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Best practices using automated titrators

Achieving speed and accuracy in your lab

ThermoFisher SCIENTIFIC

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Top 10 Tips for Titrating

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1 Choose an Autotitrator

Convert from manual titrations to an autotitrator to get the benefits of improved accuracy and precision, safe handling of corrosive titrants, ease-of-use, better use of technician time, automated calculations and automatic data logging. If you are currently outsourcing your titrations, use an autotitrator to run your samples in-house. This can save time and money and provide quick turnaround for faster results.

2 Pre-Program to Save Time

Converting to an automatic titration is often a simple one-time task, resulting in a saved programmed method that can be copied, shared, and used for all future titrations. To convert a manual method, use a preprogrammed method that is already available for the titrator, or enter the parameters of the manual method directly into the titrator. Either process typically takes only a few minutes to complete.

3 Standardize Your Titrant

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

4 Choose the Right pH Electrode

The best pH electrodes respond quickly to large and small pH changes, are stable, and accurate. A fast and accurate pH electrode leads to fast and accurate pH titrations, so choosing the right one is important. For example, ASTM has written standards for acid number and base number titrations that recommend the type of pH electrodes to be used and the test procedures to verify electrode performance. The pH electrodes that we recommend in our non-aqueous pH titration application notes (for acid number and base number) meet the recommendations and performance tests of the ASTM standards.

5 Calibrate pH for Best Accuracy

In most cases, it is recommended that you calibrate your pH electrode once a day when titrating acid/base samples. If in doubt about the stability of the calibration over the course of the day, read a pH buffer standard (in measure mode) that is close to the endpoint pH. If the buffer reads close to the accepted value at the measured temperature, your calibration is still good. In some cases, for example, if the titration technique is “equivalence point” (rather than preset endpoint) and the measurement units chosen are mV units (rather than pH units), calibration is not necessary for accurate titration results. However, calibration still gives valuable information about the performance of the electrode and can indicate the need for maintenance or replacement.

6 Measure Temperature

Using an automatic temperature compensation (ATC) probe or triode to measure temperature provides valuable temperature information that is needed for an accurate pH calibration and for adjusting the pH calibration slope when the temperature changes. This is very important for the accuracy and precision of a pH titration that uses the preset endpoint titration technique.

7 Titrate Faster and Run More Samples

When speed and sample throughput are important, there are different options for maximizing your titration. One option is to make use of the pre-dose parameter. If your titration typically takes a known amount of titrant, program a pre-dose into your method to dose most of the titrant in one shot. For example, if a titration typically takes about 8 mL, you might chose a 7 mL pre-dose. The titrator will only have to search for the endpoint in the last mL or so. Another option is to choose a different titration process control parameter. For example, if the control is “routine” try changing to “quick” to speed up the titration. Another option is to titrate less sample. If a 10 mL sample takes 10 mL of titrant, try using 2 mL of sample, which will take only 2 mL of titrant. When using an autotitrator, 2 mL can be added in 0.001 mL increments. That allows plenty of precision, even though only a small amount of titrant is used.

8 Care For Your Electrodes

Good electrodes require some routine care, just like a car. Flush and refill the filling solution regularly—weekly or biweekly is usually effective. Store the electrode in the recommended storage solution and change the storage solution biweekly. Depending on the type of samples analyzed, periodic cleaning may improve the performance of the electrode. Follow the recommendations in our application notes or the pH electrode user guide.

9 Choose the Best Endpoint Technique

The autotitrator can find the pH endpoint in one of two ways: 1) by going to a preset pH value that we specify (e.g., pH 8.3) or 2) by finding the endpoint based on mathematical evaluation of the titration curve. These techniques are the preset endpoint and equivalence point techniques, respectively. When choosing your endpoint technique, follow the recommendation from the core method application note that is the same or similar to your titration. If your titration is different, follow your current manual titration method. For example, if you are currently doing a manual titration with a pH electrode to a pH of 8.3, you would choose the preset end point titration technique and specify pH 8.3. If you are currently doing a manual titration of a strong acid/strong base or titrating to a color end point, you might choose the equivalence point titration technique and let the titrator determine the location of the endpoint. (Note: These are general guidelines. Some titrations differ. If in doubt, contact your local sales specialist or our technical service team).

10 Preserve the Integrity of Your Titrant

To preserve the integrity of your titrant, use the recommended titrant bottles, caps, and tubing, which are designed to minimize evaporation and prevent particles from getting into the titrant. Some titrants, such as sodium hydroxide titrants for certain titrations, can be protected from carbon dioxide absorption. Place a carbon dioxide sorbent (scrubber) tube on the titrant cap air intake. Other titrants, such as iodine/iodide or silver nitrate, should be protected from light by use of opaque or brown glass titrant bottles.

Titratable acidity in orange juice by automatic titration

Water Analysis Instruments,
Thermo Fisher Scientific

Key words
TA, Total acidity, citric acid, acidified foods, fruit juice, citrus, grapefruit, lemon, lime, beverage, wine, food, pH, AOAC 942.15, Orion 8172BNWP, Orion 8102BNUMD, Orion Star T910, Orion Star T940.

Introduction

Titratable acidity (TA), as citric acid, in orange juice is determined using the preprogrammed method T1 TitraAcidity. This method is a direct titration to a preset endpoint at pH 8.2 using 0.1M (0.1N) sodium hydroxide titrant. The method may be edited to perform titratable acidity in other samples as well.

Recommended equipment

- Thermo Scientific™ Orion Star™ T910 pH Titrator or T940 All-In-One Titrator or equivalent
- Thermo Scientific™ Orion™ ROSS™ SureFlow™ pH electrode (Cat. No. 8172BNWP) or equivalent
- Orion Automatic Temperature Compensation (ATC) probe
- Analytical balance (for sample measurement by weight) or graduated 10 mL pipet (for sample measurement by volume)

Required reagents and solutions

- Purchased or prepared sodium hydroxide (NaOH) standard titrant solution, 0.1 M (0.1 N)
- Reagent grade water (RGW)
- pH buffers: pH 4, 7, and 10

Optional:
Potassium hydrogen phthalate (KHP) acidimetric standard

Use suitable personal protective equipment (PPE) as recommended by the Safety Data Sheets (SDS) for the chemicals utilized during this procedure.

Titrator setup

Connect the Orion pH electrode, ATC, and the stirrer probe to the titrator. If not previously done, import the T1 TitraAcidity preprogrammed method into the titrator from the Methods screen[1]. Rinse and fill the burette with 0.1 M (0.1 N) sodium hydroxide titrant. See the titrator user manual for details. If bubbles are visible in the tubing, dispense titrant (from the Burette screen) until the bubbles have been expelled. Consider standardizing the titrant before titrating samples. See the following Titrant section.

T1 TitraAcidity Method: Preprogrammed parameters

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

Titrant	Parameter
Titrant Name	NaOH
Titrant ID	
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	0 mL
Max. Total Titrant Volume	5 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	8.2
Titration Type	Direct
Blank Required	No
Result Units	%w/w
Reaction Ratio	0.333
Sample Mol. Wt.	192.1
Sample Amount	Variable weight
Pre-dose Titrant Volume	0 mL
Max total titrant volume	10 mL
Titration Process Control	Routine
Pre-stir Duration	5 sec
Stir Speed	Medium
Sample ID	Manual

Electrode preparation

Remove electrode from storage solution. Top up the fill solution to the bottom of the fill hole and leave the fill hole open during testing. Rinse thoroughly with RGW before and between titrations.

Sample preparation

Place a clean 100 or 150 mL beaker on a balance and tare it. Add about 3 grams of orange juice sample to the beaker and record the exact weight to 0.001g or better. Add RGW to the 60 mL mark on the beaker. The sample is ready to titrate.

Sample titration

1. From the Home screen, select option to use a saved method, then select the T1 TitraAcidity reprogrammed method.
2. At the pre-titration screen, select the Calibrate option and calibrate the electrode with pH 4, 7, and pH 10 buffers.
3. After calibration, place the electrode, ATC, stirrer, 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.
4. When prompted, enter the exact weight of the sample.

Results

Parameter	Sample	Average (n = 4)	RSD	Analysis Time
Titratable Acidity (as citric acid)	Orange Juice	0.710% (w/w)	0.28%	1.1 minutes[2]

Range

This preprogrammed titration method covers a range from 0.5 to 2% acid by weight as citric acid. See below for method modifications to run other concentrations.

Method modifications

- **For other concentrations:** For less acidic samples, use double the weight of sample. For more acidic samples, use half the weight of sample or change the maximum titration volume to 20 mL by editing the Titration section of the method.
- **For other result units:** Edit the Titration section of the method and choose the desired unit. If volume-based units are chosen (i.e., % w/v or g acid/100 mL), choose a fixed volume of 3 mL.
- **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 0.5 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 other standardization frequencies may be suitable.

1. Standardizing the Titrant
    a. Weigh about 0.05 g KHP into a clean 100 or 150 mL beaker. Record the exact weight to the nearest 0.0001g. 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.
    b. If the KHP purity is not 100%, edit the Titrant section of the method to enter the actual purity.
    c. Select the Titratable Acidity preprogrammed method on the titrator.
    d. At the pre-titration screen, select the Standardize option and follow the prompts to standardize the titrant.
    e. The new standardized titrant concentration will automatically be saved and used for subsequent T1 TitraAcidity 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).

Titrator and electrode care

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

Daily Care	Weekly or Biweekly Care	As Needed
• If bubbles are visible in the titrator tubing, dispense titrant until bubbles have been expelled • Top up the electrode fill solution and leave the fill hole open during measurement • Rinse electrode well with RGW between titration cycles • Cover the fill hole and store electrode in storage solution overnight	• Drain and replace the fill solution of the electrode. • Change the storage solution in the electrode storage bottle • Consider standardizing the titrant on a weekly basis	• For slow or drifty electrode response, soak 15 minutes in 1% laboratory detergent while stirring. Rinse well with RGW afterwards • If still slow or drifty, use Orion pH cleaning solution D per instructions • See the user manuals for maintenance details

Notes

[1]Refer to the user manual for detailed instructions, if desired.

[2]With a suitable pre-dose, as described in the Method Modifications section.

Total alkalinity in water by automatic titration

Water Analysis Instruments,
Thermo Fisher Scientific

Key words
m-alkalinity, p-alkalinity, p and m alkalinity, carbonate, bicarbonate, hydroxyl, wastewater, Standard Methods 2320, ASTM D1067, ISO 9663, Orion 8172BNWP, Orion 8102BNUWP, Orion Star T910, Orion Star T940.

Introduction

Total alkalinity (or m-alkalinity) in a water sample is determined using the preprogrammed method T2 TotAlkalinity. This method is a direct titration to a preset endpoint at pH 4.5 using acidic titrant. The method may be edited to perform total alkalinity in other samples as well.

Recommended equipment

- Thermo Scientific™ Orion™ Star™ Titrator T910 pH, or T940 All-In-One, or equivalent with a 20 mL burrette
- Thermo Scientific™ Orion™ ROSS™ SureFlow™ 8172BNWP pH electrode, or equivalent
- Thermo Scientific™ Orion™ Automatic Temperature Compensation (ATC) probe
- Analytical balance (for standardization)
- Volumetric flask, 1L (for standardization)
- Graduated cylinders: 100 mL and 250 mL
- Beakers: 150 mL and 250 mL

Required reagents and solutions

- Purchased or prepared hydrochloric acid (HCl) standard titrant solution, 0.1 M (0.1 N) or 0.02 M (0.02 N)
- Reagent grade water (RGW)
- pH buffers: pH 4 and 7

Optional (for standardization):

- Tris (hydroxymethyl) aminomethane (known as Tris or THAM) primary base/alkalimetric standard, solid

Use suitable personal protective equipment (PPE) as recommended by the Safety Data Sheets (SDS) for the chemicals utilized during this procedure.

Titrator setup

Connect the Orion pH electrode, ATC, and the stirrer probe to the titrator. If not previously done, import the T2 TotAlkalinity preprogrammed method into the titrator from

the Methods screen[1]. Rinse and fill the burette with 0.1 M (0.1 N) HCl titrant. See the titrator user manual for details. If bubbles are visible in the tubing, dispense titrant (from the Burette screen) until the bubbles have been expelled. Consider standardizing the titrant before titrating samples. See the following Titrant section.

T2 TotAlkalinity Method: Preprogrammed Parameters

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

Titrant	Parameter
Titrant Name	HCl
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	Tris (THAM)
Standard Amount	Variable Weight
Standard Molecular Wt	121.14
Standard Purity	100%
Pre-dose Titrant Volume	0 mL
Max total titrant volume	15
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	4.5
Titration Type	Direct
Blank Required	No
Result Units	mg/L
Reaction Ratio	0.5
Sample Mol. Wt.	100.09
Sample Amount	Fixed vol, 100 mL
Pre-dose Titrant Volume	0.05
Max total titrant volume	20 mL
Titration Process Control	Routine
Pre-stir Duration	5 sec
Stir Speed	Medium
Sample ID	Manual

Electrode preparation

Remove electrode from storage solution. Add electrode fill solution to the bottom of the fill hole and leave the fill hole open during testing. Rinse thoroughly with RGW before and between titrations.

Sample preparation

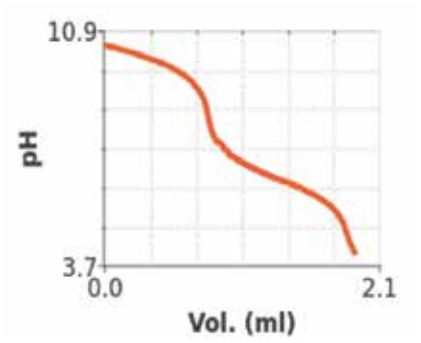
Measure 100 mL of sample into a graduated cylinder. Transfer the sample to a clean 150 mL beaker for titration.

Sample titration

1. From the Home screen, select option to use a saved method, then select TotAlkalinity.
2. At the pre-titration screen, select the Calibrate option and calibrate the electrode with pH 4 and 7 buffers.
3. After calibration, rinse well, and place the electrode, stirrer, ATC, and dispenser into the sample in the beaker. Ensure that the dispenser tip is inserted below.
4. Results are reported as mg/L as $CaCO_3$.

Results

Parameter	Sample	Average (n = 3)	RSD	Analysis Time
Total Alkalinity	Alkaline	98.7 mg/L as $CaCO_3$ (1.97 mmol/l as H^+)	0.30%	02:39 minutes[2]
Total Alkalinity	Tap Water	28.2 mg/L as $CaCO_3$ (0.564 mmol/l as H^+)	0.42%	04:26 minutes



Range

This preprogrammed titration method covers a range from about 25 to 1000 mg/L total alkalinity as $CaCO_3$, when using 0.1 M (0.1 N) acid titrant and 100 mL of sample. See below for method modifications to run other concentrations.

Method modifications

- **For other concentrations:** For best accuracy with samples of lower alkalinity (e.g., <100 mg/L), switch to 0.02 M HCl titrant and titrate 200 mL of sample. Edit the Titrant section of the method to enter the correct titrant concentration. Edit the titration section of the method to enter a fixed volume of 200 mL.
- **For other result units:** For units of mmol/l (per ISO 9963-1), edit the Titration section of the method as follows: choose the unit "mM" (which is mmol/l) and change the reaction ratio to "1".
- **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 0.5 mL less than the expected endpoint volume.
- **To use sulfuric acid (H_2SO_4) standard titrant solution instead of HCl:** For 0.1 N H_2SO_4, edit the Titrant section of the T2 method to indicate the titrant is H_2SO_4. Leave the concentration as 0.1 M. For 0.02N H_2SO_4, edit the Titrant section of the T2 method to indicate the titrant is H_2SO_4. Change the concentration to 0.02M. Note that molarity of HCl is equivalent to normality of H_2SO_4.

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 the titrant
    a. 0.1 M (0.1 N) acid titrant
        i. Use the analytical balance to weigh 0.10 to 0.15 g Tris (THAM) into a clean 100 or 150 mL beaker. Record the exact sample weight to the nearest 0.0001 g. Repeat twice more for a total of three beakers of Tris. Add RGW to the 60 mL mark on each beaker and stir for about 2 minutes or so until the Tris is completely dissolved.
        ii. If the Tris purity is not 100%, edit the Titrant section of the method to enter the actual purity.
        iii. Select the TotAlkalinity preprogrammed method on the titrator.
        iv. At the pre-titration screen, select the Standardize option and follow the prompts to standardize the titrant.
        v. The new standardized titrant concentration will automatically be saved and used for subsequent T2 TotAlkalinity method titrations.
    b. 0.02 M (0.02 N) acid titrant
        i. Prepare a 0.01 M Tris (THAM) standard by weighing 1.211 g into a 1 L volumetric flask. Dilute with RGW and mix until dissolved.
        ii. Pipet 5.0 mL of the 0.01M Tris standard into a 150 mL beaker. Add RGW to the 60 mL mark on the beaker. Repeat twice more for a total of three beakers of Tris.
        iii. Edit the Titrant section of the TotAlkalinity preprogrammed method to enter the Standard Amount as "Fixed Volume", "5 mL". Save the method.
        iv. At the pre-titration screen, select the Standardize option and follow the prompts to standardize the titrant.
        v. The new standardized titrant concentration will automatically be saved and used for subsequent T2 TotAlkalinity 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).

Titrator and electrode care

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

Daily Care	Weekly or Biweekly Care	As Needed
• If bubbles are visible in the titrator tubing, dispense titrant until bubbles have been expelled. • Add electrode fill solution to the bottom of the fill hole and leave the fill hole open during measurement. • Rinse electrode well with RGW between titration cycles. • Cover the fill hole and store electrode in storage solution overnight.	• Drain and replace the fill solution of the electrode. • Change the storage solution in the electrode storage bottle. • Consider standardizing the titrant on a weekly basis.	• For slow or drifty electrode response, soak 15 minutes in 1% laboratory detergent while stirring. Rinse well with RGW afterwards. • If still slow or drifty, use Orion pH cleaning solution D per instructions. • See the user manuals for maintenance details.

Notes

[1]Refer to the user manual for detailed instructions.

[2]With a suitable pre-dose, as described in the Method Modifications section.

References

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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 burrette
- Thermo Scientific™ Orion™ ROSS™ SureFlow™ pH electrode 8172BNWP or equivalent
- Thermo Scientific™ Orion™ Automatic Temperature Compensation (ATC) probe
- Analytical balance, capable of weighing to 0.0001 g
- 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 (0.1 N)
- Purchased or prepared titration solvent (50:45:5 toluene/isopropanol/water)
- Purchased or prepared 1–3 M 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, 0.05 M.

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

Titrator 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 screen[1]. 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.

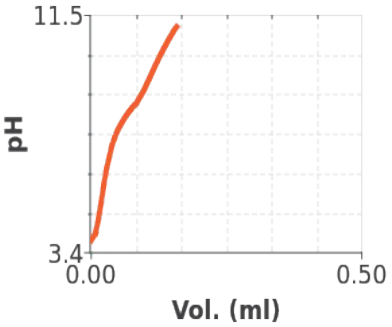
Sample titration

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.

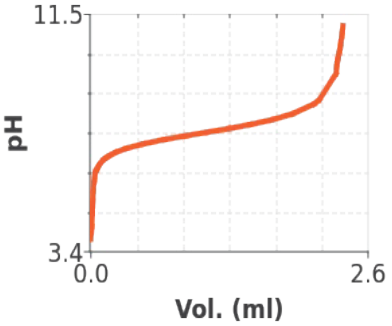
Results

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]

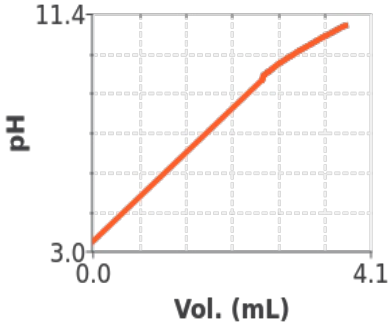
TAN Blank



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 0.1 M (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. 0.05 M KHP standard solution

        i. Accurately pipet 10.0 mL 0.05 M KHP standard solution into a clean 100 or 150 mL beaker. Add RGW to the 60 mL mark on each beaker.

        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., 0.05 M). 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.

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).

Titrator and electrode care

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

Daily Care	Weekly or Biweekly Care	As Needed
• If bubbles are visible in the titrator 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.	• 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.	• 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 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 burrette multiple times with fresh titrant.

Notes

[1]Refer to the user manual for detailed instructions.

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

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 burrette
- 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 1–3 M 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.

Titrator 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 screen[1]. 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

Titrant	Parameter
Titrant Name	Acetate in GAA
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	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
Titrant 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:

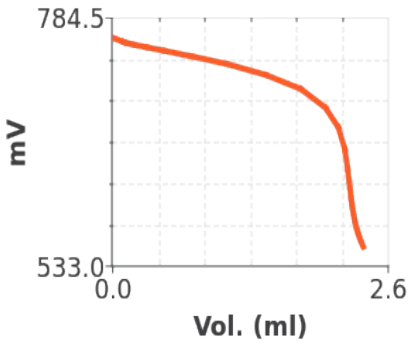
Before titrations, remove the electrode from the RGW soak and rinse it in this order, before placing in the prepared sample:

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

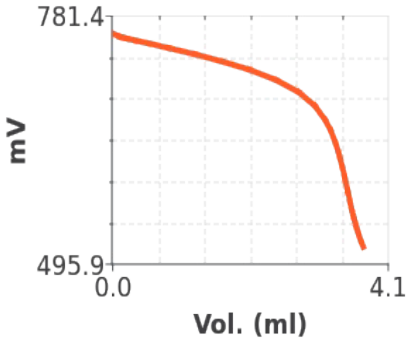
Sample titration

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.

TBN of oil



TBN of used oil



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]

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).

Titrator and electrode care

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

Daily Care	Weekly or Biweekly Care	As Needed
• If bubbles are visible in the titrator 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.	• 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.	• 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

[1]Refer to the user manual for detailed instructions.

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

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