

Total Acid Number in petroleum products by automatic titration

Water Analysis Instruments,
Thermo Fisher Scientific

Key words

TAN, ASTM D664, ISO 6619, oil, used oil, lubricant, lubricant degradation, acidic contamination, Orion 8172BNWP, Orion 8102BNUWP, Orion Star T910, Orion Star T940.

Preprogrammed method

T3 TAN

Introduction

Total Acid Number (TAN) in a petroleum product is determined using the preprogrammed method T3 TAN. The sample is dissolved in the prescribed solvent and is directly titrated to a preset endpoint at pH 11 using an alkaline titrant prepared in isopropanol. A blank is analyzed and automatically subtracted.

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
- 10.0 mL pipette
- 100 mL graduated cylinder
- 150 mL beakers



Required reagents and solutions

- Purchased or prepared potassium hydroxide in isopropanol (KOH in IPA) standard titrant solution, 0.1 M (0.1N)
- Purchased or prepared titration solvent (50:45:5 toluene/isopropanol/water)
- Purchased or prepared 1-3M lithium chloride in ethanol electrolyte fill solution (8.5 g LiCl in 100 mL ethanol)
- Reagent Grade Water (RGW)
- pH buffers: pH 4, 7, and 10
- Electrode storage solution
- Carbon dioxide adsorbent

See ASTM D664 for details on preparing titrant, titration solvent, and/or electrolyte fill solution.

Optional (for standardization):

- Potassium hydrogen phthalate (KHP) primary acidimetric standard, solid or purchased standard solution, 0.05M.

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 T3 TAN preprogrammed method into the titrator from the Methods screen¹. Rinse and fill the burette with 0.1M (0.1N) KOH in IPA titrant. Fill the adsorber tube on the titrant bottle cap with carbon dioxide absorbent and plug with glass wool or cover with Parafilm perforated with a few ventilation holes. 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.

T3 TAN method: Preprogrammed parameters

Electrode	Parameter
Electrode Type	pH
Electrode Name	edit as desired
Resolution	0.01
Buffer Group	USA

Titrant	Parameter
Titrant Name	NaOH_IPA
Titrant 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	KHP
Standard Amount	Variable Weight
Standard Molecular Wt	204.2
Standard Purity	100%
Pre-dose Titrant Volume	2 mL
Max total titrant volume	8 mL
Stand. Process Control	Routine
Pre-stir Duration	5 sec
Stir Speed	Medium

Titration	Parameter
Titration Technique	Preset End Pt.
Number of Endpoints	1
Endpoint Values	pH 11
Display Units	pH
Titration Type	Direct
Blank Required	Variable
Titration Units	TAN
Reaction Ratio	1
Sample Amount	Variable weight
Pre-dose Titrant Volume	0 mL
Max total titrant volume	6 mL
Titration Process Control	Routine
Pre-stir Duration	20 sec
Stir Speed	Fast
Sample ID	Manual

Electrode preparation

First time use: Drain the aqueous fill solution from the electrode. 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 the electrode 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.

Rinsing: Rinse thoroughly with IPA before titrations. Rinse thoroughly with IPA, then RGW after titrations. Between titrations soak 5 minutes in pH 4 solution that has been diluted 1:10 with RGW.

Sample and blank preparation

Sample: Weigh sample into a beaker or suitable titration vessel according to the expected acid number value and record the exact weight. See table below for guidance on suitable sample weights. Measure 75 mL of titration solvent in a graduated cylinder and add to the sample. The sample is ready to titrate.

Blank: Measure 75 mL of titration solvent in a graduated cylinder and pour into a beaker or suitable titration vessel. The blank is ready to titrate.

See ASTM D664 Standard Test Method for Acid Number of Petroleum Products by Potentiometric Titration for more details on sample preparation. Some samples, such as used oils, may require heating and/or straining before preparation for titration.

Acid Number	Weight of Sample	Accuracy of Weight, g
0.05 to < 1.0	20.0 ±2.0	0.10
1.0 to < 5.0	5.0 ±0.5	0.02
5 to < 20	1.0 ±0.1	0.005
20 to < 100	0.25 ±0.02	0.001
100 to <260	0.1 ±0.01	0.0005

Blank titration

1. From the Home screen or Methods screen, select option to use a saved method, then select TAN.
2. At the titration pre-check screen, select the Calibrate option and calibrate the electrode with pH 4, 7, and 10 buffers. In each buffer, stir and wait at least 2 minutes before accepting the calibration value. Slope should be 92% or better.
3. After calibration, rinse electrode, stirrer, ATC, and dispenser with RGW, then rinse well with IPA.
4. Place the electrode, stirrer, ATC, and dispenser into the prepared blank sample in the beaker. Ensure that the dispenser tip is inserted below the surface of the sample and start the titration.
5. Results are reported as mmole TAN. For best accuracy, calibrate and run a blank daily.
6. After the titration, remove the electrode, stirrer, ATC, and dispenser from the sample. Rinse well with IPA, then rinse well with RGW, and soak 5 minutes in diluted pH 4 buffer (diluted 1:10 with RGW) between titrations.

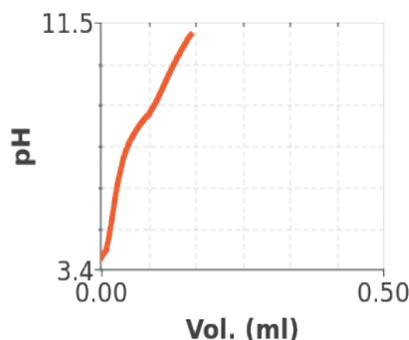
Sample titration

7. From the titration pre-check screen, select the Start Titration option.
8. Rinse the electrode, stirrer, ATC, and dispenser well with RGW, then rinse well with IPA.
9. Place the electrode, stirrer, ATC, and dispenser into the prepared sample in the beaker. Ensure that the dispenser tip is inserted below the surface of the sample and start the titration.
10. Results are reported as TAN/acid number in mg KOH/g.
11. After the titration, remove the electrode, stirrer, ATC, and dispenser from the sample. Rinse well with IPA, then rinse well with RGW, and soak 5 minutes in diluted pH 4 buffer between titrations.
12. For best accuracy, run a total of three cycles for each sample and report the average result.

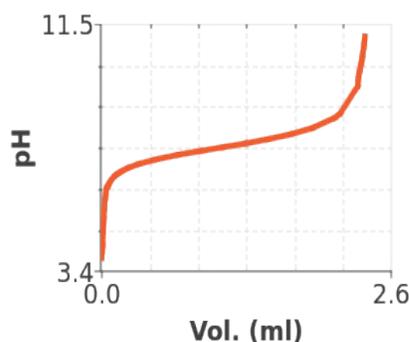
Results

Parameter	Sample	Average (n = 3)	RSD	Analysis Time
TAN Blank	Titration solvent	0.01465 mmol	1.60%	6 minutes
TAN (Acid Number)	Oil	2.275 mg KOH/g	1.49%	5 minutes
TAN (Acid Number)	Used oil	3.373 mg KOH/g	1.44%	3 minutes ²

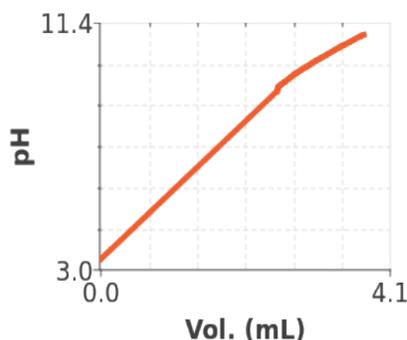
TAN Blank



TAN of Oil



TAN of Used Oil



Range

This preprogrammed titration method covers a range from about 0.1 to 150 mg KOH/g, when using 0.1M (0.1 N) KOH in IPA titrant and the prescribed weight of sample.

Method modifications

For shorter titrations: For routine titrations with well-established endpoint volumes, use a pre-dose to shorten the analysis time. Edit the pre-dose in the Titration section of the method. In general, set the pre-dose at a volume that is 1 mL less than the expected endpoint volume.

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 a daily standardization frequency, may be suitable for this titrant.

1. Standardizing the 0.1M (0.1N) KOH in IPA titrant. Choose option a (using a solid standard) or choose option b (using a standard solution).
 - a. Solid KHP standard
 - i. Accurately weigh out about 0.10 g KHP ± 0.01 g into a clean 100 or 150 mL beaker. Record the exact weight to 0.0000g. Repeat twice more for a total of three beakers of KHP. Add RGW to the 60 mL mark on each beaker and stir for about 2 minutes or so until the KHP is completely dissolved
 - If the KHP purity is not 100%, edit the Titrant section of the TAN method to enter the actual purity.
 - ii. Select the TAN preprogrammed method on the titrator.
 - iii. At the titration pre-check screen, select the Standardize option and follow the prompts to standardize the titrant.
 - iv. For best accuracy, run three cycles of the standard. The titrator will determine the average value.
 - v. The new standardized titrant concentration will automatically be saved in the TAN method and used for subsequent TAN method titrations.
 - b. 0.05M KHP standard solution
 - i. Accurately pipet 10.0 mL 0.05M KHP standard solution into a clean 100 or 150 mL beaker. Add RGW to the 60 mL mark on each beaker.
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 each method (TAN Blank and TAN) method and enter the certified concentration and titrant ID (i.e., lot number, if desired).
 - ii. From the Methods screen, access the TAN preprogrammed method and edit the Titrant section. Change the sample amount to fixed volume and enter a volume of 10.0 mL. Enter the standard concentration (e.g., 0.05M). Save the method.
 - iii. At the titration pre-check screen, select the standardize option and follow the prompts to standardize the titrant.
 - iv. For best accuracy, run three cycles of the same standard. The titrator will determine the average value.
 - v. The new standardized titrant concentration will automatically be saved and used for subsequent TAN method titrations.

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 the tubing to dislodge bubbles.• Add electrode fill solution up to the bottom of the fill hole and leave the fill hole open during measurement.• Calibrate the electrode with pH 4, 7, and 10. If desired, measure pH 12.45 buffer to verify calibration.• Prepare a soaking solution of pH 4 buffer diluted 1:10 with RGW.• Rinse electrode well with IPA before each titration cycle.• Rinse electrode well with IPA, then RGW after each titration cycle.• Between titration cycles, soak the electrode for 5 minutes in diluted pH 4 buffer.• Cover the fill hole and store electrode in storage solution overnight.• Determine the TAN Blank value daily.	<ul style="list-style-type: none">• Flush, rinse, and replace the fill solution of the electrode.• Change the storage solution in the electrode storage bottle.• Consider standardizing the titrant on a weekly or even a daily 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, rinse, and replace the fill solution of the electrode after cleaning. Soak in storage solution 30 minutes or more before use.	<ul style="list-style-type: none">• For slow or drift electrode response, clean the electrode in warm 1% laboratory detergent, as noted in the Weekly Care section.• If still slow or drift, 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 D664 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.• If precipitate forms in the burette, empty the burette and flush with warm tap water until dissolved. Then flush the burette multiple times with fresh titrant.

Notes

¹Refer to the user manual for detailed instructions.

²With a 2.5 mL pre-dose, as described in the Method Modifications section. Without a pre-dose, titration time is 15 minutes.

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 Sure-Flow kit with 8172BNWP ROSS Sure-Flow pH electrode and ATC probe	START9102
	Orion Star T940 All-in-One Titrator Sure-Flow kit with 8172BNWP ROSS Sure-Flow 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 Sure-Flow pH Electrode	8172BNWP
	Automatic Temperature Compensation (ATC) probe	927007MD
Accessories	100 or 150 mL beakers	
	100 mL graduated cylinder	
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 pH 12.46 buffer, NIST traceable, 475 ml	910112
	Orion ROSS pH electrode storage solution, 475 ml	810001
Reagent Grade Water	Thermo Scientific™ Barnstead™ Smart2Pure™ 12 UV Water Purification System	50129890*
Reagents	0.1M (0.1N) Potassium Hydroxide in isopropanol standard titrant	
	Potassium hydrogen phthalate, primary standard grade, solid or 0.05M solution	
	Titration Solvent (50:45:5 toluene/isopropanol/water)	
	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/labwater.

References

ASTM International. *Standard Test Method for Acid Number of Petroleum Products by Potentiometric Titration* (D664). West Conshohocken, PA. www.astm.org.

Find out more at thermofisher.com/titrator

