AQUACOUNTER Application Sheet	COM series	DATA No. E1	1st edition
Plating	Quantification of silver and free cyanides in silver cyanide plating solution		

1. Measurement outline

Analysis of silver plating solution is a daily analysis work that is important in controlling the quality of products, and it needs to be conducted regularly.

The general analysis items for silver cyanide plating solution are:

(1) Silver

(2) Free cyanides

(3) Carbonate salt

Among these, analysis on silver and free cyanides is considered most important.

(1) Measurement on silver (Volhard method)

In the measurement method that is most generally conducted in measurement of silver concentration, the sample solution is acidified to strong acid and cyanides are decomposed by heating. This solution is then titrated by the Volhard method with ammonium thiocyanate titrant (indicator: ferric ion, red color indicated) or the Mohr method with sodium chloride titrant (indicator: potassium chromate, brown color indicated).

$$Ag^+ + SCN^- \rightarrow AgSCN\downarrow$$
$$Ag^+ + Cl^- \rightarrow AgCl\downarrow$$

These measurement methods require caution since preprocessing involves the dangerous cyan gas. The measurement procedure by Volhard method is as follows:

Approximately 1mL sample is precisely collected and added with several mL of purified water, approximately 3mL concentrated hydrochloric acid and 1mL concentrated nitric acid within a draft with caution for generation of cyan gas. This is heated in the draft until white smoke of sulfuric acid is generated. It is kept to be cooled, and 50mL purified water is added for titration with 0.1mol/L ammonium thiocyanate titrant.

(2) Selective measurement method for silver and free cyanide ion (improved Liebig method)

Besides these measurement methods, there is a method which does not require preprocessing. This section introduces an example of measurement on silver concentration and cyanides with fractionated(Selective) titration (successive titration). Liebig method (neutral – basic solution), Mohr method (neutral solution) and Volhard method (acidic solution) are methods for quantifying cyanides. The following explains Liebig method which is most popularly used among these.

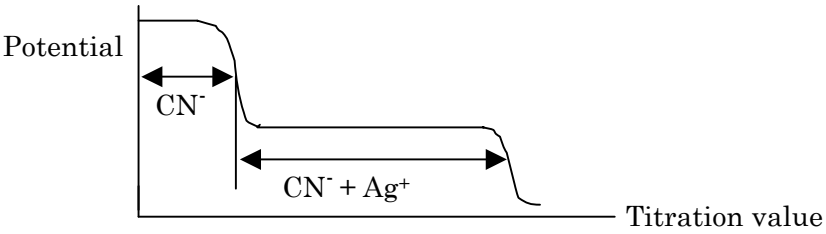
When $AgNO_3$ solution is titrated into a neutral or basic solution that contains cyanides, white precipitation of AgCN forms locally first, but it gradually dissolves and disappears. This is due to the generation of cyano complex which is dissolved easily.

$$Ag^+ + 2CN^- \rightarrow Ag(CN)_2^- \quad \cdots\cdots \text{First end point}$$

When $AgNO_3$ is continued to be titrated after all of the free cyanides form cyano complex, white clouding that does not dissolve forms. This is due to the generation of dicyanoargentate salt (silver cyanide) as shown by the formula below:

$$Ag^+ + Ag(CN)_2^- \rightarrow Ag\left[Ag(CN)_2\right] = 2AgCN\downarrow \quad \cdots\cdots \text{Second end point}$$

When titration is continued in this condition, all $Ag(CN)_2^-$ ions are titrated to precipitate as AgCN and titration is completed. The results of titration to this point are illustrated as follows:



The first end point indicates the titration value for free cyanides, and the second end point indicates the titration value for $Ag(CN)_2^-$. Therefore, it is possible to calculate the concentration of silver by subtracting the titration value for the first end point from the titration value of the second end point. The measurement procedure in this method is provided below:

5mL of 0.1mol/L sodium tetraborate solution is added to 5mL sample for pH adjustment and then 40mL D/I water is added for potentiometric titration with 0.05mol/L silver nitrate titrant.

2. Reagents and Electrodes

(1) Reagents	Titrant	0.1mol/L NH_4SCN titrant (Volhard method) 0.05mol/L $AgNO_3$ titrant (Liebig method)
	Loading buffer	Concentrated sulfuric acid, concentrated nitric acid
	pH adjustment solution	0.1mol/L $Na_2B_4O_7$ aqueous solution
(2) Electrodes	Indicator electrode	Silver indicator electrode AG-311 to IE jack (P/N E231245-A)
	Reference electrode	Silver reference electrode MS-231 to RE jack (P/N D231243-A)
	Note) Silver reference combination electrode AGR-801 (P/N D231269-A) may also be used. Reference electrode RE-201 (standard accessory) cannot be used.	

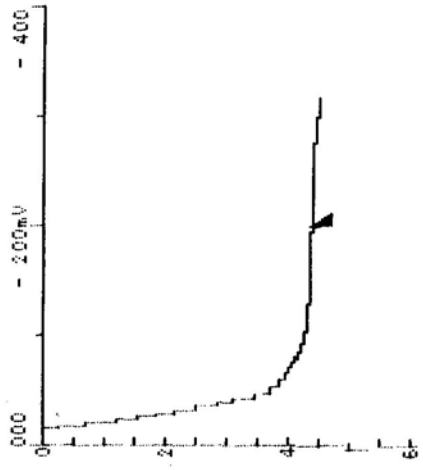
3. Measurement conditions example (for COM-1600S)

(1) Method	Auto
(2) End Sens	500(Volhard), 100(Liebig)
(3) Mode	5
Pre Int	1
Del K	5
Del Sens	0
Int Time	3
Int Sens	3
Brt Speed	2
Pulse	80

Mode No.5	
Pre Int	0 sec
Del K	5
Del Sens	0 mV
Int Time	3 sec
Int Sens	3 mV
Brt Speed	2
Pulse	40

4. Measurement example

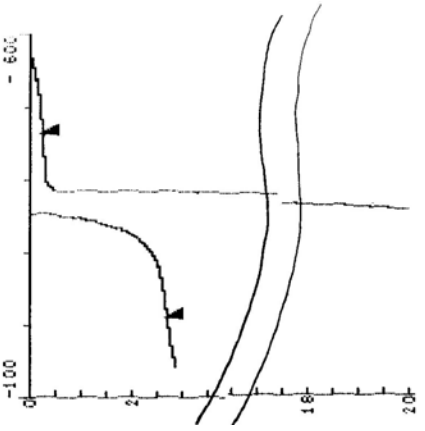
(1) Measurement example on Ag^+ in plating solution by Volhard method



Measurement results

Sample No.	Sample volume (mL)	Titration value (mL)	Concentration (g/L)
1	1	4.3500	56.04
2	1	4.3662	56.24
3	1	4.3570	56.13
Avg. (Average value)			56.14 g/L
Std. Dev. (Standard deviation)			0.104 g/L
C.V. (Coefficient of variation)			0.10 %

(2) Measurement example on free cyanides and Ag^+ by improved Liebig method



Measurement results

Sample No.	Sample volume (g)	Free Cyanide ion		AgCN	
		Titration value (mL)	Concentration (g/L)	Titration value (mL)	Concentration (g/L)
1	5	0.21625	0.282	22.246	29.83
2	5	0.21059	0.275	22.237	29.82
3	5	0.21613	0.282	22.241	29.83
Avg. (Average value)			0.280 g/L		29.83 g/L
Std. Dev. (Standard deviation)			0.004 g/L		0.006 g/L
C.V. (Coefficient of variation)			1.42 %		0.02 %

5. Outline

(1) About improved Liebig method

This method has no heating preprocess and delivers excellent safety while also enabling fractionation titration on free cyanides and silver ion compared to Volhard method. However, caution is required since the titration curve for silver ion may become unclear depending on the type of sample.

(2) Generation of AgCN precipitation

In titration of silver ion, precipitation of AgCN may occur in large amount and interfere with the measurement by adsorption to the indicator electrode, etc. As one measure against this, it is possible to reduce the size of precipitation and improve the measurement precision while also delivering the effect of electrode adsorption prevention by adding “silver chloride precipitate cohesion prevention agent” in advance.

Key words

Silver plating solution, free cyanides, silver cyanide, Liebig method, Volhard method, Mohr method

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