 495 mL of isopropyl alcohol and add 500 mL of chloroform

Filling solution for the reference electrode: Dissolve 4.2 g of LiCl in 100 mL of isopropyl alcohol

Basic buffer:

1. **Prepare a stock solution**: weigh 27.8 g of m-nitrophenol, add 100 mL of isopropyl alcohol and 500 mL of KOH 0.1 N (in isopropyl alcohol), dilute to 1000 mL with isopropyl alcohol in a volumetric flask. Store the solution in a brown glass bottle and use within 2 weeks.
2. **Prepare the basic buffer solution**: add 10 mL of the stock solution to 100 mL of solvent. Use this solution within 1 hour.

Standard for titrant calibration: Potassium hydrogen phthalate, molar weight = 204.22 g/mol

pH standards: Colored 4.01, 7.00, 10.01 (part numbers 2283449, 2283549, 2283649)

Deionized water

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4. Ranges and settings

4.1. Default parameters

The working procedure is described using the following parameters:

- m sample = 2.000 g
- Syringe volume = 5 mL

The default syringe volume for the AT1000 is set to 10 mL. This application needs a 5 ml syringe. When loading an application, if the message **syringe to replace** is displayed, change the syringe volume in the **Syringe management** option of the **Maintenance** menu.

4.2. Working range

For a 2 g (± 0.2 g) sample and maximum KOH volume of 10 mL (two syringes of 5 mL), samples of up to 20 mg/g can be analyzed.

For more concentrated oils, it is recommended to weigh a smaller amount of sample. For low concentrations it is also possible to analyze more than 2 g of oil. The ASTM D664 standard gives the following indications:

Total Acid Number (mg/g)	Sample mass (g)	Weighing accuracy (g)
0.05 – < 1.0	20.0 ± 2.0	0.10
1.0 – < 5.0	5.0 ± 0.5	0.02
5.0 – < 20	1.0 ± 0.1	0.005
20 – < 100	0.25 ± 0.02	0.001
100 – < 260	0.1 ± 0.01	0.0005

4.3. Settings

Name	Default parameter	Unit
Sample		
Name	Sample	
Amount	2	[g]
Amount min	0.1	[g]
Amount max	22	[g]
Titrant		
Name	KOH	
Titrant concentration	0.1000	[eq/L]
Syringe	Syringe 1	
Probes		
Recommended pH probe	PHG201	
Recommended reference probe	REF361	
Rinsing step 1 (solvent)		
Active	Yes	
Time	30	[s]
Stirring speed	25	[%]
Rinsing step 2 (water)		
Active	Yes	
Time	30	[s]
Stirring speed	25	[%]
Rinsing step 3 (solvent)		
Active	Yes	
Time	30	[s]
Stirring speed	25	[%]
IP titration		
Stirring speed	20	[%]
Measured parameter		[mV]
Predose	0	[mL]
Max volume stop point	10	[mL]
Stop on last EQP	Yes	
Delay	15	[s]

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Min increment size	0.03	[mL]
Max increment size	0.15	[mL]
Result 1 name	TAN (mgKOH/g)	
R1 resolution	3 decimals	
R1 min	0.05	[mg/g]
R1 max	260	[mg/g]
R1 QC min	0.05	[mg/g]
R1 QC max	260	[mg/g]
R1 EQP index	1	
R1 molar weight	56.11	[g/mol]

4.4. Modification of the settings

The parameters are defined in order to have the best compromise between accuracy and titration time.

For higher concentration with a high titrant volume, titration time can be reduced with an addition of titrant (predose) at the beginning of the titration. Enter the predose volume (in mL) and the stirring time after the addition in the application edit window.

5. Titration procedure

Launch the application **TAN**.

On the first screen, in **Sample type** choose **Define blank** and press **Start**. Follow the rinsing instructions on the screen. Then, place an empty beaker with a stir bar under the probe holder. Add 75 mL and press **OK**. Make sure that both electrodes are immersed. At the end of the titration, the equivalent volume corresponding to the blank is displayed and automatically recorded. Press **Next** and chose **New sample**.

Weigh approximately 2 g of oil in a 100 mL beaker. In **Sample type** choose **Sample with blank** and press **Start**. Follow the rinsing instructions on the screen. Then, place the beaker containing the sample and a stir bar under the probe holder. Add 75 mL of solvent and press **OK**. Make sure that both electrodes are immersed. At the end of the titration, TAN is displayed in mg of KOH per g of sample. This result is calculated taking into account the blank determined previously.

By pressing **Next** it is possible to:

- Replicate the sample. This is used to study the repeatability by analyzing several samples successively. At the end of each titration, a window displays the average value, the standard deviation (SD in g/L) and the relative standard deviation (RSD in %).
- Analyze a new sample. Another titration can be started but no Standard Deviation and RSD value will be made.

If no inflection is detected then it is possible to use endpoint detection.

- First, the endpoint potential must be determined. Immerse the electrodes in the basic buffer solution. Press **Maintenance > Live measure**, wait for a stable mV signal and read the mV value. Then, in **Settings > Applications > Edit** chose **TAN Endpoint**. In section **Method: Titration** type this mV value as the ordinate for the equivalence point. Launch the application **TAN Endpoint** and proceed as for the **TAN** application.

6. Results

6.1. Result calculation

The calculation used is:

$$\mathrm{TAN\ (mgKOH/g)} = \frac{C_{titrant}\ (\mathrm{eq/L}) \times V_{titrant}\ (\mathrm{mL})}{n_{e\text{-}\ titrant} \times m_{sample}\ (\mathrm{g})} \times M_{KOH}\ (\mathrm{g/mol})$$
$$= \frac{0.1\ (\mathrm{eq/L}) \times V_{titrant}\ (\mathrm{mL})}{1 \times m_{sample}\ (\mathrm{g})} \times 56.11\ (\mathrm{g/mol})$$

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6.2. Experimental results

These results are indicative and have been obtained for 3 TAN standards (0.52, 2.02 and 4.57 mg/g) with 5 determinations for each standard.

- Inflection

Standard 0.52 mg/g	
Mean TAN (mg/g)	0.518
Standard deviation (mg/g)	0.019
Relative standard deviation (%)	3.6

Standard 2.02 mg/g	
Mean TAN (mg/g)	2.114
Standard deviation (mg/g)	0.085
Relative standard deviation (%)	4.0

Standard 4.57 mg/g	
Mean TAN (mg/g)	4.661
Standard deviation (mg/g)	0.175
Relative standard deviation (%)	3.8

- Endpoint

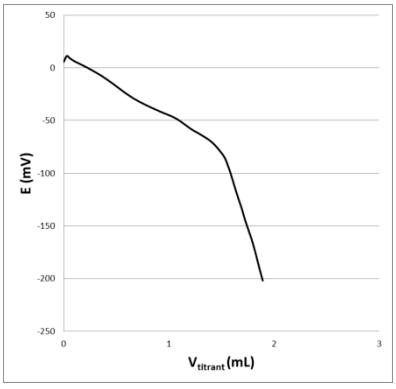
Standard 0.52 mg/g	
Mean TAN (mg/g)	0.507
Standard deviation (mg/g)	0.028
Relative standard deviation (%)	5.5

Standard 2.02 mg/g	
Mean TAN (mg/g)	1.923
Standard deviation (mg/g)	0.024
Relative standard deviation (%)	1.2

Standard 4.57 mg/g	
Mean TAN (mg/g)	4.793
Standard deviation (mg/g)	0.194
Relative standard deviation (%)	4.1

6.3. Example of a titration curve

This curve has been obtained during the analysis of one of the standards.



7. Recommendations

Always rinse the pH probe and the delivery tip between measurements.

Refill the electrode regularly with LiCl 1M in isopropyl alcohol to maintain the level of internal solution around 1 cm (0.4 inches) below the refill hole.

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8. Bibliography

- *Standard ASTM D664*

9. Appendices

9.1. Electrode testing and storage

It is recommended to check the electrodes behavior when first put into use, or when new electrodes are installed, and retest at intervals thereafter. Rinse the electrodes with solvent and then with deionized water. Dip them into the pH 4 aqueous buffer solution. Press **Maintenance > Live measure**.

Read the mV value after stirring for 1 minute. Remove the electrodes, rinse with water and dip them into the pH 7 aqueous buffer solution. Read the mV value after stirring for 1 minute. Calculate the mV difference. A good electrode system will have a difference of at least 162 mV (20 to 25 °C). If the difference is less than 162 mV, lift the sleeve of the reference electrode and make sure of the electrolyte flow. Repeat the measurements. If the difference is still less than 162 mV, clean or replace the electrode(s).

When not in use, store the reference electrode in LiCl electrolyte and the glass electrode in an acidic aqueous media (pH 4 to 5.5).

9.2. Titrant calibration

The sodium hydroxide solution can be calibrated. Its exact concentration can be determined from an acid-base titration using potassium hydrogen phthalate.

Weigh 60 mg of potassium hydrogen phthalate powder in a 100 mL beaker and use a graduated cylinder to add 70 mL of boiled deionized water (CO_2-free). Put in a stir bar, dip the probes and the delivery tip into the solution and launch the titrant calibration sequence. When prompted, type in the exact weighed amount of powder.

At the end of the titrant calibration, titer (eq/L) is displayed and the user can reject, replicate, or save the result. The saved value will be used for calculations.

Default settings for titrant calibration

Name	Default parameter	Unit
Titrant		
Name	KOH	
Titrant concentration	0.1000	[eq/L]
Syringe	Syringe 1	
Standard		
Name	Potassium hydrogen phthalate	
Amount	60	[mg]
Amount min	40	[mg]
Amount max	80	[mg]
Molar weight	204.22	[g/mol]
EP titration		
Stirring speed	20	[%]
Measured parameter		[mV]
Predose	0	[mL]
Max volume stop point	10	[mL]
Stop on last EQP	True	
Delay	0	[s]
Min increment size	0.05	[mL]
Max increment size	0.5	[mL]
Result name	Titer	
Result resolution	4 decimals	
Result min	0.09	[eq/L]
Result max	0.11	[eq/L]

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