AQUACOUNTER Application Sheet	COM series	DATA No. E3	1st edition
Plating	Quantification of Fe^{2+}, Fe^{3+} and Cu^{2+} in etching solution		

1. Measurement outline

Ferrous ion (Fe^{2+}), ferric ion (Fe^{3+}) and copper ion (Cu^{2+}) contained in the etching solution for copper foil on printed wiring board are quantified using chelate titration method and oxidation-reduction titration method.

(1) Measurement of Fe^{2+}

Oxidation-reduction titration is conduced on Fe^{2+} using $KMnO_4$ titrant in solution acidified with phosphoric acid.

$$5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} \quad 4H_2O$$

(2) Measurement of Fe^{3+} and Cu^{2+}

Ferric ion (Fe^{3+}) and copper ion (Cu^{2+}) are titrated with fractionation by chelate titration in solution acidified with acetic acid.

$$Fe^{3+} + Na_2EDTA \rightarrow FeEDTA + 2Na^+$$
$$Cu^{++} + Na_2EDTA \rightarrow CuEDTA + 2Na^+$$

In this method, each component is quantified with fractionation by applying the difference in EDTA chelate formation constant among ferrous, ferric and copper ions. At pH3 and below, the EDTA chelate conditional formation constant for Fe^{3+} is approximately 13.9 and that of Fe^{2+} is approximately 3.7. Thus it is possible to selectively quantify only Fe^{3+} when it is titrated at pH3 or below. In addition, the EDTA chelate formation constant for Cu^{2+} at pH3 is approximately 8.3, and is at the enough for titration with EDTA. This section introduces a measurement example in which potentiometric titration on Fe^{3+} is conducted first in monochloroacetic acid-acetic acid buffer to obtain the first end point and then titration is continued with EDTA to quantify Cu^{2+}.

2. Reagents and Electrodes

(1) Reagents	Titrant	0.01mol/L EDTA titrant 0.10 mol/L $KMnO_4$ titrant (for Fe^{2+} measurement)
	Loading buffer	2mL pH2 monochloroacetic acid-acetic acid buffer 5mL phosphoric acid (for Fe^{2+} measurement)
	Indicator	0.2mL PAN indicator (0.1% ethanol solution)
(2) Electrodes	Indicator electrode	Platinum electrode PT-301 (P/N D231244-A)
	Reference electrode	*Reference electrode RE-201 *standard accessory

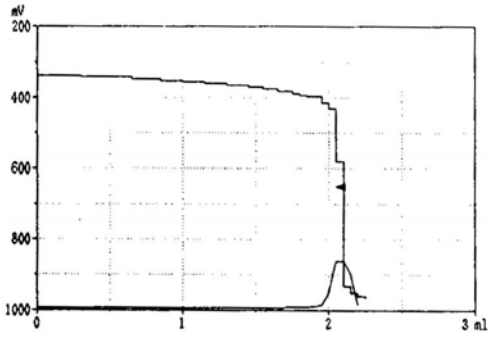
3. Measurement conditions example (for COM-1600S)

Master File No.1 **Condition file : 1 + 2** (for Fe^{3+} and Cu^{2+})					
Parameters for Condition file 1 (For 1st EP)		**Parameter for Condition file 2** (For 2nd EP)		**Mode No. 5**	
Method	AUTO	Method	AUTO	Pre Int	0 sec
Amp No.	2	Amp No.	2	Del K	5
Buret No.	1	Buret No.	1	Del Sens	0 mV
Meas Unit	mV	Meas Unit	mV	Int Time	3 sec
S Timer	0 sec	S Timer	0 sec	Int Sens	3 mV
CP mL	0 mL	CP mL	0 mL	Brt Speed	2
DP mL	0 mL	DP mL	0 mL	Pulse	40
End Sens	200	End Sens	300		
Over mL	0 mL	Over mL	0 mL		
Max. Vol.	20 mL	Max. Vol.	20 mL		
Unit	g/L	Unit	g/L		
Size	0.1 g	Size	0.1 g		
Blank	0	Blank	0		
Factor	Titre of the titrant	Factor	Titre of the titrant		
Molarity	0.05	Molarity	0.05		
K	55.85 (as Fe^{3+})	L	63.55 (as Cu^{2+})		
Formula	VA×F×M×K/S	Formula	VB×F×M×L/S		
Mode No.	5	Mode No.	5		

Master File No.2 **Condition file: 1 (for Fe^{2+})**	
Parameters for Condition file 1	
Method	Auto
Buret No.	1
Amp No.	2
Meas Unit	mV
S-Timer	0 sec
CP	0 mL
DP	0 mL
End Sens	1000
Over mL	0 mL
Max Vol	20 mL
Mode No.	5
Unit	g/L
Formula	(D-B)×K×F×M/S
Blank	0
Molarity	0.1
Factor	Titre of the titrant
K	55.85 (as Fe^{2+})

4. Measurement example

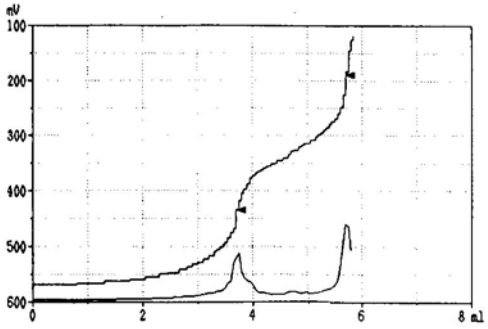
(1) Example of Fe^{2+}



Measurement results on Fe^{2+}

Sample No.	Sample volume (mL)	Titration value (mL)	Concentration (g/L)
1	1	2.052	11.53
2	1	2.051	11.52
	Avg.		11.53 g/L
	Std. Dev.		0.004 g/L
	C.V.		0.035 %

(2) Example of Fe^{3+} and Cu^{2+}



Measurement results on Fe^{3+}

Sample No.	Sample volume (mL)	Titration value (mL)	Concentration (g/L)
1	1	2.052	11.53
2	1	2.051	11.52
	Avg.		11.53 g/L
	Std. Dev.		0.004 g/L
	C.V.		0.035 %

Measurement results on Cu^{2+}

Sample No.	Sample volume (mL)	Titration value (mL)	Concentration (g/L)
1	0.1	1.920	61.37
2	0.1	1.983	63.39
	Avg.		62.38 g/L
	Std. Dev.		1.42 g/L
	C.V.		2.28 %

5. Outline

(1) About chelate titration by potentiometric detection method

This section used potentiometric method for end point detection in chelate titration to titrate two components with fractionation. While it is generally measured by photometric titration using an indicator, photometric titration is not appropriate when two components are titrated with fractionation as was this sample.

(2) About measurement of Cu^{2+}

Besides this method, there is another quantification method for Cu^{2+} in which the reductive power of I^- ion against Cu^{2+} is applied. Though it cannot be applied for this sample since Fe^{3+} exists, it is applicable if there are no other components that may oxidize the iodide ion. In this method, iodide ion is oxidized quantitatively by Cu^{2+} and iodine is released in the equivalent quantity to Cu^{2+} when the sample is added to an acidic solution containing potassium iodide.

$$2Cu^{2+} + 4I^- \rightarrow 2CuI + I_2$$

Then potentiometric titration is conduced on the released iodine using sodium thiosulfate titrant.

Key words

Etching solution, ferrous, ferric, cupric, fractionation titration

Hitachi High-Technologies Corporation
Head Office 1-24-14, Nishishinbashi,Minato-Ku,Tokyo 105-8717, Japan
Tel : 81-3-3504-7239 Fax : 81-3-3835-7302
http://www.hitachi-hitech.com

Hiranuma Sangyo Co.,Ltd.
1739, Motoyoshidacho, Mito-City, Ibaraki 310-0836, Japan
Tel : 81-29-247-6411 Fax : 81-29-247-6942
http://www.hiranuma.com