

Determination of the total base number in petroleum products

Branch

General analytical chemistry; petrochemical industry

Keywords

Titration; non aqueous titration; potentiometric titration; photometric titration; thermometric titration; Solvotrode easyClean; Optrode; Thermoprobe; Conductivity measuring cell; TET; TBN; total base number; branch 1; branch 5; 6.0229.010; 6.1115.000; 6.9011.020; 6.0916.040

Summary

The determination of the base number plays a significant part 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 base number in petroleum products by applying different types of titration.

The potentiometric determination is described according to ISO 3771 and the photometric adapted from ASTM D974. For the thermometric titration an ASTM standard method is in planning. Furthermore the conductometric determination according to IP 400 is described.

Potentiometric determination

Instruments

- Titrator with DET mode
- 10 mL buret
- 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.
- Glacial acetic acid
- Acetone, p.a.
- CO₂-free H₂O

Solutions

Titrant	c(HClO ₄) = 0.1 mol/L
HClO ₄ in acetic acid	This solution should be bought from a supplier.
Solvent	600 mL toluene + 300 mL glacial acetic acid + 100 mL acetone.
Electrolyte for electrode	Lithium chloride, c(LiCl) = 2 mol/L in ethanol

Standards

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 7 of the norm ISO 3771:2011.

Analysis

Titer

Approximately 100 – 200 mg dried potassium hydrogen phthalate are weighed into a titration vessel and 60 mL glacial acetic acid are added. The solution is then titrated using $c(\text{HClO}_4) = 0.1 \text{ mol/L}$ as titrant.

Blank

A blank titration is performed using the same amount of solvent as for the titration of the sample, and $c(\text{HClO}_4) = 0.1 \text{ mol/L}$ as titrant.

Sample

An appropriate amount of well-mixed sample (see table below) is weighed into a titration vessel and 60 – 100 mL of the solvent are added. The sample is then stirred until it is completely dissolved, proceed with the titration using $c(\text{HClO}_4) = 0.1 \text{ mol/L}$.

After the titration the electrode and buret tips are rinsed first with the solvent mixture followed by IPA and then CO_2 -free H_2O . Prior to the next measurement the electrode is rinsed with IPA.

Sample size in dependency of the expected TBN

TBN / (mg KOH / g sample)	Sample weight / g	Weighing accuracy / mg
3 – 15	2.00 g	1 mg
15 – 30	1.00 g	1 mg
30 – 45	0.25 g	0.1 mg

Parameters

Titer

Mode	DET U
Meas. point density	4
Min. increment	50 μL
Max. increment	100 μL
Signal drift	10 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	10 mV/min
Max. waiting time	60 s
EP criterion	5
EP recognition	all

Sample

Mode	DET U
Meas. point density	4
Min. increment	10 μL
Max. increment	0.5 mL
Signal drift	10 mV/min
Max. waiting time	20 s
EP criterion	15
EP recognition	all

Calculation

Titer

$$\text{Titer} = \frac{m_s}{V_{\text{EP1}} \times c_{\text{HClO}_4} \times M_A}$$

- 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_{HClO_4} : Concentration of the selected titrant in mol/L; here $c(\text{HClO}_4) = 0.1 \text{ mol/L}$
 M_A : Molecular weight of the analyte; here 204.2 g/mol

Sample

$$\text{TBN} = \frac{(V_{\text{last EP}} - V_{\text{blank}}) \times c_{\text{HClO}_4} \times f \times M_A}{m_s}$$

- TBN: Total base number in mg KOH/g sample
 $V_{\text{last EP}}$: Titrant consumption in mL to reach the last equivalence point (EP).
 V_{blank} : Blank value consumption for the used quantity of solvent
 c_{HClO_4} : Concentration of the selected titrant in mol/L; here $c(\text{HClO}_4) = 0.1 \text{ mol/L}$
 f : Correction factor (titer) without unit
 M_A : Molar mass of KOH; 56.106 g/mol
 m_s : Sample weight in g

Example determination

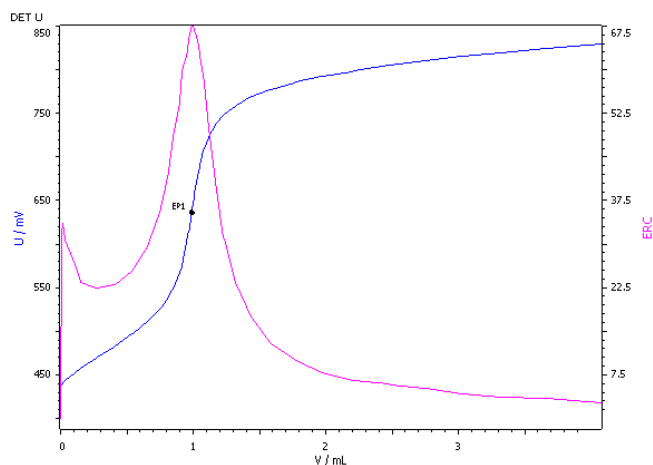


Fig. 1: Potentiometric determination of TBN
(blue = titration curve, red = ERC)

Comments

- Electrostatic charges of the electrodes and titration vessels can strongly interfere with non-aqueous titrations. These interferences are reduced to a minimum when using the recommended electrode, which has been specially developed for this type of titration.
- 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. H₂O. 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 good electrode the mV difference will be > 162 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.

- The norm ASTM D2896 is similar to ISO 3771. The differences are:

- Solvent mixture of glacial acetic acid and chlorobenzene (1/2, (v/v))

As chlorinated solvents are harmful to the environment it is not recommended to use them for analysis. ASTM D2896 therefore suggest to replace the chlorobenzene by xylene.

References

- ASTM D2896-11
Standard test method for base number of petroleum products by potentiometric perchloric acid titration
- ISO 3771:2011
Petroleum products– determination of base number – perchloric acid potentiometric titration method

Photometric determination

Instruments

- Titrator with MET mode
- 10 mL buret
- Stirrer

Electrodes

Optrode	6.1115.000
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Reagents

- Tris(hydroxymethyl) amino methane (TRIS), p.a.
- 2-propanol (IPA) anhydrous, p.a.
- Toluene, p.a.
- Methyl orange, puriss
- CO₂-free H₂O

Solutions

Titrant	HCl in IPA; c(HCl) = 0.1 mol/L, if possible this solution should be bought from a distributor.
Solvent	500 mL toluene + 495 mL IPA + 5 mL CO ₂ -free H ₂ O.
Methyl orange indicator solution	0.1 g methyl orange is dissolved in 100 mL CO ₂ -free H ₂ O.

Standards

TRIS	TRIS is dried at 105 °C for 1 h and cooled down in a desiccator.
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Sample preparation

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

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

Analysis

Titer

Approximately 50 – 60 mg dried TRIS are weighed into the titration vessel and 100 mL CO₂-free water and 0.5 mL methyl orange indicator are added. After a pause of 30 s, the solution is titrated using alcoholic c(HCl) = 0.1 mol/L as titrant.

Blank

As the solvent mixtures contains weak acidic impurities, one has to perform an acid number blank according to Application Bulletin 404.

Sample

An appropriate amount of well-mixed sample (see tables below) is weighed into the titration vessel and 100 mL of solvent and 0.5 mL methylorange indicator are added. The solution is stirred for 30 s in order to dissolve the sample, proceed the titration with c(HCl) = 0.1 mol/L.

After the titration the electrode and buret tips are rinsed with the solvent mixture.

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

TBN / (mg KOH / g sample)	Sample weight / g	Weighing accuracy / mg
≤ 3	20 ± 2 g	50 mg
> 3 to 25	2 ± 0.2 g	10 mg
> 25 to 250	0.2 ± 0.02 g	1 mg

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

TBN / (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	520 nm
Pause	30 s
Start volume	3 mL
Signal drift	20 mV/min
Max. waiting time	38 s
Volume increment	0.05 mL
EP criterion	30 mV
EP recognition	greatest

Sample

Mode	MET U
λ	520 nm
Pause	60 s
Signal drift	20 mV/min
Max. waiting time	38 s
Volume increment	0.05 mL
Evaluation	Break point evaluation
EP criterion	0.5
Slope	0.9
Smoothing factor	5

Calculation
Titer

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

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_{HCl} :	Concentration of the selected titrant in mol/L; here $c(HCl) = 0.1 \text{ mol/L}$
M_A :	Molecular weight of the analyte; here 121.14 g/mol

Sample

$$\text{TBN} = \frac{(V_{BP1} - V_{blank}) \times c_{HCl} \times f \times M_A}{m_s}$$

TBN	Total base number in mg KOH/g sample
V_{BP1} :	Titration consumption in mL to reach the first break point
V_{blank} :	Blank value consumption for the used quantity of solvent
c_{HCl} :	Concentration of titrant in mol/L; here $c(HCl) = 0.1 \text{ mol/L}$
f:	Correction factor (titer) without unit
M_A :	Molar mass of KOH; 56.106 g/mol
m_s :	Sample weight in g

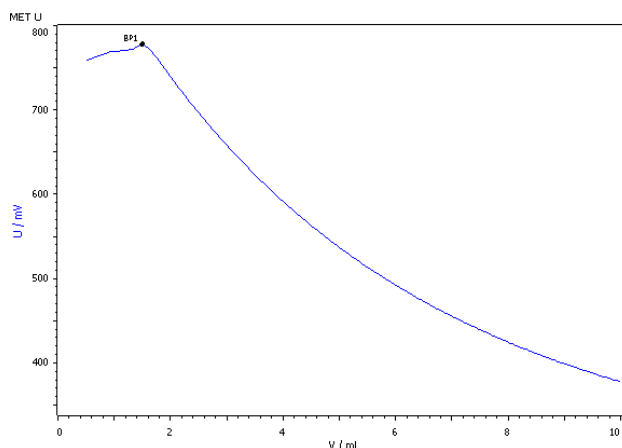
Example determination


Fig. 2: Photometric determination of TBN

Comments

- Titrations should be carried out at temperatures under 30 °C.
- 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, one has to wait five minutes before starting a determination.
- The differences to the norm ASTM D974 are:
 - Methyl orange as indicator for the titration
 - Titer determination with a standard instead of a standardized solution
- The norm DIN ISO 6618 is similar to the ASTM D974. For the determination of the base number no differences are observed.
- The titration solvent usually contains weak acid impurities which react with the strongly basic components of the test portion. To correct the base number for the test portion, it is thus necessary to determine an acid number blank of the solvent.

References

- ASTM D974-11
Standard test method for acid and base number by colour-indicator titration
- DIN ISO 6618-11
Petroleum products and lubricants – determination of acid or base number – colour-indicator titration method

Thermometric determination

Instruments

- Thermometric titrator
- 5 mL buret
- Stirrer

Electrodes

Thermoprobe	6.9011.020
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Reagents

- Toluene, p.a.
- Isobutyl vinyl ether
- Glacial acetic acid, p.a.
- Potassium hydrogen phthalate (KHP), p.a.

Solutions

Titrant	Trifluoro methane sulfonic acid c(TFMSA) = 0.1 mol/L in glacial acetic acid or perchloric acid
Solvent	Toluene

Standard

Potassium hydrogen phthalate	Potassium hydrogen phthalate is dried in a drying oven for 2 h at 105 °C and then allowed to cool down to room temperature in a desiccator
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Sample preparation

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

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

Analysis

Titer

0.04 – 0.07 g KHP are weighed into the titration vessel and dissolved in 20 mL glacial acetic acid. After the sample is homogenized for 2 min, 40 mL toluene and 1 mL isobutyl vinyl ether are added, while stirring. The solution is stirred thoroughly for 20 s before titration with c(TFMSA) = 0.1 mol/L to a single endothermic end point.

Titrate at least 3 different values of KHP in an ascending order to the first endothermic end point.

Blank

An appropriate aliquot of the sample (see table below) is pipetted directly into the titration vessel, 1 mL isobutyl vinyl ether and 40 mL solvent are added. The solution is stirred thoroughly for 20 s before titration with c(TFMSA) = 0.1 mol/L to a single endothermic end point.

Titrate at least 3 different aliquots of the sample in an ascending order to the first endothermic end point.

Sample

An appropriate aliquot of the sample (see table below) is pipetted directly into the titration vessel, 1 mL isobutyl vinyl ether and 40 mL solvent are added. The solution is stirred thoroughly for 20 s before titration with c(TFMSA) = 0.1 mol/L to a single endothermic end point.

Sample size in dependency of the expected TBN

TBN / (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	3 mL/min
Filter factor	70
Damping until	0 mL
Stop slope	off
Volume after stop	0.5 mL
Evaluation start	0 mL
End points	endothermic
EP criterion	1000

Blank

Pause	20 s
Stirring rate	15
Dosing rate	3 mL/min
Filter factor	70
Damping until	0 mL
Stop slope	off
Volume after stop	0.5 mL
Evaluation start	0 mL
End points	endothermic
EP criterion	120

Sample

Pause	20 s
Stirring rate	15
Dosing rate	3 mL/min
Filter factor	70
Damping until	0 mL
Stop slope	off
Volume after stop	0.5 mL
Evaluation start	0 mL
End points	endothermic
EP criterion	120

Calculation
Titer

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

$$\text{Titer} = \frac{1000}{a \times c_{\text{TFMSA}} \times M_A}$$

Titer	Titer of the selected titrant
1000:	Conversion factor
a:	Slope of the linear regression
c_{TFMSA} :	Concentration of titrant in mol/L
M_A :	Molecular weight of the analyte; here 204.22 g/mol

Blank

A linear regression of the different sizes of the sample against the mL of titrant consumed is plotted automatically by **tiamo**TM. The blank is defined by the interception of the y-axis.

Sample

$$\text{TBN} = \frac{(V_{\text{EP1}} - \text{Blank}) \times c_{\text{TFMSA}} \times f \times M_A}{m_s}$$

TBN	Total base number in mg KOH/g sample
V_{EP1} :	Titration consumption in mL to reach the first endothermic end point.
Blank:	Blank value consumption for the used quantity of solvent
$c(\text{TFMSA})$:	Concentration of titrant in mol/L
f:	Correction factor (titer) without unit
M_A :	Molar mass of KOH; 56.106 g/mol
m_s :	Sample weight in g

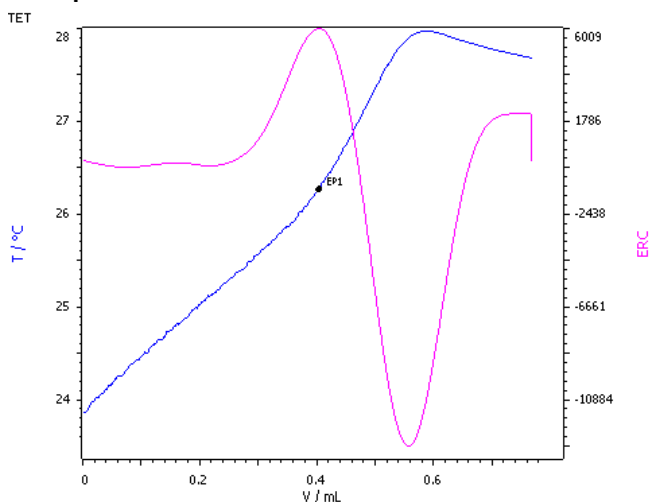
Example determination


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

Comments

- The thermometric TBN titration is a catalytic indication titration, isobutyl vinyl ether is used for the endpoint indication. Isobutyl vinyl ether reacts strongly exothermic with an excess of titrant, resulting in an endothermic endpoint.
- Instead of TFMSA perchloric acid (HClO_4) can be used as titrant. If HClO_4 is used as titrant, the temperature jump is not as steep anymore and the ERC becomes smaller. With HClO_4 the obtained TBN might be smaller as it is a weaker acid than TFMSA (pK_a -9 vs. pK_a -20).
- 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, see also Metrohm Application Note H-131.

- 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.
- The amount of sample 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.

References

- Metrohm Monograph
Practical thermometric titration

Conductometric determination

Instruments

- Titrator with MET mode
- 10 mL buret
- Stirrer

Electrodes

Conductivity measuring cell, 0.1 cm ⁻¹ with Pt1000	6.0916.040
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Reagents

- 2-propanol (IPA) anhydrous, p.a.
- Ethanol, p.a.
- Toluene, p.a.
- CO₂-free H₂O
- Sodium carbonate, p.a.

Solutions

Titrant	HCl in IPA; c(HCl) = 0.1 mol/L, if possible this solution should be bought from a distributor.
Solvent	500 mL toluene + 495 mL IPA + 5 mL CO ₂ -free H ₂ O.

Standards

Sodium carbonate standard solution	Sodium carbonate is dried at 120 °C for 2 h and cooled down in a desiccator. A standard solution is prepared by dissolving approximately 1 g Na ₂ CO ₃ in 100 mL CO ₂ -free H ₂ O.
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Sample preparation

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

For used oils containing sediments see paragraph 7 of the norm IP 400/01.

Analysis

Titer

1 – 3 mL of the standard solution and 75 mL of CO₂-free H₂O are dosed into a titration vessel. The solution is stirred for 30 s, the conductivity cell is then dipped three times into the sample solution in order to avoid air bubbles before titrating with c(HCl) = 0.1 mol/L.

After the titration the buret tip and conductivity measuring cell are rinsed with solvent until no more visible oil is present. The conductivity measuring cell is then rinsed with CO₂-free H₂O, followed by solvent.

Sample

An appropriate amount of sample (see calculation below) is weighed into the titration vessel. 75 mL solvent are added and the conductivity cell is placed in the titration vessel. The solution is stirred for 30 s to dissolve the sample, the conductivity cell is then dipped three times into the sample solution before titrating with c(HCl) = 0.1 mol/L.

After the titration the buret tip and conductivity measuring cell are rinsed with solvent until no more oil is visible. The conductivity measuring cell is then rinsed with CO₂-free H₂O, followed by solvent.

$$m_s = \frac{10}{BN_{\text{expected}}}$$

m_s : Sample amount in mg
 BN_{expected} : Expected base number

Parameters

Titer

Mode	MET Cond
Signal drift	Off
Min. waiting time	10 s
Max. waiting time	10 s
Volume increment	0.1 mL

Sample

Mode	MET Cond
Pause	30 s
Signal drift	Off
Min. waiting time	10 s
Max. waiting time	10 s
Volume increment	0.1 mL

Calculation

Titer

$$\text{Titer} = \frac{V_{\text{Std}} \times c_{\text{Std}} \times 2}{V_{\text{EP1}} \times c_{\text{HCl}}}$$

Titer:	Titer of the selected titrant
V_{Std} :	Added volume of standard solution in mL
c_{Std} :	Exact concentration of standard solution in mol/L
2:	Stoichiometric factor
V_{EP1} :	Titration consumption until the first equivalence point in mL
c_{HCl} :	Concentration of titrant in mol/L; here $c(\text{HCl}) = 0.1 \text{ mol/L}$

Sample

$$\text{TBN} = \frac{V_{\text{EP1}} \times c_{\text{HCl}} \times f \times M_{\text{A}}}{m_{\text{s}}}$$

TBN	Total base number in mg KOH/g sample
V_{EP1} :	Titration consumption in mL to reach the first equivalence point.
c_{HCl} :	Concentration of titrant in mol/L; here $c(\text{HCl}) = 0.1 \text{ mol/L}$
f:	Correction factor (titer) without unit
M_{A} :	Molar mass of KOH; 56.106 g/mol
m_{s} :	Sample weight in g

Example determination

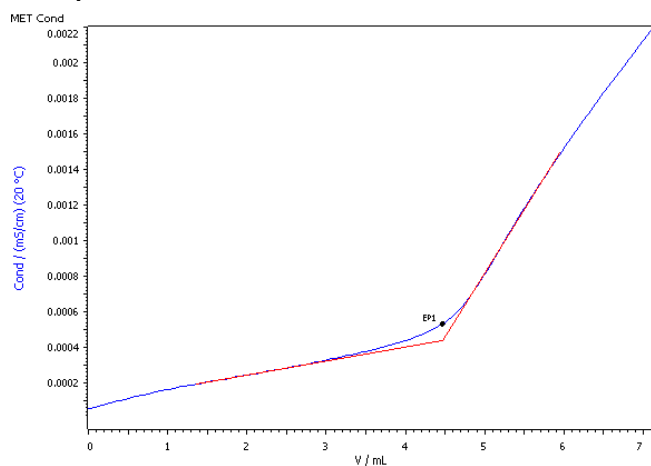


Fig. 4: Conductometric determination to TBN
(blue = measured curve, red = extrapolation)

Comments

- This method may be used for samples having a base number up to 40 mg KOH/g, but it will be necessary to dilute these samples in order to obtain a suitable sample weight. This will only give an approximate base number because this method is only validated in the range of 1 to 20 mg KOH/g.

References

- IP 400/01
Determination of base number of petroleum products – conductometric titration method

Author

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