

Total acid number titration of petroleum products

Industry sector

Chemical; petroleum & petrochemicals

Keywords

Titration; nonaqueous titration; potentiometric titration; Solvotrode easyClean; dSolvotrode; Optrode; Thermoprobe; dThermoprobe; photometric titration; thermometric titration; TET; TAN; total acid number; oil; petroleum products; 6.0229.010; 6.00203.300; 6.1115.000; 6.01117.300; 6.9011.020; ASTM; DIN; ISO; D664; D974; DIN ISO 6618; D8045; S01; S010; S05; S050

Summary

The determination of the acid number plays a significant role in the analysis of petroleum products. This is manifested in the numerous standard procedures in use worldwide (e.g., internal specifications of multinational companies, national and international specifications of ASTM, DIN, IP, ISO, etc.). These procedures differ mainly in the composition of the solvents and titrants used.

This Application Bulletin describes the determination of the total acid number (TAN) in petroleum products by applying different types of titration.

The [potentiometric determination](#) is described according to ASTM D664, the [photometric determination](#) according to ASTM D974, and the [thermometric titration](#) according to ASTM D8045.

Potentiometric determination according to ASTM D664

Instruments and accessories

- Titrator with the mode DET U
- Stirrer
- Buret(s)

Electrodes

dSolvotrode	6.00203.300
Solvotrode easyClean	6.0229.010

Reagents

- Potassium hydrogen phthalate (KHP), p.a.
- KOH in IPA, $c(\text{KOH}) = 0.1 \text{ mol/L}$
- 2-propanol (IPA) anhydrous, p.a.
- Toluene, p.a.
- Lithium chloride in ethanol, $c(\text{LiCl}) = 2 \text{ mol/L}$ in ethanol
- CO_2 -free H_2O

Solutions

Titration	KOH in IPA; $c(\text{KOH in IPA}) = 0.1 \text{ mol/L}$, if possible this solution should be bought from a supplier
Solvent	500 mL toluene + 495 mL IPA + 5 mL CO_2 -free H_2O
Electrolyte for electrode	Lithium chloride, $c(\text{LiCl}) = 2 \text{ mol/L}$ in ethanol

Standard

Potassium hydrogen phthalate	Potassium hydrogen phthalate is dried at $120 \text{ }^\circ\text{C}$ for 2 h and cooled down in a desiccator for at least 1 h.
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Sample preparation

No sample preparation required for new oils or for used oils visibly free of sediments.

For used oils containing sediments, see ASTM D664 procedure.

Analysis

Titer

Approximately 100–150 mg dried potassium hydrogen phthalate is weighed into a titration vessel and 100 mL CO₂-free H₂O is added. The solution is then titrated using c(KOH in IPA) = 0.1 mol/L as titrant until after the equivalence point.

Blank

A blank titration is performed using either 125 mL or 60 mL solvent and c(KOH in IPA) = 0.1 mol/L as titrant.

The same amount of solvent must be used for the blank and sample determination.

Sample

An appropriate amount of well-mixed sample according to **Table 1** is weighed into a titration vessel and either 125 mL or 60 mL solvent is added. The sample is then titrated with c(KOH in IPA) = 0.1 mol/L until after the equivalence point.

After the titration, the electrode and buret tip are rinsed first with the solvent mixture followed by IPA and then CO₂-free H₂O. In order to rehydrate the membrane, the electrode is placed in distilled H₂O for 3 to 5 min. The electrode is rinsed with IPA Before the next measurement.

Table 1. Ratio of the standard concentration and sample concentration, dependent on the buret volume.

Acid number	Sample weight (g) Solvent = 125 mL	Sample weight (g) Solvent = 60 mL
0.05–<1.0	20.0 ± 2.0	10.0 ± 1.0
1.0–<5.0	5.0 ± 0.5	2.5 ± 0.25
5.0–<20	1.0 ± 0.1	0.5 ± 0.05
20–<100	0.25 ± 0.02	0.25 ± 0.02
100–<260	0.1 ± 0.01	0.1 ± 0.01

Parameters

Titer

Mode	DET U
Stirring rate	8
Meas. point distance	4
Min. volume increment	50 µL
Max. volume increment	100 µL
Signal drift	60 mV/min
Max. waiting time	60 s
Stop EP	off
EP criterion	10
EP recognition	Greatest

Blank

Mode	DET U
Stirring rate	8
Meas. point distance	4
Min. volume increment	10 µL
Max. volume increment	50 µL
Signal drift	60 mV/min
Max. waiting time	60 s
EP criterion	5
EP recognition	All

Sample

Mode	DET U
Stirring rate	8
Meas. point distance	4
Min. volume increment	50 µL
Max. volume increment	0.5 mL
Signal drift	60 mV/min
Max. waiting time	60 s
Stop EP	Off
EP criterion	5
EP recognition	Last

Calculations

Titer

$$\text{Titer} = \frac{m_s}{V_{EP1} \times c_{KOH} \times M_A}$$

Titer: Titer of the selected titrant

m_s : Mass of standard in mg

V_{EP1} : Titrant consumption until the first equivalence point in mL

c_{KOH} : Concentration of the selected titrant in mol/L; here $c(KOH \text{ in IPA}) = 0.1 \text{ mol/L}$

M_A : Molecular weight of the analyte; here 204.2 g/mol

Sample

$$\text{TAN} = \frac{(V_{\text{last EP}} - V_{\text{blank}}) \times c_{KOH} \times f \times M_A}{m_s}$$

TAN: Total acid number in mg KOH/g sample

$V_{\text{last EP}}$: Titrant consumption in mL to reach the last equivalence point (EP). Normally one EP is obtained, but in the presence of strong acids there may also be several EPs. Always use the last EP for the calculation of the acid number. (The volume of the first EP can be used additionally for the calculation of the strong acid number).

V_{blank} : Blank value consumption for the used quantity of solvent

c_{KOH} : Concentration of titrant in mol/L; here $c(KOH \text{ in IPA}) = 0.1 \text{ mol/L}$

f : Correction factor (titer), dimensionless

M_A : Molecular weight of KOH; here 56.106 g/mol

m_s : Sample weight in g

Example

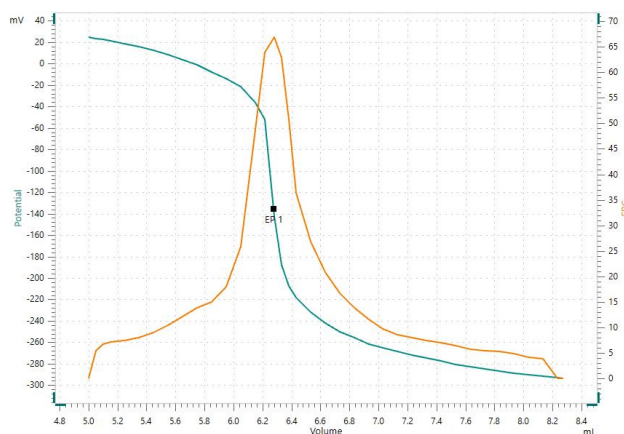


Figure 1. Potentiometric determination of TAN (green = titration curve, orange = ERC).

Comments

Electrostatic charges of the electrodes and titration vessels can strongly interfere with nonaqueous titrations. These interferences are reduced to a minimum when using a Solvotrode, which was specially developed for this type of titration.

Very high pH values may occur during the determination of the acid number. This means that in these ranges the glass electrode exhibits an increased alkali error. It is therefore recommended to use $c(\text{TEABr}) = 0.4 \text{ mol/L}$ instead of LiCl as electrolyte for the reference electrode in such cases.

To replace the electrolyte of the electrode, first all electrolyte is drained from the electrode. The electrode is then rinsed several times with the new electrolyte before replacing the flexible sleeve diaphragm. Finally, the electrode is filled with the new electrolyte. When refitting the sleeve, make sure a free flow of the electrolyte is possible.

A performance test of the electrode can be done as follows:

The electrode is thoroughly rinsed, first with solvent then with distilled H_2O . The electrode is then placed in a pH 7.00 buffer solution (Metrohm 6.2307.110) and after stirring for one minute, the voltage (in mV) is read off. After rinsing the electrode, the same procedure is repeated in pH 4.00 buffer solution (Metrohm 6.2307.100). For a good electrode, the mV difference will be $>162 \text{ mV}$ (at 20 to 25 °C). If the difference is smaller than 162 mV, release some electrolyte and repeat the measurements.

As used oil can change appreciably when in storage, samples should be tested as soon as possible after collection. The dates of sampling and testing should be noted.

For certain kinds of used oils, the titration using differential amplification is recommended.

The standard BS DIN EN 12634 is similar to ASTM D664. The differences are as follows:

- Tetramethyl ammonium hydroxide in methanol and IPA as titrant.
- Benzoic acid for the titer determination.
- Solvent mixture of dimethyl sulfoxide, IPA, and toluene.

References

ASTM D664

Standard test method for acid number of petroleum products by potentiometric titration

BS DIN EN 12634

Petroleum products and lubricants – determination of acid number, non-aqueous potentiometric titration method

Monograph: Electrodes in Potentiometry, [8.015.5013](#)

Leaflet: LL Solvotrode, [8.109.8046](#)

Photometric determination according to DIN ISO 6618 and ASTM D974

Instruments and accessories

- Titrator with the mode MET U
- Stirrer
- Buret(s)

Electrode

Optrode	6.1115.000
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Reagents

- Potassium hydrogen phthalate (KHP), p.a.
- KOH in IPA, $c(\text{KOH}) = 0.1 \text{ mol/L}$
- 2-propanol (IPA) anhydrous, p.a.
- Ethanol, p.a.
- Toluene, p.a.
- p-naphtholbenzein, indicator grade
- Phenolphthalein, puriss
- CO_2 -free H_2O

Solutions

Titrant	KOH in IPA; $c(\text{KOH in IPA}) = 0.1 \text{ mol/L}$, if possible this solution should be bought from a supplier
Solvent	500 mL toluene + 495 mL IPA + 5 mL CO_2 -free H_2O
p-naphtholbenzein indicator solution	1.0 g of p-naphtholbenzein is dissolved in 100 mL solvent.
Phenolphthalein indicator solution	0.1 g phenolphthalein is dissolved in 100 mL of a mixture of CO_2 -free H_2O and ethanol, $\Phi(\text{ethanol}) = 50\% \text{ (v/v)}$ This solution can also be bought from a supplier.

Standard

Potassium hydrogen phthalate	KHP is dried at 120 °C for 2 h and cooled down in a desiccator for at least 1 h.
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Sample preparation

No sample preparation required for new oils or for used oils visibly free of sediments.

For used oils containing sediments, see ASTM D974.

Analysis

Titer

Approximately 100–150 mg dried potassium hydrogen phthalate is weighed into a titration vessel and 100 mL CO₂-free H₂O and 0.05 mL phenolphthalein indicator are added. After a pause of 30 s, the solution is then titrated using c(KOH in IPA) = 0.1 mol/L as titrant until after the equivalence point.

Blank

A blank titration is performed using 100 mL of solvent, 0.05 mL p-naphtholbenzein indicator solution, and c(KOH in IPA) = 0.1 mol/L as titrant.

Sample

An appropriate amount of well-mixed sample according to **Table 2** and **Table 3** is weighed into the titration vessel and 100 mL of solvent and 0.05 mL p-naphtholbenzein indicator are added. The solution is stirred for 30 s in order to dissolve the sample. The sample is then titrated with c(KOH in IPA) = 0.1 mol/L until after the equivalence point.

After titration, the Optrode and buret tip are rinsed with the solvent mixture.

Table 2. Sample size in dependency of the expected TAN for new or light-colored oil.

TAN in mg KOH/g sample	Sample weight in g	Weighing accuracy in mg
≤3.0	20 ± 2.0	50
>3.0 to 25	2.0 ± 0.2	10
>25 to 250	0.2 ± 0.02	1.0

Table 3. Sample size in dependency of the expected TAN for used or dark-colored oil.

TAN in mg KOH/g sample	Sample weight in g	Weighing accuracy in mg
≤25	2.0 ± 0.2	10
>25 to 250	0.2 ± 0.02	1.0

Parameters

Titer

Mode	MET U
Wavelength	574 nm
Stirring rate	8
Pause	30 s
Start volume	2 mL
Signal drift	20 mV/min
Max. waiting time	38 s
Volume increment	50 µL
EP criterion	30 mV
EP recognition	All

Blank

Mode	MET U
Wavelength	610 nm
Stirring rate	8
Signal drift	20 mV/min
Max. waiting time	38 s
Volume increment	20 µL
EP criterion	30 mV
EP recognition	All

Sample

Mode	MET U
Wavelength	610 nm
Stirring rate	8
Pause	30 s
Signal drift	20 mV/min
Max. waiting time	38 s
Volume increment	50 µL
EP criterion	30 mV
EP recognition	All

Calculations

Titer

$$\text{Titer} = \frac{m_s}{V_{EP1} \times c_{KOH} \times M_A}$$

Titer: Titer of the selected titrant

m_s : Mass of standard in mg

V_{EP1} : Titrant consumption until the first equivalence point in mL

c_{KOH} : Concentration of the selected titrant in mol/L; here $c(\text{KOH in IPA}) = 0.1 \text{ mol/L}$

M_A : Molecular weight of the analyte; here 204.2 g/mol

Sample

$$\text{TAN} = \frac{(V_{EP1} - V_{\text{blank}}) \times c_{KOH} \times f \times M_A}{m_s}$$

TAN: Total acid number in mg KOH/g sample

V_{EP1} : Titrant consumption in mL to reach the first equivalence point

V_{blank} : Blank value consumption for the used quantity of solvent

c_{KOH} : Concentration of titrant in mol/L; here $c(\text{KOH in IPA}) = 0.1 \text{ mol/L}$

f : Correction factor (titer), dimensionless

M_A : Molecular weight of KOH; here 56.106 g/mol

m_s : Sample weight in g

Example

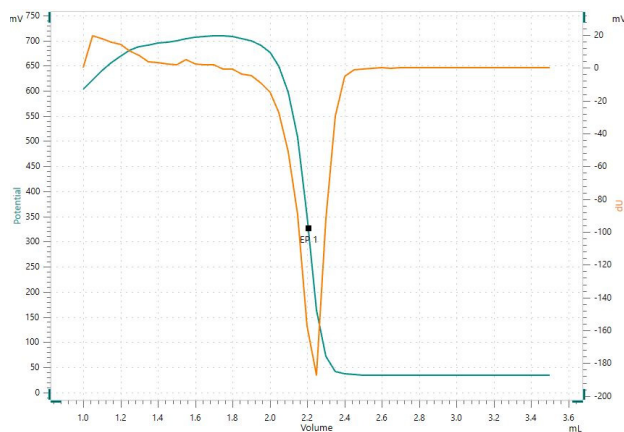


Figure 2. Photometric determination of TAN (green = titration curve, orange = ERC).

Comments

Titrations should be carried out at temperatures below 30 °C.

The p-naphtholbenzein should contain less than 0.5% (w/w) of chloride.

As used oil can change appreciably during storage, samples should be tested as soon as possible after collection. The dates of sampling and testing should be noted.

The light intensity of the LED must be sufficiently stabilized before use. Each time the Optrode is switched on or the wavelength is changed, wait at least five minutes before starting a determination.

A better reproducibility may be obtained by degassing the water with N_2 or by working under a vacuum.

The standard DIN ISO 6618 is similar to that of ASTM D974. The only difference is:

- Phenolphthalein in IPA is used as indicator solution for the titer determination.

References

ASTM D974
Standard test method for acid and base number by color-indicator titration

DIN ISO 6618
Petroleum products and lubricants – determination of acid or base number – color-indicator titration method

Monograph: Complexometric (chelometric) Titrations, **8.108.5042**

Leaflet: Manual for Optrode, **8.109.8054**

Thermometric determination according to ASTM D8045

Instruments and accessories

- Titrator with the mode TET
- Rod Stirrer
- Buret(s)

Electrodes

dThermoprobe	6.01117.300
Thermoprobe	6.9011.020

Reagents

- Potassium hydroxide $c(\text{KOH}) = 0.1 \text{ mol/L}$ in 2-propanol
- 2-propanol, isopropanol, IPA, p.a.
- Xylenes, (mixture of isomers), p.a.
- Paraformaldehyde, >95% pure
- Benzoic acid, p.a.

Solutions

Titrant	KOH in IPA; $c(\text{KOH in IPA}) = 0.1 \text{ mol/L}$, if possible this solution should be bought from a supplier.
Solvent	250 mL isopropanol and 750 mL xylene are mixed in a volumetric flask.

Standard solution

Benzoic acid standard solution	Benzoic acid is dried in a desiccator overnight. 0.61 g dried benzoic acid is weighed into a 250 mL volumetric flask and dissolved in the solvent. After the complete dissolution the flask is filled up to the mark with solvent.
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Sample preparation

Some samples may require slight warming or pre-dissolution in 10 mL of xylene prior to titration. It is possible to titrate warm samples ($<60 \text{ }^\circ\text{C}$) without a loss of resolution or precision.

In case of a pre-dissolution, this has to be considered in the blank determination.

Analysis

Titer

30 mL benzoic acid standard solution is pipetted into a titration vessel and 0.5 g paraformaldehyde is added. The solution is then titrated with $c(\text{KOH}) = 0.1 \text{ mol/L}$ to a single exothermic endpoint.

Blank

An appropriate aliquot of the sample is weighed into the titration vessel, and 30 mL solvent and 0.5 g paraformaldehyde are added. The solution is stirred thoroughly for 30 s before titration with $c(\text{KOH}) = 0.1 \text{ mol/L}$ to a single exothermic endpoint.

Titrate at least three different aliquots of the sample. Use **Table 4** as a guideline for the sample weight.

Sample

An appropriate aliquot of the sample according to **Table 4** is weighed into the titration vessel and 30 mL solvent and 0.5 g paraformaldehyde are added. The solution is stirred thoroughly for 30 s before titration with $c(\text{KOH}) = 0.1 \text{ mol/L}$ to a single exothermic endpoint.

Table 4. Guideline for the sample size in dependency of the expected TAN.

Expected TAN in mg KOH/g sample	Sample weight in g
0.05–0.99	10–20
1.00–4.99	5
5.00–15.00	1

Parameters

Titer

Mode	TET
Stirring rate	15
Pause	60 s
Dosing rate	3.00 mL/min
Stop volume	10.00 mL
Stop slope mode	Off
Filtering factor	60
Damping until	0.10 mL
Evaluation start	0.20 mL
Sort equivalence points by	Volume (ascending)
Define EP conditions	
End point(s)	1
Reaction type	Exothermic
EP criterion	-300

Blank and sample

Mode	TET
Stirring rate	15
Pause	30 s
Dosing rate	3.00 mL/min
Stop volume	10.00 mL
Stop slope mode	Off
Filtering factor	50*
Damping until	0.50 mL
Evaluation start	0.20 mL
Sort equivalence points by	Volume (ascending)
Define EP conditions	
End point(s)	1
Reaction type	Exothermic
EP criterion	-50

* The filter factor depends on the sample and thus may vary. It is important that the same filter factor is used for the blank and sample determination.

Calculations

Titer

$$\text{Titer} = \frac{C_{\text{BA}} \times V_{\text{BA}}}{V_{\text{EP1}} \times C_{\text{KOH}}}$$

Titer: Titer of the selected titrant

C_{BA} : Exact concentration of the benzoic acid standard solution in mol/L

V_{BA} : Added volume of benzoic acid standard solution in mL

V_{EP1} : Titrant consumption until the first equivalence point in mL

C_{KOH} : Concentration of the selected titrant in mol/L; here $c(\text{KOH in IPA}) = 0.1 \text{ mol/L}$

Blank

A linear regression of the different sizes of the sample in g against the mL of titrant consumed is plotted automatically by OMNIS or *tiamo*TM. The blank is defined as the intercept of the linear regression line with the y-axis.

Sample

$$\text{TAN} = \frac{(V_{\text{EP1}} - V_{\text{blank}}) \times c_{\text{KOH}} \times f \times M_{\text{A}}}{m_{\text{s}}}$$

TAN: Total acid number in mg KOH/g sample

V_{EP1} : Titrant consumption in mL to reach the first equivalence point

V_{blank} : Blank value consumption for the used quantity of solvent

C_{KOH} : Concentration of titrant in mol/L; here $c(\text{KOH in IPA}) = 0.1 \text{ mol/L}$

f: Correction factor (titer), dimensionless

M_{A} : Molecular weight of KOH; here 56.106 g/mol

m_{s} : Sample weight in g

Example

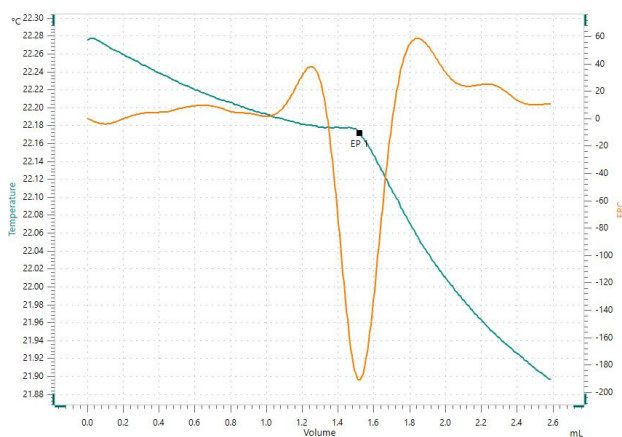


Figure 3. Thermometric titration curve for a raw crude oil sample (green = titration curve, orange = ERC).

Comments

The linear regression for the titer and the blank can be determined automatically from the results using appropriate software such as OMNIS or *tiamo*[™].

For more information about the titer and blank determination in *tiamo*[™], see Metrohm Application Note AN-H-131.

Various types of paraformaldehyde exist. Therefore, it is recommended to use the one mentioned under the reagents section, as not every paraformaldehyde is suited for the catalysis of this reaction.

In a titration, the titrant reacts with the analyte in the sample either exothermically or endothermically. The thermoprobe measures the temperature of the titrating solution. When all of the analyte in the sample has reacted with the titrant, the temperature of the solution will change, and the endpoint of the titration is revealed by an inflection in the temperature curve.

Catalytically enhanced titrations using paraformaldehyde as catalyst are based on the endothermic hydrolysis of the paraformaldehyde in the presence of an excess of hydroxide ions.

The amount of analyte determined is not related to the change in temperature of the solution. Therefore, it is not necessary to use insulated titration vessels.

Thermometric titrations are conducted under conditions of constant titrant addition rate. In this respect, they differ from potentiometric titrations, where the titrant addition rate may be varied during the titration according to the electrode response. In thermometric titrations, a constant addition rate of titrant equates to a constant amount of heat being given out or consumed, and hence a more or less constant temperature change up to the endpoint.

For the automation of the analysis, it is also possible to add the paraformaldehyde as a suspension with the solvent. When approximately 17 g paraformaldehyde is dissolved in 1 L of solvent, then 30 mL solvent contains approximately 0.5 g paraformaldehyde. The suspension can then be added using pumps. For a correct ratio of solvent and paraformaldehyde, the suspension must be stirred constantly during an analysis series.

As an alternative to the pumps, the paraformaldehyde-solvent suspension can be added using a Dosino. The automated addition of a suspension is described in AN-T-095.

References

ASTM D8045
Standard Test Method for Acid Number of Crude Oils and Petroleum Products by Catalytic Thermometric Titration

AN-H-131
Determination of titer and method blank for thermometric titrations using *tiamo*[™]

AN-H-141
Determination of acid number in raw oil in accordance with ASTM D8045

AN-T-095
Automated mixing of a suspension and a solvent using a 50 mL dosing unit

Monograph: Practical thermometric titrimetry, [8.036.5003](#)

Brochure: Thermometric Titration with OMNIS, [8.000.5446](#)

Leaflet: Sensor dThermoprobe, [8.0109.8018](#)

Leaflet: Thermoprobe, [8.109.8055](#)

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