



## ***Acid Number of Petroleum Products*** ***(Potentiometric titration ASTM D664-95 reapproved 2001)***

### **Introduction**

This method is a determination of the acidic components of a petroleum product. The titration is run in non-aqueous media using potassium hydroxide in alcoholic solution as titrant. If no inflection point is detected during the titration, an end point titration will be necessary (see application note TTEP01.01PET).

### **Principle**

The titration performs an inflection point determination, taking into account the total volume of titrant necessary to detect an inflection point at a potential close to that of a non-aqueous basic buffer solution.

The result is expressed as mg of potassium hydroxide necessary to titrate 1 g of product.

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

### **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

REF361 Reference Electrode (part no. E21M003) filled with LiCl 1M in isopropyl alcohol as reference electrode

M241Pt Metal Electrode (part no. E31M001) as cell grounding KOH 0.1M in isopropyl alcohol: Add 6 g of KOH to approximately 1000 ml of isopropyl alcohol. Boil gently for 10 minutes. Allow the solution to rest for 2 days, filter, store in a chemically resistant bottle and standardise versus potassium hydrogen phthalate. This titrant is also commercially available.

Titration solvent

Mix 5 ml of distilled water with 495 ml of isopropyl alcohol, then add 500 ml of toluene.

Basic buffer solution (stock solution):

Weigh 27.8 of m-nitrophenol, add 100 ml of isopropyl alcohol and 500 ml of KOH 0.1M (in isopropyl alcohol), dilute to 1000 ml with isopropyl alcohol in a volumetric flask.

Store the solution in a brown glass bottle.

Use this solution within 2 weeks

Prepare the basic buffer solution by dilution of 10 ml of the stock solution in 100 ml of titration solvent.

Use this solution within 1 hour (solution A).

Filling solution for the reference electrode:  
Dissolve 4.2 g of LiCl in 100 ml of isopropyl alcohol.

Buffer solutions pH 4.00 (S11M012) and pH 10.00 (S11M014)

For strong acid number determination

Acid buffer solution:

Weigh 24.2 g of 2,4,6-trimethylpyridine, add 750 ml of 0.2 mol/l HCl in isopropyl alcohol and dilute to 1000 ml with isopropyl alcohol using a volumetric flask. Use this solution within 2 weeks.

Prepare the acid buffer solution by dilution of 10 ml of the stock solution in 100 ml of titration solvent. Use this solution within 1 hour (solution B).

**Warning:** Reagents used in this application note are flammable. They can cause severe burns and are hazardous if swallowed, breathed or come into contact with the skin or eyes. Always respect laboratory health and safety regulations when using these reagents. Also refer to ASTM Standard D664.

### **Inflection Detection settings**

#### **CONTINUOUS ADDITION MODE (CONTINUOUS IP)**

Cell grounding:	M241Pt
Measure:	mV
Blank:	YES
Stirring speed:	550 rpm

Stirring delay: 30 s  
 Burette volume: 10 ml  
 Maximum volume: 5 ml (see notes)  
 Stop point: -300 mV  
 Smoothing parameter: 8  
 Inflexion points number: 2  
 Minimum speed: 0.05 ml/min  
 Maximum speed: 1ml/min  
 Direction: Decreasing mV  
 Inflection1: see notes  
 Min. ordinate: -250 mV  
 Max. ordinate: 60mV  
 Inflection 2  
 Min. ordinate: -250 mV  
 Max. ordinate: 60 mV  
 Sample unit: g  
 Sample amount: see working range

Results:  
 Results by: cumulate  
 Number of results: 2

Result 1  
 Result unit: mg/g  
 Molar weight: 56.11  
 Reaction: 1 smp + 1 titr  
 Calculate with IP: 1

Result 2  
 Result unit: mg/g  
 Molar weight: 56.11  
 Reaction: 1 smp + 1 titr  
 Calculate with IP: 2

#### INCREMENTAL MODE (Dynamic IP)

Speed: 5 ml/min  
 Dynamic dose: 12  
 Maximum dose: 0.3 ml  
 Stability: 10 mV/min  
 Acceptation: 00:30 min:s  
 IP filter: 1  
 IP reject: 15

*Others settings similar to Continuous IP*

#### Procedure

**It is strongly recommended to work under a hood.**

When performing the application for the first time, prepare the REF361 Reference Electrode.

The REF361 is delivered filled with aqueous KCl solution, empty this solution, rinse the electrode with isopropyl alcohol and fill it with the LiCl solution in isopropyl alcohol.

Check the electrodes behaviour

Measure the potential indicated by the electrodes dipped in the solution A and solution B. The potential is normally close to -140/-160 mV for solution A and around 200 mV for solution B with the abovementioned electrodes.

Use the icon ELECTRODES and "DISPLAY MEASUREMENT"

Run a blank determination using 125 ml of titration solvent

Prepare the sample by dilution of the necessary amount of product in 125 ml of titration solvent (see notes).

Run the titration.

#### Electrodes maintenance and storage

a) When a titration is finished, rinse the electrodes with titration solvent, then with ethyl alcohol and distilled water and dip them in the pH 4.00 buffer solution for 30/60 seconds.

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 first 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 Analytical GK ANNEX Electrode Maintenance Kit (part no. S91M001).

#### Results

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

$$R(\text{mg/g}) = (V_{\text{titr}} - V_{\text{blk}}) * C(\text{titr}) * 56.11 / W(\text{smp})$$

$V_{\text{titr}}$  = Total volume of titrant used in ml

$V_{\text{blk}}$  = Blank volume used for solvent titration

$C(\text{titr})$  = Concentration of titrant in mol/l

$W(\text{smp})$  = Sample weight in g

56.11 = molecular weight of KOH

#### Results with used motor oil

Mean: 2.8 mg/g  
 Standard deviation: 0.05 mg/g  
 Rel. Standard dev.: 2%

#### Working range

According to the calculation formula for 1 g of product and a 10 ml burette, the experimental range is between 5 mg/g and 40 mg/g for the Acid Number.

In addition, ASTM Standard D664 gives for the sample size:

Acid number	Sample weight (in g)
0.05-1	20
1.0-5.0	5
5.0-20	1
20-100	0.1

## Notes

### Note regarding the inflection and the result numbers

As a general rule, with oils containing only weak acidic functions (Acid Number determination), only one inflection occurs during the titration. A second inflection may occur (consequence of a noisy titration curve). If the curve parameters are entered, 2 inflections with results by CUMULATE can give the expected result even in this situation.

### Note regarding Strong Acid Number

Minimum and maximum ordinates indicated for inflection point determination are indicated for products with Acid Number. For products with Strong Acid Number, change the first inflection as indicated below:

Inflection 1

Min. ordinate: 60 mV

Max. ordinate: 200 mV

The indicated maximum ordinate corresponds to the starting potential of the solution.

### Note regarding titrant standardisation

If necessary, standardise the KOH 0.1M in isopropyl alcohol against weighed potassium acid phthalate (KOOCC<sub>6</sub>H<sub>4</sub>COOH with a molar weight of 204.22 g/mol and 1 smp + 1 titrant) and dissolved in CO<sub>2</sub> free distilled water.

### Note regarding the maximum volume

Depending on the expected result, it may be necessary (especially in continuous IP) to modify this setting. Try to enter a maximum volume corresponding to 2 ml above the last inflection volume. Note that if the titration curve is well defined, you can use the stop after the last inflection point.

Titration Manager settings:

Inflection point number: 1

Stop at last IP: YES

(other settings similar to those indicated before)

## Curve

