Application Note

Quantifying the nickel chloride and nickel sulphate in a nickel plating solution

Industry	Metals
Instrument	Automatic potentiometric titrator
Measurement method	Potentiometry / precipitation titration, Photometric titration / chelatometric titration
Standards	

1. Scope

The concentration of nickel salts in nickel plating solutions is an important factor in controlling the plating bath. This Application Note describes an example of measuring the concentration of nickel salts in a plating solution containing nickel sulphate and nickel chloride as the nickel salts.
The measurement details are shown below (Figure).

① Nickel chloride : $NiCl_2 + 2AgNO_3 \rightarrow Ni(NO_3)_2 + 2AgCl$
② Total Nickel : Ni(II) + EDTA → Ni-EDTA chelate
②−① Nickel sulfate : $NiSO_4$

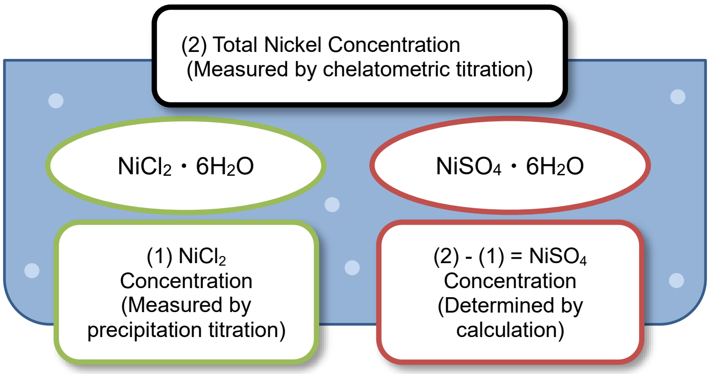


Fig. Calculation method for each nickel salt concentration

For the nickel chloride (1), the chloride ions are measured by precipitation titration with silver nitrate as the titration solution. The concentration of nickel chloride hexahydrate is then determined from this titration volume.
For the nickel sulphate (calculated by subtracting (1) from (2)), the total nickel concentration (2) is determined by chelatometric titration with an ethylenediaminetetraacetic acid (EDTA) solution as the titration solution. The nickel chloride (2) component determined in the previous step is subtracted from this to determine the concentration of nickel sulphate hexahydrate. The precipitation titration is carried out by potentiometric titration using a combined silver electrode. For the chelatometric titration, murexide was used as the indicator with the solution buffered to a pH of 10. The change in color of the indicator was detected by a photometric sensor in order to determine the endpoint.

2. Post-measurement procedure

The detecting unit on the combined silver electrode must have a metallic luster when used. If there is contamination or an oxidation film, polish it as needed using polishing paper, and keep it clean.

The electrolyte for the combined silver electrode should be replaced about every two weeks. After use, clean the photometric sensor well with pure water. Then wipe away any excess water, and dry it before storage.

3. Apparatus

Main unit	Automatic potentiometric titrator (preamplifier, STD) Photometric preamplifier PTA
Electrode	Combined silver electrode reference electrode internal solution (1 mol/L potassium nitrate)
Photometric sensor	Interference filter, wavelength 530 nm

4. Reagents

—Precipitation Titration—

Titrant	0.1 mol/L aqueous silver nitrate solution

—Chelatometric Titration—

Titrant	0.1 mol/L aqueous EDTA solution
Indicator	Diluted murexide powder (0.2 g of murexide ground and mixed into 100 g of potassium sulfate)
Additive reagents	1 mol/L aqueous ammonium chloride solution, with 28 % ammonia

5. Procedure

—Nickel Chloride—

1) Introduce exactly 2.0 mL of the sample into a beaker, and add 100 mL of water.
2) Titrate with a 0.1 mol/L aqueous silver nitrate solution.
3) Take the inflection point on the titration curve as the endpoint, and determine the concentration of nickel chloride hexahydrate from the titration volume.

—Nickel Sulphate—

1) Introduce exactly 1.0 mL of the sample into a beaker, and add 150 mL of water.
2) Add 10 mL of the ammonium chloride solution. Then add ammonia solution until the solution turns yellow.
3) Titrate with a 0.1 mol/L EDTA solution.
4) Take the inflection point on the titration curve as the endpoint, and determine the total nickel concentration from the titration volume. Subtract the equivalent of the nickel chloride from this volume to determine the concentration of nickel sulphate hexahydrate.

6. Calculation

Nickel chloride hexahydrate (g/L) = (EP1 - BL1) × TF × C1 × K1/S
Concentration conversion for nickel sulphate (g/L) = CO1 × 262.9/237.7

EP1 Titration volume (mL)
BL1 Titration volume for a blank test (mL) = 0
TF Titrant factor = 1.0042
C1 Concentration conversion coefficient = 237.7
K1 Unit conversion coefficient = 0.05
S Amount of sample introduced (mL) = 2.0
CO1 First calculated result (measurement result for nickel chloride hexahydrate (g/L))

Nickel sulphate hexahydrate (g/L) = ((EP1 - BL1) × TF × C1 × K1/S) - R

EP1 Titration volume (mL)
BL1 Titration volume for a blank test (mL) = 0
TF Titrant factor = 0.9794
C1 Concentration conversion coefficient = 262.9
K1 Unit conversion coefficient = 0.1
S Amount of sample introduced (mL) = 1.0
R Corrected nickel chloride amount (g/L)
(Concentration converted from the above measured value for nickel chloride)

7. Example

— Parameter —

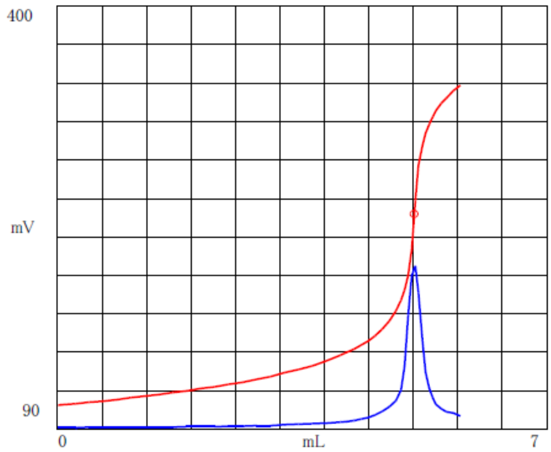
<Titr. Mode>	Auto Int.	**<Ctrl. Para.>**	
<Titr. Form>	Level Stop	Number of EP	1
		End Sense	Standard
<Titr. Para.>		Gain	1
Max Volume	20 (mL)	Data Sampling	On
Channel/Unit (Ctrl.)	*	Ctrl. Speed	Standard
Wait Time	0 (s)	Other Control	Standard
Dose Mode	None	Stirrer Speed	4
		Auto Intermit mode	Standard

*Note For nickel chloride (precipitation titration), Ch1, mV
For nickel sulphate (chelatometric titration), Ch3, %T

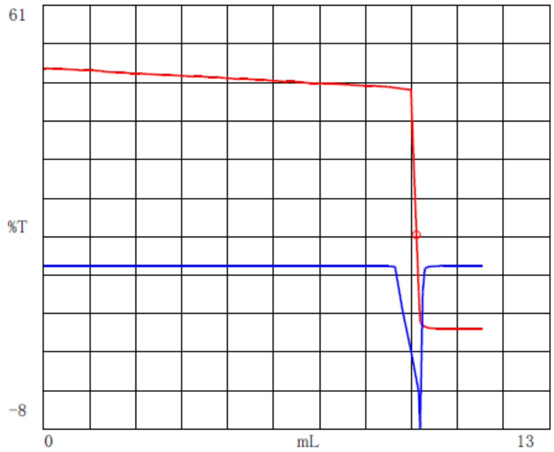
(The above condition is an example. The setting condition depends on the model.)

— Example of Titration curve —

・Precipitation titration



・Chelatometric titration



— Measurement results —

Table 1 Measurement results of Nickel chloride hexahydrate

	Sample (mL)	Titration volume (mL)	$NiCl_2 \cdot 6H_2O$ (g/L)
1	2	5.1114	30.50
2	2	5.1210	30.56
3	2	5.1176	30.54
Average	-	-	30.53
SD	-	-	0.03
RSD (%)	-	-	0.10

Table 2 Measurement results of Nickel sulfate hexahydrate

	Sample (mL)	Titration volume (mL)	$NiSO_4 \cdot 6H_2O$ (g/L)
1	1	9.5938	216.49
2	1	9.5738	215.98
3	1	9.5379	215.05
Average	-	-	215.84
SD	-	-	0.73
RSD (%)	-	-	0.34