# ACID-BASE TITRATIONS
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

Whether in aqueous or non-aqueous media, acid-base titrations are the most frequently performed titrations in analytical laboratories in all fields. Instructions for performing some of the most commonly used applications are given in this booklet together with calibration procedures for the corresponding titrants and electrodes. Certain modifications may be needed to take into account specific regulations or standards in force in certain countries, in particular regarding results presentation.
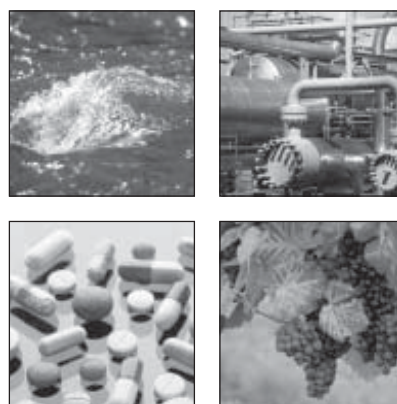
Radiometer Analytical produces other technique-based applications booklets as well as a range of applications dedicated to particular sectors. Ask your local representative for the following booklets:

Technique	Part No.
Precipitation titrations	D41T010
Complexometric titrations	D41T011
Redox titrations	D41T012

Dedicated	Part No.
Food and beverage analysis	D41T004
Plating bath analysis	D41T005
Water and environmental analysis	D41T006
Chemical industries	D41T007

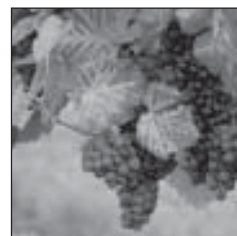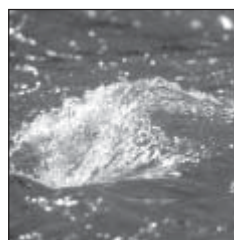Our Applications Laboratory is continually developing new applications.

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

ACID-BASE TITRATIONS

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End Point Titration Manager
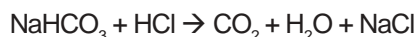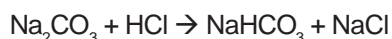# Operational Qualification

Introduction

The operational qualification procedure demonstrates that an instrument runs according to the operational specifications in the selected environment. For an end point titration manager, 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

$$Na_2CO_3 + HCl \rightarrow NaHCO_3 + NaCl$$

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

corresponding to 2 different end points.
The operational qualification takes into account the second equivalence point (pH 3.90) corresponding to the complete neutralisation of sodium carbonate.

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) and 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

End Point 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
Predose:	see below
Start timer:	45 sec
Max. volume:	see below
Number of EP:	1
Min. speed:	0.2 ml/min
Max. speed:	5.00 ml/min
Direction:	decreasing pH
End point:	3.90 pH
Delay:	10 sec
Proportional band:	3.00 pH

Results

Sample unit:	mg
Number of result:	1
Acceptation criteria:	YES
Result unit:	%
Molar weight:	105.99
Reaction:	1 smp + 2 titr
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 combined pH 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.

End point titration operation qualification

Fit 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.

End point titration

To determine the necessary amount of sodium carbonate

With a 25 ml burette capacity

Weigh exactly 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 predose corresponding to 10 ml and a maximum volume of 25 ml

With a 10 ml burette capacity

Use the same settings as the 25 ml burette capacity

With a 5 ml burette capacity

Weigh exactly 40-45 mg of Na_2CO_3

Use a maximum volume of 10 ml

No predose.

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 with 3 different samples. Results should be accepted between 99 and 101%.

# Inflection Point Titration Manager Operational Qualification
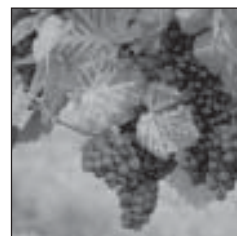
Introduction

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:

$$Na_2CO_3 + HCl \rightarrow NaHCO_3 + NaCl$$

$$NaHCO_3 + HCl \rightarrow CO_2 + H_2O + NaCl$$
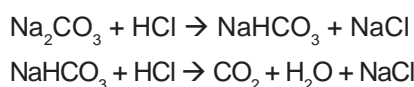
The operational qualification takes into account the second equivalence point (close to pH 4.00)

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

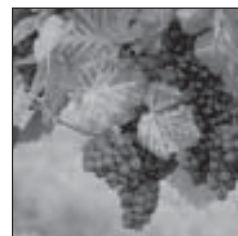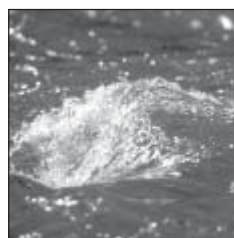These settings were tested with a 10 ml burette. The others settings are unchanged.

Calibration of an Acidic Solution

Reagent preparation

In aqueous media, 2 acids are mainly used as titrants: HCl (concentrated commercial solution is around 12M) or H_2SO_4 (18M or 36N). It is also possible to use HNO_3 (concentrated commercial solution is nearly 12.8M). To prepare 1000 ml of 0.1 eq/l strong acid solution, dilute X ml of concentrated acid (see table) in 200 ml of distilled water and, by means of a volumetric flask, dilute to 1000 ml. **CAUTION:** These operations are highly exothermic. Observe laboratory safety regulations.

Acid	Conc. % w/w	Density g/l	Conc. M (mol/l)	X = Vol (ml)
HNO_3	60%	1.35	12.8	7.8
H_2SO_4	96%	1.83	18	2.8
HCl	37%	1.18	12	8.3

Standard preparation

To calibrate acid solution, use analytical grade $Na_2B_4O_7,10 H_2O$ as standard (molecular weight 381.4 g/mol); it reacts with H^+ ions according to

$$B_4O_7^{--} + 2H^+ + H_2O \rightarrow 4HBO_2$$
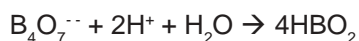
A 0.1 eq/l borax solution contains 0.05 mol/l (or 1/20 mol/l) of borax. To prepare 1000 ml of 0.1 eq/l of standard, weigh exactly 19.070 g of analytical grade $Na_2B_4O_7,10 H_2O$ and dilute to 1000 ml with a volumetric flask.

A 0.1 eq/l solution can be stored for 1 month.

Electrode and reagents

pHC2401-8 Combined pH Electrode (part no. E16M336)

Freshly distilled water

0.1 eq/l borax standard solution

IUPAC Series pH standards pH 4.005 (part no. S11M002) and pH 10.012 (part no. S11M007)

End Point titration settings

Burette volume:	25 ml
Stirring speed:	400 rpm
Working mode:	pH
Number of end points:	1
End point:	5.10 pH
Stirring delay:	10 seconds
Minimum speed:	0.2 ml/min
Maximum speed:	6.0 ml/min
Proportional band:	3.0 pH
End point delay:	5 seconds
Direction:	Decreasing pH
Sample unit:	ml
Standard amount:	20
Standard conc.:	0.1 eq/l
Result:	eq/l

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Procedure

Prepare the titration system with a 25 ml burette and 0.1 eq/l acid solution as titrant.

Calibrate the pHC2401-8 electrode using IUPAC standards.

Do not forget to fill the reagent bottle absorption chamber with absorbent.

Pipette exactly 20 ml of borax 0.1 eq/l.

Complete to 100 ml with distilled water.

Dip electrode and delivery tip in the solution.

Start method by pressing the RUN key.

Results

The result is expressed as eq/l concentration and based on the following formula:

Vol(acid sol) * C(acid sol) = Vol(borax sol) * C(borax sol)

The calibration result can be accepted if 5 determinations give a result with a relative standard deviation of less than 0.5%.

Notes

a) Using a solution as standard, it is best to use a standard concentration close to the titrant concentration. This allows closed volumes for titrant and standard.

For the best result accuracy, pipette a standard volume corresponding to a delivered titrant volume greater than 50% of the used burette cylinder.

b) The application note uses a 25 ml cylinder capacity. If you use a 5 or 10 ml cylinder for the burette, pipette 5 ml of standard and modify the method as follows:

Predose:	2 ml
Maximum volume:	8 ml

c) It is possible to calibrate an acid titrant by weighing an amount of borax.
With a 25 ml burette cylinder capacity.
Exactly weigh approximately 380 mg of borax.

In the STANDARD screen ENTER

Standard unit:	mg
Standard amount:	xx.x
Concentration unit:	%
Concentration:	100
(or purity of the standard)	
Molecular weight:	381.4

And in the RESULT screen ENTER

Result:	eq/l

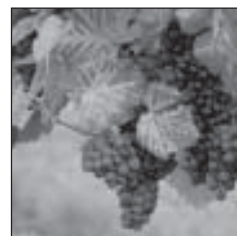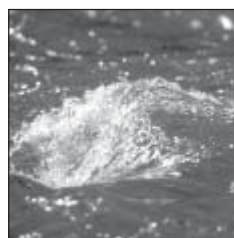For HCl or HNO_3 (result in eq/l or mol/l)
Coefficients: 1 Standard + 2 Titrant

For H_2SO_4 (result in eq/l)
Coefficients: 2 Standard + 2 Titrant

For H_2SO_4 (result in mol/l)
Coefficients: 1 Standard + 1 Titrant

Calibration of an Alkaline (NaOH or KOH) Solution

Reagent preparation

There are several ways to prepare free carbonate NaOH or KOH solution.
To prepare 0.1 eq/l NaOH or KOH solution the easiest way is to:

Take a new bottle of NaOH or KOH pellets and quickly weigh 4.00 g of NaOH or 5.60 g of KOH

(NaOH has a molecular weight of 40 g/mol and KOH 56 g/mol)

Using a conical flask, dissolve the pellets in 200 ml of hot (40°C approx.) freshly boiled distilled water, cover the flask with plastic film and leave to cool to room temperature.

Using a volumetric flask, quickly complete to 1000 ml with the same freshly boiled distilled water.

For long storage, use a polythene flask.

Standard preparation

To calibrate NaOH solution, use oxalic acid $H_2C_2O_4$, $2H_2O$ as standard (molecular weight 126.0 g/mol). As in aqueous media, the 2 acid functions are titrated together; **a 0.1 eq/l oxalic solution contains 0.05 mol/l (or 1/20 mol/l) of oxalic acid.**

To prepare 1000 ml of 0.1 eq/l of standard.
Weigh exactly 6.300 g (126.0/20) of oxalic acid. Using a volumetric flask, dissolve to 1000 ml with freshly boiled distilled water.

Electrode and reagents

pHC2401-8 Combined pH Electrode (part no. E16M336)

Freshly boiled distilled water

0.1 eq/l oxalic acid standard solution

IUPAC Series pH standards
pH 4.005 (part no. S11M002) and
pH 10.012 (part no. S11M007)

End Point titration settings

Burette volume:	25 ml
Stirring speed:	400 rpm
Working mode:	pH
Number of end points:	1
End point:	8.55 pH
Stirring delay:	10 seconds
Minimum speed:	0.2 ml/min
Maximum speed:	6.0 ml/min
Proportional band:	3.0 pH
Direction:	Increasing pH
End point delay:	5 seconds
Sample unit:	ml
Standard amount:	20
Standard conc.:	0.1 eq/l
Result:	eq/l

Procedure

Prepare the titration system with a 25 ml burette and 0.1 eq/l NaOH solution as titrant.

Calibrate the pHC2401-8 electrode using IUPAC standards.

Do not forget to fill the reagent bottle absorption chamber with absorbent CO_2.

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Calibration of an Alkaline (NaOH or KOH) Solution

Pipette exactly 20 ml of oxalic acid 0.1 eq/l.

Complete to 100 ml with distilled water.

Dip electrode and delivery tip in the solution.

Start method by pressing the RUN key.

Results

The result is expressed as eq/l concentration and based on the following formula

Vol(NaOH sol) * C(NaOH sol) = Vol(oxalic acid sol) * C(oxalic acid sol)

The calibration result can be accepted if 5 determinations give a result with a relative standard deviation of less than 0.5%.

Notes

a) Using a solution as standard, it is best to use a standard concentration close to the titrant concentration. This allows closed volumes for titrant and standard. For the best result accuracy, pipette a standard volume corresponding to a delivered titrant volume greater than 50% of the used burette cylinder.

b) The application note uses a 25 ml cylinder capacity. If you use a 5 or 10 ml cylinder for the burette, pipette 5 ml of standard and modify the method as follows:

Predose: 2 ml
Maximum volume: 8 ml

c) It is possible to calibrate a basic titrant by weighing an amount of oxalic acid.

With a 25 ml burette cylinder capacity

Exactly weigh approximately 120 mg of oxalic acid

In the STANDARD screen ENTER
Standard unit: mg
Standard amount: xx.x
Concentration unit: %
Concentration: 100
        (or purity of the standard)
Molecular weight: 126.0
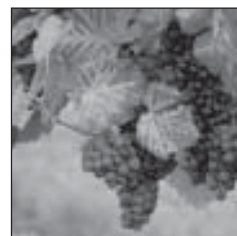
And in the RESULT screen ENTER

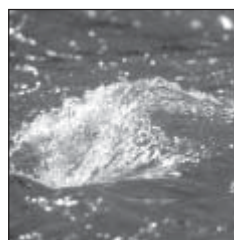Result: eq/l
Coefficients: 1 Standard + 2 Titrant

Note that for NaOH and KOH, concentration in eq/l is the same as in mol/l.

d) For alkaline solutions with higher concentration (1M or 1N for example), use the same procedure but take 40 g of NaOH, or 56 g of KOH, for 1000 ml of solution and calibrate the solution by exactly weighing approximately 1200 mg of oxalic acid.

Alkalinity of Bleach
(NaClO Solution)

Introduction

A bleach solution contains mainly NaClO plus basic products such as NaOH and Na_2CO_3.
The concentration of basic products is generally expressed as NaOH concentration, which is around 8 g/l NaOH, i.e. 0.2N concentration.
The alkalinity determination uses an acid/base titration.

Principle

The OH^- content is simply determined by an acid/base titration using a 0.1 eq/l strong acid as titrant.
Depending on the bleach solution, the titration curve generally shows 2 inflections. The most common method involves a titration of all the basic functions by a predetermined end point titration at pH 4.00. Before this titration, it is necessary to reduce the ClO^- ions present in the solution.

Electrode and reagents

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

H_2O_2 30% (volume)

Hydrochloric acid 0.1 eq/l (or 0.1 mol/l)

Slowly add 8.3 ml of concentrated hydrochloric acid to 500 ml of distilled water and dilute to exactly 1000 ml. Calibrate the titrant versus $Na_2B_4O_7$, 10 H_2O (sodium borate) as standard.

(See separate application note)

Distilled water

IUPAC Series pH standards pH 4.005 (part no. S11M002) and pH 10.012 (part no. S11M007)

End Point titration settings

Burette volume:	25 ml
Stirring speed:	400 rpm
Working mode:	pH
Number of end points:	1
End point:	4.00 pH
Stirring delay:	45 seconds
Minimum speed:	0.2 ml/min
Maximum speed:	8.0 ml/min
Proportional band:	3.00 pH
End point delay:	5 seconds
Sample unit:	ml
Sample amount:	5
Titration:	Decreasing pH
Result:	g/l

Procedure

Calibrate the electrode using the two IUPAC standards

Pipette 5 ml of sample

Always dilute the sample with the same volume of distilled water (max. 50 ml)

Slowly add 5 ml of H_2O_2 for 5 ml of sample

Dip electrode and delivery tip in the solution

Start method by pressing the RUN key

![Radiometer analytical logo]

Results

Expressed as NaOH content (MW = 40 g/mol) in g/l

As 1 molecule of titrant reacts with 1 molecule of NaOH

$$R(NaOH) = V(titr) * C(titr) * 40 / V(smp)$$

-V(titr) = total volume of titrant to reach the end point in ml

-V(smp) = sample amount

-C(titr) = exact concentration of the titrant in eq/l

For a result in g/l

Enter

The sample amount in the SAMPLE screen

The titrant concentration in the TITRANT screen

1 Titrant and 1 Sample in the COEFFICIENTS display

40 for NaOH molecular weight

The Titration Manager gives a result according the above formula.

For a result as a %

As the Titration Manager cannot give a result in % if the sample unit is a volumetric unit, you can use the equation feature:

Equation number:	1
Equation result:	% NaOH
Equation formula:	
R1 / 10	

R1 is the titration result calculated in g/l.

5 determinations on a commercial concentrated bleach

Mean (as NaOH):	7.25 g/l
Standard deviation:	0.07 g/l
Rel. standard deviation:	1%

Working range

Results are expressed in g/l of NaOH (MW = 40 g/mol)

1 ml of HCl 0.1 eq/l represents 4 mg of NaOH or, with a 5 ml sample volume a NaOH content corresponding to 0.8 g/l

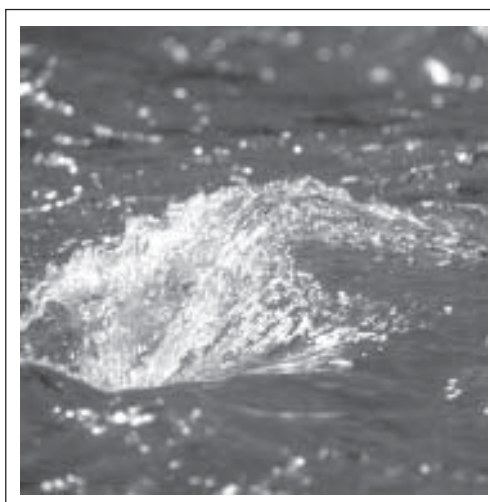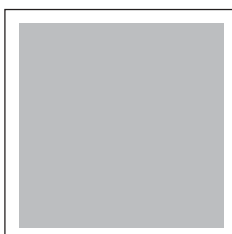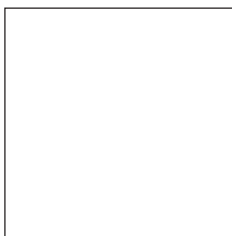The working range can be calculated as the following formula:

$$\text{Result (in g/l)} = V(titr \text{ in ml}) * 0.8 * 1000 / V(smp)$$

Using the conditions given in this applicatin note (5 ml sample and a 25 ml burette for titrant), it is possible to obtain results between 7 g/l (for 35% capacity of the burette) and 20 g/l (total capacity of the burette) with the best possible accuracy and reproducibility.

Notes

Addition of H_2O_2 is necessary to reduce the ClO^- ion to Cl^- before running the alkalinity titration.

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Alkalinity of Water

Introduction

Alkalinity of water is determined by end point titration with a strong acid solution. "Phenolphthalein" alkalinity corresponds to titratable alkalinity at pH 8.3 and total alkalinity corresponds to titratable alkalinity at pH 4.5. This application note is an application of international standard ISO 9963-1.

Principle

The current standard uses HCl 0.1 eq/l as titrant but another strong acid such as H_2SO_4 0.1 eq/l can also be used. If the pH of the water sample is below 8.3, the "Phenolphthalein" alkalinity is, by definition, equal to zero.
Results are normally expressed as mmoles/l (or meq/l) of "alkalinity", but other units can be used (see notes).
If a suitable sensor is used, the alkalinity determination can be linked with a pH and temperature measurement of the sample.

Electrode and reagents

pHC3081-8 Combined pH Electrode with temperature sensor (part no. E16M305)

HCl 0.1 eq/l solution in distilled water

Distilled water

IUPAC Series pH standards pH 4.005 (part no. S11M002) or pH 7.000 (part no. S11M004) and pH 10.012 (part no. S11M007)

End Point Titration settings

2 linked methods, one for pH measurement and the second for alkalinity measurement

pH measurement

Temperature:	Probe
Stability:	25 mpH/min
Acceptation time:	45 seconds
Max stabilisation time:	2 min

TCA and TA determination

Burette volume:	10 ml
Stirring speed:	400 rpm
Working mode:	pH
Number of end points:	2
TCA end point:	8.30 pH
Proportional band:	0.5 pH
TA end point:	4.50 pH
Proportional band:	1.0 pH
Stirring delay:	30 seconds
Minimum speed:	0.2 ml/min
Maximum speed:	4 ml/min
End point delay:	10 seconds
Sample unit:	ml
Sample amount:	100
Titration:	Decreasing pH
Results:	meq/l
Results:	cumulate

Procedure

This standard can be used with natural, drinking and wastewaters with TA between 0.4 and 20 mmoles/l.

Calibrate the electrode with pH 4.005 and pH 10.012 IUPAC Series pH standards.

Pipette 100 ml of water.

 Radiometer analytical

Dip electrode and delivery tip in the sample.

Start method by pressing the RUN key.

Results

Expressed as milliequivalents/l (or millimol/l) of OH⁻ alkalinity

$$R = V(titr) * C(titr) * 1000 / V(smp)$$

-V(titr) = Total volume of titrant in ml, delivered to reach the end point (pH 8.3 or pH 4.5)
-C(titr) = titrant concentration in eq/l (currently 0.1)
-V(smp) = Volume of the sample (currently 100 ml)

For a result in mmol/l

Enter

The sample amount in the SAMPLE screen

The titrant concentration in the TITRANT screen

1 Titrant and 1 Sample in the COEFFICIENTS display

The Titration Manager gives a result according the above formula.

Results for 5 determinations in milliequivalents/l

Mean: 3.6
Standard deviation: 0.038
Relative standard deviation: 1%

Working range

The sample size and titrant concentration depend on the quality of the water.
Using the application note settings

V sample = 100 ml
Burette volume = 10 ml
Titrant concentration = 0.1 eq/l

For the best accuracy and reproducibility, the result range is between 3.5 meq/l (or 175 mg/l $CaCO_3$) for 35% of the cylinder burette capacity and 10 meq/l (or 500 mg/l $CaCO_3$) for the burette capacity.

With the same conditions, the "experimental" limit corresponding to a titrant volume of 0.5 ml is 0.5 meq/l (or 25 mg/l $CaCO_3$). For alkalinity below this value, it is recommended to use a low alkalinity method with 0.02 eq/l titrant and 200 ml for sample volume, using the calculation above.

Notes

1) The results are normally expressed in mmoles/l (or meq/l) of alkalinity.
1 ml of 0.1 eq/l of strong acid represents 0.1 meq or mmol of alkalinity.

2) Depending on the country, many other units can be used for the results

-mmol/l $CaCO_3$ (= meq/l * 0.5)
(CO_3^- has 2 alkalinity functions per molecule)

-mg/l $CaCO_3$ (= meq/l * 50)
(MW of $CaCO_3$ is 100.09 g/mol with 2 alkaline functions per molecule)

-mg/l HCO_3^- (= meq/l * 61)
(MW of HCO3- is 61 g/mol with 1 alkaline function per molecule)

-Clark degree   (= meq/l * 3.50)

-German degree   (= meq/l * 2.80)

-French degree   (= meq/l * 5.0)

-U.S. degree   (= meq/l * 2.90)

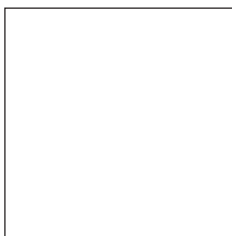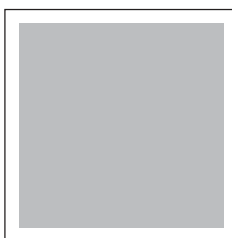It is easy to express results in all these units thanks to the equation features of the Titration Manager.

Bibliography

International standard ISO 9963

EPA method number 310.1

Standard methods for water and wastewater 18th edition (1992) 2-25 part 2320

Titratable Acidity
in Wines or Juices

Introduction

Titratable acidity is used as a guide to determine how acidic the product will taste. This determination measures the concentration of all available hydrogen ions present in the sample, wine or juice.

It is a weak acid titration using a strong base such as NaOH and the equivalence point (or end point) occurs at a pH greater than pH 7.00. Depending on local procedures, the end point can vary between pH 7.5 and pH 8.4.

We use pH 8.2, the most commonly used value, in the following application.

Principle

The end point titration at pH 8.2 is very easy to run. The titrant is normally NaOH 0.1 eq/l. The wine sample needs to be degassed before determination.

The result is normally expressed in g/l tartaric acid (MW = 150.09 g/mol and 2 acid functions).

Tartaric acid =
$HOOC\text{-}(CHOH)_2\text{-}COOH$

Electrode and reagents

pHC2401-8 Combined pH Electrode (part no. E16M400)

NaOH 0.1 eq/l solution in distilled water (see Application Note TTEP01-02MIN)

Distilled water

Check the pH of the distilled water. Using the titration manager as a pH-meter, adjust the distilled water to pH 8.2 by means of a few drops of base or acid solution.

IUPAC Series pH standards pH 4.005 (part no. S11M002) or pH 7.000 (part no. S11M004) and pH 10.012 (part no. S11M007).

End Point titration settings

Burette volume:	10 ml
Stirring speed:	400 rpm
Working mode:	pH
Number of end points:	1
End point:	8.20 pH
Stirring delay:	30 seconds
Minimum speed:	0.2 ml/min
Maximum speed:	5 ml/min
Proportional band:	4.00 pH
End point delay:	5 seconds
Sample unit:	ml
Sample amount:	10
Titration:	Increasing pH
Result:	g/l

Procedure

A wine sample can be degassed in two ways:

1) Pour the wine into a Buchner flask and connect it to a vacuum system for 3 minutes.

2) Boil the wine for a few seconds then allow the wine to cool to room temperature.

Calibrate the combined pH electrode using the 2 IUPAC standards above.

Pipette 10 ml of sample.

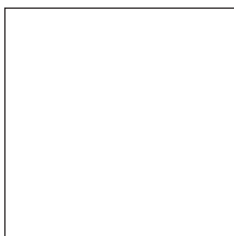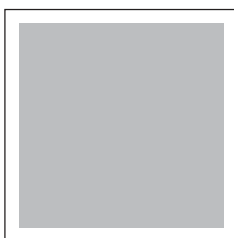If necessary, add pH adjusted distilled water.

Dip electrode and delivery tip in the solution.

Start method by pressing the RUN key.

Radiometer analytical

Results

Expressed as g/l of tartaric acid using eq/l or mol/l as titrant unit

2 molecules of NaOH react with 1 molecule of tartaric acid

$$R = V(titr) * C(titr) * 150.09 / V(smp) * 2$$

-V(titr) = total volume of titrant to reach the end point in ml

-C(titr) = Titrant concentration in eq/l (currently 0.1)

-V(smp) = sample volume

150.09 = molecular weight of tartaric acid

2 = Ratio between titrant and sample (2 titrants react with 1 sample)

For a result in g/l

Enter

The volume sample in the SAMPLE screen

The titrant concentration in the TITRANT screen,

2 Titrants and 1 Sample in the COEFFICIENTS display

150.09 as molecular weight.

The Titration Manager will give a result according the formula above.

For 5 determinations on wine

Mean (as tartaric acid in g/l): 5.3 g/l
Standard deviation: 0.025 g/l
Rel. standard deviation: 0.5%

Working range

With current figures (0.1 for C(titr) and 10 for V(smp) and a low limit around 0.5 for V(titr) we can consider 0.375 g/l as an experimental limit.

Using application note conditions (10 ml volume sample and 10 ml titrant burette) it is possible to obtain results between 2.60 g/l (for 35% capacity of the burette) and 7.40 g/l (capacity of the burette) with the best possible accuracy and reproducibility.

If the result is different from that expected, change cylinder capacity of the burette and/or the sample volume.

For samples with very low acidity you can also use a low concentration titrant (0.02 eq/l titrant gives a low limit for the result equal to 0.075 g/l for a 10 ml sample).

You can also take a larger amount of sample.

Notes

1) Normally the result is expressed as g/l of tartaric acid
1 ml of NaOH 0.1 eq/l represents 7.5 mg of tartaric acid

2) Depending on local regulations, other acids can be used for the expressed result; for example

Acetic acid (1 ml of NaOH 0.1 eq/l = 6.005 mg)

Citric acid (anhydrous) (1 ml of NaOH 0.1eq/l = 6.40 mg)

Lactic acid (1 ml of NaOH 0.1 eq/l =9.01 mg).

Acidity of Milk

Introduction

As the acidity has a major influence on the taste of the product, this parameter is used to test the quality of milk.
As the acidity of milk increases with the storage time, this parameter is also a means of checking storage conditions.

Principle

The acidity of milk is determined by end point titration using 0.1 eq/l NaOH. The end point value is generally fixed at pH 8.7 and the result is expressed in dg/l of lactic acid. This result is also called DORNIC acidity.

Electrode and reagents

pHC2401-8 Combined pH Electrode (part no.E16M400)

NaOH 0.1 eq/l solution in distilled water (see Application Note TTEP01-02MIN)

IUPAC Series pH standards pH 4.005 (part no. S11M002) or pH 7.000 (part no. S11M004) and pH 10.012 (part no. S11M007).

End Point titration settings

Burette volume:	10 ml
Stirring speed:	400 rpm
Working mode:	pH
Number of end points:	1
End point:	8.70 pH
Stirring delay:	20 seconds
Minimum speed:	0.2 ml/min
Maximum speed:	6.0 ml/min
Proportional band:	4.00 pH
End point delay:	5 seconds
Sample unit:	ml
Sample amount:	20
pH:	Increasing
Result:	g/l
Equation:	Result * 10

Procedure

Calibrate the combined pH electrode using the two IUPAC standards above.

Pipette 20 ml of sample into a low volume beaker (Radiometer Analytical beakers part no. 904-488 for 50 pcs. can be used).

Dip electrode and delivery tip in the solution.

Do not dilute the sample.

Start method by pressing the RUN key.

Results

Expressed as decigrams/l of lactic acid (CH_3-CHOH-COOH) and MW=90 g/mol
As in this case 1 molecule of NaOH reacts with 1 molecule of lactic acid

$$R = V(titr) * C(titr) *90 * 10* / V(smp)$$

-V(titr) = total volume of titrant to reach the end point in ml

-C(titr) = Titrant concentration in eq/l (currently 0.1)

-V(smp = sample volume in ml

90 = Molecular weight of lactic acid

10 = Factor for result expression in decigram/l

If you enter the correct data for titrant concentration, sample amount, molecular weight, the titration manager's reaction coefficients and equations allow the result to be calculated.

R Radiometer analytical

For a result in g/l
Enter

The sample amount in the SAMPLE screen

The titrant concentration in the TITRANT screen

1 Titrant and 1 Sample in the COEFFICIENTS display

90 for lactic acid molecular weight

The Titration Manager gives a result according to the formula above.

You can obtain a first result directly in g/l of lactic acid and then use an equation to obtain another result in decigrams/l

For a result in decigrams/l use the equation feature
Equation number: 1
Equation result: dg/l
Equation formula
R1 * 10

R1 is the titration result calculated in g/l

Results for 10 determinations
Mean (as decigrams/l of lactic acid):   15.17
Standard deviation: 0.106
Relative standard deviation: 0.7%

Working range

The acidity of fresh milk is around 15 to 17 when expressed, as indicated, in decigrams/l of lactic acid (some articles give a mean value of around 18). According to the calculation formula and for 20 ml of sample, this value corresponds to approximately 4 ml of 0.1 eq/l titrant.

Notes

1) Depending on local applications, it is recommended to use a N/9 (0.1111 eq/l) titrant.
With this titrant concentration and a sample volume equal to 10 ml:

Acidity (in decigrams/l of lactic acid) = V(titrant) * 10

2) According to another definition, acidity of milk can be expressed in Soxlet-Henkel acidity: i.e. the number of ml of 0.25 eq/l titrant needed to titrate 100 ml of milk.
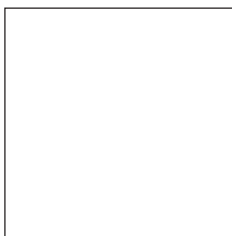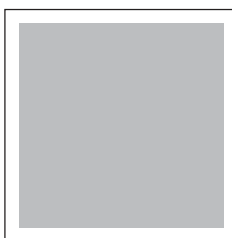
For a 10 ml sample volume

Acidity in °S-H = V(titrant) * 10 /2.5

Fresh milk corresponds to a Soxlet-Henkel acidity of around 7.2 (generally between 6.5 and 7.5).

3) The end-point value is important for this method. Please refer to local rules or standards.

4) This method frequently uses a coloured indicator. To adapt the pH determination, use the coloured indicator the first time and read the pH of the sample according to the colour change.

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Acidity of Mustard and Associated Products

Introduction

The total acidity of mustard and many associated products such as mayonnaise refers to the sum of titratable acids using a strongly alkaline titrant like NaOH.
An end point titration can easily be used with pH 7.50 as end point.
Depending on the sample and local regulations, results are expressed as acetic acid content in g/l or mg/g or even as a %.
This method is not suitable for edible oils, because they are not miscible with water.

Principle

The end point titration is very easy to run. The titrant is normally NaOH 0.1 eq/l.
As the result is expressed as acetic acid content, the MW of CH_3COOH is 60 g/mol.

Electrode and reagents

pHC2401-8 Combined pH Electrode (part no. E16M400)

NaOH 0.1 eq/l solution in distilled water (see Application Note TTEP01-02MIN)

Distilled water

IUPAC Series pH standard solutions pH 4.005 (part no. S11M002) and pH 7.000 (part no. S11M004)

End Point titration settings

Burette volume:	25 ml
Stirring speed:	400 rpm
Working mode:	pH
Number of end points:	1
End point:	7.50 pH
Stirring delay:	30 seconds
Minimum speed:	0.2 ml/min
Maximum speed:	8.0 ml/min
Proportional band:	3.50 pH
End point delay:	5 seconds
Sample unit:	g
(depending to the sample can be also ml)	
Sample amount:	(see below)
Titration:	Increasing pH
Result:	%

Procedure

Dilute the sample in 50 or 100 ml of freshly distilled water.
For some samples an efficient stirring procedure may be necessary.

Calibrate the combined pH electrode using pH 4.005 and pH 7.000 IUPAC standards.

Dip electrode and delivery tip the sample.

Start method by pressing the RUN key.

Results

As in this case 1 molecule of titrant reacts with 1 molecule of CH_3COOH

Expressed as g/l acetic acid
R = V(titr) * C(titr) * 60.0 / V(smp)

Expressed as mg/g acetic acid (or g/kg)
R = V(titr) * C(titr) * 60.0 *FDIL / W(smp)

Expressed as % acetic acid
R = V(titr) * C(titr) * 60.0 *FDIL / 10 * W(smp)

-V(titr) = total volume of titrant to reach the end point in ml

-C(titr) = Titrant concentration in eq/l (currently 0.1)

-W(smp) = sample amount in g

-V(smp) = Sample volume in ml

-FDIL = Dilution factor between the total volume used to dilute the sample and the aliquot used for titration.

For a result as a %
Enter

The actual sample amount in the SAMPLE screen

The titrant concentration in the TITRANT screen

1 Titrant and 1 Sample in the COEFFICIENTS display

60 as molecular weight

The Titration Manager gives the result according the above formula.

As the above-mentioned dilution factor FDIL is directly calculated by the titration manager, if necessary enter the following in the SAMPLE screen.

DILUTION:YES

The total sample amount
The final dilution volume
The aliquot volume

5 determinations on mustard
Mean: 1.8%
Standard deviation: 0.009
Rel. standard deviation: 0.5%

Working range

Using application note conditions (0.1 for titrant concentration and 25 ml burette cylinder and 10 ml for sample volume), the working range is between 5.25 g/l (for 35% capacity of the burette) and 15 g/l (for the burette capacity) for the best reproducibility.
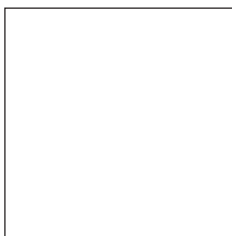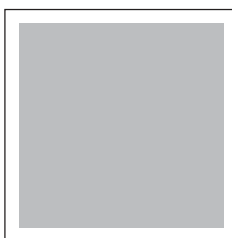For 10 g of sample and FDIL=1 the experimental working range is between 5.25 g/kg and 15 g/kg or between 0.52% and 1.5%.

Notes

1) With some non-homogeneous products, it is necessary to ensure efficient stirring during titration. In this case, you can also use lower addition speeds and a longer end point delay (15 seconds for example)

2) According to different regulations or standards, the pH of the end point can be changed but other settings stay identical.

Acidity of Cheese

Introduction

As the acidity of cheese has a major influence on the taste of the product, this parameter is used to test the quality.

Principle

The acidity of cheese is determined by end point titration using 0.1 eq/l NaOH. The end point value is generally fixed at pH 8.4 and the result is expressed in % of lactic acid, which has a MW of 90.08 g/mol.

Electrode and reagents

pHC2401-8 Combined pH Electrode (part no.E16M400).

NaOH 0.1 eq/l solution in distilled water (see Application Note TTEP01-02MIN).

IUPAC Series pH standards pH 4.005 (part no. S11M002) or pH 7.000 (part no. S11M004) and pH 10.012 (part no. S11M007).

End Point titration settings

Burette volume:	10 ml
Stirring speed:	400 rpm
Working mode:	pH
Number of end points:	1
End point:	8.40 pH
Stirring delay:	30 seconds
Minimum speed:	0.2 ml/min
Maximum speed:	10 ml/min
Proportional band:	4.00 pH
End point delay:	5 seconds
Titration:	Increasing pH
Sample unit:	g
Sample amount:	see below
Result:	%

Procedure

Sample preparation

Place a known amount of cheese (generally between 10 and 20 g) in a 250 ml beaker, add 100 ml of distilled water at 40°C and homogenise with a high speed homogeniser. Filter or centrifuge according to particular recommendations and dilute to 250 ml using a volumetric flask. Titrate an aliquot of 25 or 50 ml for example.

Titration

Calibrate the combined pH electrode using the 2 IUPAC standards above.

Pipette 25 or 50 ml of sample.

Dip electrode and delivery tip in the solution.

Start method by pressing the RUN key.

Results

Expressed as % of lactic acid (CH_3-CHOH-COOH with a MW of 90.08 g/mol)

As in this case 1 molecule of titrant reacts with 1 molecule of lactic acid

$R = V(titr) * C(titr) * 90.08 * 100 * F / 1000 * W(smp)$

-V(titr) = total volume of titrant to reach the end point in ml

-C(titr) = Titrant concentration in eq/l (currently 0.1)

-W(smp = sample amount in g

90.08 = Molecular weight of lactic acid

Radiometer analytical

F = Dilution factor between total volume and aliquot

100 = Factor needed for a result expressed in %

For a result in %
Enter

The actual sample amount in the SAMPLE screen

The titrant concentration in the TITRANT screen

1 Titrant and 1 Sample in the COEFFICIENTS display

90.08 as molecular weight

The Titration Manager gives a result according to the above formula.

You can also use the dilution calculation formula of the titration manager.

In the SAMPLE screen

Dilution YES
Enter the total sample amount
Enter the final dilution volume in ml
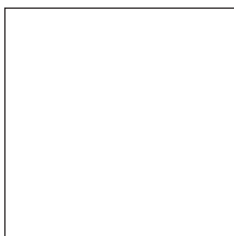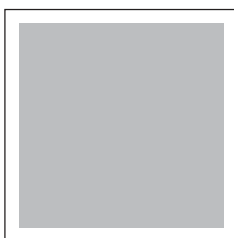Enter the aliquot volume in ml

5 determinations

Mean:	0.97%
Standard deviation:	0.01%
Rel. standard deviation:	1%

Working range

For a dilution factor of 10 and 10 g as sample amount, and for a titrant volume corresponding to 0.5 ml as an experimental detection limit for titrant consumption, the result limit is close to 0.45%.

Total Titratable Acidity in Vinegar

Introduction

Besides the taste, the quality of a vinegar depends on various factors such as pH and total titratable acidity. As this determination is run by titration with a strong basic solution (NaOH 1 or 0.5 M), the end point titration is between pH 8.0 and pH 8.8 depending on the manufacturing conditions.

Principle

The end point titration for this application note, based on experiments at pH 8.2, is very easy to run. Vinegar is diluted before analysis with freshly distilled water; the titrant is NaOH 1M or 0.5 M. The result is expressed in g/100 ml (or %) of CH_3COOH (MW=60 g/mol)

Electrode and reagents

pHC2401-8 Combined pH Electrode (part no. E16M400)

NaOH 0.5 or 1 eq/l solution in distilled water (see Application Note TTEP01-02MIN)

Distilled water

IUPAC Series pH standards pH 4.005 (part no. S11M002) or pH 7.00 (part no. S11M004) and pH 10.012 (part no. S11M007).

End Point titration settings

Burette volume:	25 ml
Stirring speed:	400 rpm
Working mode:	pH
Number of end points:	1
End point:	8.20 pH
Stirring delay:	30 seconds
Minimum speed:	0.2 ml/min
Maximum speed:	10 ml/min
Proportional band:	3.00 pH
End point delay:	5 seconds
Sample unit:	ml
Sample amount:	10
Titration:	Increasing pH
Result:	g/l

Procedure

As the end point of the titration depends on the vinegar, refer to your local procedure or determine the end point value by means of a manual titration (manual dosing).

Calibrate the pHC2401-8 electrode using 2 of the 3 above-mentioned IUPAC standards.

Prepare the burette with the 1M or 0.5M NaOH titrant.

Pipette 10 ml of sample.

Add 50 ml of freshly distilled water.

Dip electrode and delivery tip in the solution.

Start method by pressing the RUN key.

Results

Expressed as g/100 ml (or %) of CH_3COOH

$R = V(titr) * C(titr) * 60 * 100 / V(smp) * 1000$

-V(titr) = total volume of titrant to reach the end point in ml

-C(titr) = Titrant concentration in eq/l (currently 0.1)

-V(smp) = sample volume in ml

60 = molecular weight of CH_3COOH

Radiometer analytical

For a result in %
Enter

A first result unit as g/l

The actual sample amount in the SAMPLE screen

The titrant concentration in the TITRANT screen

1 Titrant and 1 Sample in the COEFFICIENTS display

60 as molecular weight

As the Titration Manager cannot give a result as a % if the sample unit is a volumetric unit, use the equation feature:

Equation number: 1
Equation result : % CH_3COOH
Equation formula
R1 / 10

R1 is the titration result calculated in g/l.

For 5 determinations
Mean (as g/100 ml of CH_3COOH):
7.2 g/100 ml
Standard deviation: 0.058 g/100 ml
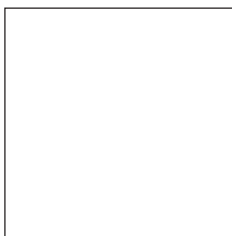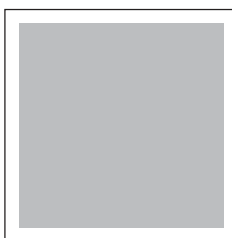Rel. standard deviation: 0.8%

Working range

Irrespective of manufacturing differences, commercially available vinegars generally have a total titratable acidity of between 4 and 8%. For a 10 ml sample amount, this corresponds to 0.4 to 0.8 g of acetic acid and 1 ml of NaOH 1M corresponds to 0.06 g of CH_3COOH.

Notes

Differences in standards or procedures may lead the end point to be fixed at a pH higher than 9.5.

In this case, use the pHC2011-8 Combined pH Electrode (part no. E16M317) instead of the pHC2401-8.

Titratable Acidity and Formol Number in Fruit Juices

Introduction

The formol number, or formol titration, measures the total amino acid (NH_2-R-COOH) concentration. Using 2 successive end point titrations, it is possible to determine total titratable acidity and formol number.

Principle

The determination of formol number takes place in three steps:

1) Neutralisation of titratable acidity by means of an end point titration at pH 8.2 with NaOH 0.1 eq/l

2) Addition of an excess of formol (HCHO) to the solution. This operation locks the NH_2 groups of amino acids due to the decrease in pH and allows titration of the COOH groups of amino acids with an end point titration at pH 8.2

3) Second endpoint titration at pH 8.2 to determine total amino acid content. The result is then expressed as milliequivalents/100 ml or milliequivalent/l

Electrode and reagents

pHC2401-8 Combined pH Electrode (part no. E16M400)

NaOH 0.1 eq/l solution in distilled water (see separate application note)

Distilled water

Check the pH of the distilled water. Using the titration manager as a pH meter, adjust the distilled water to pH 8.2, by means of few drops of base or acid solution, with NaOH 0.1 as titrant

Formol (HCHO) solution at 37% adjusted to pH 8.2

IUPAC Series pH standards pH 4.005 (part no. S11M002) or pH 7.000 (part no. S11M004) and pH 10.012 (part no. S11M007)

End Point titration settings

Two linked methods
First method (can be used as titratable acidity)

Burette volume:	10 ml
Maximum volume:	30 ml
Stirring speed:	400 rpm
Working mode:	pH
Number of end points:	1
End point:	8.20 pH
Stirring delay:	30 seconds
Minimum speed:	0.2 ml/min
Maximum speed:	10 ml/min
Proportional band:	3.00 pH
End point delay:	10 seconds
Sample unit:	ml
Sample amount:	10
Result expression:	g/l
(of tartaric acid or citric acid)	
Titration:	Increasing pH

Second method (Formol number determination)

Burette volume:	10 ml
Maximum volume:	10 ml
Stirring speed:	400 rpm
Working mode:	pH
Number of end points:	1
End point:	8.20 pH
Stirring delay:	60 seconds
Minimum speed:	0.2 ml/min
Maximum speed:	5 ml/min
Proportional band:	2.00 pH
End point delay:	10 seconds
Sample unit:	ml
Sample amount:	10
Result expression:	meq/100 ml
Titration:	Increasing pH

Radiometer analytical

Procedure

Connect the electrode to the electrode input.

Calibrate the electrode using the two IUPAC standards above.

Stir and pipette 10 ml of sample.

Always dilute the sample with the same volume of distilled water (25 ml for example).

Dip electrode and delivery tip in the solution

Start titration by pressing the RUN key.

At the end of the first method manually add 5 ml of HCHO solution for 10 ml of sample to the sample solution.

Results

For titratable acidity expressed as g/l of tartaric acid (HOOC-(CHOH)$_2$-COOH)

Result is normally expressed as g/l of tartaric acid (MW= 150.09 g/mol and 2 acid functions).
As 2 molecules of NaOH react with 1 molecule of tartaric acid:

$$R = V(titr) * C(titr) * 150.09 / V(smp) * 2$$

-V(titr) = total volume of titrant to reach the end point in ml

-C(titr) = Titrant concentration in eq/l (currently 0.1)

-V(smp) = sample volume

150.09 = molecular weight of tartaric acid

2 = Ratio between titrant and sample

For titratable acidity in g/l of tartaric acid
Enter in the first method

The actual sample amount in the SAMPLE screen in ml

The titrant concentration in the TITRANT screen in mol/l or eq/l

2 Titrants and 1 Sample in the COEFFICIENTS display

150.09 as molecular weight

The Titration Manager gives a result according the above formula.

For titratable acidity in g/l of citric acid (that has 3 acid functions with a MW of 192.4)
Enter in the first method

The actual sample amount in the SAMPLE screen in ml

The titrant concentration in the TITRANT screen in mol/l or eq/l

3 Titrants and 1 Sample in the COEFFICIENTS display

192.4 as molecular weight

The Titration Manager gives a result according the above formula.

For Formol number expressed as meq/l

Formol no. = V(titr) * C(Titr) *1000/ V(smp)

-V(titr) = total volume of titrant to reach the end point in ml
-C(titr) = Titrant concentration in eq/l or mol/l (currently 0.1)
-V(sample) = sample volume in ml

For formol number in meq/100ml
Enter in the second method

The actual sample amount in the SAMPLE screen in ml

The titrant concentration in the TITRANT screen in mol/l or eq/l

1 Titrant and 1 Sample in the COEFFICIENTS display (if necessary)

Enter in the RESULT screen
Result: 1
Unit: eq/l
Equation: 1
Formula: R1/10
Name: meq/100 ml

The Titration Manager gives 2 results:
Result expressed in meq/l
Result from equation formula, expressed in meq/100 ml

3 determinations on grapefruit juice
Acidity
Mean: 15.28 g/l tartaric acid
Standard deviation:
0.02 g/l tartaric acid
Rel. standard deviation: 0.13%

Formol number
Mean: 2.19 meq/100 ml
Standard deviation:
0.038 meq/100 ml
Rel. standard deviation: 1.7%

Working range

Related to the calculation formula, using 10 ml for sample volume and 0.1 eq/l titrant concentration. For acidity determination 1 ml of titrant corresponds to 0.75 g/l of tartaric acid.
For formol number determination:

Formol no. (meq/100 ml) = V(titr) in ml

For a 10 ml burette, formol number range can be estimated between 0.2 (experimental low limit corresponding to 0.2 ml) and 10 (nominal value of cylinder capacity):

Formol no. (meq/l) =
Formol no. (meq/100 ml) * 10

Notes

Depending on local procedures, the first end point can vary between pH 8.0 and pH 8.4.

The most commonly used value is pH 8.2. We use this value in this application.

It is also possible to have different values for the pH end points (for example, pH 8.1 for the first and pH 8.4 for the second).

Adjust the pH of the formol solution to the same value as that used in the second end point titration (formol number determination).
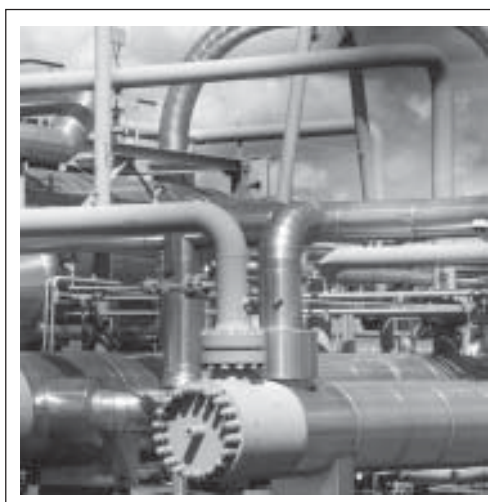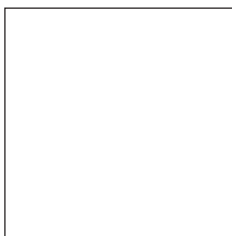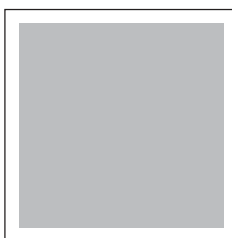
Analysis of a Finishing Bath

Introduction

In the car industry, the finishing bath is used just before the phosphatation bath. The main components of this bath are metallic phosphates, titanium for example. The analysis of the bath consists of measuring the total alkalinity of the solution with H_2SO_4 0.1N as titrant. As the titration curve is very well defined, it is possible perform an automatic titration with a combined glass electrode with a pre-set end point detection.

Principle

The results are expressed as "points", i.e. the number of ml of titrant 0.1N used to titrate a given sample amount.

As this titration was initially run with a coloured indicator (bromocresol green), the pre-set end point can be fixed to pH 4.77.

The sample amount is generally about 100 ml.

Electrode and reagents

pHC2401-8 Combined pH Electrode (part no. E16M400)

H_2SO_4 0.1 eq/l solution in distilled water

Distilled water

IUPAC Series pH standards pH 4.005 (part no. S11M002) or pH 7.000 (part no. S11M004) and pH 10.012 (part no. S11M007).

End Point titration settings

Burette volume:	10 ml
Stirring speed:	400 rpm
Working mode:	pH
Number of end points:	1
Endpoint:	4.77 pH
Stirring delay:	30 seconds
Minimum speed:	0.4 ml/min
Maximum speed:	6.0 ml/min
Proportional band:	2.0 pH
End point delay:	5 seconds
Sample unit:	ml
Sample amount:	100
Titration:	Decreasing pH
Result:	ml

Procedure

Calibrate the electrode with pH 4.005 and pH 10.012 IUPAC standards.

Pipette 100 ml, or the asked volume of sample.

If dilution is necessary, always take the minimum and constant volume of distilled water.

Dip electrode and delivery tip in the sample.

Start method by pressing the RUN key.

Results

Expressed as ml of 0.1 eq/l titrant for 100 ml of sample

$R = V(titr)$

If the titrant used is not exactly 0.1 eq/l in concentration and if the sample amount is not 100 ml, correct as follows:

$R = V(titr) * 100 * C(titr) / V(smp) * 0.1$

Radiometer analytical

-V(titr) = total volume of titrant to reach the end point (pH 4.77) in ml

-V(smp) = current sample amount

-C(titr) = exact concentration of the titrant

Depending on local industry regulations, the reference volume may not be 100 ml.

4 determinations. Results in points for 100 ml samples

Mean: 2.50 ml
Standard deviation: 0.050 ml
Rel. standard deviation: 2%

Working range

As the result for a 100 ml sample volume and a 0.1 eq/l titrant is directly the delivered volume of titrant (for the best possible accuracy and reproducibility), the working range is between 3.5 and 10 ml for the application note conditions.

Notes

1) Reliability of an end point titration depends on the behaviour of the working electrode.

2) For this bath, it is necessary to regularly check the electrode.

3) After a cycle of measurements (10 or even 5 titrations) check the electrode, for example by measuring the IUPAC standard pH 10.012 or by a new calibration procedure.

Total and Free Alkalinity of a Cleaning Bath
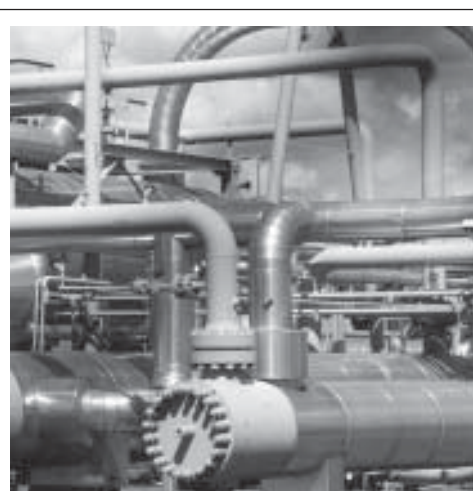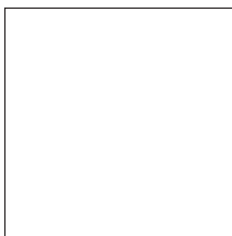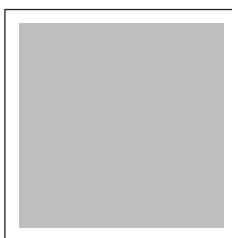
Introduction

In the car industry, a cleaning bath is generally a mixture of a strong base (typically NaOH) with other salts, phosphates, silicates or borates for example. The analysis aims to determine the free or strong alkalinity (free OH$^-$) and the total alkalinity corresponding to the sum of weak bases.
Free and total alkalinity can be determined on the same sample by end point acid-base titration at two different end points, pH 7.7 for the first and pH 4.0 for the second. Usually the titrant is 0.1 eq/l H_2SO_4.

Principle

The sample amount is generally between 25 and 100 ml.

Results are expressed as a number of ml of 0.1 eq/l titrant necessary to reach the end point (pH 7.7 or pH 4.0) for a 100 ml sample volume.

Electrode and reagents

pHC2401-8 Combined pH Electrode (part no. E16M400)

0.1 eq/l H_2SO_4 in distilled water

Distilled water

IUPAC Series pH standards pH 4.005 (part no. S11M002) or pH 7.000 (part no. S11M004) and pH 10.012 (part no. S11M007).

End Point titration settings

Burette volume:	25 ml
Stirring speed:	400 rpm
Working mode:	pH
Number of end points:	2
First end point:	7.70 pH
Proportional band:	2.0 pH
Second end point:	4.00 pH
Proportional band:	2.0 pH
Stirring delay:	30 seconds
Minimum speed:	1.25 ml/min
Maximum speed:	10 ml/min
End point delay:	5 seconds
Sample unit:	ml
Sample amount:	100
Titration:	Decreasing pH
Result:	ml
Results:	cumulate

Procedure

Calibrate the electrode with pH 4.005 and pH 10.012 IUPAC standards.

Pipette 100 ml or the required volume of sample.

If dilution is necessary, always take the minimum and constant volume of distilled water.

Dip electrode and delivery tip in the sample.

Start method by pressing the RUN key.

Results

Expressed as ml of 0.1 eq/l titrant for 100 ml of sample

R = V(titr)

If the titrant used is not exactly 0.1 eq/l in concentration and if the sample amount is not 100 ml, correct as follows:

R = V(titr) * 100 * C(titr) / V(smp) * 0.1

-V(titr) = total volume of titrant to reach the end point (pH 7.7 or pH 4.0) in ml

-V(smp) = current sample amount

-C(titr) = exact concentration of the titrant

Depending on local industry regulations, the reference volume may not be 100 ml.

5 determinations. Results in points

FREE ALKALINITY
Mean:	6.46 ml
Standard deviation:	0.009 ml
Rel. standard deviation:	0.15%

TOTAL ALKALINITY
Mean:	14.76 ml
Standard deviation:	0.012 ml
Rel. standard deviation:	0.09%

Working range

As the result for a 100 ml sample volume and a 0.1 eq/l titrant is directly the delivered volume of titrant (for the best possible accuracy and reproducibility), the working range is between 8.75 and 25 ml for the application note conditions.

Taking into account the difference between free and total alkalinity, the free alkalinity is sometimes below the range but the reproducibility is nevertheless acceptable.
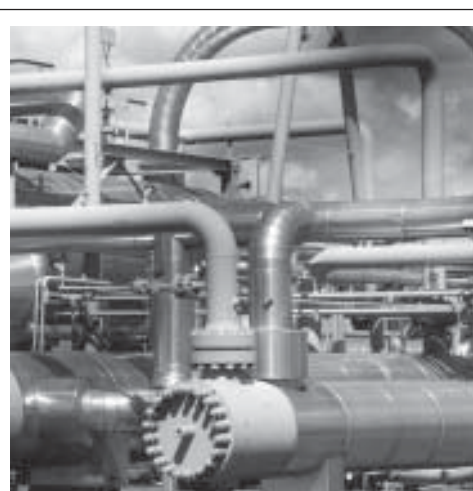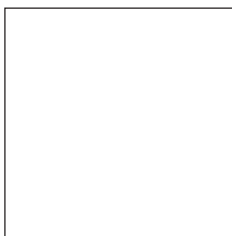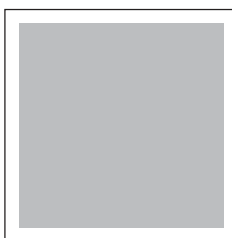
Notes

1) It is not difficult to run this end point titration method. Pay attention to the result, which is not always calculated as indicated in this application note. Do not forget that the volumes used for results are total volumes from starting titration to the end point.

2) Reliability of an end point titration depends on the electrode used. Check the combined pH electrode regularly, for example after a series of 5 determinations.

NaOH and HCHO in Electroless Copper Bath

Introduction

Chemical copper baths, used in particular in the manufacture of printed circuits, contain copper salts, sodium hydroxide stabilising agents and formol.
The sodium hydroxide concentration of the bath is generally between 8 and 12 q/l. Formol concentration is between 3 and 8 g/l. The HCHO determination uses an end point acid/base titration after OH^- titration (end point titration at pH 10.00) and addition of Na_2SO_3.

Principle

HCHO determination in a copper bath takes place in three steps:

1) Neutralisation of the sample to pH 10.00. This first step can be used as a NaOH determination (see separate application note)

2) Addition to the sample of a Na_2SO_3 solution. This addition allows the following reaction

$$HCHO + Na_2SO_3 + H_2O \rightarrow NaSO_3CH_2OH + NaOH$$
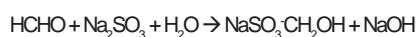
which releases one OH^- ion for one HCHO molecule

3) End point titration of released OH^- which allows the HCHO determination

Electrode and reagents

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

Hydrochloric acid 0.1 eq/l

Slowly add 8.3 ml of concentrated hydrochloric acid to 500 ml of distilled water and dilute to exactly 1000 ml. Calibrate the titrant versus $Na_2B_4O_7$,10 H_2O (sodium borate) as standard.

Distilled water

1M Na_2SO_3 solution:

Dissolve 126 g of Na_2SO_3 in a beaker containing 800 ml of distilled water. With a few drops of 1M NaOH, adjust the pH of the solution to 10.00 using the Titration Manager fitted with the pHC2011-8 electrode as a pH meter. Adjust to 1000 ml with distilled water.
It is necessary to adjust the pH of the Na_2SO_3 solution to 10.00 because the first step of the procedure is performed by end point titration at pH 10.00.

IUPAC Series pH standards pH 4.005 (part no. S11M002) and pH 10.012 (part no. S11M007)

End Point titration settings

Two linked methods
First method (can be used as OH^- determination)

Burette volume:	25 ml
Stirring speed:	400 rpm
Working mode:	pH
Number of end points:	1
End point:	10.00 pH
Stirring delay:	30 seconds
Minimum speed:	0.2 ml/min
Maximum speed:	10 ml/min
Proportional band:	3.00 pH
End point delay:	10 seconds
Sample unit:	ml
Sample amount:	5
Result expression:	g/l
Titration:	Decreasing pH

Second method (HCHO determination)

Burette volume:	25 ml
Stirring speed:	400 rpm
Working mode:	pH
Number of end points:	1

 Radiometer analytical

End point: 10.00 pH
Stirring delay: 60 seconds
Minimum speed: 0.2 ml/min
Maximum speed: 10 ml/min
Proportional band: 3.00 pH
End point delay: 10 seconds
Sample unit: ml
Sample amount: 5
Result expression: g/l
Titration: Decreasing pH

Procedure

Connect the combined pH electrode to the E1 electrode input

Calibrate the combined pH electrode using the 2 above IUPAC standards

Pipette 5 ml of sample

Always dilute the sample with the same volume of distilled water (do not exceed 50 ml)

Dip electrode and delivery tip in the solution

Start titration by pressing the RUN key

At the end of the first method, manually add 10 ml of Na_2SO_3 solution to the sample solution for 5 ml of sample aliquot.

Results

As in this case 1 molecule of titrant reacts with 1 molecule of NaOH or HCHO
Expressed as NaOH content (MW = 40 g/mol) and HCHO content (MW = 30 g/mol) in g/l

$R(NaOH) = V(titr) * C(titr) * 40 / V(smp)$

$R(HCHO) = V(titr) * C(titr) * 30 / V(smp)$

-V(titr) = total volume of titrant to reach the end point in ml

-V(smp) = current sample amount

-C(titr) = exact concentration of the titrant

For a result in g/l
Enter

The sample amount used in the SAMPLE screen

The titrant concentration in the TITRANT screen

1 Titrant and 1 Sample in the COEFFICIENTS display for the two methods

40 for NaOH molecular weight in the first method

30 for HCHO molecular weight in the second method

The Titration Manager gives a result according to the above formula.

Results and statistics for NaOH and HCHO

10 determinations on the same bath (NaOH)
Mean (as NaOH): 8.8 g/l
Standard deviation: 0.04 g/l
Rel. standard deviation: 0.5%

5 determinations on the same bath (HCHO)
mean (as HCHO): 2.66 g/l
Standard deviation: 0.011 g/l
Rel. standard deviation: 0.43%

Working range

Results are expressed in g/l of NaOH (MW = 40 g/mol) and g/l of HCHO (MW = 30 g/mol)

1 ml of HCl 0.1 eq/l represents 4 mg of NaOH and 3 mg of HCHO or, with a 5 ml sample volume, a NaOH content corresponding to 0.8 g/l and a HCHO content of 0.6 g/l

The working range can be calculated as the following formula

Result (in g/l) = V(titr in ml) * 0.8 * 1000 / V(smp) for NaOH

And

Result (in g/l) = V(titr in ml) * 0.6 * 1000 / V(smp) for HCHO

Using application note conditions (5 ml volume sample and 25 ml titrant burette), it is possible to obtain results between 7 g/l NaOH and 5 g/l HCHO (for 35% capacity of the burette) and 20 g/l NaOH and 15 g/l HCHO (total burette capacity) with the best possible accuracy and reproducibility.

Notes

1) The stirring delay set in the second method allows the operator to add the Na_2SO_3 solution. You can choose to reduce this time.

2) Result is expressed in g/l HCHO

1 eq/l represents 3 mg of HCHO

Ensure you use a high alkalinity electrode such as the pHC2011-8

3) Always calibrate the pH combined electrode using IUPAC standard pH 10.012 (part no. S11M007)

4) If your own procedure works at a pH other than pH 10.00, adjust the Na_2SO_3 solution to the same pH.
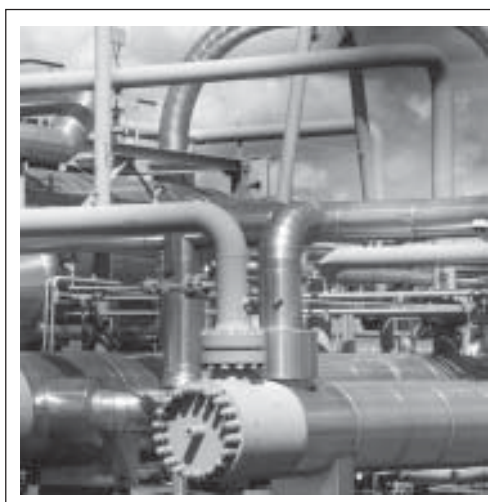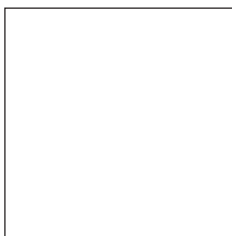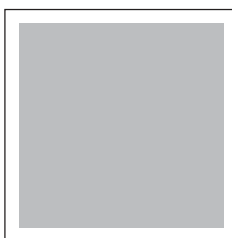
NaOH in Electroless Copper Bath

Introduction

Chemical copper baths, used in particular in the manufacture of printed circuits, contain copper salts, sodium hydroxide stabilising agents and formol.
The sodium hydroxide concentration of the bath is generally between 8 and 12 g/l. Formol concentration is between 3 and 8 g/l. The NaOH determination uses an acid/base titration.

Principle

The OH$^-$ content is simply determined by an acid/base titration using a 0.1 eq/l strong acid as titrant.

Electrode and reagents

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

Hydrochloric acid 0.1 eq/l

Slowly add 8.3 ml of concentrated hydrochloric acid to 500 ml of distilled water and dilute to exactly 1000 ml. Calibrate the titrant versus $Na_2B_4O_7$,10 H_2O (sodium borate) as standard (see separate note)

Distilled water

IUPAC Series pH standards
pH 4.005 (part no. S11M002) and pH 10.012 (part no. S11M007)

End Point titration settings

Burette volume:	25 ml
Stirring speed:	400 rpm
Working mode:	pH
Number of end points:	1
End point:	10.00 pH
Stirring delay:	30 seconds
Minimum speed:	0.2 ml/min
Maximum speed:	10 ml/min
Proportional band:	3.00 pH
End point delay:	10 seconds
Sample unit:	ml
Sample amount:	5
Titration:	Decreasing pH
Result:	g/l

Procedure

Calibrate the combined pH electrode using the 2 IUPAC standards above.

Pipette 5 ml of sample.

Dilute the sample with the same volume of distilled water each time (no more than 50 ml maximum).

Dip electrode and delivery tip in the solution.

Start method by pressing the RUN key.

Results

Expressed as NaOH content (MW = 40 g/mol) in g/l
As in this case 1 molecule of titrant reacts with 1 molecule of NaOH:

R(NaOH) = V(titr) * C(titr) * 40 / V(smp)

-V(titr) = total volume of titrant to reach the end point in ml

-V(smp) = current sample amount

-C(titr) = exact concentration of the titrant in eq/l

For a result in g/l
Enter

The sample amount in the SAMPLE screen

The titrant concentration in the TITRANT screen

1 Titrant and 1 Sample in the COEFFICIENTS display

40 for NaOH molecular weight in the first method

The Titration Manager gives a result according to the above formula.

10 determinations on the same bath
Mean (as NaOH):	8.8 g/l
Standard deviation:	0.04 g/l
Rel. standard deviation:	0.5%

Working range

Results are expressed in g/l of NaOH (MW = 40 g/mol)

1 ml of HCl 0.1 eq/l represents 4 mg of NaOH or, with a 5 ml sample volume, a NaOH content corresponding to 0.8 g/l
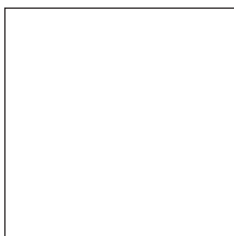
The working range can be calculated according to the following formula

Result (in g/l) = V(titr in ml) * 0.8 * 1000 / V(smp)

Using application note conditions (5 ml volume sample and 25 ml titrant burette), it is possible to obtain results between 7 g/l (for 35% capacity of the burette) and 20 g/l (for burette capacity) with the best possible accuracy and reproducibility.

For other NaOH contents, change the burette cylinder capacity and/or sample volume.

Notes

1) Ensure you use use a high alkalinity electrode such as the pHC2011-8.

2) Before starting a determination cycle, always calibrate the combined pH electrode using pH 10.012 standard (part no. S11M007).

3) According to certain bath manufacturer's protocols, the pH value for the end point titration can change and be between 9.5 and 10.50.

Boric Acid in Plating Baths

Introduction

Nickel, cobalt or zinc acid plating baths generally consist of a mixture of boric acid and a metallic salt of the corresponding metal. The boric acid can be determined by means of an acid-base titration after addition of D-mannitol. Depending on the formulation of the bath, boric acid concentration is generally around 25 g/l.

Principle

In the presence of excess D-mannitol, boric acid forms a complex giving a strong acidic compound easily titratable by sodium hydroxide.

The reaction is

For boric acid neutralisation (molar weight = 61.83 g/mol)

$$H_3BO_3 + OH^- \rightarrow H_2BO_3^- + H_2O$$
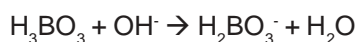
Electrode and reagents

pHC2401-8 Combined pH Electrode (part no. E16M317)

1M NaOH (1.0 mol/l or eq/l) (see separate note)

Distilled water

IUPAC Series pH standards pH 4.005 (part no. S11M002) and pH 10.012 (part no. S11M007)

D-Mannitol 200 g/l in distilled water

End Point titration settings

Burette volume:	25 ml
Maximum volume:	See below (working range)
Stirring speed:	400 rpm
Working mode:	pH
Number of end points:	1
First end point:	6.60 pH (see note 6)
Stirring delay:	45 seconds
Minimum speed:	0.2 ml/min
Maximum speed:	5 ml/min
Proportional band:	3.00 pH
End point delay:	10 seconds
Sample unit:	ml

Sample amount:	5
Titration:	Increasing pH
Result:	g/l
Molar weight:	61.83
Coefficients:	1 sample and 1 titrant

Procedure

Calibrate the electrode using the 2 IUPAC standards above.

Pipette 5 ml of sample.

Add 50 ml of the mannitol solution.

If necessary add a few ml of distilled water.

Dip electrode and delivery tip in the solution.

Start method by pressing the RUN key.

Results

Generally expressed in g/l boric acid
As 1 mole of titrant reacts with 1 mole of boric acid

R(Boric acid) = V(titr) * C(titr) * 61.83/ V(smp)

-V(titr) = total volume of titrant to reach the end point in ml

-V(smp) = current sample amount

-C(titr) = exact concentration of the titrant in mol/l

-61.83 = molecular weight of boric acid

For results in g/l
Settings indicated above for END POINT TITRATION allow the Titration Manager to give results according to the above formula.

3 determinations on a zinc bath
Mean: 25.10 g/l boric acid
Standard deviation:
                       0.08 g/l boric acid
Rel. standard deviation: 0.32%

Working range

Corresponding to the application note conditions (titrant concentration 1 mol/l, 5 ml for sample volume) and the above-mentioned formulas.

1 ml of titrant:

Corresponds to 12.36 g/l of boric acid content

Corresponding to the expected values for results, this calculation can easily determine the maximum volume for titration.

An acid nickel bath contains between 40 and 50 g/l of boric acid and also 80 g/l of nickel; an acid zinc bath contains around 25 g/l of boric acid and 30 to 40 g/l of zinc.

Notes

1) In order to obtain correct results, this titration needs a large amount of excess mannitol, especially for zinc baths.

2) Solid state mannitol can be added to the solution, in this case add distilled water and 10 g of mannitol.

3) If the amount of excess mannitol is correct, the starting pH is normally below 4.00.

4) It may be necessary to heat the plating bath to 60°C before pipetting just to dissolve the precipitate.

5) Using a titrant with a lower concentration (0.2 M or 0.5 M for example) can improve the accuracy of the results.

6) Depending on the bath composition (nickel, zinc or cobalt) the pH of the end point can change. To determine the value of the end point, for the first run, take an end point of 10.00 pH to obtain the complete curve, and then by visual examination, determine the end point generally situated between 6.4 pH and 7.5 pH.

Boric Acid and Nickel Content Determination
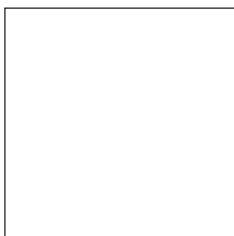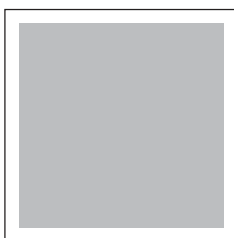
Introduction

Nickel is commonly used as plating in surface treatment or preparation industries. In some cases, in particular for bright plating, the bath consists of a mixture of boric acid and nickel salt.
The boric acid can be determined by means of an acid-base titration. Bright nickel baths generally contain 40 to 50 g/l of boric acid and 60 to 80 g/l of Ni (MW of Ni 58.69 g/mol)

Principle

In the presence of excess D-mannitol, boric acid forms a complex giving a strong acidic compound easily titratable by sodium hydroxide.
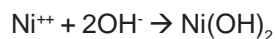
The reaction is

For boric acid neutralisation (molar weight = 61.83 g/mol)

$$H_3BO_3 + OH^- \rightarrow H_2BO_3^- + H_2O$$
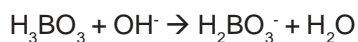
After boric acid neutralisation, the precipitation of $Ni(OH)_2$ occurs according to the following reaction

$$Ni^{++} + 2OH^- \rightarrow Ni(OH)_2$$

A two end-point acid-base titration allows determination for boric acid and Ni content.

Electrode and reagents

pHC2401-8 Combined pH Electrode (part no. E16M317)

1M NaOH (1.0 mol/l or eq/l) (see separate note)

Distilled water

IUPAC Series pH standards pH 4.005 (part no. S11M002) and pH 10.012 (part no. S11M007)

D-Mannitol 200 g/l in distilled water or solid state D mannitol

End Point titration settings

Burette volume:	25 ml
Maximum volume:	See below (working range)
Stirring speed:	400 rpm

Working mode:	pH
Number of end points:	2
First end point: 6.80 pH (boric acid)	
Proportional band:	3.00 pH
End point delay:	10 seconds
Second end point:	10.00 pH
(nickel)	
Proportional band:	3.00 pH
End point delay:	10 seconds
Stirring delay:	45 seconds
Minimum speed:	0.4 ml/min
Maximum speed:	6 ml/min
Sample unit:	ml
Sample amount:	5
Titration:	Increasing pH
Results:	difference
Result1:	g/l
Calculate with EP:	1
Molar weight:	61.83 g/mol
Coefficients: 1 sample and 1 titrant	
Result2:	g/l
Calculate with EP:	2
Molar weight:	58.69 g/mol
Coefficients: 1 sample and 2 titrants	

Procedure

Calibrate the combined pH electrode using the 2 IUPAC standards above

Pipette 5 ml of sample

Add 50 ml of the mannitol solution or 10 g of solid-state D mannitol

If necessary add a few ml of distilled water

Dip electrode and delivery tip in the solution

Start method by pressing the RUN key

Results

Generally expressed in g/l for boric acid and Ni content

Boric acid
As 1 mole of titrant reacts with 1 mole of boric acid

$$R(Boric\ ac) = V(titr) * C(titr) * 61.83 / V(smp)$$

-V(titr) = total volume of titrant to reach the first end point in ml

-V(smp) = Current sample amount

-C(titr) = Exact concentration of the titrant in mol/l

-61.83 = molecular weight of boric acid

Nickel content
As 2 moles of titrant react with 1 mole Ni^{++}

$$R(Nickel) = V(titr) * C(titr) * 58.69/2* V(smp)$$

-V(titr) = volume of titrant used between the first and the second endpoint

-V(smp) = Current sample amount

-C(titr) = Exact concentration of the titrant in mol/l

-58.69 = molecular weight of Nickel

For results in g/l
Settings indicated above for END POINT TITRATION allow the Titration Manager to give results according to the above formula.

3 determinations on the same bath

Boric acid
Mean: 44.40 g/l boric acid
Standard deviation: 0.2 g/l boric acid
Relative standard deviation: 0.45%

Nickel
Mean: 65.90 g/l nickel
Standard deviation: 0.66 g/l boric acid
Relative standard deviation   1.0%

Notes

For this titration, the curve shape is normally well defined, so end point determination is suitable.

Precipitation of $Ni(OH)_2$ is not a quick reaction so do not use too high a burette speed.

After D mannitol addition the pH of the sample is normally near by 5.00 pH.

Sometimes it may be necessary to heat the plating bath to 60°C before pipetting just to dissolve the precipitate.

Using a titrant with a lower concentration (0.2 M or 0.5 M for example) can improve the accuracy of the results.

NaOH 1M, used as titrant, carbonates easily. Check the concentration by means of a strong acid 1M every day if possible.

Determination of Gastric Acidity
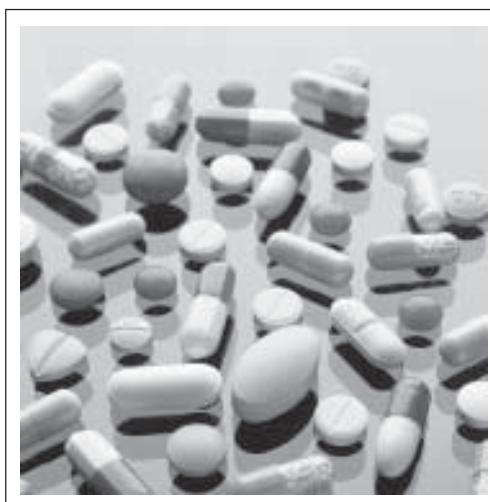
Introduction

The gastric secretions are a complex mix of HCl, pepsin, rennet, mineral chlorides (Na, K, Ca, Mg), calcium phosphate and organic material (especially mucus). Generally the acid concentration is 0.1 N, for an healthy human, but this concentration can be modified by many external factors as food or drug ingestion or stress.
In case of illness it can be necessary to determine the hyper-acidity or the acidity of the gastric secretion.

Principle

Acidity of gastric juice is determined by an end-point titration at pH 7.00 using as titrant a NaOH solution 0.1 equivalent/l. The sample amount is generally between 0.1 ml (100 µl) and 1 ml (1000 µl). The result is expressed as meq/ml (or eq/l).
As for pathological situations, expected results should be between 0.01 meq/ml and may be up to 8 meq/ml, it is very difficult to have only one titration method covering this whole range.

According to this fact the pre-programmed method "**Gastric acidity**" is suitable for orientation test and 0.1-2 meq/ml range. Copying this method, it is possible to create 2 others methods changing only few parameters.

GASTRIC AC L
(for 0.01-0.1 meq/ml range)
Minimum speed: 0.02 ml/min
Maximum speed: 0.5 ml/min
Sample amount: 500 µl
(possibly 1000µl)

GASTRIC AC H
(for range > 2 meq/ml)
Maximum volume: 20 ml
Minimum speed: 0.1 ml/min
Maximum speed: 5.0 ml/min
Sample amount: 100 µl
(possibly 200µl)

Electrode and reagents

PHC3101 Combined pH electrode (E16M327) with CL114 (A94L114) cable

25 mm magnetic barrels A90A410

NaOH 0.1 equivalent/l solution in distilled water (see separate application note but commercially available solution can be used). The pre-programmed titrant for the method is labelled as "**NaOH Gastric 0.1**"

pH standard IUPAC pH 4.005 (S11M002) and pH 7.00 (S11M004)

Distilled or de-ionised water

Titration Vessel PP 22-45 ml 904-489 (50 pcs) with special holder 923-172 (code number for 10 pcs)

Pipettes for 100µl, 500µl and 1 ml

End Point titration settings (Gastric Acidity)

Burette volume: 10 ml
Maximum volume: 40 ml
Stirring speed: 500 rpm
Working mode: pH
Number of end points: 1
End point: 7.00 pH
Stirring delay: 10 seconds
Minimum speed: 0.02 ml/min
Maximum speed: 3.0 ml/min
Proportional band: 5.00 pH
End point delay: 10 seconds
Sample unit: µl

Radiometer analytical

Sample amount: 1000
(see working range)
pH: Increasing

Result 1: ml
Equation unit: meq/ml
Equation : V1*CT*1000/SA

Procedure

Put in place the pHC3101-9 combined electrode in the suitable hole of the electrode head (see Guide to bayonet accessories booklet)

Calibrate the combined glass electrode with the above mentioned buffer solution

Place the electrode and the delivery tip in opposite positions on electrode head. The ends of electrode and delivery tip should be at the same level in the beaker.

Install the titrant (**NaOH gastric 0.1N**) and enter its concentration

Pour 20 ml of distilled or de-ionised water into the 22-45 ml beaker and place it on the sample stand of the Titration Manager using a beaker holder

Add the recommended volume of sample

If the expected result is approximately known run the appropriate method

If the expected result is unknown, run, as orientation test with 100µl of sample amount the "Gastric Acidity" method and according to this first result choose the suitable method

Working ranges

Titrant volume in ml as a function of the gastric acid concentration (in meq/ml) and sample amount (in µl)

	0.01 meq/ml	0.1 meq/ml	1.0 meq/ml	2.0 meq/ml	8.0 meq/ml
100µl	(0.01 ml)	(0.1 ml)	1.0 ml	2.0 ml	8.0 ml
500µl	(0.05 ml)	0.5 ml	5.0 ml	10.0 ml	(40.0 ml)
1000µl	0.1 ml	1.0 ml	10.0 ml	(20.0 ml)	(80.0 ml)

In brackets: titration case not recommended for good accuracy or for titrant consumption , increase or decrease the sample size respectively.

Results with "Gastric Acidity" and an healthy person

Used sample: 500 µl of a mix of HCl and pepsin in de-ionised water
The result corresponds to:

$$R1 = V(titr) * C(titr) / V(smp)$$

V(titr) = Titrant volume in ml
C(titr) = Titrant concentration in eq/l
V(smp) = sample volume in ml

Results (3 determinations)
Mean: 0.1067 meq/ml
Standard deviation: 0.0004

Notes

1) The pHC3101-9 can be interesting for low maintenance level; Do not forget to store this electrode in KCl 3M solution as recommended by Radiometer Analytical. Note that this electrode is used in the pre-programmed method.

2) Place the electrode and the delivery tip in opposite positions on electrode head. Extremities of electrode and delivery tip are at the same level in the beaker.

3) As the programmed time between two electrodes calibrations is **1 day** the corresponding icon on the main menu will always be "cloudy" after a calibration. See the user's guide (D21T043) chapter 2, p. 12.

4) For quick determinations, it is possible to use an end-point Titration Manager fitted with a 25 ml burette cylinder, 1000 µl of sample volume and the pre-programmed method without change. With these conditions the working range is 0.02 meq/ml - 4.0 meq/ml.

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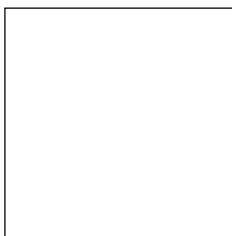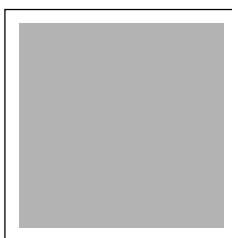
(Potentiometric titration ASTM D664-95 reapproved 2001)

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)

Radiometer analytical

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.
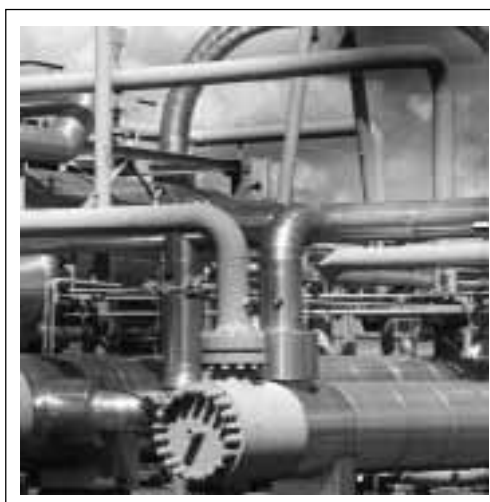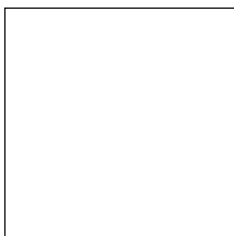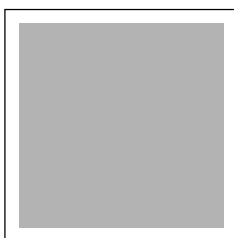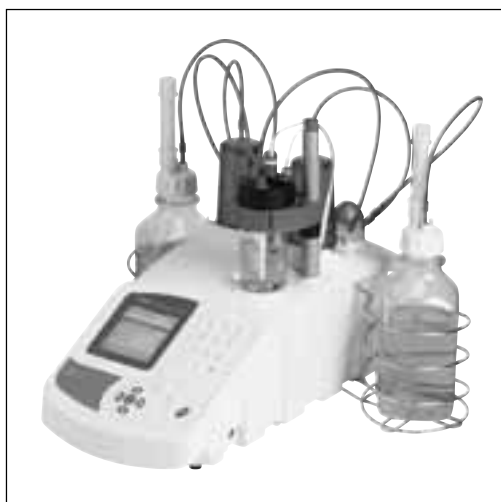
R A D I O M E T E R   A N A L Y T I C A L   S A S
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Acid Number of Petroleum Products

(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)

Radiometer analytical

For strong acid number determination

Acid buffer solution

Weigh 24.2 g of 2.4.6-trimethyl-pyridine, 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

Radiometer analytical

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-C_6H_4-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
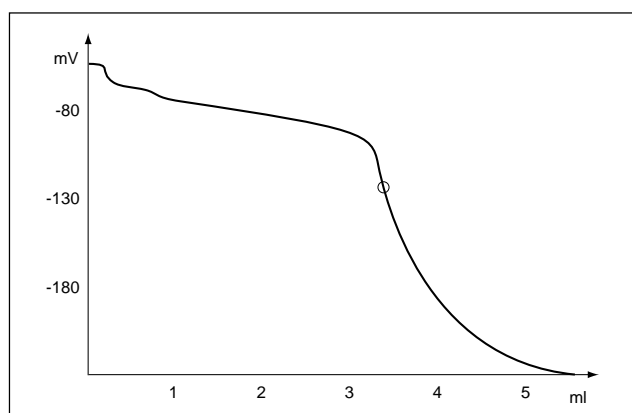
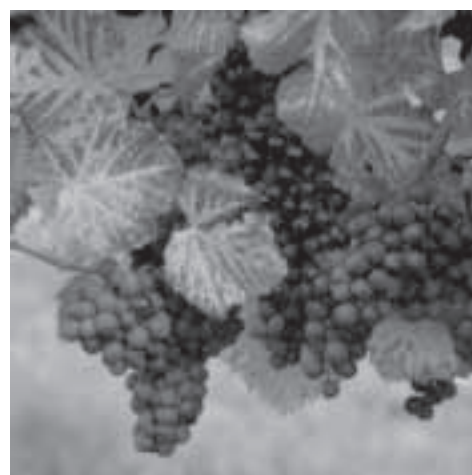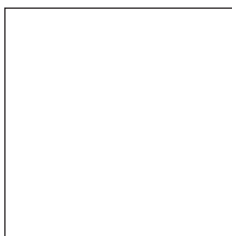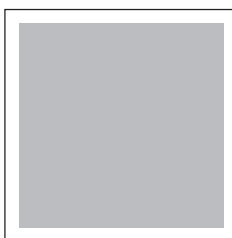**R A D I O M E T E R   A N A L Y T I C A L   S A S**
72 rue d'Alsace, 69627 Villeurbanne Cedex, France
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Acidity of Edible Oils

(According to standard NF.EN.ISO 660-1999)

Introduction

In the edible oils industry, the degree of acidity is an important parameter for classifying the various oils. Acidity also has an influence on the product taste. As the titration is performed in non-aqueous media, it is recommended to use a titration with inflection point detection.

Principle

The sample is dissolved in methyl-isobutyl ketone (methyl4-pentanone2) and titrated with KOH (generally 0.1M) in isopropanol. The result is expressed as mg/g of KOH for acid number and also as a % of oleic (or lauric or palmitic) acid **(see results)**.

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 as titrant solution

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.

Ethyl alcohol as cleaning solution for the glass electrode

Titration solvent: methyl-isobutyl ketone (methyl4-pentanone2)

Filling solution for reference electrode: Dissolve 4.2 g of LiCl in 100 ml of ethyl alcohol

Buffer solutions pH 4.00 (part no. S11M012) and pH 10.00 (part no. S11M014)

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 ADDITION MODE (CONTINUOUS IP)

Cell grounding:	M241Pt
Measure:	mV
Blank:	YES
Min. ordinate: -185 mV **(see notes)**	
Max. ordinate:	100 mV
Stirring speed:	550 rpm
Stirring delay:	30 s
Burette volume:	10 ml
Maximum volume:	10 ml

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Stop point: -300 mV
Smoothing parameter: 7
Inflection point number: 1
Minimum speed: 0.2 ml/min
Maximum speed: 1 ml/min
Direction: Decreasing mV
Stop at last IP: YES

Inflection1
Min. ordinate: -220 mV
Max. ordinate: -50 mV

Sample unit: g
Sample amount: **see working range**

Results:
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: %
Molar weight: 282 **(see results)**
Reaction: 1 smp + 1 titr
Calculate with IP: 1

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.

Weigh and dissolve the necessary amount of sample in 50 ml of titration solvent.

Dip electrodes and delivery tip in the solution.

Run the titration.

Electrode 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. Before starting a new titration rinse electrodes with ethyl alcohol.

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 for one day.

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 10.00 buffer solutions. The difference between the two measurements should be at least 165 mV.

d) Once a week clean the glass electrode using the Radiometer Analytical GK ANNEX Electrode Maintenance Kit (part no. S91M001).

Oil	Acid	Acid formula	Molar Weight
Coconut oil	Lauric acid	$CH_3\text{-}(CH_2)_{10}\text{-}COOH$	200 g/mol
Palm oil	Palmitic acid	$CH_3\text{-}(CH_2)_{14}\text{-}COOH$	256 g/mol
Other oils	Oleic acid	$CH_3\text{-}(CH_2)_7\text{-}CH{=}CH\text{-}(CH_2)_7\text{-}COOH$	282 g/mol

Results

As indicated before results can be expressed in 2 different ways:

expressed as acid number in mg/g of KOH

$$R(mg/g) = V_{titr} * C_{titr} * 56.11/W_{smp}$$

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

C_{titr} = Concentration of titrant in mol/l

W_{smp} = Sample weight in g

56.11 = molecular weight of KOH

expressed as acidity as a % of acid

$$R(\%) = V_{titr} * C_{titr} * M * 100/1000 * W_{smp}$$

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

C_{titr} = Concentration of titrant in mol/l

W_{smp} = Sample weight in g

M = Molar weight of organic acid used for result expression (see below)

Depending on the oil, three different organic acids are used for result expression:

Results on olive oil (3 determinations)
Acid number
Mean: 0.5124 mg/g
Standard deviation: 0.0056 mg/g
Acidity
Mean: 0.275%
Standard deviation: 0.0028%

Radiometer analytical

Acidity of Edible Oils (According to standard NF.EN.ISO 660-1999)

Working range

Depending on the expected result, take a sample amount as indicated opposite:

Acid number (mg/g)	Acidity (%) (*)	Sample in g	Titrant volume in ml (**)
<1	<0.5	20	<3.6
1-4	0.5-2	10	1.8-7.2
4-15	2-7.5	2.5	1.8-6.75
15-75	7.5-37.5	0.5	1.3-6.75
>75	>37.5	0.1	>1.35

(*) Calculated with oleic acid molar weight
(**) For a 0.1M titrant

Notes

Note regarding ordinates
The indicated values for the different ordinates are experimentally measured using the above-mentioned electrodes and methyl-isobutyl ketone as titration solvent. These values may change depending on electrode behaviour (especially the reference electrode) and solvent quality.

Note regarding titrant standardisation
If necessary, standardise the KOH 0.1M in isopropyl alcohol against weighed potassium acid phthalate (KOOC-C_6H_4-COOH with a molar weight of 204.22 g/mol and 1smp + 1 titrant) and dissolved in CO_2-free distilled water.

Note regarding neutralisation of titration solvent
As the titration solvent has a slight acid reaction it is necessary to run a blank for every new batch of solvent.

Note regarding some particular oils
As indicated in standard ISO 660-1999, some oils do not give detectable inflections. In this case, it is possible to run an end point titration with an end point value corresponding to the equivalent point of oleic acid dissolved in the titration solvent.
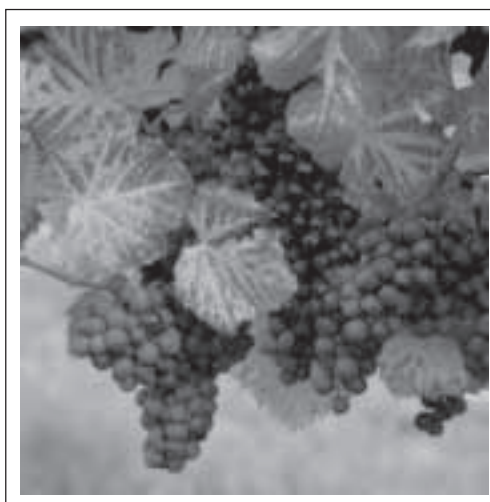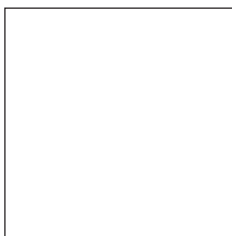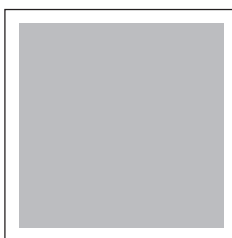Using the above-mentioned electrodes, this end point value is close to -179 mV.

To determine this value, weigh around 100-120 mg of purified oleic acid and run a titration with KOH 0.1M in isopropyl alcohol as titrant solution.
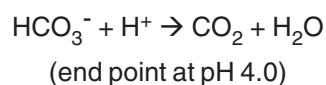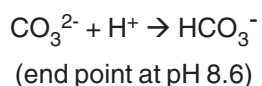
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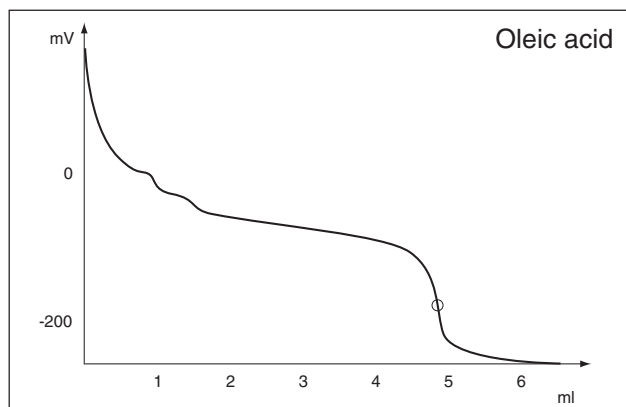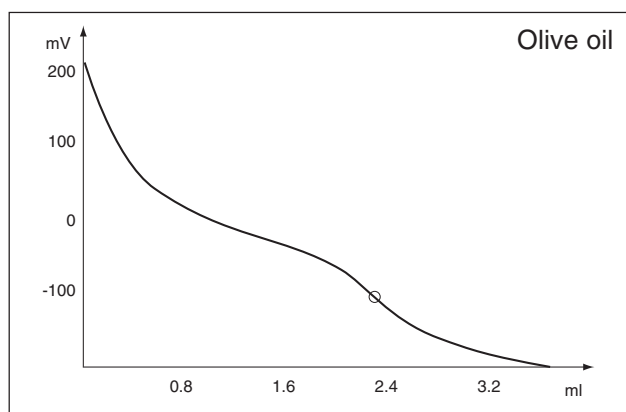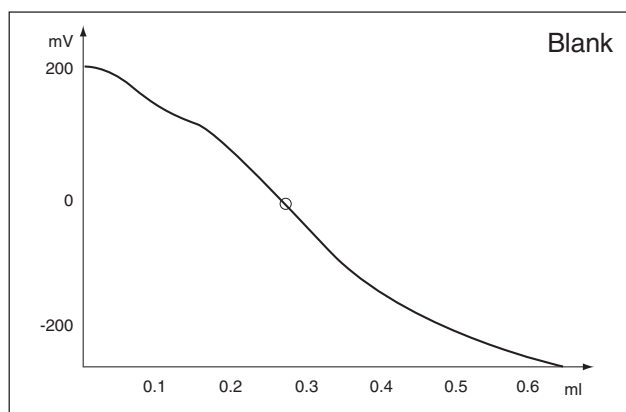
Carbon Dioxide in Wines

Introduction

Carbon dioxide (CO_2) is generally present in wines. This is due to fermentation and the use of CO_2 for transfer operations during winemaking.
The principle is to make the sample strongly alkaline, by adding concentrated sodium hydroxide solution that converts all the CO_2 into CO_3^{2-} and titrating with 0.1M hydrochloric acid.

Principle

As the wine made strongly alkaline (pH10-12) contains only CO_3^{2-}, the titration occurs in two steps

$$CO_3^{2-} + H^+ \rightarrow HCO_3^-$$

(end point at pH 8.6)

$$HCO_3^- + H^+ \rightarrow CO_2 + H_2O$$

(end point at pH 4.0)

The end point titration is then performed with two successive end points (pH 8.6 and pH 4.0) and the titrant volume delivered from pH 8.6 to pH 4.0 is used to quantify the CO_2 level in the wine in g/l. The molar weight of CO_2 is 44.0 g/mol.

A blank titration run with the same, but degassed, wine is necessary.

Electrode and reagents

pHC2401-8 Combined pH Electrode (part no. E16M400)

HCl 0.1 mol/l solution in distilled water (see Application Note TTEP01-01MIN)
This solution is also commercially available.

NaOH 50% w/v in distilled water

Dilution of 50 g of NaOH pellets in 100 ml of freshly boiled distilled water is highly exothermic. The solution is also very caustic for the skin and eyes. Observe laboratory safety regulations.

Distilled water

In order to have a reproducible blank result, use freshly boiled, distilled water which has been cooled to room temperature.

IUPAC Series pH standards pH 4.005 (part no. S11M002) and pH 10.012 (part no. S11M007)

End Point titration settings

Burette volume:	25 ml
Stirring speed:	500 rpm
Working mode:	pH
Blank:	YES **(see notes)**
Predose:	0 ml **(see notes)**
Stirring delay:	10 seconds
Maximum volume:	40 ml
Minimum speed:	0.2 ml/min
Maximum speed:	10 ml/min
Direction:	Decreasing pH
Number of end points:	2
End point 1:	8.6 pH
Proportional band:	2.0 pH
End point delay:	5 seconds
End point 2:	4.0 pH
Proportional band:	2.0 pH
End point delay:	5 seconds
Sample unit:	ml
Dilution:	YES
Sample amount:	100
Final dilution amount:	102 **(see notes)**
Aliquot:	10

Result
No of results: 1
Result by: difference
Calculate with EP: 2
Result unit: g/l
Molar weight: 44.0 g/mol
Reaction: 1 smp + 1 titr

Procedure

Calibrate the combined pH electrode
Let the wine cool to 5°C

Blank preparation
Degassing a wine sample.
Pour the wine into a Buchner flask and connect it to a vacuum system for 3 minutes.
Degassing is also possible by heating the wine and boiling for few seconds only. Then allow the wine to cool to room temperature.
Pipette 100 ml of this degassed wine; add 2 ml or more of the NaOH 50% solution as accurately as possible. Make sure that the pH of this solution is around pH 10-12.
Pipette 10 ml of this solution.
Add the necessary volume of distilled water; dip electrode and delivery tip in the solution.
Run a blank titration.
You can run more than one test on the blank; in this case the Titration Manager takes into account the mean value.

Sample preparation
Taking care not to lose carbon dioxide, take 100 ml of the wine at 5°C using a measuring tube.
Pour it in a conical flask, add the same volume of the NaOH 50% solution as for the blank, seal the flask and mix thoroughly.
To avoid losing carbon dioxide, ensure that the flasks handling the sample are always at low temperature (near 0°C). Use an ice bath or refrigerator.

Make sure that the pH of this solution is around pH 10-12.
Pipette 10 ml of this solution.
Add the necessary volume of distilled water, dip electrode and delivery tip in the solution.
Run the titration.

Results

Expressed as g/l of CO_2 (molar weight of CO_2 = 44 g/mol)

$$R_{CO2} = (V_{titr} - V_{blk}) * C_{titr} * 44 / V_{smp}$$

V_{titr} = Delivered titrant volume between pH 8.6 and pH 4.00 for sample

V_{blk} = Delivered titrant volume between pH 8.6 and pH 4.00 for blank

C_{titr} = Titrant concentration in mol/l (generally 0.1)

V_{smp} = Sample volume (generally 10 ml)

The above-mentioned END POINT SETTINGS take in account:

- the blank calculation,
- the dilution factor due to the addition of 2 ml of NaOH 50% solution.

Result on red wine
No carbon dioxide measured
Verification of the method by addition of Na_2CO_3 directly in the sample beaker before titration with the same wine.

Na_2CO_3 added in mg	V_{titr} - V_{blk}
24	2.57 ml
45	4.5 ml
61	6.08 ml

As indicated in this table the method allows the added Na_2CO_3 be measured with a recovery ratio close to 98%.

Results on sparkling white wine
Sample dilution settings for this wine
Sample amount: 50 ml
Final dilution amount: 52 ml
Aliquot: 10 ml

Blank on degassed wine
5.37 ml of titrant (mean on 3 determinations)

Results (3 determinations)
Mean: 6.83 g/l CO_2
Standard deviation: 0.02 g/l CO_2

Working range

According to the formula mentioned under "Results":

1 ml for (V_{titr} - V_{blk}) corresponds to 0.44 g/l of CO_2

Note that this result is calculated for 10 ml of sample and does not take into account the dilution factor due to addition of NaOH 50% solution.

Notes

Note regarding the "blank"
As the behaviour of every wine is different, it is necessary to run a blank titration for every different type of wine.

As the blank titration depends on the composition of the studied wine, do not forget to use the same sample amount of wine and dilution settings for the blank determination and for the sample.

Note regarding the "predose"
To save time it is possible to use the "predose" function of the Titration Manager.

Bear in mind that the "predose" volume of titrant is effective during sample titration and also "blank titration.

Note that using "predose" can eliminate the first end point.

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Carbon Dioxide in Wines

Note regarding the final amount dilution

This amount is the sum of the volume sample (generally 100 ml) and the volume of the NaOH 50% solution added (in this application note 2 ml).

The volume of the NaOH 50% can change according to the wine.

Note regarding the result

As the method itself offers good reproducibility, the accuracy of the result depends on the handling of the non-degassed sample. It is important to avoid losing carbon dioxide especially with sparkling wines.
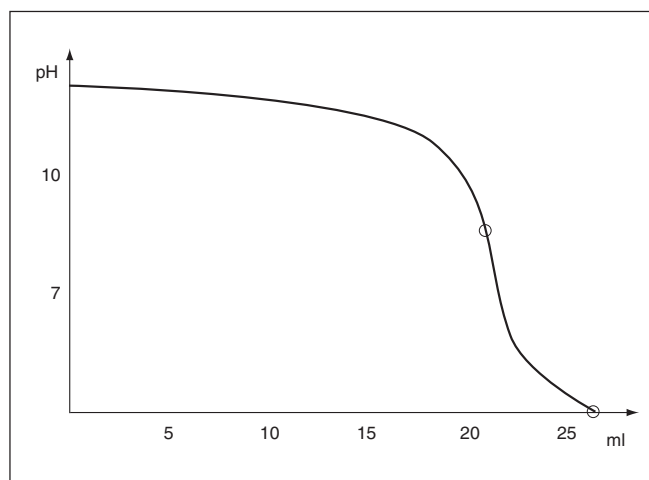
Ensure that a sufficient volume of NaOH 50% solution is added.
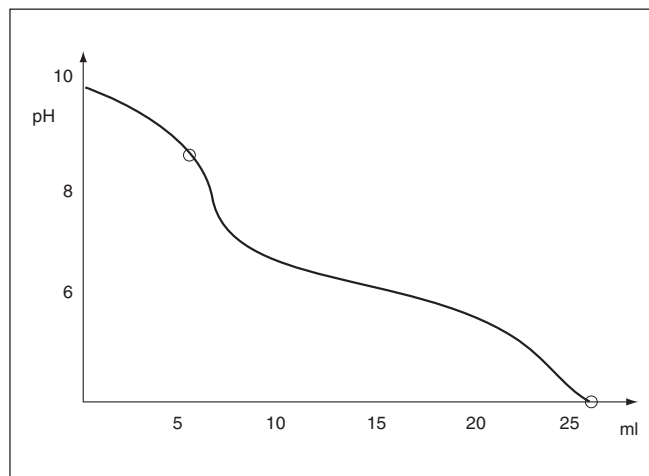
Bibliography

Techniques for chemical analysis and quality monitoring during wine-making

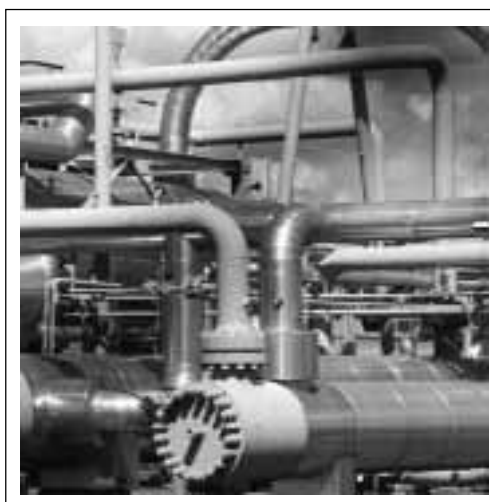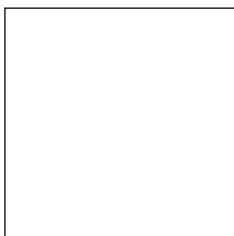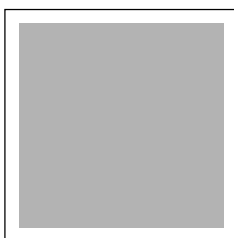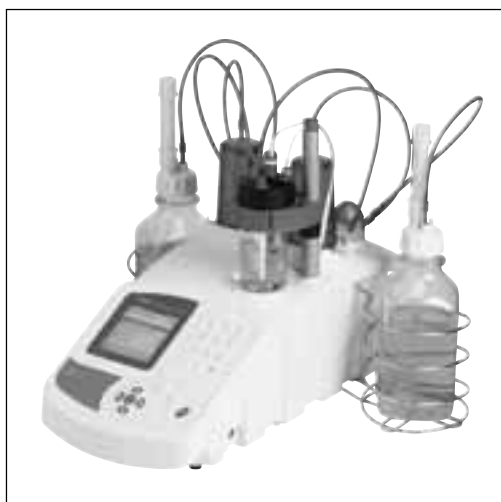Ed: Patrick ILAND wine promotion Campbelltown AUSTRALIA

Curves

Blank

Sample: sparkling wine

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).

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Base Number of Petroleum Products (Perchloric acid titration ASTM D 2896-01 and ISO 3771)

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 (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).

Curves

Blank solvent

Sample

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.
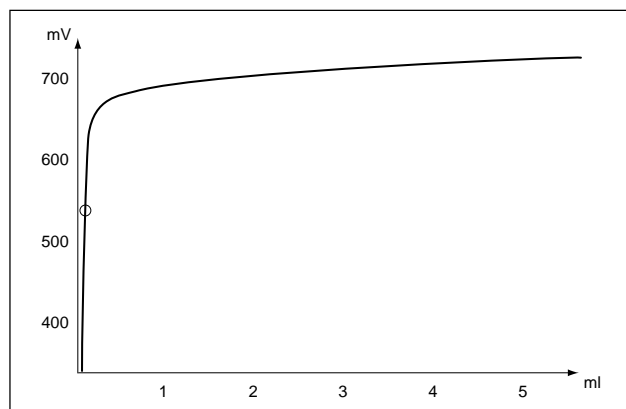Note the volume V_1 of the sodium acetate solution.
Weigh no more than 5 g of product and add the same volume of titration solvent and the same volume of perchloric acid that should be in excess.
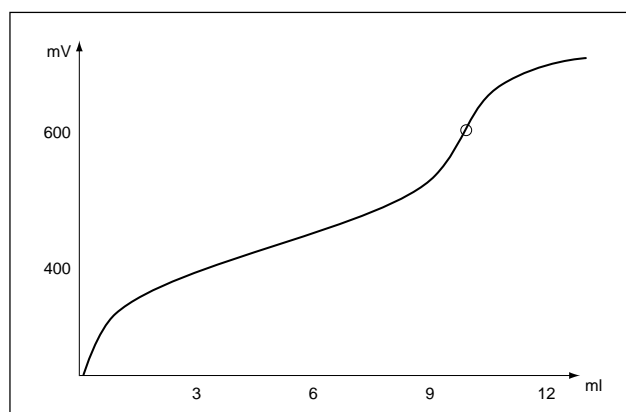Titrate the solution with the sodium acetate solution, note the volume V_2 used.
If C_{ac} is the titrant concentration and W the sample amount:

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