PRECIPITATION 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

Precipitation titration is used in many industries. The most important applications are halide (especially chloride) and silver determinations. Some precipitation titrations are also acid-base titrations in the plating bath industry. 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.*
Acid-base titrations	D41T009
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

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PRECIPITATION TITRATIONS

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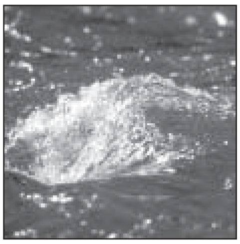
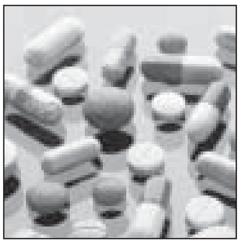
End Point Titration Manager
Operational Qualification





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

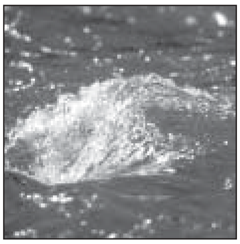
No predose.

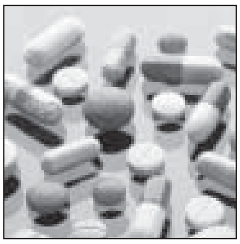
Dissolve the weighed sodium carbonate quantitatively in the titration beaker with 50 to 80 ml of freshly distilled water.

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

Radiometer analytical

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.

Chloride in Mineral Water

Introduction

Many mineral waters contain an easily titratable amount of chloride ions. The most accurate method for chloride determination is inflection point titration, but for quick measurement, if the sample matrix is reproducible, end point titration can be used with a combined silver electrode.

Principle

The titrant reagent for chloride determination is silver nitrate ($AgNO_3$); using end point titration, the titrant concentration must be at least 0.05 eq/l and generally between 0.1 and 0.05 eq/l. The water sample must be acidic at around pH 4.5. That can be obtained by means of acetic acid but for mineral waters with high pH, nitric acid 1M can be also used.

The reaction corresponds to:

$Ag^+ + Cl^- \rightarrow AgCl$ (precipitate)

Results are normally expressed as mg/l of chloride (AW = 35.45 g/mol) or sometimes as mg/l of sodium chloride (NaCl with MW = 58.45 g/mol).

Electrode and reagents

MC6091Ag Metal Electrode, combined silver/reference (part no. E34M004) with CL114 cable (part no. A94L114)

$AgNO_3$ 0.05 eq/l solution

Dissolve 8.494 g of analytical grade $AgNO_3$ in distilled water and dilute to 1000 ml using a volumetric flask. As $AgNO_3$ can be found as very pure grade, it can be considered as reference material.

HNO_3 1M solution

Dilute 78 ml of concentrated HNO_3 in 500 ml of distilled water. Let it cool to room temperature and dilute to 1000 ml using a volumetric flask.

End Point titration settings

Burette volume:	25 ml
Stirring speed:	400 rpm
Working mode:	mV (with i=0)
Number of end points:	1
End point:	-100 mV
Stirring delay:	30 seconds
Minimum speed:	0.1 ml/min
Maximum speed:	4.0 ml/min
Proportional band:	100 mV
End point delay:	10 seconds
Sample unit:	ml
Standard amount:	50 or 100 ml (depending on chloride in the sample)
Titration:	Increasing mV
Result:	mg/l

Procedure

For carbonated mineral waters, or waters containing a high level of carbonate ions, it is necessary to add 5 or 10 ml of HNO_3, boil the sample and let it cool to room temperature before the titration.

For other samples, add 10 ml of HNO_3 0.1 eq/l and titrate directly.

Pipette 50 or 100 ml of sample.

If necessary, add distilled water.

Connect the electrode.

Dip electrode and delivery tip in the solution.

Start method by pressing the RUN key.

Results

As 1 molecule of titrant reacts with 1 molecule of Cl^-
Generally expressed as mg/l of chloride ion (AW = 35.453 g/mol)

R = V(titr)* C(titr) * 35.453 * 1000 / V(smp)

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

-C(titr) = titrant concentration in eq/l (currently 0.05)

-V(smp) = sample volume in ml
35.453 = Atomic weight of chloride ion

For a result expressed as mg/l of NaCl, replace 35.453 with 58.453 (MW of NaCl).

For a result in mg/l of Cl or NaCl
Enter

The sample amount in the SAMPLE screen

The titrant concentration in the TITRANT screen,

1 Titrant and 1 Sample in the COEFFICIENTS display

58.44 as molecular weight (for NaCl) or 35.453 (for Cl)

The Titration Manager gives a result according the above formula.

For 5 determinations of a mineral water

Mean:	88 mg/l
Standard deviation:	0.7 mg/l
Rel. standard deviation;	0.8%

Working range

With 100 ml for the sample volume and 0.5 ml as experimental lower limit for titrant delivery, we can consider a chloride concentration corresponding to approx. 8.5 mg/l as experimental limit.

For the best possible accuracy, the working range starts at 130 mg/l for a 25 ml burette cylinder (corresponding to 35% of the capacity).

Notes

Because this application note works with an end point titration, it is not recommended to titrate with a reagent lower than 0.05 eq/l.

If you use a reagent with a concentration below 0.05, change the end point delay to 20 or 25 seconds because the AgCl precipitation is a low speed reaction for low chloride concentration.

Starting measured potential can indicate presence of halides other than chloride in the sample. Normally chloride ions give a measured potential around -220/-300 mV; if the measured potential is below these values, you can expect Br^- or I^-; if presence of S^{2-} is expected, it is necessary to prepare the sample as a carbonated mineral water to eliminate H_2S.

Chloride in Food Products

Introduction

Salt (NaCl) is present in many foods such as ham, sausage, canned products, dried soups and meats. As NaCl is soluble in water, the most common way to determine the amount of salt is a titration with silver nitrate after sample dissolution in water.

Principle

The titrant reagent for chloride determination is silver nitrate ($AgNO_3$); using end point titration for food products, the titrant concentration is generally 0.1 eq/l.
The sample solution must have an acid pH. 1 M/l nitric acid is generally used.
The reaction corresponds to:

$Ag^+ + Cl^- \rightarrow AgCl$ (precipitate)

Results are normally expressed as a % of sodium chloride (NaCl with MW= 58.45 g/mol).

Electrode and reagents

MC6091Ag Combined Metal Electrode, silver/mercurous sulphate (part no. E34M004) with CL114 cable (part No. A94L114).

$AgNO_3$ 0.1 eq/l solution

Dissolve 16.988 g of analytical grade $AgNO_3$ in distilled water and dilute to 1000 ml using a volumetric flask. As $AgNO_3$ can be found as very pure grade, it can be considered as reference material.

HNO_3 1M solution

Dilute 78 ml of concentrated HNO_3 in 500 ml of distilled water, let it cool to room temperature and dilute to 1000 ml using a volumetric flask.

End Point titration settings

Burette volume:	25 ml
Stirring speed:	400 rpm
Working mode:	mV
Number of end points:	1
End point:	-100 mV
Stirring delay:	30 seconds
Minimum speed:	0.1 ml/min
Maximum speed:	5.0 ml/min
Proportional band:	200 mV
End point delay:	10 seconds
Direction:	Increasing mV
Sample unit:	g
Sample amount:	(see below)
Result:	%

Procedure

Sample preparation
Sample preparation varies according to the product.

Ham (preserved meats): Mix 10 g of product with 190 g of distilled water and weigh an aliquot (around 50 g) for the titration.

Dried soup: Dilute 5 g of product with 250 ml of hot distilled water, allow to cool to room temperature and dilute to 1000 ml in a volumetric flask. Pipette an aliquot (around 20 ml) for titration.

Canned food: Shake the can and open it. Weigh 100 g of the product, mix with 900 g of distilled water and weigh an aliquot (around 5 g) for titration.

These are general recommendations. Use your own particular procedures for special samples.

Titration procedure
Take the required amount of the aliquot sample.

As sample amount, enter either the current amount, or the total amount and also the dilution factor, allowing a result corresponding exactly to the real sample amount.

Add 5 ml of HNO_3 1M and, if necessary, distilled water.

Connect the combined metal electrode to the titration manager.

Dip electrode and delivery tip in the solution.

Start method by pressing the RUN key.

Results

As in this case 1 molecule of titrant reacts with 1 molecule of Cl^-
Generally expressed as % of salt (NaCl) (MW = 58.44 g/mol)

$$R = V(titr) * C(titr) * 58.44 * 100 / SA * 1000$$

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

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

-SA = sample amount used during the titration (in g)

58.44 = Molar weight of NaCl

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

58.44 as molecular weight (for NaCl)

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

If necessary, 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 weight (in g) as final dilution volume in ml

Enter the aliquot weight (in g) as aliquot volume in ml

The Titration Manager does not use g or mg as units for dilution. In this case, you can use volumetric units instead.

For 5 determinations on a dried beef soup

Mean:	45.3%
Standard deviation:	0.45
Rel. standard deviation:	1%

Working range

Depending on the type of sample, the result will vary.

Examples
For canned food: around 2%
For preserved meat: between 2 and 5%
For dried soups: around 45%

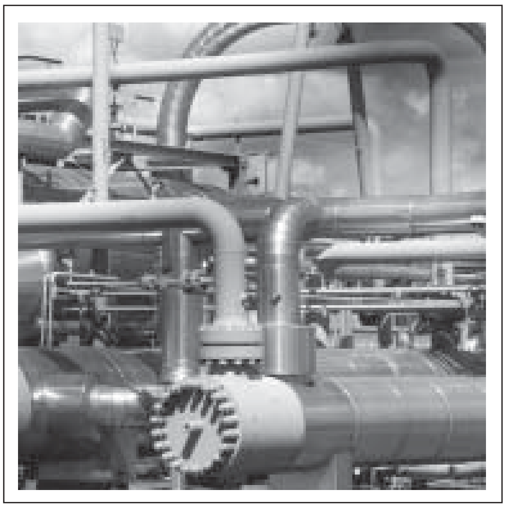
For the application note conditions (titrant concentration of 0.1M) and for **1 g of titrated sample**, 1 ml of titrant corresponds to 0.58% of NaCl in the food product.

Notes

The main differences between local procedures concern sample preparation procedures.

For example, for sausage, some procedures make use of Soxlet extraction with boiling distilled water instead of mixing, as indicated above.

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 Chloride in Water

(ISO and NF ISO 9297)

Introduction

As tap water or surface water contains chloride ions at low concentration levels, chloride determination should be performed by titration with silver nitrate ($AgNO_3$) as titrant. Standard NF ISO 9297 uses a colorimetric determination (with silver chromate) of the equivalent point but it is possible with the same titrant to use a potentiometric determination of the equivalent point.
This application uses a potentiometric titration with a combined silver/reference electrode.

Principle

The silver nitrate reacts with chloride ion according to

$$(Ag^+, NO_3^-) + Cl^- \rightarrow AgCl \downarrow + NO_3^-$$

1 mole of $AgNO_3$ reacts with 1 mole of chloride.
The titrant concentration is generally 0.02 M (ISO and NF ISO standard)
The results are expressed in mg/l of chloride (Cl^- with a molecular weight of 35.453 g/mol)

Electrode and reagents

MC6091Ag Combined metal/reference (Hg/Hg_2SO_4) electrode (part no. E34M002) with CL114 cable.

HNO_3 1M

Dilute 78 ml of concentrated nitric acid in 1000 ml of distilled water

This operation is highly exothermic. Observe laboratory safety regulations.

$AgNO_3$ 0.02M

Dry $AgNO_3$ for 2 hours at 105°C and leave it to cool to room temperature in a dessicator

Using a volumetric flask, dissolve 3.3974 g of $AgNO_3$ in 1000 ml of distilled water.

pH 4. Buffer solution

Dissolve 146 g of CH_3COONa (or 246 g of $CH_3COONa, 3H_2O$) in 400 ml of distilled water, add 480 g of concentrated CH_3COOH and dilute to 1000 ml with distilled water.

Inflection Detection settings

CONTINUOUS ADDITION MODE

Stirring speed :	450 rpm
Stirring delay:	30 s
Burette volume:	10 ml
Maximum volume:	10 ml (see notes)
Stop point:	0 mV
Smoothing parameter:	6
Inflexion points number:	1
Minimum speed:	0.1 ml/min
Maximum speed:	2 ml/min
Direction:	Increasing mV

Inflexion 1

Min. ordinate:	-200 mV **(see notes)**
Max. ordinate:	-35 mV **(see notes)**

Sample unit:	ml
Sample amount:	50 or 100

Results

Unit:	mg/l
Reaction:	1 sample + 1 Titrant
Molar weight:	35.45 g/mol

Procedure

For tap and surface water, pipette 50 or 100 ml of sample, add 10 ml of nitric acid 1M.

For tap and drinking water, it is possible to replace nitric acid 1M by the same volume of pH 4 buffer solution.

Dip electrodes and delivery tip in the beaker.

Run the titration.

For wastewater, the sample should be treated first as laid down in the regulations.

Results

Generally expressed as mg/l of chloride ion (AW = 35.453)
As 1 molecule of titrant reacts with 1 molecule of Cl-

R = V(titr)* C(titr) * 35.453 * 1000 / V(smp)

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

-C(titr) = Titrant concentration in mol/l (currently 0.02)

-V(smp) = sample volume in ml
35.453 = Atomic weight of chloride ion

The above inflection detection settings allow the Titration Manager to calculate the result directly in mg/l of chloride.

For 6 determinations on tap water

Mean:	9.48 mg/l
Standard deviation:	0.12 mg/l
Relative standard deviation:	1.28 %

Working range

As this application note works with continuous addition of titrant, it is recommended to work with one burette capacity. It is also recommended to have around 1 ml of titrant before and after the inflection point.

For a 10 ml burette, the "experimental" titrant volume should be between 1 ml and 9 ml. These volumes correspond to **7 to 63 mg/l of chloride for a sample volume of 100 ml** and **0.02 M titrant**.

Notes

If you need to treat the sample before titration, run a "blank" titration with distilled water instead of the sample. The Titration Manager takes into account a blank titration.

Use slow speeds for titrant delivery to avoid "over-titration". For low concentrations of chloride ions, the precipitation kinetics of AgCl is not a fast reaction.

Between titrations, just rinse the silver electrode with distilled water; do not use abrasive strips to clean the silver rod.

Analytical grade silver nitrate can be considered as a standard, but you can also standardise the silver nitrate solution versus a NaCl solution with the same molar concentration.

Prepare a 0.02 M solution using very pure NaCl.

Dry the pure NaCl at 105°C and leave it to cool to room temperature in a dessicator.

Dissolve 1.1688 g of NaCl in 1000 ml of distilled water using a volumetric flask.

Pipette and weigh a volume of NaCl solution corresponding to half the capacity of the burette.

As the solution density can be taken as 1, enter the measured weight as a volume.

Dilute the NaCl standard with 70 ml of distilled water and add 10 ml pH 4 buffer solution.

Calibrate the titrant using the above-mentioned sample inflection detection settings and follow the titrant calibration procedure of the Titration Manager.

NOTE REGARDING MAXIMUM VOLUME
You can save time and titrant by choosing a maximum volume of 1 or 2 ml above the expected volume at the inflection point.

NOTE REGARDING MINIMUM AND MAXIMUM ORDINATE
Using the combined metal/reference electrode described above, the starting potential is around -200 mV, the final potential close to 0 mV and the inflection point close to -130 mV. You can improve the indicated settings as

Minimum ordinate = E(IP)-50 mV
in our case, -180 mV

Maximum ordinate = E(IP)+50 mV
in our case, -80 mV

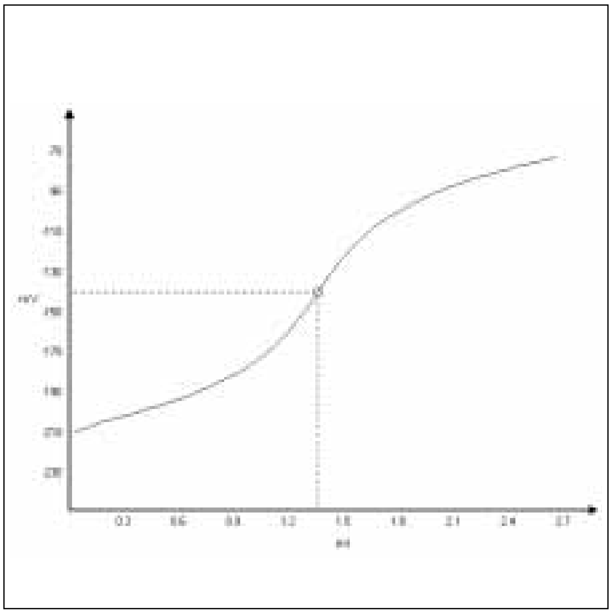
With E(IP)= Experimental measured potential at the inflection point

DYNAMIC INCREMENTAL ADDITION OF THE TITRANT (Dynamic IP)

In this particular case corresponding to relatively low delivered volumes of titrant, running an incremental addition of titrant is not as easy as continuous addition.
The curve shape depends on a slight modification of the settings. The number of stored points may be too low to ensure good reproducibility.
However you can work with the following settings tested with the sample used with continuous addition

Dynamic dose:	12
Maximum dose:	1 ml
Burette speed:	5 ml/min
Stabilisation:	6 mV/min
Acceptation:	30 s
Filter:	1
I.P. reject:	15

Curve



Determination of Chloride in Water

(Standard methods for water 20th edition 4.51 4500 D)

Introduction

As tap water or surface water contains chloride ions at low concentration levels, chloride determination should be performed by titration with silver nitrate ($AgNO_3$) as titrant. The Standard method for water uses a potentiometric determination with a silver rod as measuring electrode and a glass electrode as reference electrode. This application uses a potentiometric titration with glass and silver electrodes.

Principle

The silver nitrate reacts with chloride ion according to

$(Ag^+, NO_3^-) + Cl^- \rightarrow AgCl \downarrow + NO_3^-$

1 mole of $AgNO_3$ reacts with
1 mole of chloride
The titrant concentration should be 0.0141 M (standard methods)
The results are expressed in mg/l of chloride (Cl^- with a atomic weight of 35.45 g/mol)

Electrode and reagents

pHG301 Glass Electrode (part no. E11M001) connected to the measuring input of the Titration Manager with CL114 cable (part no. A94L114).

M291Ag Metal Electrode (part no. E34M002) connected to the reference input of the Titration Manager with CL114 cable.

Note that you can use a M295Ag (part no. E34M003) connected to the reference input with adapter part no. A94P807 instead of the M291Ag.

- HNO_3 1M

Dilute 78 ml of concentrated nitric acid in 1000 ml of distilled water. This operation is highly exothermic. Observe laboratory safety regulations.

- $AgNO_3$ 0.0141 M

Dry the $AgNO_3$ for 2 hours at 105°C and leave it to cool to room temperature in a dessicator. Using a volumetric flask, dissolve 2.395 g of $AgNO_3$ in 1000 ml of distilled water.

- Distilled water

Inflection Detection settings

CONTINUOUS ADDITION MODE
Stirring speed: 450 rpm
Stirring delay: 30 s
Burette volume: 10 ml
Maximum volume: 10 ml **(see notes)**
Stop point: -50 mV **(see notes)**
Smoothing parameter: 6
Number of inflection points: 1
Minimum speed: 0.1 ml/min
Maximum speed: 2 ml/min

Direction: Decreasing mV **(see notes)**

Inflection 1
Min. ordinate: -20 mV **(see notes)**
Max. ordinate: +140 mV **(see notes)**

Sample unit: ml
Sample amount: 50 or 100

Results
Unit: mg/l
Coefficients: 1 sample and 1 Titrant
Molar weight: 35.45 g/mol

Procedure

For tap and surface water, pipette 50 or 100 ml of sample, add 10 ml of nitric acid 1M.

Dip electrodes and delivery tip in the beaker.

Run the titration.

For wastewater, the sample should be treated first as laid down in the regulations.

Results

Generally expressed as mg/l of chloride ion (AW = 35.453)

As 1 molecule of titrant reacts with 1 molecule of Cl^-

$$R = V(titr) * C(titr) * 35.453 * 1000 / V(smp)$$

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

-C(titr) = Titrant concentration in mol/l (0.0141 for Standard method)

-V(smp) = sample volume in ml

35.453 = Atomic weight of chloride ion

The above inflection detection settings allow the Titration Manager to calculate the result directly in mg/l of chloride.

For 6 determinations on tap water

Mean:	9.52 mg/l
Standard deviation:	0.14 mg/l
Relative standard deviation:	1.47%

Potential value for inflection: close to 80 mV

Working range

As this application note works with continuous addition of titrant, it is recommended to work with one burette capacity. It is also recommended to have around 1 ml of titrant before and after the inflection point.

For a 10 ml burette, the "experimental" titrant volume should be between 1 ml and 9 ml. These volumes correspond **to 5 to 45 mg/l of chloride for a sample volume of 100 ml and 0.0141 M titrant**.

Notes

If you need to treat the sample before titration, run a "blank" titration with distilled water instead of the sample. The Titration Manager takes into account a blank titration.

Use slow speeds for titrant delivery to avoid "over-titration". For low concentrations of chloride ions, the precipitation of AgCl is not a fast reaction.

Between titrations, just rinse the silver electrode with distilled water, do not use abrasive strips to clean the silver rod.

Maintenance of the glass electrode:
Follow the Radiometer Analytical procedures given in the operating instructions. You can also clean the electrode by immersion in diluted NH_4OH (1 vol. of concentrated NH_4OH for 20 vol. of distilled water) to dissolve the AgCl at the surface of the glass bulb.

Analytical grade silver nitrate can be considered as a standard, but you can also standardise the silver nitrate solution versus a NaCl solution with the same molar concentration.

Prepare using very pure NaCl a 0.0141 M solution.

Dry the pure NaCl at 140°C and leave it to cool to room temperature in a dessicator.

Dissolve 0.824 g of NaCl in 1000 ml of distilled water using a volumetric flask.

Pipette and weigh a volume of NaCl solution corresponding to half the capacity of the burette.

As the solution density can be taken as 1, enter the measured weight as a volume.

Dilute the NaCl standard with 70 ml of distilled water and add 10 ml of nitric acid.

Calibrate the titrant using the above-mentioned sample inflection detection settings and follow the titrant calibration procedure of the Titration Manager.

NOTE REGARDING MAXIMUM VOLUME
You can save time and titrant by choosing a maximum volume of 1 or 2 ml above the expected volume at the inflection point.

NOTE REGARDING MINIMUM AND MAXIMUM ORDINATE AND STOP POINT
Using the glass and metal electrodes as described above, **initial and final potentials depend on the pH of the solution**.

For tap water diluted with nitric acid experimental values are generally close to
140 mV for initial potential
-20 mV for final potential (or stop point)
85 mV for equivalent point potential

For the same tap water diluted with a pH 4.0 buffer solution values are close to

-35 mV for initial potential
-180 mV for final potential
-103 mV for equivalent point potential

You can improve the indicated settings:

Minimum ordinate = E(IP)-50 mV
Maximum ordinate = E(IP)+50 mV

With E(IP)= Experimental measured potential at the inflection point

NOTE REGARDING TITRATION DIRECTION

Using the Titration Manager, it is **necessary to connect** glass and metal electrodes as indicated:

pHG301 Glass Electrode to the measuring input

M291Ag Metal Electrode to the reference input

The titration direction is therefore the opposite of the titration direction using a ($Hg/HgSO_4$) reference electrode and a silver electrode connected in the normal way.

NOTE REGARDING ELECTRODE CREATION

With the Titration Manager

First create the reference electrode

Function: Reference/ ID from other / ID: M291Ag Cl^- (for example)

Then create the measuring electrode

Function: mV (i=0) / ID from catalogue / pHG301/ ID: Cl^-/

Reference / from user / M291AgCl^-/

DYNAMIC INCREMENTAL ADDITION OF THE TITRANT (Dynamic IP)

In this particular case corresponding to relatively low delivered volumes of titrant, running an incremental addition of titrant is not as easy as continuous addition.

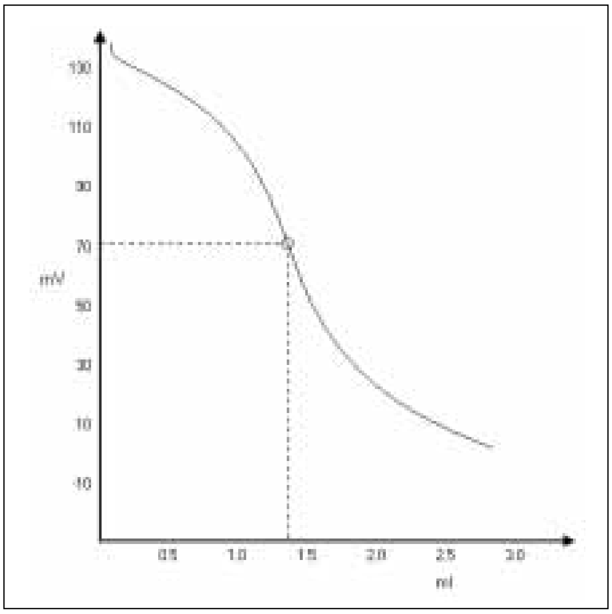
The curve shape depends on a slight modification of the settings.

The number of stored points may be too low to ensure good reproducibility.

However you can work with the following settings tested with the sample used with continuous addition:

Dynamic dose:	12
Maximum dose:	1 ml
Burette speed:	5 ml/min
Stabilisation:	6 mV/min
Acceptation:	30 s
Filter:	1
I.P. reject:	15

Curve



Determination of Salt in Butter

(According to ISO 1738.1997)

Introduction

Salt, as sodium chloride, is present in or added to butter. The chloride determination should be performed by titration with silver nitrate ($AgNO_3$) as titrant. Standard **NF ISO 9297** uses a colorimetric determination of the equivalence point (with potassium chromate) but it is possible with the same titrant to make a potentiometric determination of the equivalence point.
This application uses a potentiometric titration with a silver electrode as measuring electrode and a mercury/mercurous sulphate as reference electrode. It is suitable for butters containing more than 0.03% of sodium chloride.

Principle

The silver nitrate reacts with the chloride ion according to

$$(Ag^+, NO_3^-) + Cl^- \rightarrow AgCl \text{ (precipitate)} + NO_3^-$$

Then 1 mole of $AgNO_3$ corresponds to 1 mole of chloride.
The titrant concentration is generally 0.1M.
The results are expressed as a % of salt (NaCl with a molecular weight of 58.453 g/mol).

Electrode and reagents

M291Ag Silver Metal Electrode (part no. E34M002) connected to the Titration Manager with cable part no. A94L114.

REF601 Hg/Hg_2SO_4 Reference Electrode (part no. E21M012) connected to the Titration Manager with adapter part no. A94P807 **(see notes).**
(Other electrodes can be used such as the M295Ag Silver Metal Electrode (part no. E34M002) with adapter part no. A94P807 or the REF621 Reference Electrode (part no. E21M006) connected with the CL114 cable (part no. A94L114).

If temperature control of the solution is required: T201 Temperature Sensor (part no. E51M001)

HNO_3 1M
Dilute 78 ml of concentrated nitric acid in 1000 ml of distilled water.

This operation is highly exothermic. Observe laboratory safety regulations.

$AgNO_3$ 0.1M
Dry the $AgNO_3$ at 105°C for 2 hours and let it cool to room temperature in a dessicator.

Using a volumetric flask, dissolve 16.9873 g of $AgNO_3$ in 1000 ml of distilled water. This solution is also available commercially.

Hot distilled water (approximately 60°C for electrodes and beaker cleaning).

Inflection Detection settings

CONTINUOUS ADDITION MODE

Stirring speed:	500rpm
Stirring delay:	30 s
Burette volume:	25 ml

Maximum volume:
25 ml **(see working range)**
Stop point: 0 mV
Smoothing parameter: 5
Inflection point number: 1
Minimum speed: 0.2 ml/min
Maximum speed: 5 ml/min
Direction: Increasing mV
Stop at last IP: YES

Inflection 1:
Min. ordinate: -200 mV **(see notes)**
Max. ordinate: -50 mV **(see notes)**

Sample unit: g
Sample amount: 4 **(see notes)**

Results:
Unit: %
Reaction: 1 smp + 1 Titr
Molar weight: 58.453 g/mol

Procedure

Accurately weigh around 4 or 5 g of butter in the titration beaker.

Add 100 ml of hot distilled water (60°C) and mix the solution until the butter is properly mixed in.

(It is also possible to add cold water and to warm up the solution).

Add 1 ml of HNO_3 **(see notes).**

Dip electrodes and delivery tip in the solution.
It is recommended to dip electrodes and delivery tip in a stirred solution to avoid butter deposit at the reference junction.

Run the titration with a beaker temperature of around 50 - 60°C **(see notes)**.

Results

As in this case 1 molecule of titrant reacts with 1 molecule of Cl^-

Generally expressed as a % of sodium chloride ion (MW = 58.453 g/mol)

R =
V(titr)*C(titr)*58.453*100/W(smp)*1000
(1)

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

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

-W(smp) = sample weight in g

58.453 = Molar weight of sodium chloride (NaCl)

100 = To have a result for 100g of product (%)

1000 = To have a result expressed in g

Using the above inflection detection settings, the Titration Manager directly calculates the result in mg/l of chloride.

For three determinations on salted butter
Mean: 1.995%
Standard deviation: 0.0018%
Rel. standard deviation: 0.09%
(Butter with a salt content of 2%)

For three determinations on butter (with a 10 ml burette)
Mean: 0.036%
Standard deviation: 0.0003%
Rel. standard deviation: 0.8%

Working range

Using a 25 ml burette, the experimental titrant volume should be between 1 and 23 ml.

According to formula (1), 1 ml of titrant corresponds to approximately 0.145% of salt for 4 g of sample.

For a 25 ml burette, this corresponds to a working range of 0.145% to 3.33%.

Although the ISO standard specifies a low limit corresponding to a salt content of 0.1%, it is possible to measure salt content below this value using a 10 ml burette and a sample amount of about 6 g. In this case, set the maximum volume to 10 ml.

Notes

Note regarding electrodes
As the sample solution can cause the porous pin of the reference electrode to become clogged, it is advisable to use separate rather than combined electrodes.
At the end of each titration, immediately rinse the electrodes with hot water.

Note regarding sample amount
Try to have a sample test representative of the raw product.
If necessary, warm and mix the product before weighing.

Radiometer
analytical

Note regarding HNO_3 addition
This optional addition allows a more stable and reproducible starting potential.
If you do not add HNO_3 check the minimum and maximum ordinate values and correct them if necessary.

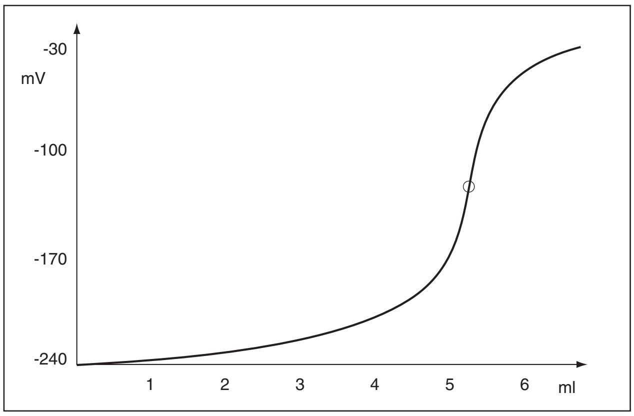
Note regarding titration temperature
According to the ISO standard, it is also possible to run the titration at room temperature. However, it is essential to always work with the same conditions.
As the Hg/Hg_2SO_4 electrode is used as reference electrode, it is recommended to run the titration at a temperature below 65°C.

Note regarding a blank titration
Depending on the purity of the reactants, it may be necessary to run a blank titration. For this purpose just enter:

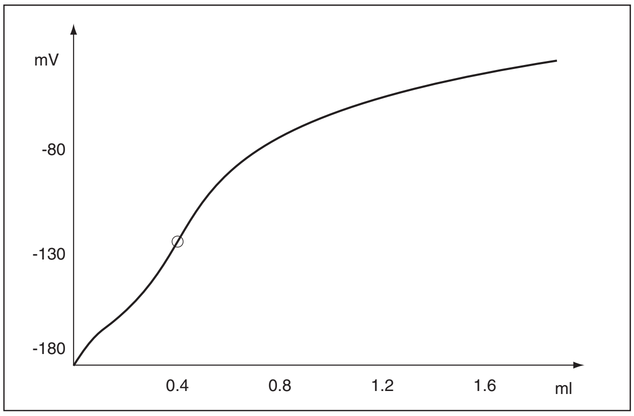
Titration with blank: YES

Other settings are unchanged.
For this application blank was checked and corresponded to 0.00 ml.

Curves



Salted butter



Butter

Thiols (Mercaptans) in Fuels

(According to ASTM D3227-00)

Introduction

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

Principle

The Ag^+ ion reacts with the thiols according to

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

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

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

Electrode and reagents

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

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

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

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

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

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

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

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

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

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

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

Inflection Detection settings

CONTINUOUS IP

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

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

Titration:	Decreasing mV
Inflection number:	1

Inflection 1

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

Sample

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

Number of results:	2

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

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

Procedure

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

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

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

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

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

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

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

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

Results

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

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

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

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

For 3 determinations on untreated kerosene

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

Test on a gasoline S95

Result:	$5.18.10^{-4}$ % 5.18 mg/kg

Sample amount around 30 g
Titrant volume around 0.45 ml

Working range

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

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

According to the formula for 20 g of sample,

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

Notes

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

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

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

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

Curve