
Application Bulletin

Of interest to: Petrochemical industry

A 1, 5

Determination of the acid and base number in petroleum products

Summary

The determination of the acid or base number plays a significant part in the analysis of petroleum products. This is manifested in the numerous standard procedures in use the world over (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. Fortunately, the days seem to be over where one laboriously worked with pH meter, rod burette and colour indicators. Modern titrators are gradually replacing the time-consuming, manual titrations as well as the calculation of the results.

This bulletin describes the determination of the acid and base number in petroleum products by means of automatic potentiometric titration.

Instruments and accessories

- 702 SET/MET Titrino, 716 DMS Titrino, 736 GP Titrino, 751 GPD Titrino or 785 DMP Titrino or
 - 726 Titroprocessor with 700 Dosino or 685 Dosimat
 - 2.728.0040 Magnetic Stirrer
 - 6.3014.223 Exchange Units 20 mL (with flat PCTFE/PTFE stopcock)
 - 6.0229.100 LL Solvotrode with 6.2104.020 electrode cable or
 - 6.0431.100 Pt Titrode and 6.0729.100 Double junction Ag/AgCl reference electrode with two 6.2104.020 electrode cables (for three electrode technique with differential amplifier input of the titrator).
-

Reagents

This bulletin does not include advice concerning the use and handling of the described chemicals or the safety precautions to be taken. For this information, we recommend that you refer to the relevant literature.

Reagents for the determination of the acid number

- Titrant: c(TBAOH) = 0.1 mol/L in isopropanol (IPA) or
c(KOH) = 0.1 mol/L in IPA
- Solvent: 500 mL toluene + 495 mL IPA + 5 mL H₂O
For environmental reasons one should refrain from using chlorinated solvents.

- Electrolyte for the electrodes: Tetraethylammonium bromide $c(\text{TEABr}) = 0.4 \text{ mol/L}$ in ethylene glycol (Metrohm no. 6.2320.000)
- Standard: $c(\text{benzoic acid}) = 0.100 \text{ mol/L}$ in ethanol (1.220 g benzoic acid in 100 mL ethanol)

Reagents for the determination of the base number

- Titrant: $c(\text{HClO}_4) = 0.1 \text{ mol/L}$ in glacial acetic acid or $c(\text{HCl}) = 0.1 \text{ mol/L}$ in IPA
- Solvent: Toluene : glacial acetic acid = 1 : 1 (volume ratio)
- Electrolyte for the electrodes: LiCl sat. in ethanol (Metrohm no. 6.2312.000)
- Standard: $c(\text{CH}_3\text{COONa}) = 0.100 \text{ mol/L}$ in glacial acetic acid (0.820 g anhydrous CH_3COONa in 100 mL glacial acetic acid)

Treatment of the electrode(s), control of the electrode's slope

- When not in use, store the Solvotrode and the reference electrode in the respective electrolyte solutions. The Pt Titrode should be stored in dist. water.
- Upon completion of the titration, rinse the electrodes first with toluene/IPA, then with ethanol and finally with dist. water. (In sample changer operation, immerse the electrodes, while stirring, for 10 s each in toluene/IPA, then ethanol, and finally rinse well in a separate beaker with dist. water.)
- Control of the electrode's slope:
Rinse the electrodes with dist. water and gently dry with a soft paper towel (do not rub). Dip them in buffer solution pH = 7.00 (Metrohm no. 6.2307.110), stir and after 1 min read off the voltage value in mV. After rinsing the electrodes with dist. water, repeat the same procedure with buffer solution pH = 4.00 (Metrohm no. 6.2307.100).
For good electrodes the resulting voltage difference is > 150 mV (at 20 ... 25 °C). If the difference is less than 150 mV, loosen the ground sleeve of the diaphragm, so that a little electrolyte can flow out. Then repeat the measurements using the two buffer solutions.

Example:

Voltage for buffer pH = 7.00: 18 mV
Voltage for buffer pH = 4.00: 195 mV
Resulting voltage difference: 177 mV

Assessment: The electrode is OK.

Analyses

1. Determination of the acid number

An appropriate amount of the well-mixed sample (see table below) is weighed into the titration vessel and 50... 125 mL of the solvent (toluene/IPA/H₂O) are added. Proceed with the titration with TBAOH or KOH using one of the following methods:

DET U	drift controlled	time controlled
meas.pt.density	2	2
min.incr.	100 µL	100 µL
signal drift	10 mV/min	OFF
equibr.time	20 s	20 s
pause (before titration)	50 s	50 s

Sample size

Expected acid number mg KOH / g sample	Sample weight	Weighing accuracy
0.05 ... 0.9	10 ± 2 g	100 mg
1 ... 4.9	5 ± 0.5 g	20 mg
5 ... 19	1 ± 0.1 g	5 mg
20 ... 99	0.25 ± 0.02 g	1 mg
100 ... 250	0.1 ± 0.01 g	0.5 mg

Calculation

$$\text{Acid number in mg KOH / g sample} = (\text{EPn} - \text{C31}) * \text{C01} * \text{C02} * \text{C03} / \text{C00}$$

EPn = Titrant consumption in mL to reach the nth (last) equivalence point.
Normally one equivalence point is obtained. In the presence of strong acids there may also be several EPs. Always use the last EP for the calculation of the acid number. (EP1 can be used additionally for the calculation of the strong acid number.)

C00 = Sample weight in g

C01 = 0.1 (concentration of the titrant in mol/L)

C02 = Titre of the titrant

C03 = 56.106 [M(KOH) in g/mol]

C31 = Blank value consumption for the used quantity of solvent (also see Application Bulletin No. 210)

2. Determination of the base number

Depending on the expected base number, weigh 0.1 ... 5 g of the well-mixed sample into the titration vessel. Add 50 ... 125 mL of the solvent (toluene/glacial acetic acid) and titrate with HClO₄ or HCl using one of the following methods:

DET U	drift controlled	time controlled
meas.pt.density	2	2
min.incr.	100 µL	100 µL
signal drift	10 mV/min	off
equibr.time	20 s	20 s
pause (before titration)	50 s	50 s

Calculation

Base number in mg KOH / g sample = $(EP_n - C_{31}) * C_{01} * C_{02} * C_{03} / C_{00}$

EP_n = Titrant consumption in mL to reach the nth (last) equivalence point.
 Normally one equivalence point is obtained. In the presence of strong bases there may also be several EPs. Always use the last EP for the calculation of the base number. (EP₁ can be used additionally for the calculation of the strong base number.)

C₀₀ = Sample weight in g

C₀₁ = 0.1 (concentration of the titrant in mol/L)

C₀₂ = Titre of the titrant

C₀₃ = 56.106 [M(KOH) in g/mol]

C₃₁ = Blank value consumption for the used quantity of solvent (also see Application Bulletin No. 210)

Remarks

- 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 electrodes, which have been 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. c(TEABr) = 0.4 mol/L should therefore be used as electrolyte for the reference electrode.

Figures

The determinations were carried out using the 785 DMP Titrimo.

Parameters for drift controlled titration:

```
'pa
785 DMP Titrimo      02287  785.0010
date 1999-04-13    time 15:11    20
DET U              TAN drif
parameters
>titration parameters
  meas.pt.density      2
  min.incr.            100 µl
  dos.rate             max. ml/min
  signal drift         10 mV/min
  equilibr.time        20 s
  start V:             OFF
  pause                50 s
  meas.input:          1 or diff.
  temperature          25.0 °C
>stop conditions
  stop V:              abs.
  stop V               4 ml
  stop U               OFF mV
  stop EP              9
  filling rate         max. ml/min
>statistics
  status:              OFF
>evaluation
  EPC                  5
  EP recognition:      last
  fix EP1 at U        OFF mV
  pK/HNP:             OFF
>preselections
  req.ident:           OFF
  req.smpl size:      value
  limit smpl size:    OFF
  activate pulse:     OFF
=====
```

Parameters for time controlled titration:

```
'pa
785 DMP Titrimo      02287  785.0010
date 1999-04-13    time 10:01    11
DET U              TBN time
parameters
>titration parameters
  meas.pt.density      2
  min.incr.            100 µl
  dos.rate             max. ml/min
  signal drift         OFF mV/min
  equilibr.time        20 s
  start V:             OFF
  pause                50 s
  meas.input:          1 or diff.
  temperature          25.0 °C
>stop conditions
  stop V:              abs.
  stop V               10 ml
  stop U               OFF mV
  stop EP              9
  filling rate         max. ml/min
>statistics
  status:              OFF
>evaluation
  EPC                  5
  EP recognition:      last
  fix EP1 at U        OFF mV
  pK/HNP:             OFF
>preselections
  req.ident:           OFF
  req.smpl size:      value
  limit smpl size:    OFF
  activate pulse:     OFF
=====
```

Fig. 1: Parameter settings for drift or time controlled titration.

```
'fr
785 DMP Titrino      02287  785.0010
date 1999-04-13    time 15:11    20
card label:       751
U(init)           85 mV DET U    TAN drif
smp1 size         5.3686 g
EP1                2.183 ml      -314 mV
TAN                2.28 mg/g
stop V reached
=====
```

```
'fr
785 DMP Titrino      02287  785.0010
date 1999-04-13    time 14:40    18
card label:       751
U(init)           132 mV DET U    TAN dri3
smp1 size         4.8872 g
EP1                1.936 ml      -256 mV
TAN                2.22 mg/g
stop V reached
=====
```

```
'cu
785 DMP Titrino      02287  785.0010
date 1999-04-13    time 15:11    20
start V           0.000 ml DET U    TAN drif
1.0 ml/div        dU=100.0 mV/div
```

```
'cu
785 DMP Titrino      02287  785.0010
date 1999-04-13    time 14:40    18
start V           0.000 ml DET U    TAN dri3
1.0 ml/div        dU=100.0 mV/div
```

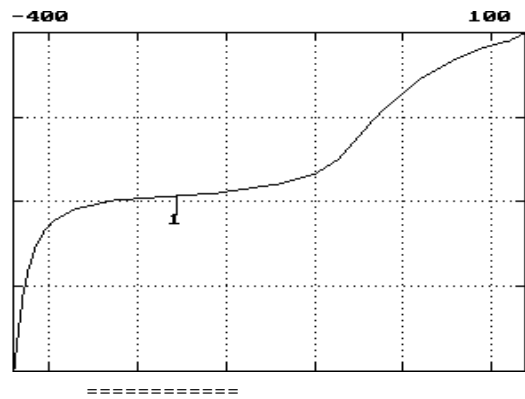
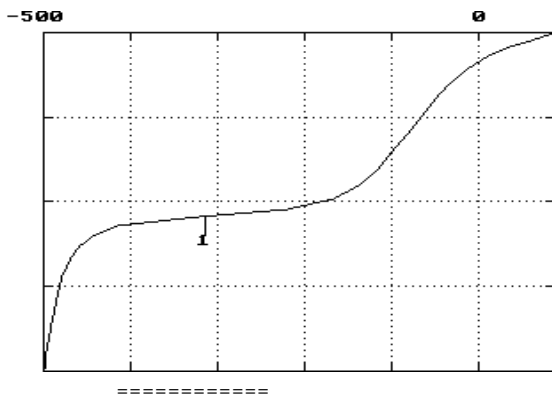


Fig. 2: Acid number in spindle oil, drift controlled, 6.0229.100 Solvotrode.

Fig. 3: Acid number in spindle oil, drift controlled, «three electrode technique».

```
'fr
785 DMP Titrino      02287  785.0010
date 1999-04-13    time 09:27    10
card label:       751
U(init)          392 mV DET U    TBN time
smpI size       5.4219 g
EP1             5.671 ml          727 mV
TBN             5.87 mg/g
stop V reached
=====
```

```
'cu
785 DMP Titrino      02287  785.0010
date 1999-04-13    time 09:27    10
start V         0.000 ml DET U    TBN time
2.0 ml/div      dU=100.0 mV/div
```

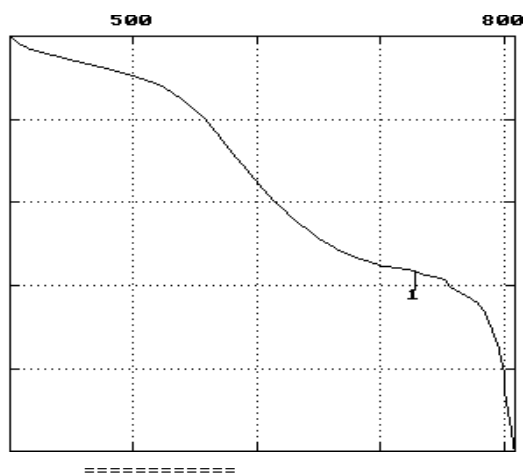


Fig. 4: Base number in motor oil, time controlled, 6.0229.100 Solvotrode.

```
'fr
785 DMP Titrino      02287  785.0010
date 1999-04-13    time 13:13    15
card label:       751
U(init)          390 mV DET U    TBN tim3
smpI size       5.0663 g
EP1             5.344 ml          675 mV
TBN             5.92 mg/g
stop V reached
=====
```

```
'cu
785 DMP Titrino      02287  785.0010
date 1999-04-13    time 13:13    15
start V         0.000 ml DET U    TBN tim3
2.0 ml/div      dU=100.0 mV/div
```

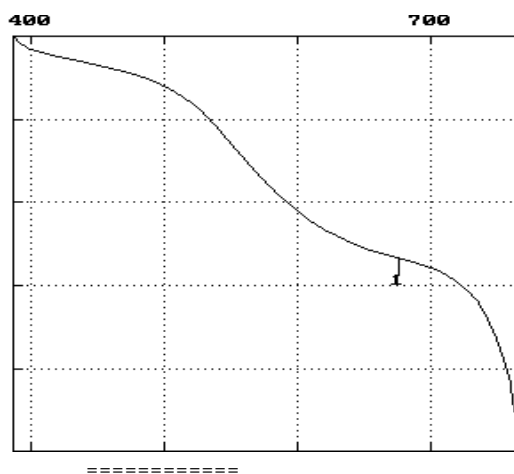


Fig. 5: Base number in motor oil, time controlled, «three electrode technique».

Literature

- ASTM D 4739-87
Standard Test Method for Base Number Determination by Potentiometric Titration.
- ASTM D 2896-88
Standard Test Method for Base Number of Petroleum Products by Potentiometric Perchloric Acid Titration.
- ASTM D 664-89
Standard Test Method for Acid Number of Petroleum Products by Potentiometric Titration.
- ISO 3771: 1994
Petroleum Products – Determination of base number – Perchloric acid potentiometric titration method.