Total Base Number (TBN) Back titration (ASTM D2896-11)

DOC316.52.93115

Potentiometric titration
Application: Petrochemical oils and lubricants

1. Introduction

Oils and lubricants have a base reserve designed to neutralize the acids produced after the combustion process in order to avoid corrosion of engine components. A low Total Base Number (TBN) indicates that oil has to be changed.

2. Principle

When no inflection is detected in a forward titration, TBN can be determined in a back titration. Excess standard perchloric acid solution is added to the sample, and then the excess $HClO_4$ solution is back titrated with standard sodium acetate solution:

$$HO^- + HClO_4 \rightarrow H_2O + ClO_4^- + HClO_{4\ excess}$$

$$HClO_{4\ excess} + CH_3COONa \rightarrow ClO_4^- + CH_3COOH + Na^+$$

TBN is expressed in mg of KOH per g of sample.

Since samples are non-aqueous, they are diluted in a mix of chlorobenzene and acetic acid. The solvent for perchloric acid and sodium acetate is acetic acid.

3. Electrodes and reagents

Electrodes: Glass pH electrode, PHG311-9 + CL114 cable

Red Rod reference electrode, double junction, REF251. The outer compartment of the REF251 reference electrode has to be filled with a saturated sodium perchlorate solution

Legacy adapter: the working electrode PHG311 is plugged on the BNC socket using the CL114 cable, and the reference electrode is plugged on the banana socket

Titrant: Sodium acetate 0.1 eq/L in acetic acid: Dissolve 5.3 g of anhydrous Na_2CO_3 in 300 mL of glacial acetic acid. Dilute to 1 L with acetic acid after solution is complete

Excess titrant: HClO4 0.1 eq/L in acetic acid: It is recommended to buy a commercial 0.1 eq/L perchloric acid solution. Otherwise, mix 8.5 mL of 70 to 72% perchloric acid with 500 mL of glacial acetic acid and 30 mL of acetic anhydride. Dilute to 1 L with glacial acetic acid and allow the solution to stand for 24h

Titration Solvent: Chlorobenzene + acetic acid; Add one volume of glacial acetic acid to two volumes of chlorobenzene

Filling solution for the reference electrode: Saturated solution of $NaClO_4$ in glacial acetic acid

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 $(g) = \frac{10}{\text{expected BN (mg/g)}}$ weighed with the following precision:

Sample weight (g)	Weighing precision (g)
1 – 2.5	0.005
0.25 – 1.0	0.001
0.1 – 0.25	0.0005

Note: *The sample size for the back titration modification does not exceed 2.5 g. When, with a 2.5 g-sample no inflection point is found, reduce the sample size to 1.5 g and repeat the analysis. Reducing the sample size generally improves the clarity of the inflection point.*

- Burette volume = 10 mL

4.2. Working range

The sample weights and precisions given in section **4.1** allow the determination of base numbers between 4 and 100 mg/g.

However ASTM D2896-11 standard specifies that this test method can be used to determine base numbers higher than 300 mg/g. In this case, weigh 0.1 g of sample for expected base numbers up to 450 mg/g. For even more concentrated samples, weigh a smaller amount of sample.

4.3. Settings

Name	Default parameter	Unit
Application		
Application name	TBN Back Titration	
Sample		
Name	sample	
Amount	2.000	[g]
Probe		
Recommended probe	PHG311-9	
Titrant		
Name	Sodium acetate	
Titrant concentration	0.1000	[eq/L]
Syringe	Syringe 1	
Rinsing step 1 (solvent)		
Active	Yes	
Time	30	[s]
Stirring speed	25	[%]
Rinsing step 2 (DI water)		
Active	Yes	
Time	30	[s]
Stirring speed	25	[%]
Rinsing step 3 (solvent)		
Active	Yes	
Time	30	[s]
Stirring speed	25	[%]
Back titration		
Type	Manual	
Excess volume	4	[mL]
Stirring speed	25	[%]
Measured parameter		[mV]
Predose	0	[mL]
Max volume stop point	10	[mL]
Stop on last EQP	Yes	

Delay	120	[s]
Min increment size	0.08	[mL]
Max increment size	0.25	[mL]
Result 1 name	TBN (mgKOH/g)	
R1 resolution	2 decimals	
R1 min	0.01	[mg/g]
R1 max	300	[mg/g]
R1 QC min	0.01	[mg/g]
R1 QC max	300	[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

A titration is divided into two parts:

- A rinsing procedure for the electrodes, comprising three steps: 30 seconds in solvent (chlorobenzene + acetic acid), 30 seconds in deionized water and another 30 seconds in solvent.
- A titration of Total Base Number.

5.1 Sample analysis

Launch the application **TBN Back Titration**.

Weigh the sample in the titration beaker according to the recommendations given in section **4.1**.

In **Sample type** choose **Sample** and press **Start**.

Follow the rinsing indications on the screen. Then, place the beaker containing the sample and a stir bar under the probe holder, press **OK**. Add 60 mL of solvent with a graduated cylinder, make sure that both electrodes are immersed and press **OK**. Add 4 mL of $HClO_4$ 0.1 eq/L with a pipette. Titration will start after a 2 min delay. At the end of the titration, TBN is displayed in mg of KOH per g of sample.

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 mg/g) 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.

Note: *In* ***Sample type****,* ***Define blank*** *and* ***Sample with blank*** *are not available for Back Titration.*

6. Results

6.1. Result calculation

With $HClO_4$ as back titrant and sodium acetate as titrant, the calculation is:

$$\text{TBN (mgKOH/g)} = \frac{C_{\text{back titrant}}\,(\text{eq/L}) \times V_{\text{back titrant}} - C_{\text{titrant}}\,(\text{eq/L}) \times V_{\text{titrant}}\,(\text{mL})}{m_{\text{sample}}\,(\text{g})} \times M_{\text{KOH}}\,(\text{g/mol})$$

$$= \frac{0.1\,(\text{eq/L}) \times 4\,(\text{mL}) - 0.1\,(\text{eq/L}) \times V_{\text{titrant}}\,(\text{mL})}{m_{\text{sample}}\,(\text{g})} \times 56.11\,(\text{g/mol})$$

6.2. Experimental results

These results are indicative and have been obtained for a given sample for six successive determinations. Results are given for the titration of 3 standards and a sample of used motor oil.

Standard 1.01 mg/g	
Mean TBN (mg/g)	1.17
Standard deviation (mg/g)	0.05
Relative standard deviation (%)	3.8

Standard 6.06 mg/g	
Mean TBN (mg/g)	6.10
Standard deviation (mg/g)	0.11
Relative standard deviation (%)	1.8

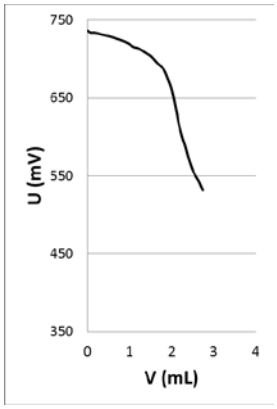
Standard 40.40 mg/g	
Mean TBN (mg/g)	40.33
Standard deviation (mg/g)	1.87
Relative standard deviation (%)	4.6

Used motor oil	
Mean TBN (mg/g)	10.29
Standard deviation (mg/g)	0.32
Relative standard deviation (%)	3.1

The titration typically lasts around 2 min.

6.3. Example of a titration curve

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



7. Recommendations

Refill the reference electrode regularly to maintain the level of both internal solutions (inner and outer) at around 1 cm (0.4 inches) below the refill hole.

Rinsing steps can be skipped (right button) or disabled (in Edit mode), although it is highly recommended to consistently rinse the electrodes between each measurement in order to maintain good accuracy.

8. Bibliography

- *Standard ASTM D2896-11*

9. Appendix

9.1 Electrodes testing and storage

It is recommended to check the electrode's behavior when first put into use, or when new electrodes are installed, and retest at intervals thereafter. Dip the electrodes into a well-stirred mixture of 60 mL of glacial acetic acid plus 0.1 g of potassium hydrogen phthalate and record the reading (**Maintenance** > **Live Measure**).

Rinse the electrodes with chlorobenzene and immerse in a 50 mL of glacial acetic acid plus 0.75 mL of 0.1 eq/L $HClO_4$ solution. The difference between readings is to be at least 0.3 V.

When not in use, store both electrodes in deionized water.

9.2 Titrant calibration

The sodium acetate solution can be calibrated. Its exact concentration can be determined from an acid-base titration using $HClO_4$.

Use a pipette to take precisely 4 mL of 0.1 eq/L $HClO_4$ standard solution and pour it into the titration beaker. Add 60 mL of solvent with a graduated cylinder. Put in a stir bar, dip the probes and the delivery tip into the solution and launch the titrant calibration sequence.

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	Sodium acetate	
Titrant concentration	0.1000	[eq/L]
Syringe	Syringe 1	
Standard		
Name	HClO4	
Amount	4	[mL]
Concentration	0.1	[eq/L]
IP titration		
Stirring speed	30	[%]
Measured parameter		[mV]
Predose	2	[mL]
Max volume stop point	10	[mL]
Stop on last EQP	True	
Delay	0	[s]
Min increment size	0.05	[mL]
Max increment size	0.2	[mL]
Result name	Titer	
Result resolution	4 decimals	
Result min	0.09	[eq/L]
Result max	0.11	[eq/L]