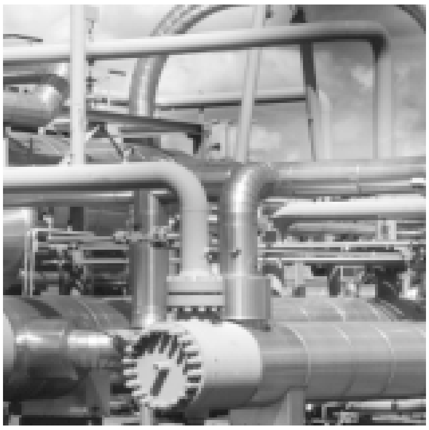
# COMPLEXOMETRIC TITRATIONS
# Introduction

## 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



Complexometric titrations are generally run in order to determine divalent cations. The most important applications are the titration of calcium and magnesium for example for water hardness and the determination of nickel, zinc, copper and cobalt for the plating industry. Certain modifications may be needed to take into account the composition of specific baths or standards in force in certain industries.
The equivalence point was and still is frequently determined using a colorimetric method but ion specific electrodes can also be used as measuring electrodes.

In addition to dedicated application booklets, Radiometer Analytical also produces technique-based applications. Ask your local representative for the following booklets:

| Technique | Part No. |
|---|---|
| Acid-base titrations | D41T009 |
| Precipitation titrations | D41T010 |
| 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.

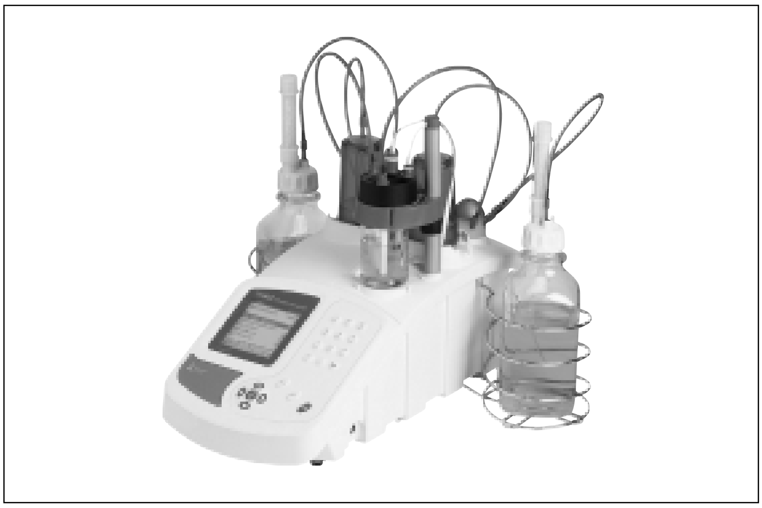
# COMPLEXOMETRIC TITRATIONS

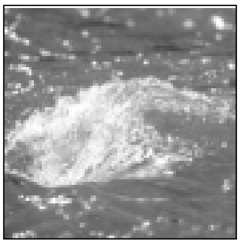
---

D41T011 • © • Radiometer Analytical S.A. • France • 2002-02B

Radiometer
analytical

# 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.

# Determination of Hardness in Water

## (ISO 6059 and Standard methods for water 18th edition 2.36 2340C)

## Introduction

Hardness of water measures the sum of calcium and magnesium ions present in the water. The above-mentioned standard lays down a titration with EDTA at pH 10.00, using a $NH_4Cl$ /$NH_4OH$ buffer and a colorimetric detection of the equivalent point.
**This application note also uses EDTA titration with a potentiometric determination** of the equivalent point by means of a **Calcium ion-selective electrode**. Instead of the $NH_4Cl$ /$NH_4OH$ buffer, we use a mixture of TRIS and acetylacetone. This buffer solution allows separation between Calcium and Magnesium when a Calcium selective electrode is used as measuring electrode.

## Principle

The titrant EDTA reacts with $Ca^{2+}$ or $Mg^{2+}$ according to the reaction

$$Me^{2+} + H_2Y^{2-} \rightarrow MeY + 2H^+$$

Where $Me^{2+}$ represents $Ca^{2+}$ or $Mg^{2+}$ and $H_2Y^{2-}$ the di-sodium salt of EDTA

1 mole of EDTA corresponds to
1 mole of $Ca^{2+}$ or $Mg^{2+}$

The EDTA concentration is 0.02 mol/l
The results are generally expressed as mg/l of $CaCO_3$ or mmol/l but some other units can be used (see notes).

## Electrode and reagents

ISE25Ca Calcium Ion-Selective Electrode (part no. E41M002) with a CL114 cable (part no. A94L114)

REF201 Reference Electrode (part no. E21M009)

EDTA titrant 0.02 mol/l (or 20 mmol/l)

The molecular weight of $Na_2EDTA$ is 372.24 g/mol

Dissolve 7.445 of $Na_2EDTA$ in 1000 ml of water using a volumetric flask

This titrant is also commercially available

Complexing and buffer solution

0.035 mol/l TRIS and 0.055 mol/l acetylacetone

Dissolve 3.50 g of acetylacetone and 6.65 g of TRIS (tri(hydroxy)-aminomethane) in 1000 ml of water using a volumetric flask.

Do not use this buffer for longer than one month.

$Ca^{2+}$ 0.01 mol/l and 0.1 mol/l solutions

Prepare the 0.01 mol/l solution by dilution of the 0.1mol/l solution commercially available as standard solution

## Inflection Detection Settings

**CONTINUOUS ADDITION MODE**

| | |
|---|---|
| Stirring speed: | 450 rpm |
| Stirring delay: | 20 s |
| Burette volume: | 25 ml |
| Maximum volume: | 25 ml |
| Stop point: | -80 mV |
| Smoothing parameter: | 6 |
| Inflexion points number: | 2 |
| Minimum speed: | 0.3 ml/min |
| Maximum speed: | 4 ml/min |
| Direction: | Decreasing mV |

Inflection1
Min. ordinate: -40 mV **(see notes)**
Max. ordinate: 120 mV

Inflection 2
Min. ordinate: -40 mV
Max. ordinate: 120 mV

Sample unit: ml
Sample amount: 50 or 100

Results: **(see notes)**
Results by: cumulate
Number of results: 2

Result 1
Result unit: mmol/l
Reaction: 1 smp + 1 titr
Calculate with IP: 1

Result 2
Result unit: mmol/l
Reaction: 1 smp + 1 titr
Calculate with IP: 2

## Procedure

This procedure is suitable for surface waters, tap water and drinking waters.

Prepare and fill the ISE25Ca Ion-Selective Electrode as indicated in the operating instructions and store it in $CaCl_2$ for one hour prior to the first use.

Install electrodes and titrant

Pipette the necessary amount of water (generally 50 or 100 ml)

Add 20 ml of the buffer solution

Dip electrodes and delivery tip in the beaker

Run the titration.

## Results

Depending on the ratio between concentration of $Ca^{2+}$ and $Mg^{2+}$, the titration curve can show one or two inflection points.

**For one inflection point**
It corresponds to the cumulate ($Ca^{2+}$ + $Mg^{2+}$) or $Ca^{2+}$ if there is no $Mg^{2+}$ in the water or if the ratio $Ca^{2+}/Mg^{2+}$ between relative concentrations of these 2 elements is too high.

**For two inflection points**
The first one corresponds to $Ca^{2+}$
The difference between the first and the second corresponds to $Mg^{2+}$
The total volume delivered to the second equivalent point corresponds to the cumulate ($Ca^{2+}$ + $Mg^{2+}$)

**Results are generally expressed in mmol/l or mg/l of $CaCO_3$ for the cumulate ($Ca^{2+}$ + $Mg^{2+}$)**

R (mmol/l) = V(titr) * C(titr) / V(smp)

R (mg/l $CaCO_3$) = V(titr) * C(titr) * 100 / V(smp)

- V(titr) = Total volume of titrant used in ml

- C(titr) = Concentration of titrant in mmol/l

- V(smp) = Sample volume in ml

- 100 = molecular weight of $CaCO_3$

**For 5 determinations on a mineral water**
Mean: 3.25 mmol/l
or 325 mg/l $CaCO_3$
Standard deviation: 0.03 mmol/l
Rel standard deviation: 0.9%

## Working range

For 100 ml of sample and a 20 ml burette volume, a titrant volume between 1 and 18 ml corresponds to a working range between 0.2 and 3.6 mmol/l or 20 and 360 mg/l of $CaCO_3$ (see above formulas).

## Notes

**Note regarding the inflection points ordinates**

The above-mentioned values correspond to the curve ordinates generally observed for normal tap water

For the first inflection point (Calcium determination), the inflection point is often close to 80/90 mV and for the second (Magnesium determination), it is close to 15/30 mV

**Note regarding the result**

**Result expressed in mg/l of $CaCO_3$**
The above-mentioned settings allow a result in line with the standard (total hardness expressed in mmol/l) whether the titration curve presents one or two inflection points.

If a result expressed in mg/l of $CaCO_3$ is needed, use the following settings.

Result unit: mg/l
Molar weight: 100
Reaction: 1 smp + 1 titr

**Results expressed separately in mg/l of $Ca^{2+}$ and $Mg^{2+}$ and total hardness**
If the titration curve presents 2 inflection points, the first point corresponds to the Calcium and the second to Magnesium.
The results can then be modified as follows:

Results by: Difference

Result 1
Result unit: mg/l
Molar weight: 40.1
(molar weight of Ca)
Reaction: 1 smp + 1 titr
Calculate with IP: 1

Result 2
Result unit: mg/l
Molar weight: 24.31
(molar weight of Mg)
Reaction: 1 smp + 1 titr
Calculate with IP: 2

Equation 1
Title: Hardness mmol/l
Equation: (R1/40.1) + (R2/24.31)

**OR/AND**

Equation 1 (or 2)
Title: Hardness mg/l
Equation:
(R1*100/40.1) + (R2*100/24.31)

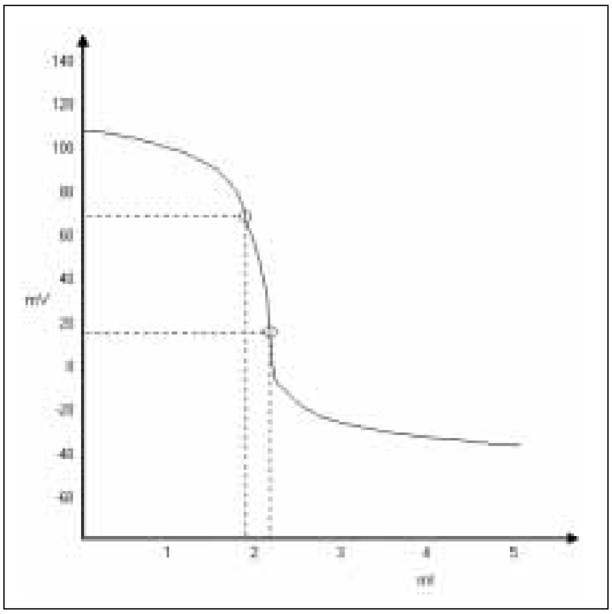
**Note regarding titrant calibration**
If necessary, the EDTA solution can be calibrated using 0.01 mol/l $Ca^{2+}$ solution. To calculate the titrant concentration, enter the $Ca^{2+}$ standard concentration in mol/l and ask for a result in mol/l with a reaction corresponding to 1 smp + 1 Titr.

**Note regarding Calcium ion-selective electrode maintenance**
Prepare and use the Calcium ion-selective electrode according to the operating instructions.

During experiments, store the electrode in a 0.01 mol/l $Ca^{2+}$ solution.

For long-term storage, empty the electrode and store it in its box.

**Curve**



# Nickel in Nickel Plating Solutions

## (EDTA Titration)

## Introduction

Nickel is commonly used as plating in surface treatment or preparation industries. In some cases, especially for bright plating, the bath is a mixture of boric acid and nickel salt. It is possible to determine boric acid and nickel content with an acid-base titration (see note TTEP01.07PLA), but as a general rule, nickel determination is performed using NiEDTA complex formation.
A typical nickel concentration in nickel plating baths is around 50-80 g/l of but some baths have greater concentrations (e.g. 400 g/l).
The molar weight of nickel is 58.71 g/mole.

## Principle

A two-step back titration is used.
First step:

Addition of an excess of EDTA that reacts with $Ni^{2+}$ forming NiEDTA complex, 1 mole of EDTA reacting with 1 mole of $Ni^{2+}$ ion according to

$$Ni^{2+} + H_2Y^{2-} \rightarrow NiY + 2H^+$$

Second step:
Titration of the excess EDTA with a copper solution according to

$$Cu^{2+} + H_2Y^{2-} \rightarrow CuY + 2H^+$$

The two reactions must take place in buffered media (for example a pH around 4.5 with acetic buffer solution). The measuring electrode is a $Cu^{2+}$ selective electrode.

## Electrode and reagents

ISE25Cu $Cu^{2+}$ selective electrode (part no. E41M006)

CL114 connecting cable (part no. A94L114)

REF201 Red Rod Reference Electrode (part no. E21M001)

EDTA solution 0.10 mol/l

The molecular weight of $Na_2EDTA$ is 372.24 g/mol.
Dissolve 37.224 of $Na_2EDTA$ in 1000 ml of water using a volumetric flask.
This solution is also commercially available.

Sodium acetate buffer solution

Dissolve 85 g of sodium acetate ($CH_3COONa$) in water, add 60 ml of glacial acetic acid and dilute to 1000 ml with distilled water. This solution contains approximately 1 mole of $CH_3COOH$ and 1 mole of $CH_3COONa$ per litre.

Titrant: 0.1 mol/l $Cu^{2+}$ solution: dissolve 24.968 g of $CuSO_4$, $5H_2O$ in 1000 ml of distilled water using a volumetric flask.
Note that it is possible to use another copper salt ($Cu(NO_3)_2$ for example).

Distilled water

## Inflection Detection Settings (with Monoburette Titration Manager)

**CONTINUOUS ADDITION MODE**

| | |
|---|---|
| Stirring speed: | 550 |
| Stirring delay: | 30 s |
| Burette volume: | 10<br>**(see procedure)** |
| Back Titration: | MANUAL<br>**(see Titration Automation)** |

Excess reagent: EDTA 0.1M
Excess volume: 10 ml

Maximum volume: 10 ml
**(see procedure)**
Stop point: 240 mV
**(see start & end potentials)**
Smoothing parameter: 6
Inflection point number: 1
Minimum speed: 0.2 ml/min
Maximum speed: 5 ml/min
Direction: Increasing mV
Stop at last IP: YES
Inflection
Min. ordinate: 170 mV
(see start and end potentials)
Max. ordinate: 230 mV

Dilution: YES
Sample unit: ml
Sample amount: 10
Total dilution volume: 200 ml
Aliquot: 10 ml

Results:
Number of results: 1

Result 1
Result unit: g/l

Molar weight: 58.71
(for a result expressed in g/l of $Ni^{2+}$)
Excess: 1 smp + 1 exc
Reaction: 1 Exc + 1 Titr

## Procedure

Connect the ISE25Cu electrode to the E1 electrode input by means of the CL114 cable

Connect the REF201 electrode to the reference electrode input

Fill the titration burette with the 0.1 mole/l copper solution

**Sample preparation**
As nickel concentration can cover a wide range, it is important to ensure the sample solution contains an excess of EDTA before titration.

As a guideline, refer to the following table

| Ni conc. g/l | Sample vol. ml | Total dil. Vol. ml | Aliquot ml | EDTA added ml | Titrant vol. ml |
|---|---|---|---|---|---|
| 60 | 10 | 200 | 10 | 10 | 5 |
| 120 | 10 | 200 | 10 | 20 | 10 |
| 240 | 5 | 200 | 10 | 20 | 10 |
| 480 | 5 | 200 | 5 | 20 | 10 |

This table takes into account concentrations of 0.1 mol/l for EDTA and Copper solution.
To simplify the table, the molar weight of Ni is taken as 60 g/mol (true value 58.71 g/mol).
Other figures may be specified in laboratory regulations.

Add 10 ml of acetate buffer solution and the necessary amount of EDTA solution to the sample aliquot.
*Depending on the composition of the bath, the volume of the acetate buffer solution may need to be increased.*
If necessary, add distilled water
Start method by pressing the RUN key.

## Results

**Generally expressed in g/l of Nickel (MW = 58.71 g/mol)**
The titration is a back titration of excess EDTA using $Cu^{2+}$ as titrant
As indicated before, 1 $Ni^{2+}$ and 1 $Cu^{2+}$ react with 1 mole of EDTA, then the result is

$$CNi = (V_{exc} * C_{exc} - V_{titr} * C_{titr}) * 58.71 / V_{smp}$$

$V_{exc}$ = Volume of EDTA added in ml
$C_{exc}$ = Concentration of the EDTA solution in mol/l
$V_{titr}$ = Volume of titrant ($Cu^{2+}$ solution) used for titration in ml
$C_{titr}$ = Concentration of the titrant in mol/l
$V_{smp}$ = Sample volume in ml present in the titration beaker
58.71 = Molar weight of Nickel

**For results in g/l**
With the settings indicated above, the Titration Manager gives a result according to the above formula taking into account the sample dilution.

**Three determinations on the same bath**
**Nickel**
Mean: 53.5 g/l nickel
Standard deviation: 0.70 g/l boric acid
Relative standard deviation: 1.3%

A Nickel/boric acid bath is used in this application.

## Notes

**Electrodes**
To avoid reference electrode contamination, it is recommended to use a REF251 double junction reference electrode (part no. E21M001) instead of the REF201 reference electrode (part no. E21M009).
Do not leave the ISE25Cu selective electrode in a solution containing excess EDTA for too long.
When the titration is finished, rinse the electrodes and store the ISE25Cu in a solution containing approximately $10^{-3}$ mol/l of $Cu^{2+}$ in distilled water.
Refer to the electrode operating instructions.

### Titration automation

Addition of EDTA solution can be automated using a bi-burette workstation.
Install the second burette with a volume corresponding to 10 or 20 ml.
Create and install the EDTA reagent with a 0.1M concentration on this burette.
Change the method settings to

| | |
|---|---|
| Back Titration: | AUTOMATIC |
| Excess reagent: | EDTA 0.1M |
| Excess volume: | 10 ml |

This automatic addition of EDTA improves accuracy and reproducibility of the results.

### Start and end potentials

Depending on the bath composition, the start and end potentials may change, but the titration always increases the measured potential and the potential jump during the titration is close to 100 mV.

### Modifying the procedure

With some Nickel baths, especially Nickel/boric acid, it is possible to use an ammonium buffer solution instead of the acetic buffer solution.

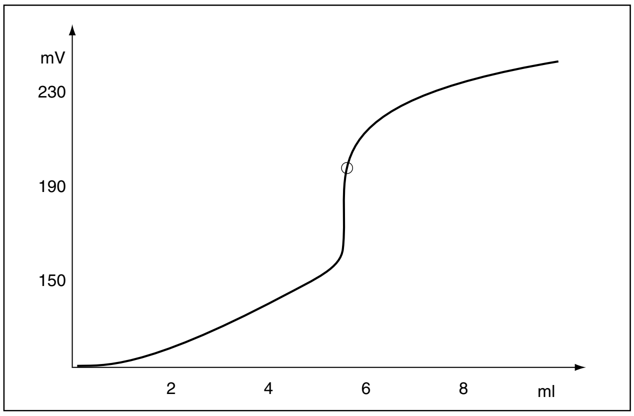
$NH_4Cl$ and $NH_4OH$ buffer solution
Dissolve 50 g of ammonium chloride ($NH_4Cl$) in 200 ml of distilled water, add 250 ml of concentrated ammonia ($NH_4OH$ 30%), complete to 1000 ml with distilled water.

The measured potential during the titration changes.
Use the following settings as experimental values:

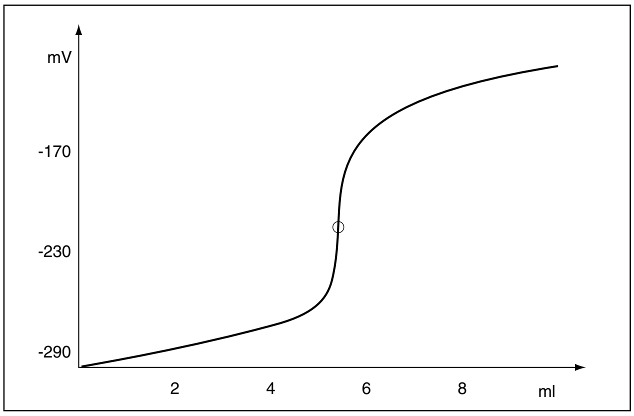
| | |
|---|---|
| Stop point: | -100 mV |
| Inflection | |
| Min. ordinate: | -300 mV |
| Max. ordinate: | -100 mV |

(These values were obtained with the nickel/boric acid bath previously used.)

### Curves



$Ni^{++}$ determination in pH 4.5 buffer



$Ni^{++}$ determination in pH 9 buffer

# Copper in Electroless Copper Baths

## (EDTA Titration)

## 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. Copper concentration is around 3 g/l.
HCHO and NaOH concentrations can be determined as indicated in application notes TTEP01.04PLA and TTEP01.05PLA.
According to bath manufacturer's procedures, copper concentration determination uses either a redox reaction (with iodide) or a complexometric reaction with E.D.T.A as in this application note.

## Principle

The titrant EDTA reacts with $Cu^{2+}$ according to the reaction

$$Cu^{2+} + H_2Y^{2-} \rightarrow CuY + 2H^+$$

Then 1 mole of EDTA corresponds to 1 mole of $Cu^{2+}$

The EDTA concentration is generally 0.1 or 0.2 mol/l
As for every complexometric titration, the reaction occurs in a pH buffered solution; in this case pH 10.0 with a mixture of $NH_4Cl$ and $NH_4OH$.
The indicating electrode should be a $Cu^{2+}$ selective electrode.

## Electrode and reagents

ISE25Cu $Cu^{2+}$ selective electrode (part no. E41M006)

CL114 connecting cable (part no. A94L114)

REF251 Red Rod Reference Electrode (part no. E21M001)

EDTA titrant 0.10 mol/l (or 0.2 mol/l)

The molecular weight of $Na_2EDTA$ is 372.24 g/mol.
Dissolve 37.224 (or 74.448 g for a 0.2 mol/l concentration) of $Na_2EDTA$ in 1000 ml of water using a volumetric flask.
This titrant is also commercially available.

$NH_4Cl$ and $NH_4OH$ buffer solution

Dissolve 50 g of ammonium chloride ($NH_4Cl$) in 200 ml of distilled water, add 250 ml of concentrated ammonia ($NH_4OH$ 30%), complete to 1000 ml with distilled water.

Distilled water

## Inflection Detection Settings

**CONTINUOUS ADDITION MODE**

| | |
|---|---|
| Stirring speed: | 550 rpm |
| Stirring delay: | 20 s |
| Burette volume: | 10 ml<br>**(see working range)** |
| Maximum volume: | 10 ml |
| Stop point: | -350 mV **(see notes)** |
| Smoothing parameter: | 6 |
| Inflection point number: | 1 |
| Minimum speed: | 0.2 ml/min |
| Maximum speed: | 4 ml/min |
| Direction: | Decreasing mV |
| Stop at last IP: | YES |

Inflection
Min. ordinate: -270 mV **(see notes)**
Max. ordinate: -140 mV

Sample unit: ml
Sample amount: 10

Results:
Number of results: 1

Result 1
Result unit: g/l
Molar weight: 63.5 **(see notes)**
Reaction: 1 smp + 1 titr

## Procedure

Connect the ISE25Cu electrode to the E1 electrode input by means of the CL114 cable.

Connect the REF201 electrode to the reference electrode input.

Pipette 10 ml of bath.

Add 50 ml of NH4Cl and NH4OH buffer solution and, if necessary, distilled water.

Dip electrodes and delivery tip in the solution.

Start method by pressing the RUN key.

## Results

**Generally expressed as mg/l of copper (Cu with a molar weight of 63.5 g/mol)**

$$R_{Cu} = V_{titr} * C_{titr} * 63.5 / V_{smp}$$

$R_{Cu}$ = result in g/l of Cu

$V_{titr}$ = delivered volume of titrant to reach the inflection point in ml

$C_{titr}$ = exact concentration of titrant in mol/l

63.5 = molar weight of Cu

$V_{smp}$ = Current sample amount in ml

With the settings indicated above, the Titration Manager gives a result according to the above formula.

**3 determinations on the same bath**
Mean: 3.02 g/l
Standard deviation: 0.01 g/l

## Working range

As the copper determination is conducted according to automatic inflection point detection, it is recommended to have 2 ml of titrant before and after the equivalence point.
With a sample amount of 10 ml and a titrant concentration of 0.1 mol/l, see the following table:

| Burette volume | Delivered vol. volume | $CuSO_4$, $5H_20$ conc. in g/l | Copper conc. In g/l |
|---|---|---|---|
| 10 ml | 2 ml<br>8 ml | 4.95<br>19.8 | 1.26<br>5.04 |
| 25 ml | 2 ml<br>23 ml | 4.95<br>57 | 1.26<br>14.6 |
| 50 ml | 2 ml<br>48 ml | 4.95<br>119 | 1.26<br>30.5 |

For other copper concentrations change the sample amount and/or titrant concentration.

## Notes

**Note regarding electrodes**
To avoid reference electrode contamination, it is recommended to use a REF251 double junction reference electrode (part no. E21M001) instead of the REF201 reference electrode (part no. E21M009).
Do not leave the ISE25Cu selective electrode in a solution containing excess EDTA for too long.
When the titration is finished, rinse the electrodes and store the ISE25Cu in a solution containing approximately $10^{-3}$ mol/l of $Cu^{2+}$ in distilled water.
Refer to the electrode operating instructions.

**Note regarding stop point and ordinate values**
These values vary depending on the chemical composition of the copper bath. The indicated values correspond to an electroless copper bath containing NaOH and HCHO. The titration always decreases the measured potential and the potential jump during the titration is close to 150 mV.

**Note regarding result unit**
The result unit used in the application note corresponds to g/l of copper (molar weight 63.5 g/mol). Some local rules use g/l of $CuSO_4$, $5H_2O$ with a molar weight of 249.5 g/mol as result unit. In this case, change the molar weight in the result screen and refer to the table for the corresponding working range.

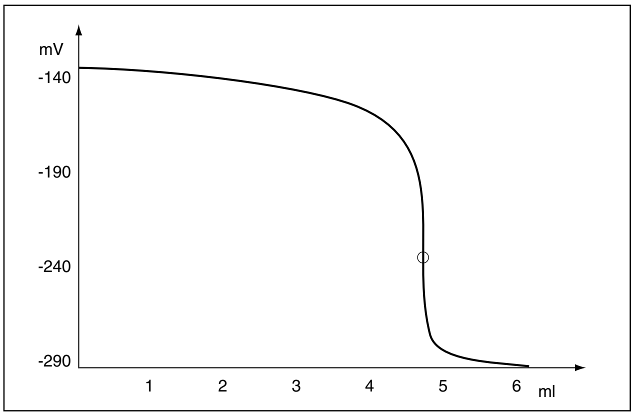
**Note regarding other copper baths**
This application note is also applicable to other copper baths such as acid baths containing copper ions and sulphuric acid.
With this kind of bath, it is necessary to neutralise the sample before buffer solution addition (pH close to 8.00/9.00).

## Dynamic Incremental Addition of the Titrant (Dynamic IP)

It is possible to work with dynamic IP
Dynamic dose: 10
Maximum dose: 0.30 ml
Burette speed: 20.00 ml/min
Stabilisation: 3 mV/min
Acceptation: 10 s
Filter: 1
I.P. reject: 50

Other settings are the same as for Continuous IP

**Curve**



Cu$^{++}$ determination in pH 9 buffer

**RADIOMETER ANALYTICAL SAS**
72 rue d'Alsace, 69627 Villeurbanne Cedex, France
E-mail: radiometer@nalytical.com Web: www.radiometer-analytical.com
Tel. : +33 (0)4 78 03 38 38 - Fax: +33 (0)4 78 68 88 12