



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. Standard ASTM D664-95 recommends to use End Point titration technique when the Inflection Point yields an ill-defined IP. As this application note also works in end point titration, it should be used if the inflection method does not produce an apparent inflection (see also application note TTIP01.01PET).

Principle

The end point titration takes into account the total volume of titrant necessary to reach a potential equal 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. Leave the solution to stand 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, cause severe burns and are hazardous if swallowed, inhaled or come into contact with the skin or eyes. Use these reagents according to the safety regulations in application in the lab; also refer to ASTM D664.

End Point titration

Cell grounding:	M241Pt
Measure:	mV
Blank:	YES
Stirring speed:	550 rpm
Stirring delay:	30 s
Burette volume:	10 ml
Maximum volume:	10 ml
Number of end points:	2
Stirring delay:	30 seconds
Minimum speed:	0.2 ml/min
Maximum speed:	1 ml/min
End point 1:	200 mV (see notes)
Proportional band:	200 mV
End point delay:	10 seconds
End point 2:	-140 mV (see notes)
Proportional band:	200 mV
End point delay:	10 seconds
Direction:	Decreasing mV

Sample unit: g
Sample amount: see working range
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

Procedure

It is strongly recommended to work under a hood

Prepare the REF361 Reference Electrode for the first time.

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 electrode behaviour:

Measure the potential indicated by the electrodes dipped in 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 above-mentioned electrodes. Enter these values as end point values. For this, use the ELECTRODES and "DISPLAY MEASUREMENT" icons.

Run a blank determination using 125 ml of titration solvent.

Prepare the sample by diluting the necessary amount of product in 125 ml of titration solvent (**see working range notes**).

Dip electrodes and delivery tip in solution.

Wait for the stability of the starting potential using the ELECTRODE and "DISPLAY MEASUREMENT" icon.

Run the titration

Electrode maintenance and storage

a) After a titration, 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 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 pH 4.00 and then in 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 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_{titr} = Total volume of titrant used in ml

V_{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

As two end points are entered, if the petroleum product has no strong acidity, the first result will be zero and the second the Acid Number of the product.

Results with used engine oil

Mean: 2.5 mg/g
Standard deviation: 0.05 mg/g
Rel. Standard dev.: 2%

Working range

Using 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 D664 gives the following 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 end point values

The above-mentioned end point values are experimental values, depending on reference and measuring electrode behaviour and also on the exact composition of the titration solvent.

The first end point corresponds to Strong Acid Number and the second to Acid Number

Regularly check the measured potential by dipping the electrodes in the basic buffer solution (or acid buffer solution) and enter this value as end point value.