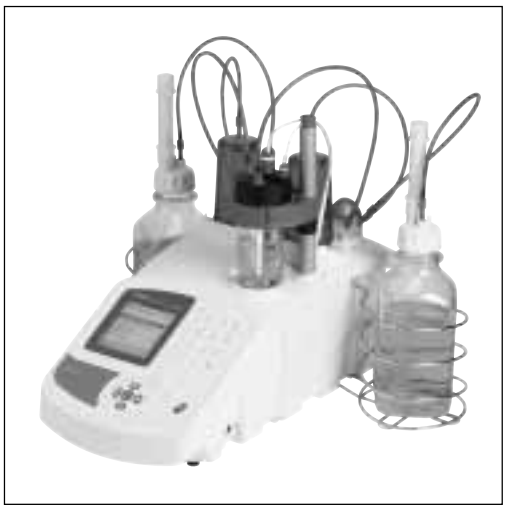
Nickel in Nickel Plating Solutions

(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 **(see procedure)**
Back Titration:	MANUAL **(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.

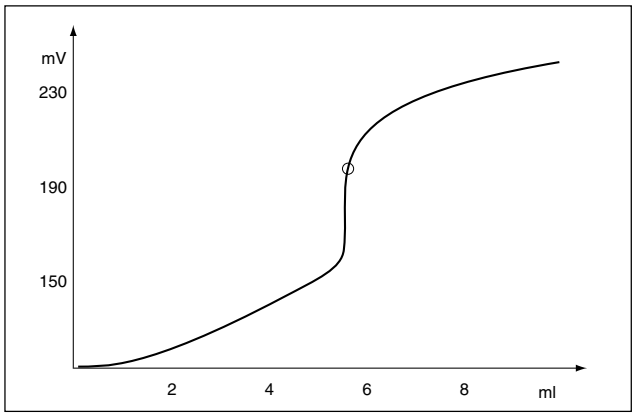
NH_4Cl and NH_4OH buffer solution
Dissolve 50 g of ammonium chloride (NH_4Cl) in 200 ml of distilled water, add 250 ml of concentrated ammonia (NH_4OH 30%), complete to 1000 ml with distilled water.

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

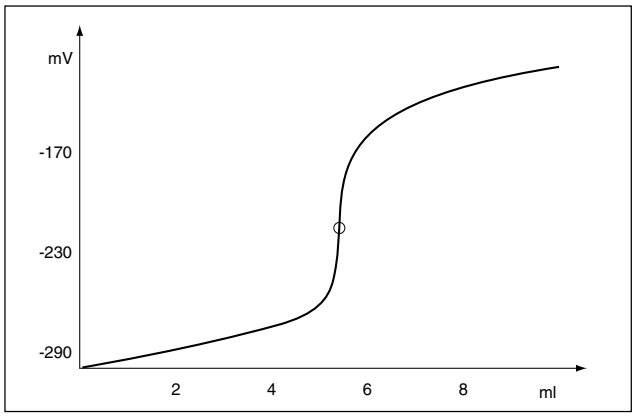
Stop point:	-100 mV
Inflection	
Min. ordinate:	-300 mV
Max. ordinate:	-100 mV

(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

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