



Base Number of Petroleum Products

(Perchloric acid titration ASTM 2896-01 and ISO 3771)

Introduction

The Base Number determination is a measurement of the basic constituents of petroleum products. This titration uses perchloric acid in glacial acetic acid as titrant in a specific non-aqueous media.

Principle

The titration performs an inflection point determination taking into account the total volume of titrant necessary to detect an inflection point.

The result is expressed as mg of potassium hydroxide for 1 g of product.

The titrant concentration is 0.1M and the molar weight of KOH is 56.11 g/mol

If the titration curve is poorly defined with no inflection point detected, it is necessary to run a back titration (see "back titration" note).

Electrode and reagents

As the titration occurs in nonaqueous media, it is recommended to work with separate electrodes and a three-electrode system (see electrode maintenance and storage notes).

pHG311 Glass Electrode (part no.E11M004) with a CL114 cable (part no. A94L114) as measuring electrode, REF451 (part no. E21M005) with salt bridge filled with saturated NaClO₄ in glacial acetic acid with a CL114 cable (part no. A94L114) as reference electrode (see Reference electrode note), M241Pt Metal Electrode (part no. E31M001) as cell grounding.

Titration solvent

Add one volume of glacial acetic acid to two volumes of chlorobenzene.

Sodium perchlorate electrolyte

Prepare a saturated solution of sodium perchlorate (NaClO₄) in glacial acetic acid.

HClO₄ 0.1M in CH₃COOH

Mix 8.5 ml of 70 to 72% HClO₄ with 500 ml of glacial

acetic acid and 30 ml of acetic anhydride and dilute to 1000 ml with glacial acetic acid.

Standardise the solution using potassium hydrogen phthalate (see standardisation note).

This solution is also commercially available.

pH 4.00 buffer solution (part no. S11M012) and pH 10.00 buffer solution (part no. S11M014)

Warning: Some reagents used in this application note are flammable. Others can cause severe burns and are hazardous if swallowed, breathed or come into contact with skin or eyes. Always respect laboratory health and safety regulations when using these reagents. Also refer to the ASTM

Inflection Detection settings

CONTINUOUS ADDITION MODE (CONTINUOUS IP)

Cell grounding:	M241Pt
Burette volume:	25 ml
Measure:	mV
Blank:	YES
Min. ordinate:	400 mV (see "ordinates" note)
Max. ordinate:	700 mV
Stirring speed:	600 rpm
Stirring delay:	30 s
Maximum volume:	15 ml (see "maximum volume" note)
Stop point:	750 mV (see "ordinates" note)
Direction:	Increasing mV
Minimum speed:	0.1 ml/min
Maximum speed:	1 ml/min
Smoothing parameter:	5
Inflection points number:	1
Inflection1	
Min. ordinate:	400 mV (see "ordinates" note)
Max. ordinate:	700 mV

Stop at last IP: YES
Sample unit: g
Sample amount: **see working range**

Results

Number of results: 1
Result unit: mg/g
Molar weight: 56.11
Reaction: 1 smp + 1 titr

Procedure (using 120 ml of titration solvent)

It is strongly recommended to work under a hood

For the first use, prepare the REF451 Reference Electrode.

The REF451 is delivered with the salt bridge filled with aqueous KCl solution, empty this solution, then rinse the bridge with water then with acetic acid and fill it with the Base Number of Petroleum Products (Perchloric acid titration ASTM D 2896-01 and ISO 3771) saturated solution of sodium perchlorate (NaClO₄) in glacial acetic acid.

Check the electrode behaviour:

Measure the potentials reached by the electrodes dipped in the pH 4.00 and then in the pH 10.0 buffer solutions. The difference between the two measurements should be at least 330 mV.

For this, use the ELECTRODES and "DISPLAY MEASUREMENT" icon.

Run a blank determination using 120 ml of titration solvent.

Prepare the sample by dilution of the necessary amount of product in 120 ml of titration solvent.

Run the titration.

Results

As indicated before, results **are expressed as mg/g of KOH**

$$R(\text{mg/g}) = (V_t - V_b) * C_t * 56.11 / W$$

V_t = Total volume of titrant used in ml

V_b = Blank volume used for solvent titration

C_t = Concentration of titrant in mol/l

W = Sample weight in g

56.11 = molecular weight of KOH

Results on 2 different oil samples

Blank volume for solvent

0.087 ml

Oil 1

Mean on 2 tests

TBN: 11.16 ±0.025 mg/g

Oil 2

Mean on 2 tests

TBN: 13.20 ±0.07 mg/g

Working range

According to the calculation formula for 1 g of product and using a 25 ml burette, the experimental range is between 5 mg/g and 110 mg/g for the Base Number.

In addition, ASTM D2896-01 gives for the sample size diluted with 120 ml of solvent

Sample weight in g	Expected Base No.
10-20	2.8-1.4
5-10	5.6-2.8
1-5	28-5.6
0.25-1	112-28
0.1-0.25	280-112

This table corresponds to an approximate titrant volume of 5.0 ml

Electrode maintenance and storage

a) When a titration is finished, rinse the electrodes with titration solvent, then with distilled water and dip them in the pH 4.00 buffer solution for 30/60 seconds. Before starting a new experiment, rinse electrodes with titration solvent. Depending on the oil, it is possible to use another solvent instead of the titration solvent.

b) After a cycle corresponding to 5/10 titrations, change the measuring glass electrode. Clean it with titration solvent, ethyl alcohol and distilled water and store it in pH 4.00 buffer solution.

c) Every morning or before starting a new titration cycle, check the electrode system. Measure the potentials reached by the electrodes dipped in the pH 4.00 and then in the pH 10.0 buffer solutions. The difference between the two measurements should be at least 330 mV.

d) Once a week, clean the glass electrode using the Radiometer

Notes

Reference electrode

Instead of the REF451, it is possible to use the REF361 Reference Electrode (part no. E21M003) filled with LiCl 1M in isopropanol. Using this electrode, it is necessary to change the potential ordinates; as experimental values you can note:

Stop point: 950 mV
Min. ordinate: 700 mV
Max. ordinate: 850 mV

Maximum volume

Depending on the expected result, it can be necessary to modify this setting (especially in continuous IP). Enter a maximum volume corresponding to 2-3 ml above the last inflection volume.

Ordinates

Indicated ordinate values are experimental values with the mentioned titration solvent and electrodes. If the reference electrode or titration solvent are changed, it should be necessary to modify the different ordinate values.

Titrant standardisation

If necessary, standardise the titrant against weighed potassium hydrogen phthalate ($\text{KOOOC-C}_6\text{H}_4\text{-COOH}$ with a molar weight of 204.22 g/mol and 1 smp + 1 titrant). Take 0.1 g of potassium hydrogen phthalate weighed to the nearest 0.1 mg. Dissolve it with care in 20 ml of warm acetic acid, add 40 ml of chlorobenzene, cool and titrate.

Carry out a blank titration on 20 ml of acetic acid plus 40 ml of chlorobenzene.

Back titration

If no inflection point is visible during direct titration, it is necessary to run a back titration to determine the Base Number.

In this case, a known volume (in excess) of 0.1M perchloric acid in acetic acid is added to the sample diluted in the solvent titration. The excess of perchloric acid is back titrated with sodium acetate in acetic acid as titrant.

0.1M sodium acetate solution

Using a volumetric flask, dilute 5.3 g of Na_2CO_3 (anhydrous sodium carbonate) in 300 ml of acetic acid, after dissolution, complete to 1000 ml with acetic acid (the molar weight of Na_2CO_3 is 106 g/mole and 1 mole of Na_2CO_3 gives in acetic acid 2 moles of CH_3COONa).

Procedure according to the ASTM standard

Using titration solvent as solvent, titrate a known volume of perchloric acid (for example 8-10 ml) with the sodium acetate solution. Note the volume V_1 of the sodium acetate solution.

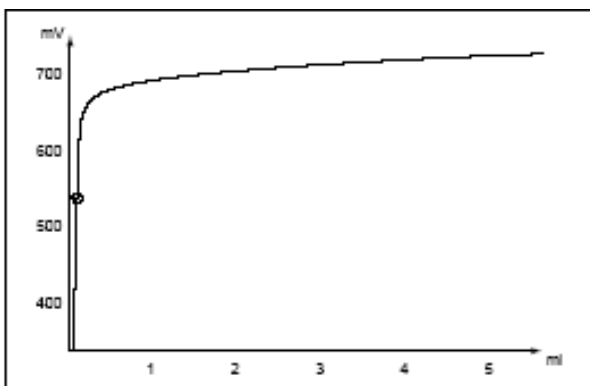
Weigh no more than 5 g of product and add the same volume of titration solvent and the same volume of perchloric acid that should be in excess.

Titrate the solution with the sodium acetate solution, note the volume V_2 used.

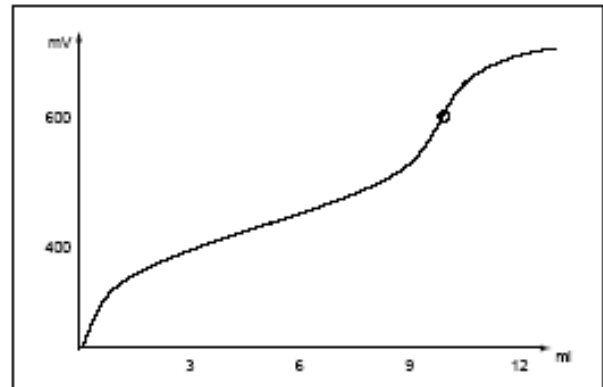
If C_{ac} is the titrant concentration and W the sample amount:

$$\text{BN (mg/g)} = ((V_1 - V_2) * C_{ac} * 56.11) / W$$

Curves



Blank solvent



Sample