

Total Base Number in petroleum products by automatic titration

Water Analysis Instruments,
Thermo Fisher Scientific

Key words

TBN, ASTM D2896, ISO 3771, oil, used oil, oil additives, lubricant, lubricant degradation, Orion 8172BNWP, Orion Star T910, Orion Star T940.

Preprogrammed methods

T4 TBN Back

Introduction

Total Base Number (TBN) in a petroleum product is determined using the preprogrammed method T4 TBN Back. The sample is dissolved in the prescribed solvents, a standard perchloric acid (PCA) reagent is added, and the sample is back titrated to an equivalence point endpoint using an alkaline titrant prepared in glacial acetic acid. The back titration is compliant with ASTM D2896, is fast, and provides reliable endpoints.

Recommended equipment

- Thermo Scientific™ Orion™ Star™ Titrator T910 pH, or T940 All-In-One, or equivalent with a 20 mL burette
- Thermo Scientific™ Orion™ ROSS™ SureFlow™ pH electrode 8172BNWP or equivalent
- Thermo Scientific™ Orion™ Automatic Temperature Compensation (ATC) probe
- Analytical balance, capable of weighing to 0.0001g
- Glass pipette, 4 mL or 10 mL graduated
- 25 mL and 100 mL graduated cylinders
- 100 mL or 150 mL beakers



Required reagents and solutions

- Purchased or prepared sodium acetate in acetic acid standard titrant solution, 0.1 N (0.1 M)
- Purchased standard solution, perchloric acid in acetic acid, 0.1 N (0.1 M)
- Purchased or prepared 1-3M lithium chloride in ethanol (8.5 g LiCl in 100 mL ethanol)
- Glacial acetic acid (GAA)
- Chlorobenzene (CBZ)
- 2:1 mixture CBZ/GAA
- Reagent grade water (RGW)
- Electrode storage solution

See ASTM D2896 for details on preparing titrant and/or electrolyte fill solution.

Optional (for kinetic electrode test):

- Purchased pH buffers, pH 4, 7, and 10

Use suitable Personal Protective Equipment (PPE) and ventilation as recommended by the Safety Data Sheets (SDS) for the chemicals utilized during this procedure.

Titration setup

Connect the Orion pH electrode, ATC, and the stirrer probe to the titrator. If not previously done, import the T4 TBN Back preprogrammed method into the titrator from the Methods screen¹. Rinse and fill the burette with titrant. See the titrator user manual for details on setting up the titrator.

If bubbles are visible in the tubing, dispense titrant (from the Burette screen) until the bubbles have been expelled. Tap the tubing to dislodge bubbles. Consider standardizing the titrant before titrating samples. See Titrant section below.

T4 TBN Back method: Preprogrammed parameters

Electrode	Parameter
Electrode Type	pH
Electrode Name	edit as desired
Resolution	0.001
Buffer Group	USA

Titration	Parameter
Titration Name	Acetate in GAA
Titration ID	Edit as desired
Conc. Input Mode	Standardization
Nominal Concentration	0.1M
Standardize Tech	Equivalence Pt.
Number of Endpoints	1
Results Units	M
Standardize Reaction Ratio	1
Standard Name	PCA
Standard Amount	Fixed volume, 4 mL
Standard Concentration	0.1000 M*
Pre-dose Titrant Volume	2 mL
Max. Total Titrant Volume	6 mL
Standard Process Control	Routine
Pre-stir Duration	20 sec
Stir Speed	Fast

Titration	Parameter
Titration Technique	Equivalence Pt.
Number of Endpoints	1
Display Units	mV
Titration Type	Back
Blank Required	No
Result Units	TBN
Reagent Reaction Ratio	1
Titration Reaction Ratio	1
Reagent Amount	Fixed volume, 4 mL
Reagent Concentration	0.1000 M*
Sample Amount	Variable weight
Pre-dose Titrant Volume	0.1 mL
Max. Total Titrant Volume	5 mL
Titration Process Control	Routine
Pre-stir Duration	60 sec
Stir Speed	Fast
Sample ID	Manual

*If the standard PCA reagent concentration is not 0.1000 M (0.1000 N), enter the true value.

Electrode preparation

First time use: Drain the aqueous fill solution from the electrode by depressing the cap to flush it out. Rinse the inner chamber with RGW to remove all traces of salt, then rinse with ethanol. Rinse and fill the electrode with the lithium chloride in ethanol electrolyte fill solution. Store overnight in Orion ROSS storage solution with the fill hole cover in place.

Daily use: Remove electrode from storage solution. Add lithium chloride in ethanol electrolyte fill solution to the bottom of the fill hole and leave the fill hole open during testing. Place electrode in a beaker of RGW for a few minutes before starting titrations.

Sample preparation

Weigh sample into a beaker or suitable titration vessel according to the expected base number value and record the exact weight. Choose the approximate weight of sample as follows:
approximate weight, g = 10/expected TBN
Do not exceed 2.5 grams of sample. Measure 40 mL of CBZ into the beaker to dissolve the sample. Then add 20 mL of GAA. Pipette 4.00 mL of standard PCA reagent into the beaker. Mix. The sample is ready to titrate. For best accuracy, prepare three portions of each sample, as noted above. Titrate all three and report the average result.

Electrode rinsing protocol

In order to transition the electrode back and forth between the aqueous environment of soaking to the non-aqueous environment of titration, follow these rinsing protocols:

Before titrations, remove the electrode from the RGW soak and rinse it in this order, before placing in the prepared sample:



After titrations, remove the electrode from the sample and rinse it in this order, before soaking in RGW:



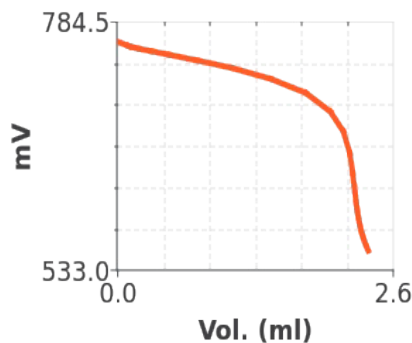
Sample titration

1. From the Methods screen, select option to run the saved method TBN.
2. Remove the electrode from RGW. Rinse the electrode, stirrer, ATC, and dispenser with GAA, then solvent mix, according to the “before titration” rinsing protocol noted above. Place the electrode, stirrer, ATC, and dispenser into the sample in the beaker. Ensure that the dispenser tip is inserted below the surface of the sample and start the titration.
3. Results are reported as TBN in mg KOH/g.
4. After the titration, remove the electrode, stirrer, ATC, and dispenser from the sample. Rinse with solvent mix, then GAA, then RGW, according to the “after titration” rinsing protocol noted above. Soak 3 minutes in clean RGW between titrations.
5. For best accuracy, repeat steps 2 to 4 to run a total of three cycles on three portions of each sample. Report the average result.

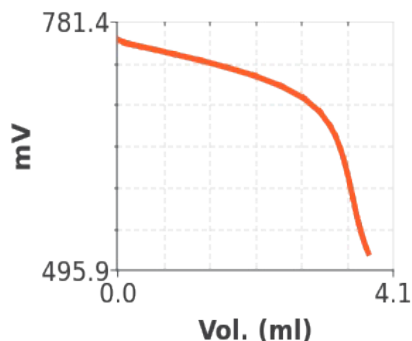
Results

Parameter	Sample	Average (n = 3)	RSD	Analysis Time
TBN (Base number)	Oil	9.802 mg KOH/g	0.30%	2.8 minutes
TBN (Base number)	Used oil	3.841 mg KOH/g	1.1%	4.4 minutes ²

TBN of oil



TBN of used oil



Range

This preprogrammed titration method covers a range of up to 300 mg KOH/g, when using 0.1 M (0.1 N) standard PCA reagent and the prescribed weight of sample.

Method modifications

For shorter titrations: Use a pre-dose to shorten the analysis time. Edit the pre-dose in the Titration section of the method. In general, a pre-dose of 1 or 1.5 mL can be expected to work well.

Titrant

Over time, standard titrant solutions age and can change concentration. For higher accuracy, determine the exact concentration by standardizing the titrant. It is common to standardize on a weekly basis, but other standardization frequencies may be suitable.

1. Standardizing titrant
 - a. Accurately pipet 4.00 mL standard PCA reagent into a clean 100 or 150 mL beaker. Add 60 mL of solvent mix.
 - b. Select the TBN Back method. At the pre-titration screen, select the standardize option and follow the prompts to standardize the titrant.
 - c. The new standardized titrant concentration will automatically be saved and used for subsequent TBN Back method titrations.

2. Certified standardized titrant solutions

- a. Some customers may prefer not to standardize their titrant, instead choosing to purchase and use certified standardized titration solutions. In this case, edit the Titrant section of the method and enter the certified concentration and titrant ID (i.e., lot number, if desired).

Titration and electrode care

Refer to the titration and electrode user manuals for details on cleaning, storage, and maintenance recommendations to keep the titration and electrode performing well. Main points for care are summarized below.

Daily Care	Weekly or Biweekly Care	As Needed
<ul style="list-style-type: none">• If bubbles are visible in the titration tubing, dispense titrant until bubbles have been expelled. Tap tubing to dislodge bubbles that stick.• Add electrode fill solution up to the bottom of the fill hole and leave the fill hole open during measurement.• Rinse electrode well with GAA, then solvent mix before each titration cycle.• Rinse electrode well with solvent mix, then GAA, then RGW after each titration cycle.• Between titration cycles, soak the electrode for 3 minutes in RGW.• Cover the fill hole and store electrode in storage solution overnight.	<ul style="list-style-type: none">• Flush and replace the electrode fill solution of the electrode.• Change the storage solution in the electrode storage bottle.• Consider standardizing the titrant on a weekly basis.• Clean the electrode by soaking 15 minutes in a warm 1% laboratory detergent solution while stirring. Then brush gently with a soft toothbrush only and rinse well with RGW. Flush and replace the fill solution of the electrode after cleaning. Soak in storage solution 30 minutes or more before use.• Prepare a supply of solvent mix by combining 2 parts of CBZ with 1 part of GAA.	<ul style="list-style-type: none">• For slow or drifty electrode response, clean the electrode in warm 1% laboratory detergent, as noted in the Weekly Care section.• If still slow or drifty, use Orion pH cleaning solution C, per instructions, or soak 30 minutes in 1M nitric acid, rinse well, then flush and replace the fill solution. Soak in storage solution 30 minutes or more before use.• See the user manuals for maintenance details.• The Kinetic Electrode Test described in ASTM D2896 Appendix X4 may be used to determine the performance of the electrode. If performance is not as expected, clean and perform maintenance on the electrode as described above.

Notes

¹Refer to the user manual for detailed instructions.

²To speed up the titration, consider changing the pre-dose to 1 or 1.5 mL.

To purchase Thermo Scientific laboratory products, please contact your local equipment distributor and reference the part numbers listed below:

Product	Description	Cat. No.
Titrator kits	Orion Star T910 pH titrator SureFlow kit with 8172BNWP ROSS SureFlow pH electrode and ATC probe	START9102
	Orion Star T940 All-In-One Titrator Sure-Flow kit with 8172BNWP ROSS SureFlow pH electrode and ATC probe	START9402
Titrators	Thermo Scientific Orion Star T910 pH Titrator without electrode	START9100
	Thermo Scientific Orion Star T9400 All-in-One Titrator without electrode	START9400
Electrodes	Thermo Scientific Orion ROSS SureFlow pH Electrode	8172BNWP
	Automatic Temperature Compensation (ATC) probe	927007MD
Accessories	100 or 150 mL beakers	
	25 mL graduated cylinder	
	100 mL graduated cylinder	
	4 mL pipet	
pH Buffers	Orion pH 4.01 buffer, NIST traceable, 475 ml	910104
	Orion pH 7.00 buffer, NIST traceable, 475 ml	910107
	Orion pH 10.01 buffer, NIST traceable, 475 ml	910110
	Orion ROSS pH electrode storage solution, 475 ml	810001
Reagent Grade Water	Thermo Scientific™ Barnstead™ Smart2Pure™ 12 UV Water Purification System	50129890*
Reagents	0.1 N (0.1 M) sodium acetate in acetic acid standard titrant	
	Chlorobenzene	
	Glacial acetic acid	
	0.1 N (0.1 M) perchloric acid in acetic acid	
	1-3 M lithium chloride in ethanol electrolyte filling solution	

*Please contact your local Thermo Scientific representative for support on ordering the best water purification system for your application. And visit our website at www.thermofisher.com/T900titratorseries.

References

ASTM International. *Standard Test Method for Base Number of Petroleum Products by Potentiometric Perchloric Acid Titration* (D2896). West Conshohocken, PA. www.astm.org.

Find out more at thermofisher.com/titrator