

## Application Bulletin AB-404/2 e

# 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; ASTM; D664; D974; D8045

### 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 D664, the photometric according to ASTM D974 and the thermometric titration according to ASTM D8045.

## Potentiometric determination according to ASTM D664

### 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.
- CO<sub>2</sub>-free H<sub>2</sub>O

### 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 <sub>2</sub> -free H <sub>2</sub> 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 ASTM D664.

## Analysis

### Titer

Approximately 100 – 150 mg dried potassium hydrogen phthalate is weighed into a titration vessel and 100 mL CO<sub>2</sub>-free H<sub>2</sub>O 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 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 (see table 1 below) is weighed into a titration vessel and 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 CO<sub>2</sub>-free H<sub>2</sub>O. In order to rehydrate the membrane, the electrode, is placed for 3 to 5 min in dist. H<sub>2</sub>O. Before the next measurement, the electrode is rinsed with IPA.

Table 1: Sample size in dependency of the expected TAN and solvent amount

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 – <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
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 <sub>s</sub> :	Mass of standard in mg
V <sub>EP1</sub> :	Titration consumption until the first equivalence point in mL
c <sub>KOH</sub> :	Concentration of the selected titrant in mol/L; here c(KOH in IPA) = 0.1 mol/L
M <sub>A</sub> :	Molecular weight of the analyte; here 204.2 g/mol

### Sample

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

TAN	Total acid number in mg KOH/g sample
$V_{\text{last EP}}$ :	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).
$V_{\text{blank}}$ :	Blank value consumption for the used quantity of solvent
$c_{\text{KOH}}$ :	Concentration of titrant in mol/L; here $c(\text{KOH in IPA}) = 0.1 \text{ mol/L}$
$f$ :	Correction factor (titer), dimensionless
$M_{\text{A}}$ :	Molar mass of KOH; 56.106 g/mol
$m_{\text{s}}$ :	Sample weight in g

### Example

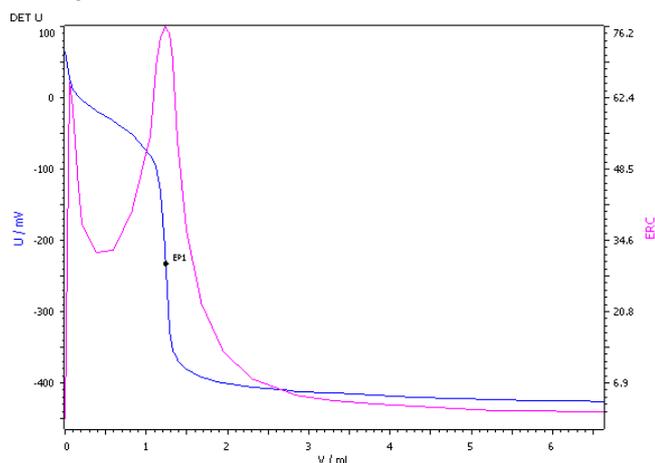


Fig. 1: Potentiometric determination of TAN (blue = titration curve, pink = ERC)

### 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.  $\text{H}_2\text{O}$ . 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 °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.
- For certain kinds of used oils the titration using differential amplification is recommended.
- The standard BS DIN EN 12634 is similar to the ASTM D664. 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 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

# Photometric determination according to ASTM D974

## 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.
- CO<sub>2</sub>-free H<sub>2</sub>O

## 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 <sub>2</sub> -free H <sub>2</sub> 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 <sub>2</sub> -free H <sub>2</sub> O and ethanol, Φ(ethanol) = 50% (v/v) This solution can also be bought from a supplier.

## 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 ASTM D974.

## Analysis

### Titer

Approximately 100 – 150 mg dried potassium hydrogen phthalate is weighed into the titration vessel and 100 mL CO<sub>2</sub>-free water and 0.05 mL phenolphthalein indicator are added. After a pause of 30 s, the solution is titrated with c(KOH in IPA) = 0.1 mol/L 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 (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. The sample is then titrated with c(KOH in IPA) = 0.1 mol/L until after the equivalence point.

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

Table 2: 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

Table 3: 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
$\lambda$	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
$\lambda$	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
$\lambda$	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
$V_{EP1}$ :	Titration 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
$V_{EP1}$ :	Titration consumption in mL to reach the first equivalence point.
$V_{\text{blank}}$ :	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

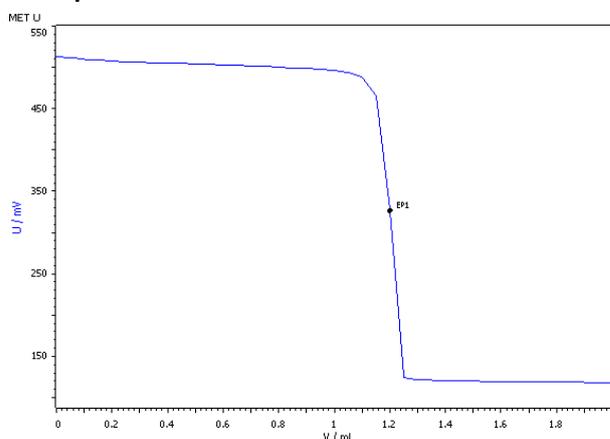


Fig. 2: Photometric determination of TAN

## 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 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

# Thermometric determination according to ASTM D8045

## Instruments

- Thermometric titrator
- 10 mL buret for the titrant
- 50 mL buret for the solvent addition
- Rod stirrer for intensive stirring

## Electrodes

Thermoprobe	6.9011.020
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## 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, Sigma-Aldrich, 158127
- Benzoic acid, p.a.

## Solutions

Titration	$c(\text{KOH}) = 0.1 \text{ mol/L}$ in IPA 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 over-night. 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 (<math>60 \text{ }^\circ\text{C}</math>) 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 4 different aliquots of the sample in an ascending order. Use the table below as a guideline for the sample weight.

### Sample

An appropriate aliquot of the sample (see table below) 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 / [mg KOH/g sample]	Sample weight / [g]
0.05 – 0.99	10 – 20
1.00 – 4.99	5
5.00 – 15.00	1

## Parameters

### Titer

Pause	60 s
Stirring rate	15
Dosing rate	4 mL/min
Filter factor	60
Damping until	1 mL
Stop slope	off
Added volume after stop	0.5 mL
Evaluation start	1 mL
End points	ex (exothermic)
EP criterion	-10

**Blank and sample**

Pause	30 s
Stirring rate	15
Dosing rate	2 mL/min
Filter factor	50 – 70*
Damping until	0.2 mL
Stop slope	off
Added volume after stop	0.5 mL
Evaluation start	0 mL
End points	ex (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.

**Calculation**
**Titer**

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

Titer	Titer of the selected titrant
$c_{\text{BA}}$ :	Exact concentration of the benzoic acid standard solution in mol/L
$V_{\text{BA}}$ :	Added volume of benzoic acid standard solution in mL
$c_{\text{KOH}}$ :	Concentration of titrant in mol/L
$V_{\text{EP1}}$ :	Titration consumption in mL to reach the first equivalence point.

**Blank**

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

**Sample**

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

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

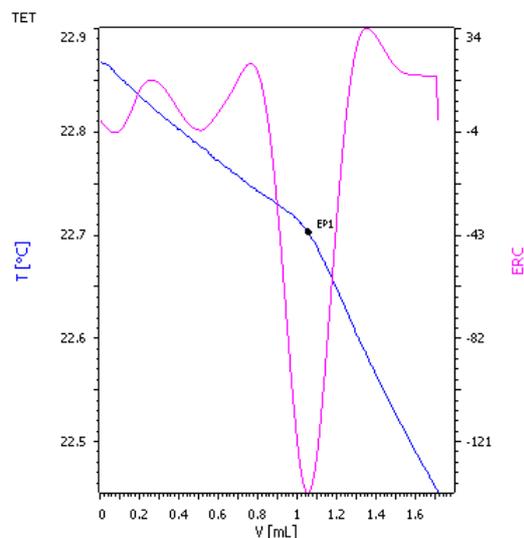
**Example determination**


Fig. 3: Thermometric titration curve for a raw crude oil sample (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**<sup>TM</sup>.
- For more information about the titer and blank determination using **tiamo**<sup>TM</sup>, 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 automation of the analysis it is also possible to add the paraformaldehyde as suspension with the solvent. Therefore approx. 17 g paraformaldehyde is dissolved in 1 L of solvent, thus 30 mL solvent contain approx. 0.5 g paraformaldehyde. The suspension can then be added using pumps.  
For correct ratio of solvent and paraformaldehyde the suspension must be stirred all the time during an analysis series.
- As an alternative to the pumps the paraformaldehyde-solvent-suspension can be added using a Dosino. The automated adding 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*<sup>TM</sup>
- AN-T-095  
Automated mixing of a suspension and a solvent using a 50 mL dosing unit

#### Author

Competence Center Titration

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