

Application Bulletin AB-404_1_EN

Determination of the total acid number in petroleum products

Branch

General analytical chemistry; petrochemistry

Keywords

Titration; nonaqueous titration; potentiometric titration; Solvotrode easyClean, Optrode; Thermoprobe; photometric titration; thermometric titration; TET; TAN; total acid number; oil; petroleum products; branch 1; branch 5; 6.0229.010; 6.1115.000; 6.9011.020

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 over the world (internal specifications of multinational companies, national and international specifications of ASTM, DIN, IP, ISO, etc.). These procedures differ mainly in the composition of the used solvents and titrants.

This bulletin describes the determination of the acid number in petroleum products by applying different types of titration.

The potentiometric determination is described according to ASTM D 664 and the photometric according to ASTM D 974. Furthermore, the thermometric titration is presented, for which an ASTM standard method is intended.

Potentiometric determination

Instruments

- Titrator with DET mode
- 10 mL burette
- Stirrer

Electrodes

Solvotrode easyClean	6.0229.010
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Reagents

- Potassium hydrogen phthalate (KHP), p.a.
- 2-propanol (IPA) anhydrous, p.a.
- Toluene, p.a.
- CO₂-free H₂O

Solutions

Titration	KOH in IPA; c(KOH in IPA) = 0.1 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 ₂ O.
Electrolyte for electrode	Lithium chloride, c(LiCl) = 2 mol/L in ethanol

Standard

Potassium hydrogen phthalate	Potassium hydrogen phthalate 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 used oils visibly free of sediments.

For used oils containing sediments, see paragraph 10 of ASTM D 664-11.

Analysis

Titer

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

Blank

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

Sample

An appropriate amount of well-mixed sample (see table below) is weighed into a titration vessel and 125 mL of the solvent are added. Proceed with the titration using c(KOH in IPA) = 0.1 mol/L.

After the titration, the electrode and burette 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 for 3 to 5 min in dist. H₂O. Before the next measurement, the electrode is rinsed with IPA.

Sample size in dependency of the expected TAN

TAN/ [mg KOH/g sample]	Sample weight/[g]	Weighing accuracy/[mg]
0.05–0.9	10 ± 2	100
1–4.9	5 ± 0.5	20
5–19	1 ± 0.1	5
20–99	0.25 ± 0.02	1
100–250	0.1 ± 0.01	0.5

Parameters

Titer

Mode	DET U
Meas. point density	4
Min. increment	50 µL
Max. 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
Meas. point density	4
Min. increment	10 µL
Max. increment	50 µL

Signal drift	60 mV/min
Max. waiting time	60 s
EP criterion	5
EP recognition	All

Sample

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

Calculation

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} :	Titration consumption until the first equivalence point in mL
c _{KOH} :	Concentration of the selected titrant in mol/L; here c(KOH in IPA) = 0.1 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 _{last EP} :	Titration 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 in IPA) = 0.1 mol/L
f:	Correction factor (titer), dimensionless
M _A :	Molar mass of KOH; 56.106 g/mol
m _s :	Sample weight in g

Example

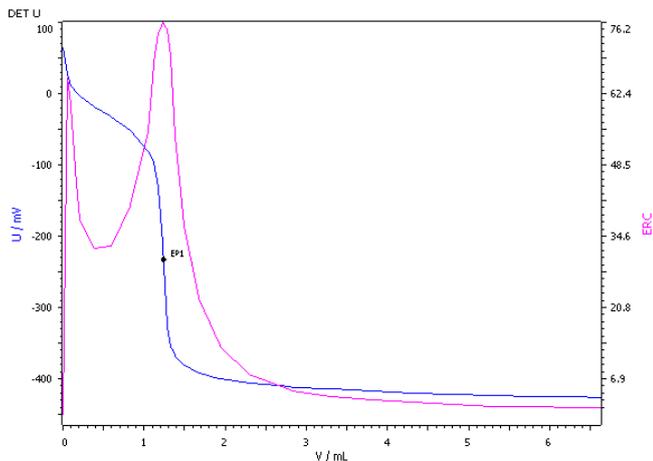


Fig. 1: Potentiometric determination of TAN
(blue = titration curve, pink = ERC)

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 easyClean, 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, all electrolyte is drained from the electrode. The electrode is then rinsed several times with the new electrolyte, before replacing the flexible sleeve diaphragm. The electrode is then finally 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 dist. H_2O . The electrode is then placed in a buffer solution pH 7.00 (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 buffer solution pH 4.00 (Metrohm 6.2307.100).
For a good electrode, the mV difference will be $> 162 \text{ mV}$ (at 20 to $25 \text{ }^\circ\text{C}$). If the difference is smaller than 162 mV , release some electrolyte and repeat the measurements.

- As used oil can change appreciably in storage, samples should be tested as soon as possible after collection. The dates of sampling and testing should be noted.
- The standard BS DIN EN 12634 is similar to the ASTM D 664. The differences are:
 - 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 D 664-11
Standard test method for acid number of petroleum products by potentiometric titration
- BS DIN EN 12634-98
Petroleum products and lubricants – determination of acid number, non-aqueous potentiometric titration method

Photometric determination

Instruments

- Titrator with MET mode
- 10 mL burette
- Stirrer

Electrodes

Optrode	6.1115.000
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Reagents

- Potassium hydrogen phthalate (KHP), p.a.
- 2-propanol (IPA) anhydrous, p.a.
- Ethanol, p.a.
- Toluene, p.a.
- p-naphtholbenzein, indicator grade
- Phenolphthalein, puriss.
- CO₂-free H₂O

Solutions

Titrant	KOH in IPA; c(KOH in IPA) = 0.1 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 ₂ O.
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 ₂ O and ethanol, Φ(ethanol) = 50% (v/v) This solution can also be bought from a supplier (e.g. Fluka 74760).

Standard

Potassium hydrogen phthalate	Potassium hydrogen phthalate 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 used oils visibly free of sediments.

For used oils containing sediments, see paragraph 8 of ASTM D974-11.

Analysis

Titer

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

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 (see tables below) 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. Proceed with the titration using c(KOH in IPA) = 0.1 mol/L.

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

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

TAN/[mg KOH/g sample]	Sample weight /[g]	Weighing accuracy/[mg]
≤ 3	20 ± 2	50
> 3 to 25	2 ± 0.2	10
> 25 to 250	0.2 ± 0.02	1

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

TAN/[mg KOH/g sample]	Sample weight/[g]	Weighing accuracy/[mg]
≤ 25	2 ± 0.2 g	10 mg
> 25 to 250	0.2 ± 0.02 g	1 mg

Parameters

Titer

Mode	MET U
λ	574 nm
Pause	30 s
Start volume	2 mL

Signal drift	20 mV/min
Max. waiting time	38 s
Volume increment	0.05 mL
EP criterion	30 mV
EP recognition	all

Blank

Mode	MET U
λ	610 nm
Signal drift	20 mV/min
Max. waiting time	38 s
Volume increment	0.02 mL
EP criterion	30 mV
EP recognition	all

Sample

Mode	MET U
λ	610 nm
Pause	30 s
Signal drift	20 mV/min
Max. waiting time	38 s
Volume increment	0.05 mL
EP criterion	30 mV
EP recognition	all

Calculation

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 :	Molar mass of KOH; 56.106 g/mol
m_s :	Sample weight in g

Example determination

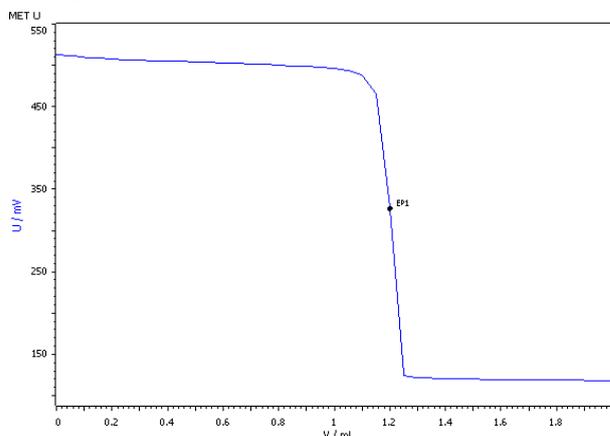


Fig. 2: Photometric determination of TAN

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 in 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 have stabilized sufficiently 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 working under vacuum.
- The standard DIN ISO 6618 is similar to the ASTM D 974. The only difference is:
 - Phenolphthalein in IPA is used as indicator solution for the titer determination

References

- ASTM D 974-11
Standard test method for acid and base number by color-indicator titration
- DIN ISO 6618-11
Petroleum products and lubricants – determination of acid or base number – color-indicator titration method

Thermometric determination

Instruments

- Thermometric titrator
- 10 mL burette
- 50 mL dosing unit
- Stirrer

Electrodes

Thermoprobe	6.9011.020
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Reagents

- 2-propanol (IPA) anhydrous, p.a.
- Toluene, p.a.
- Paraformaldehyde powder, 95% S.A. 158127
- Benzoic acid, p.a.

Solutions

Titrant	Tetrabutyl ammonium hydroxide, alcoholic c(TBAOH) = 0.1 mol/L in IPA/methanol, $\Phi(\text{IPA}) = 50\%$ (v/v) If possible this solution should be bought from a supplier.
Solvent	Toluene/IPA, $\Phi(\text{IPA}) = 50\%$ (v/v)
Catalyst	$\beta(\text{paraformaldehyde}) = 250$ g/L in solvent mixture.

Standard solution

Benzoic acid	Benzoic acid is dried in a desiccator over night. A standard solution with c(benzoic acid) = 0.1 mol/L in IPA is prepared.
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Sample preparation

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

For used oils containing sediments, sample preparation according to paragraph 10 of ASTM D 664-11 is recommended.

Analysis

Titer

2 mL catalyst and 30 mL solvent are mixed within the 50 mL dosing unit and dosed into the titration vessel. For further information about this addition, see Metrohm Application Note AN-T-095.

An aliquot (1 to 5 mL) of standardized benzoic acid solution is added. The solution is stirred thoroughly for 20 seconds and then titrated with c(TBAOH) = 0.1 mol/L to a single exothermic endpoint.

Titrate at least 4 different amounts of benzoic acid in an ascending order.

Blank

An appropriate aliquot of the sample (see table below) is pipetted directly into the titration vessel and the catalyst and the solvent mixture are added as described under *Titer*. The solution is stirred thoroughly for 30 seconds before titration with c(TBAOH) = 0.1 mol/L to a single exothermic endpoint.

Titrate at least 4 different aliquots of the sample in an ascending order.

Sample

An appropriate aliquot of the sample (see table below) is pipetted directly into the titration vessel and the catalyst and the solvent mixture are added as described under *Titer*. The solution is stirred thoroughly for 30 seconds before titration with c(TBAOH) = 0.1 mol/L to a single exothermic endpoint.

Guideline for the sample size in dependency of the expected TAN

TAN/ [mg KOH/g sample]	Sample weight/[g]	Weighing accuracy/[mg]
0.05 – 0.9	10 ± 2	100
1 – 4.9	5 ± 0.5	20
5 – 19	1 ± 0.1	5
20 – 99	0.25 ± 0.02	1
100 – 250	0.1 ± 0.01	0.5

Parameters

Titer

Pause	20 s
Stirring rate	15
Dosing rate	7 mL/min
Filter factor	60
Damping until	1 mL
Stop slope	off

Added volume after stop	0.5 mL
Evaluation start	0 mL
End points	ex (exothermic)
EP criterion	-2

Blank

Pause	30 s
Stirring rate	15
Dosing rate	4 mL/min
Filter factor	60
Damping until	0 mL
Stop slope	off
Added volume after stop	0.5 mL
Evaluation start	0 mL
End points	ex (exothermic)
EP criterion	-10

Sample

Pause	30 s
Stirring rate	15
Dosing rate	4 mL/min
Filter factor	60
Damping until	0 mL
Stop slope	off
Added volume after stop	0.5 mL
Evaluation start	0 mL
End points	ex (exothermic)
EP criterion	-10

Calculation

Titer

A linear regression of the mL of titrant consumed versus the different sizes of the standard in mL is plotted automatically by **tiamo**TM. The titer is then calculated from the slope.

$$\text{Titer} = \frac{C_{\text{Benzoic acid}}}{a \times C_{\text{TBAOH}}}$$

Titer	Titer of the selected titrant
$C_{\text{Benzoic acid}}$	Exact concentration of standard solution in mol/L
a:	Slope of the linear regression
C_{TBAOH}	Concentration of titrant in 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 **tiamo**TM. The method blank is defined as the intercept of the linear regression line with the y-axis.

Sample

$$\text{TAN} = \frac{(V_{\text{EP1}} - \text{Blank}) \times C_{\text{TBAOH}} \times f \times M_{\text{A}}}{m_{\text{s}}}$$

TAN	Total acid number in mg KOH / g sample
V_{EP1}	Titration consumption in mL to reach the first equivalence point.
Blank:	Blank value; consumption for the used quantity of solvent
C_{TBAOH}	Concentration of titrant in mol/L
f:	Correction factor (titer), dimensionless
M_{A}	Molar mass of KOH; 56.106 g/mol
m_{s}	Sample weight in g

Example determination

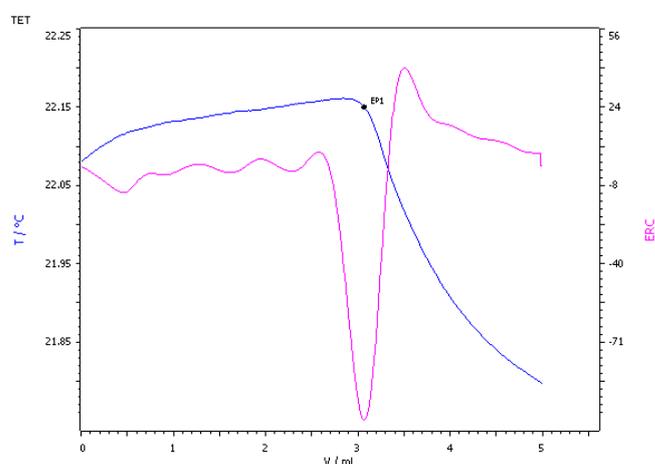


Fig. 3: Thermometric determination of TAN (blue = titration curve, pink = ERC)

Comments

- The linear regression for the titer and the blank can be determined automatically from the results using appropriate software such as **tiamo**TM.
- For more information about the titer and blank determination using **tiamo**TM, see also Metrohm Application Note AN-H-131.
- Various types of paraformaldehyde are existing. Therefore, it is recommended to use the one mentioned under reagents, 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 rate of the temperature change will change, and the endpoint of the titration is indicated 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 automated mixing of two solutions in a dosing unit, see Metrohm Application AN-T-095.

References

- Metrohm Monograph
Practical thermometric titration

Author

Competence Center Titration

Metrohm International Headquarters