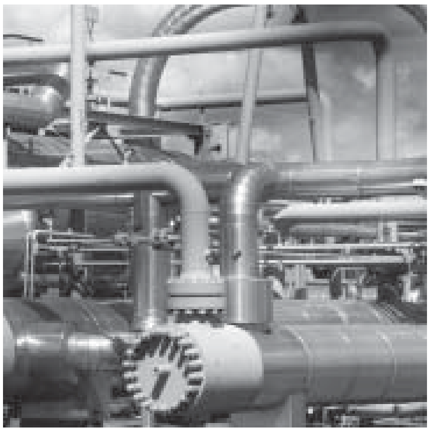
# PETROCHEMICAL INDUSTRIES
## Introduction

### The complete applications package

At Radiometer Analytical, we put applications first. When you order one of our new generation of titration workstations with a dedicated application package, you have everything you need to get started right away: electrodes, specific accessories, standards, maintenance solutions and, of course, methods and application notes.

### Application booklets



The petrochemical industry manufactures and tests two main types of products: engine and motor oils and fuels such as kerosene, gasoline and turbine fuel. This requires exclusively non-aqueous titrations using special electrodes and titration solvents. As the petrochemical industry is subjected to strict international regulations and ASTM or ISO standards, the relevant standard is specified for each application.
Analyses based on potentiometric titration are acid-base titrations (TAN or TBN determination), precipitation titrations (Mercaptan determination) and redox titrations (Bromine number or Water determination).

Radiometer Analytical produces other technique-based applications booklets as well as a range of applications dedicated to particular sectors. Ask your local representative for the following booklets:

| *Technique* | *Part No.* |
|---|---|
| Acid-base titrations | D41T009 |
| Precipitation titrations | D41T010 |
| Complexometric titrations | D41T011 |
| Redox titrations | D41T012 |

| *Dedicated* | *Part No.* |
|---|---|
| Chemical industries | D41T007 |

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For the latest updates visit us at www.titration.com.

# PETROCHEMICAL INDUSTRIES

Radiometer
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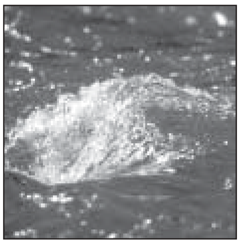
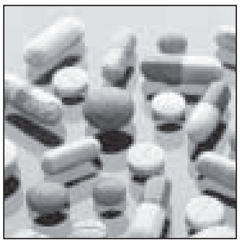
# Inflection Point Titration Manager
# Operational Qualification





## Introduction

The operational qualification procedure demonstrates that an instrument runs according to the operational specifications in the selected environment. For a titration manager using automatic inflection point determination, this operation can consist of two steps:

- Calibration and checking of a pH measurement electrode system,

- Titration of anhydrous sodium carbonate standard using a commercial standard solution of HCl.

## Principle

The reaction has 2 steps corresponding to 2 different inflection points:

$Na_2CO_3 + HCl \rightarrow NaHCO_3 + NaCl$

$NaHCO_3 + HCl \rightarrow CO_2 + H_2O + NaCl$

The operational qualification takes into account the second equivalence point (close to pH 4.00) corresponding to the complete neutralisation of sodium carbonate.

The Titration Manager settings allow the complete titration curve to be seen.

## Electrode and reagents

pHC2011-8 Combined pH Electrode (part no. E16M317)

T201 Temperature Sensor (part no. E51M001)

IUPAC Series pH standards

pH 4.005 (part no. S11M002)

pH 7.000 (part no. S11M004)

pH 10.012 (part no. S11M007)

100 g bottle of Merck "certified" sodium carbonate (part no. 1.06394.0100) or 500 g bottle of "pro analysis" Merck sodium carbonate (part no. 1.06392.0500)

1 l of "ready to use" Merck HCl 0.1 mol/l (part no. 1.09060.1000)

Distilled water

## Continuous IP titration settings

**Electrode**

| | |
|---|---|
| pH: | pHC2011-8 |
| Calibration request: | YES |
| Number of cycles: | 2 |
| Number of buffers: | 3 |
| Measurement: | Stirring |
| Temperature: | probe |

**Calibration parameters**

| | |
|---|---|
| Stability: | 15 mpH/min |
| Acceptation time: | 2.00 min |
| Max. stab. Time: | 5.00 min |
| Acceptation criteria: | YES |
| Iso. pH: | 6.65 pH |

**Calibration solutions**

| | |
|---|---|
| 1: | 4.005 (IUPAC) |
| 2: | 7.000 (IUPAC) |
| 3: | 10.012 (IUPAC) |
| Min. zero pH: | 5.8 pH |
| Max. zero pH: | 7.5 pH |
| Min. sensitivity: | 95% |
| Max. sensitivity: | 103% |

**Titrant**

| | |
|---|---|
| ID: | HCl |
| Unit: | M |
| Titre: | Entered |

**Method**

| | |
|---|---|
| Stirring speed: | 550 rpm |
| | |
| Predose: | 0 ml |
| Start timer: | 45 sec |
| Max. volume: | **(see notes)** |
| Stop point: | 2.000 pH |
| Smoothing parameter: | 8 |
| Number of IP: | 2 |
| Min. speed: | 0.2 ml/min |
| Max. speed: | 5.00 ml/min |
| Direction: | decreasing pH |
| | |
| Inflection 1 | |
| Min. ordinate: | 7.00 pH |
| Max. ordinate: | 10.00 pH |
| Inflection 2 | |
| Min. ordinate: | 2.80 pH |
| Max. ordinate: | 6.00 pH |
| | |
| Sample unit: | mg |
| Sample amount: | **(see notes)** |
| | |
| Results | |
| Results by: | cumulate |
| Number of result: | 1 |
| Acceptation criteria: | YES |
| | |
| Result 1 | |
| Result unit: | % |
| Molar weight: | 105.99 |
| Reaction: | 1 smp + 2 titr |
| Calculate with IP: | 2 |
| Minimum value: | 99 |
| Maximum value: | 101 |

## Procedure

**Electrode calibration and checking**

If the electrode is new, condition it by immersion in distilled water for at least 1 hour.

Connect the pHC2011-8 electrode and the T201 Temperature Sensor

Using the above-mentioned settings, RUN an electrode calibration with 2 or more cycles.

At the end of the last cycle, calibration results should be accepted

Ensure that the temperature of the standards does not differ by more than 2°C.

**Operation qualification in continuous IP**

Fit the burette of the titration manager with HCl 0.1 M as titrant and install the titrant

**Preparation of $Na_2CO_3$**

As indicated, dry approximately 5 g of anhydrous sodium carbonate in an oven for 4 hours at 250°C. Let it cool to room temperature in a desiccator with $P_2O_5$ or another humidity adsorber.

## Notes

To determine the necessary amount of sodium carbonate

**With a 25 ml burette capacity**

Weigh exactly approximately 85-90 mg of $Na_2CO_3$

This weight corresponds to

1.6-1.8 meq or 16-18 ml of HCl 0.1M. Use a maximum volume close to 20/22 ml

**With a 10 ml burette capacity**

Weigh exactly approximately 40 mg of $Na_2CO_3$. Use a maximum volume of 10 ml

**With a 5 ml burette capacity**

Weigh exactly approximately 20 mg of $Na_2CO_3$. Use a maximum volume of 5 ml

Dissolve the weighed sodium carbonate quantitatively in the titration beaker with 50 to 80 ml of freshly distilled water.

Immerse the electrode and the delivery tip in the solution.

Using the above-mentioned settings, run a titration on 3 different tests or replicates. Results should be accepted between 99 and 101%.

Calculations are programmed to give a result according to the delivered titrant volume at the inflection point situated in the acceptance range 2.80-6.00 pH

## Dynamic IP Titration settings

This application note can be used with incremental addition of titrant (Dynamic IP)

**Dynamic IP**

| | |
|---|---|
| Speed: | 5.00 ml/min |
| Dynamic dose: | 30 |
| Maximum dose: | 0.3 ml |
| Stability: | 100 mpH/min |
| Acceptation: | 10 s |

These settings were tested with a 10 ml burette. The others settings are unchanged.

# 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 non-aqueous 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 stay 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 settings

**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**:

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

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

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

C(titr) = Concentration of titrant in mol/l

W(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 | Mass of sample (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.

# 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 non-aqueous 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 above-mentioned 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(mg/g) =
(Vtitr - Vblk) * C(titr) * 56.11 / W(smp)

Vtitr = Total volume of titrant used in ml

Vblk  = Blank volume used for solvent titration

C (titr) = Concentration of titrant in mol/l

W (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 ($KOOC\text{-}C_6H_4\text{-}COOH$ with a molar weight of 204.22 g/mol and 1 smp + 1 titrant) and dissolved in $CO_2$ free distilled water.

**Note regarding the maximum volume**

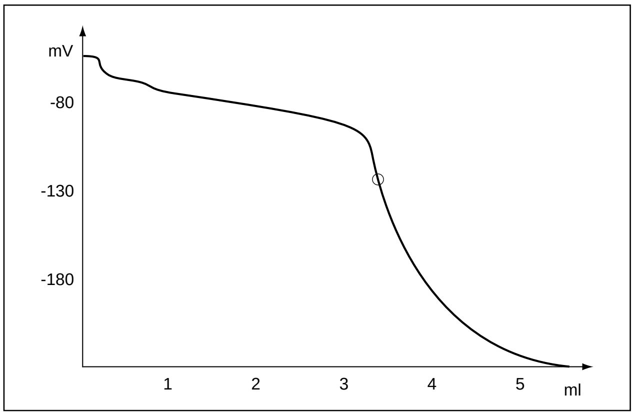
Depending on the expected result, it may be necessary (especially in continuous IP) to modify this setting. Try to enter a maximum volume corresponding to 2 ml above the last inflection volume.
Note that if the titration curve is well defined, you can use the stop after the last inflection point.

Titration Manager settings:

| | |
|---|---|
| Inflection point number: | 1 |
| Stop at last IP: | YES |

(other settings similar to those indicated before)

**Curve**



# Bromine Number of Petroleum Products

## (ASTM D1159-98 Electrometric titration)

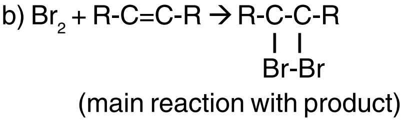
## Introduction

This method covers bromine number determination of certain petroleum products indicated in ASTM standard D1159-98. The magnitude of the bromine number is simply an indication of the bromine reactive constituents, not an indication of the constituents.
The bromine number mainly indicates the concentration of double bonds present in the product.

## Principle

Expressed as g of Bromine ($Br_2$) able to react with 100 g of product, the bromine number determination uses the reaction between a ($Br^-$/$BrO_3^-$) solution and the petroleum product according to the following reactions

a) $5\,Br^- + BrO_3^- + 6H^+ \rightarrow 3Br_2 + 3H_2O$



b) $Br_2 + R\text{-}C{=}C\text{-}R \rightarrow \underset{\text{Br-Br}}{R\text{-}C\text{-}C\text{-}R}$

(main reaction with product)

(Note that other reactions can occur such as addition, substitution or oxidation)

**To avoid secondary reactions the titration is run at low temperature (close to 5°C).**
The titrant concentration, expressed as $Br_2$ concentration, is 0.25 mol/l (or ¼ mol/l). According to reaction (a), the titrant contains 5/12 mole of KBr and 1/12 mol/l of $KBrO_3$.The molar weight of KBr is 119.9 g/mol and for $KBrO_3$ 167.9 g/mol. Titration is run according to an inflection determination with imposed current potentiometry and a double platinum wire electrode.

## Electrode and reagents

M241Pt2-8 Metal Electrode, double platinum (part no. E32M002)
or
M231Pt2 Metal Electrode, double platinum (part no. E32M001) with adapter part no. A94P801

T201 Temperature sensor (part no. E51M001)

Water-jacketed titration beaker connected to a low temperature thermostat or a bath filled with ice

Bromide-Bromate titrant solution (0.25 mol/l as bromine concentration)

Dissolve 51.0 g of KBr (5*119.9/12) and 13.92 g of $KBrO_3$ (167.01/12) in 1000 ml of distilled water using a volumetric flask.

Sulphuric acid (1+5)

Carefully mix one volume of concentrated sulphuric acid with 5 volumes of distilled water. Caution: the dilution reaction is exothermic.

Titration solvent **(see notes)**

Mix 714 ml of glacial acetic acid ($CH_3COOH$), 134 ml of dichloromethane ($CH_2Cl_2$), 134 ml of methanol ($CH_3OH$) and 18 ml of sulphuric acid (1+5).

Dichloromethane ($CH_2Cl_2$)

**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.

## Inflection Detection settings

**CONTINUOUS IP**
Titration with blank
Burette volume: 10 ml **(see notes)**
Max. volume: 7 ml
Stirring speed: 500 rpm
Working mode: mV with i >0
Current: DC
Current value: 5µA **(see notes)**
Blank: YES
Start timer: 30 s
Stop point: 0 mV

Minimum speed: 0.50 ml/min
Maximum speed: 2.00 ml/min
Smoothing param: 8

Titration: Decreasing potential
Inflection number: 1
Stop at last IP: YES

Inflection 1:
Min. ordinate: 200 mV
Max. ordinate: 800 mV

Sample

Dilution: YES
Sample unit: g
Sample amount: 2
**(see working range)**
Final dilution vol.: 50 ml
Aliquot: 5 ml
**(see working range)**

Result 1: ml

Equation 1:
Equation Unit: Bromine number
Equation: (R1*CT*15.98*DA/(SA*AL)
**(see notes)**

## Procedure

Connect the double platinum wire electrode to the corresponding input of the Titration Manager.

Connect the temperature sensor to the corresponding input on the Titration Manager.

For a new titration solvent batch run a BLANK titration with 115 ml of titration solvent and 5 ml of dichloromethane. The experimental blank volume is generally lower than 0.1 ml.

*Sample preparation*
Place 10 ml of dichloromethane in a 50 ml volumetric flask then add the weighed sample and fill the flask to the mark with dichloromethane.

Add 110 ml of titration solvent to the titration beaker.

Add an aliquot (generally 5 ml but not more than 10 ml) of the sample solution in dichloromethane.

Dip the electrode, temperature sensor and delivery tip in the beaker and immerse the beaker in an ice bath or alternatively in a low temperature thermostatic bath.

Using the electrode direct measurement function of the Titration Manager (icon ELECTRODES and "DISPLAY MEASUREMENT) allow the solution to reach the mentioned temperature (around 5°C) **(see notes)**.

Run the titration.

## Results

As indicated above, results are expressed **in g of $Br_2$ able to react with 100 g of product**.

R(bromine number) =
(Vtitr-Vblk)*C(titr)*159.8*100/W(smp)*1000

Vtitr = Total volume of titrant used in ml

Vblk = Blank volume used for solvent titration

C (titr) = Concentration of titrant in mol/l

W (smp) = Sample weight in g

159.8 = molecular weight of $Br_2$

100 = conversion factor for 100 g of product

1000 = correction factor for result in g instead of mg

**For 5 determinations on cyclohexene ($C_6H_{10}$)**
Mean delivered volume: 3.42 ml
Rel. standard deviation: 1.2%
Corresp. Bromine number: 193
Theoretical: 194.6

## Working range

For a sample amount of 1g, and a calculated dilution coefficient of 10 (50 ml for final dilution volume and 5 ml for the aliquot), 1 ml of 0.25 mol/l titrant corresponds to a Bromine number of 37.5.

The magnitude of the bromine number of a sample is often unknown and it is necessary to perform a preliminary test with 2 g of sample.

ASTM Standard D1159 gives a table for sample amount as a function of Bromine number:

| Bromine number | Sample amount in g | Titrant volume in ml |
|---|---|---|
| 0-10 | 20-16 | Around 4 |
| 10-20 | 10-8 | Around 3-4 |
| 20-50 | 5-4 | Around 5 |
| 50-100 | 2-1.5 | Around 4 |
| 100-150 | 1.6-0.8 | Around 3-4 |
| 150-200 | 0.8-0.6 | Around 3-4 |

## Notes

**Notes regarding the titration solvent**
ASTM Standard D1159 gives trichloroethane as an alternative for dichloromethane. However, the use of this solvent is forbidden in many countries.
To save time, you can store the titration solvent in a refrigerator between the experiments.

**Note regarding the maximum volume**
To avoid a two-phase system during titration, it is not recommended to use a titrant volume higher than 10 ml.

**Note regarding the imposed current**
A 1 µA imposed current can give noisy curves and 10 µA gives a curve that is not well defined around the inflection point.
Instead of DC imposed current it is possible to use AC imposed current. A 25 µA AC imposed current gives titration curves similar to those obtained with 5 µA DC current. In this case, also modify the "Br-Nb-Ctrl-Temp" method.

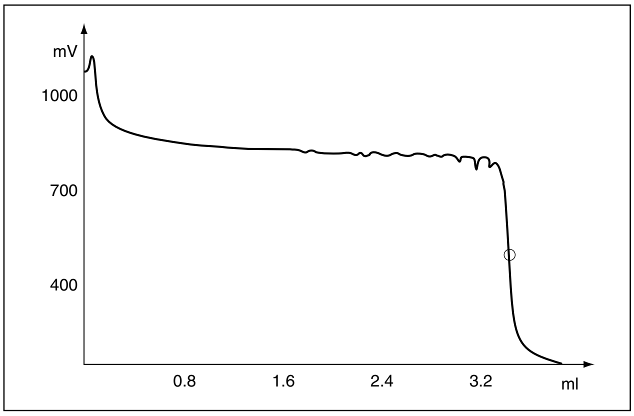
**Note regarding the equation**
The entered equation takes into account the programmed dilution of the sample.
DA is the final dilution volume and AL the aliquot volume.

**Note regarding sample handling**
For sample and dichloromethane handling, you can use a glass syringe instead of a pipette.

**Note regarding temperature measurement**
As indicated previously, you can use the DISPLAY MEASUREMENT function, but in this case you can just check the temperature of the solution (DISPLAY MEASUREMENT checks the measured potential on E1 and E2 inputs, not on Pt-Pt input). You can use this information in the pre-programmed method "Br- Nb-Ctrl-Temp" that measures the potential of the double platinum wire electrode AND the sample temperature.

**Note regarding the curve shape**
Based on experience, the starting potential may be around 1300 mV and suddenly falls to around 800 mV at the beginning of the titration. Then the curve falls very quickly to the final measured potential (generally around 100 mV) near the inflection point.

**Curve**



# Thiols (Mercaptans) in Fuels

## (According to ASTM D3227-00)

## Introduction

Thiols (or organic mercaptans) have an unpleasant odour and are corrosive. Thiols are removed during the manufacture of fuels such as gasoline, kerosene, aviation turbine and distillate fuels and it is important to check the efficiency of the treatment and the quality of the final product.
Thiol titration uses the reaction of the R-SH group with $Ag^+$ in a non-aqueous media with a silver/silver sulphide measuring electrode.

## Principle

The $Ag^+$ ion reacts with the thiols according to

$$R\text{-}SH + Ag^+ \rightarrow R\text{-}SAg + H^+$$

1 mole of thiol corresponds to 1 mole of $Ag^+$ ion
The titrant concentration is 0.01M
Results are expressed as a % (sometimes in mg/kg) of S (AW = 32.07 g/mol)

The titration is run using inflection point determination with a silver/silver sulphide measuring electrode and a glass reference electrode.

## Electrode and reagents

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

M295Ag Metal Electrode (part no. E34M003) connected to the reference INPUT by means of a adapter part no. A94P807

pHG301 Glass Electrode (part no. E11M001) connected to measuring input E1 by means of cable part no. A94L114

M241Pt Metal Electrode (part no. E31M001) connected to GROUND

$AgNO_3$ 0.01M in isopropanol (2-propanol)

Prepare a 0.1M stock solution by dissolving 16.865 g of $AgNO_3$ in 100 ml of distilled water and complete to 1000 ml in a volumetric flask with 2-propanol.

Prepare the 0.01M titrant solution by diluting 100 ml of the stock solution to 1000 ml with 2-propanol in a volumetric flask.
Store the $AgNO_3$ solutions in brown glass bottles.
*As aqueous $AgNO_3$ 0.1M is commercially available, you can also prepare the 0.01M titrant solution by diluting 100 ml of the 0.1M aqueous solution to 1000 ml with 2-propanol using a volumetric flask.*

**Alkaline titration solvent**
Dissolve 1.6 g of anhydrous $CH_3COONa$ in 25 ml of free dissolved oxygen distilled water and complete to 1000 ml with 2-propanol
*This solvent is used if low molecular weight thiols are expected*

**Acidic titration solvent**
Dissolve 1.6 g of anhydrous $CH_3COONa$ in 20 ml of free dissolved oxygen distilled water, add 4.6 ml of glacial acetic acid and complete to 1000 ml with 2-propanol

**Sodium sulphide solution**
Dissolve 10 g of $Na_2S$ in 1000 ml of water

**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.

## Inflection Detection settings

**CONTINUOUS IP**

| | |
|---|---|
| Cell grounding: | M241Pt |
| Burette volume: | 10 ml |
| Max. volume: | 10 ml |
| Stirring speed: | 500 rpm |
| Working mode: | mV |
| Start timer: | 45 s |
| Stop point: | -450 mV |

| | |
|---|---|
| Minimum speed: | 0.20 ml/min |
| Maximum speed: | 3.00 ml/min |
| Smoothing param: | 4 |

| | |
|---|---|
| Titration: | Decreasing mV |
| Inflection number: | 1 |

Inflection 1

| | |
|---|---|
| Min. ordinate: | -300 mV **(see notes)** |
| Max. ordinate: | -150 mV **(see notes)** |
| Stop at last IP: | YES |

Sample

| | |
|---|---|
| Dilution: | NO |
| Sample unit: | g |
| Sample amount: | 10 **(see working range)** |

| | |
|---|---|
| Number of results: | 2 |

| | |
|---|---|
| Result 1: | % |
| Reaction: | 1 smp + 1 Titr |
| Molar weight: | 32.060 |

| | |
|---|---|
| Result 2: | mg/kg |
| Reaction: | 1 smp + 1 Titr |
| Molar weight: | 32.060 |

## Procedure

*Electrode preparation*
*A silver/silver sulphide electrode has to be used for this application.*

To coat the silver electrode with silver sulphide proceed as follows:

For the first time, clean the silver electrode using an abrasive band (part no. 991-565).

Dip the silver electrode in a beaker with 100 ml of alkaline titration solvent and 8 ml of $Na_2S$ solution.

Using a pipette, add by increments over a 10 to 15 min. period 10 ml of $AgNO_3$ 0.1M solution.

Remove the electrode from the solution. If the sulphide coating is correct, the silver rod is black over its entire surface.

*Sample preparation*
To determine thiols according to ASTM D3227, it is necessary to eliminate any hydrogen sulphide ($H_2S$) present using acidic solution of $CdSO_4$. Refer to the standard for the exact procedure.

*Titration*
Weigh the recommended amount of sample **(see working range)**
Add 100 ml of basic titration solvent
Dip electrodes and delivery tip in the beaker
Run the titration

## Results

**Expressed, according to the ASTM standard, as a % of S but also according to local rules in mg/kg or ppm of S**

R(in %) =
V(titr)*C(titr)*32.06*100/W(smp)*1000

- 1000 = to have a result in g of S, the delivered volume is in ml
- V(titr) = total volume of titrant to reach the inflection point in ml
- C(titr) = Titrant concentration in mol/l (generally 0.01)
- W(smp) = sample amount in g
- 100 = to have a result for 100 g of sample
- 32.06 = Molar weight of S

The Titration manager calculates the result directly expressed as a % and mg/kg of S when the above inflection detection settings are applied.

**For 3 determinations on untreated kerosene**

| | |
|---|---|
| Mean: | 0.012767%<br>127.67 mg/kg |
| Standard deviation: | 0.000056 %<br>0.06 mg/kg |
| Sample amount around 10 g | |
| Titrant volume around | 3.6 ml |

**Test on a gasoline S95**

| | |
|---|---|
| Result: | $5.18.10^{-4}$ %<br>5.18 mg/kg |

*Sample amount around 30 g*
*Titrant volume around 0.45 ml*

## Working range

For low concentrations of thiols (around 5 mg/kg or $5.10^{-4}$ %), weigh 30 to 50 g of sample to obtain a titration volume of around 0.4-1.0 ml.

For high concentrations of thiols, 10 g of sample are sufficient.

According to the formula for 20 g of sample,

1 ml of titrant corresponds to 0.0016% (or 1.6 mg/kg) of S.

## Notes

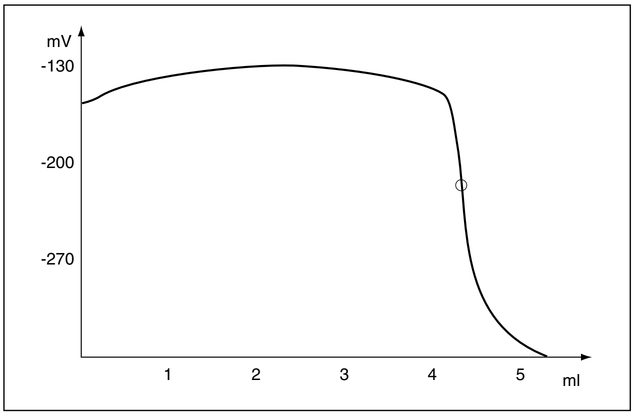
ELECTRODE STORAGE AND MAINTENANCE
At the end of the titration, rinse electrodes with distilled water and wipe the glass electrode. Store the glass electrode as indicated in the operating instructions.
Store the silver electrode in distilled water or in a solution of 100 ml of titration solvent containing 0.5 ml of the 0.1M $AgNO_3$ solution
Depending on local regulations, some laboratories use a combined Ag/Reference electrode as such as the MC6091Ag (part no. E34M004) instead of separate glass and silver electrodes.

MIN AND MAX ORDINATES
The above values correspond to the alkaline titration solvent. When a glass electrode is used as "reference", it is necessary to change these values for those of the acidic titration solvent.

NOTE REGARDING TITRATION DIRECTION
Using the Titration Manager, **you need to connect** glass and silver as indicated:
pHG301 to the measuring input
M291Ag to the reference input.
The titration direction is therefore the opposite of that using a (Hg/$HgSO_4$) reference electrode and a silver electrode connected in the conventional way.

NOTE REGARDING ELECTRODE CREATION
With the Titration Manager
**First create the reference electrode**
Function: Reference / ID from other / ID: M291Ag - (for example)
**Next create the measuring electrode**
Function: mV (i=0) / ID from catalogue / pHG301/ ID:
Reference / from user / M291Ag

**Curve**



# Base Number of Petroleum Products

## (Perchloric acid titration ASTM D 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 non-aqueous 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 $NaClO_4$ 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 ($NaClO_4$) in glacial acetic acid.

$HClO_4$ 0.1M in $CH_3COOH$
Mix 8.5 ml of 70 to 72% $HClO_4$ 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 D2896-01.

## 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 saturated solution of sodium perchlorate ($NaClO_4$) 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**

$$R(mg/g) = (V_t - V_b) * C_t * 56.11 / W$$

$V_t$ = 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 Analytical GK ANNEX Maintenance Kit (part no. S91M001).

## Notes

**Reference electrode**
Instead of the REF451, it is possible to use the REF361Reference 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 ($KOOC-C_6H_4-COOH$ 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.

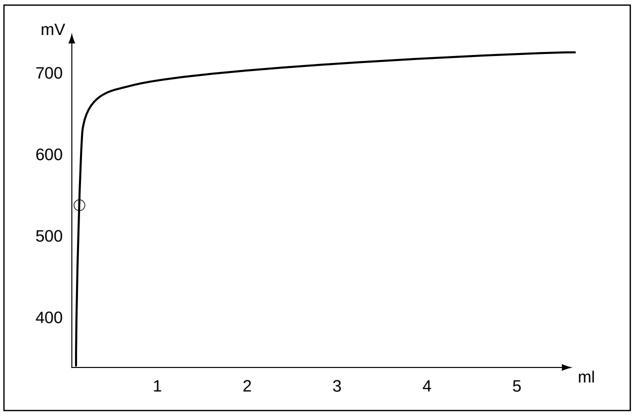
**Back titration**
If no inflection point is visible during direct titration, it is necessary to run a back titration to determine the Base Number.
In this case, a known volume (in excess) of 0.1M perchloric acid in acetic acid is added to the sample diluted in the solvent titration.
The excess of perchloric 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 $CH_3COONa$).

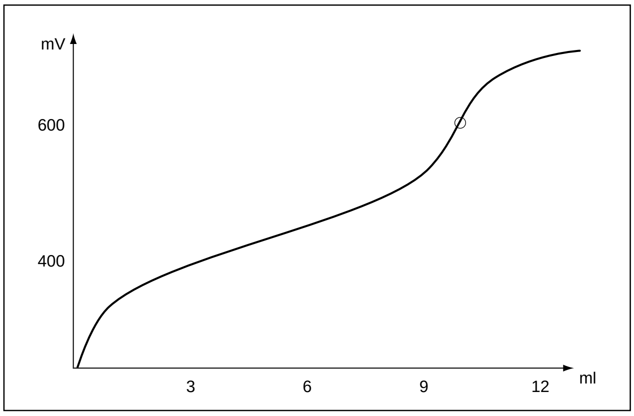
*Procedure according to the ASTM standard*
Using titration solvent as solvent, titrate a known volume of perchloric acid (for example 8-10 ml) with the sodium acetate solution.
Note the volume $V_1$ of the sodium acetate solution.
Weigh no more than 5 g of product and add the same volume of titration 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:

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

**Curves**



Blank solvent



Sample

Titration Applications – TTIP02-01PET/2002-06A