

Application Note

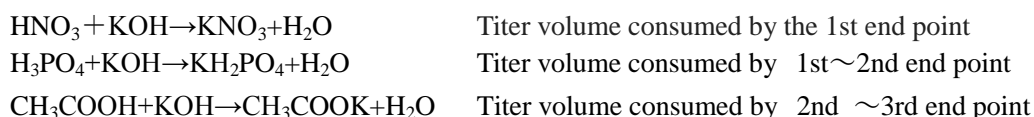
Determination of mixed acids (nitric acid, phosphoric acid, acetic acid) in etchant for aluminum

Industry	:	Metals
Instrument	:	Automatic potentiometric titrator
Measurement method	:	Potentiometric titration / Neutralization titration
Standards	:	-

1. Scope

Nitric acid, phosphoric acid and acetic acid are contained as an acidic component in the etchant under manufacturing process of aluminum. Each concentration in the acidic component affects the performance and property of the etchant. Therefore, controlling the concentration of each component is important.

In this application note, determination of nitric acid, phosphoric acid and acetic acid concentration in a non-aqueous solvent by neutralization titration are described. Strength of the each acid in water can not be detected separately, however, in organic solution, it can be detected separately and this phenomenon is taken in this application. In this titration method, three end-points are detected. Each end point corresponds to the following chemical reaction.



2. Precautions

- 1) The standardization of the titrant is in accordance with JIS K 8001 or ISO 6531-1.
- 2) Store the titrant in a container made of resin. Please attach the Zeolite cylinder to suppress the intrusion of carbon dioxide.

3. Post-measurement procedure

After measurement, wash the electrode with pure water. After that, please immerse the electrode in pure water and keep it.

4. Apparatus

Main unit : Automatic potentiometric titration system (preamplifier:STD)
 Electrode : Combined Glass Electrode
 (Internal liquid of reference electrode: 1 mol / L lithium chloride / ethanol solvent)

5. Reagents

Titration solution: 0.1 mol / L potassium hydroxide (ethanol solution)
 Titration solvent: Propylene glycol and ethanol mixed in the same volume

6. Procedure

- Measurement -

- 1) Weigh approximately 0.5 g of sample into a 200 mL beaker.
- 2) Add about 100 mL titration solvent and dissolve the sample.
- 3) Titrate with 0.1 mol / L potassium hydroxide (ethanol solution).

7. Calculation

$$\text{HNO}_3(\text{wt}\%) = (\text{EP1} - \text{BL1}) \times \text{TF1} \times \text{C1} \times \text{K1} / \text{S}$$

$$\text{H}_3\text{PO}_4(\text{wt}\%) = (\text{EP2} - \text{EP1} - \text{BL1}) \times \text{TF1} \times \text{C2} \times \text{K1} / \text{S}$$

$$\text{CH}_3\text{COOH}(\text{wt}\%) = (\text{EP3} - \text{EP2} - \text{BL1}) \times \text{TF1} \times \text{C3} \times \text{K1} / \text{S}$$

- EP1 : Titer volume consumed by the 1st end point(mL)
- EP2 : Titer volume consumed by the 2nd end point(mL)
- EP3 : Titer volume consumed by the 3rd end point(mL)
- BL1 : Blank value(0.000mL)
- TF1 : Factor value of titrant (1.0340)
- C1 : Concentration conversion factor 1(6.300 mg/mL)
- C2 : Concentration conversion factor 2(9.800 mg/mL)
- C3 : Concentration conversion factor 3(6.005 mg/mL)
- K1 : Unit conversion factor(0. 1)
- S : Sample size(g)

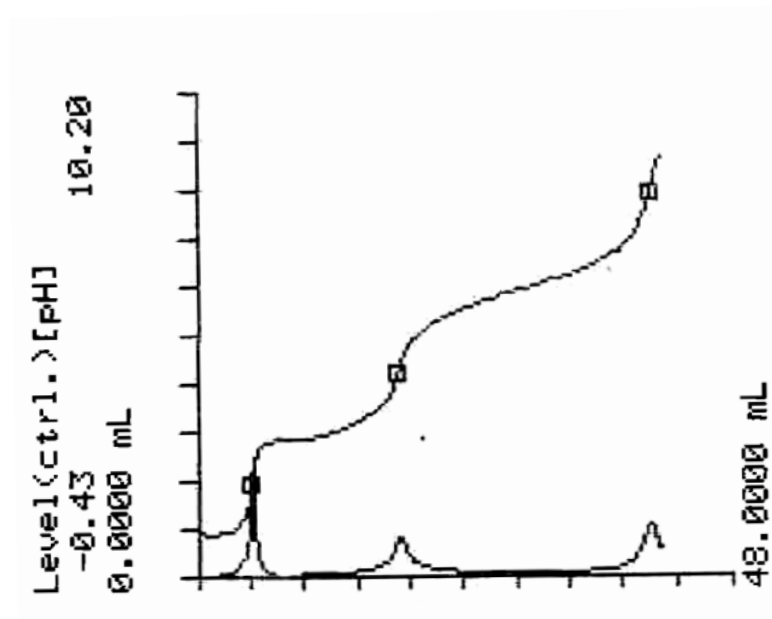
8. Example

-Titration parameter-

<u><Titr.Mode></u>	:Auto Intermit	<u><Ctrl.Para></u>	
		Number of EP	: 3
<u><Titr.Form></u>	:EP Stop	End Sense	: Set
		dE	: 20dE
<u><Titr.Para></u>	: 1	dmL	: 30dE/dmL
Burette No.	: 80(mL)	Gain	: 1
Max. Volume	: Ch1, pH	Stirrer Speed	: 4
Channel/Unit(Ctrl.)	: Off	Data sampling	: standard
Channel/Unit(Ref.)	: standard	Ctrl. Speed	: standard
pH Polarity	: Negative	Other Control	: standard
Titr.Type Check	: Auto		
Direction	: 3 (s)		
Wait Time	: None		

(The measurement parameter and the titration curve are an example.)

-Titration curve and results-



Five types of samples (●, ■, ▲, ○, △) were prepared and titrated. The measurement results are shown in Table 1.

Table1 Measurement result of each sample

Sample symbol	nitric acid			phosphoric acid			Acetic acid		
	concentration (%)	Average value (%)	Absolute error (%)	concentration (%)	Average value (%)	Absolute error (%)	concentration (%)	Average value (%)	Absolute error (%)
▲	6.65	6.69	-0.04	29.58	29.79	-0.21	30.28	30.91	-0.63
■	8.31	8.37	-0.06	15.10	15.47	-0.36	61.60	62.87	-1.28
●	11.67	11.78	-0.11	10.23	10.63	-0.40	4.14	4.20	-0.06
○	0.99	0.96	0.03	60.01	60.42	-0.42	14.31	14.57	-0.26
△	3.02	3.00	0.02	60.24	60.90	-0.66	1.04	1.08	-0.04
Correlation coefficient	1.0000			1.0000			1.0000		

Table 2 shows detailed measurement results of each sample.

Table 2 Details of measurement results

Sample symbol		Sample (g)	Titrant Factor	EP1 Titer (mL)	nitric acid (wt%)	EP2 Titer (mL)	phosphoric acid (wt%)	EP3 Titer (mL)	Acetic acid (wt%)
▲	1	0.4527	1.0340	4.6493	6.69	17.9383	29.75	40.4771	30.91
	2	0.4210	1.0340	4.3138	6.67	16.6736	29.75	37.7722	31.12
	3	0.4206	1.0340	4.3215	6.69	16.7168	29.86	37.5139	30.70
	Mean(wt%)	-	-	-	6.69	-	29.79	-	30.91
	S.D.(wt%)	-	-	-	0.01	-	0.07	-	0.21
	R.S.D.(%)	-	-	-	0.15	-	0.22	-	0.67
	MAX-MIN(wt%)	-	-	-	0.02	-	0.12	-	0.42
■	1	0.4370	1.0340	5.6033	8.35	12.2516	15.42	56.1940	62.44
	2	0.4174	1.0340	5.3682	8.38	11.7725	15.55	54.1236	63.00
	3	0.4153	1.0340	5.3460	8.39	11.6714	15.43	53.9290	63.18
	Mean(wt%)	-	-	-	8.37	-	15.47	-	62.87
	S.D.(wt%)	-	-	-	0.02	-	0.07	-	0.39
	R.S.D.(%)	-	-	-	0.21	-	0.46	-	0.62
	MAX-MIN(wt%)	-	-	-	0.03	-	0.13	-	0.74
●	1	0.4456	1.0340	8.0615	11.79	12.7429	10.65	15.7251	4.16
	2	0.4671	1.0340	8.4363	11.77	13.3425	10.64	16.5074	4.21
	3	0.4863	1.0340	8.7997	11.79	13.8880	10.60	17.2069	4.24
	Mean(wt%)	-	-	-	11.78	-	10.63	-	4.20
	S.D.(wt%)	-	-	-	0.01	-	0.02	-	0.04
	R.S.D.(%)	-	-	-	0.10	-	0.23	-	0.99
	MAX-MIN(wt%)	-	-	-	0.02	-	0.04	-	0.08
○	1	0.5196	0.9935	0.7974	0.96	33.1008	60.53	45.7143	14.48
	2	0.5237	0.9935	0.8049	0.96	33.3279	60.47	46.1954	14.66
	3	0.5197	0.9935	0.7940	0.96	32.9639	60.27	45.6523	14.57
	Mean(wt%)	-	-	-	0.96	-	60.42	-	14.57
	S.D.(wt%)	-	-	-	0.00	-	0.14	-	0.09
	R.S.D.(%)	-	-	-	0.31	-	0.23	-	0.60
	MAX-MIN(wt%)	-	-	-	0.01	-	0.26	-	0.18
△	1	0.5371	0.9935	2.5577	2.98	36.1562	60.91	37.1457	1.10
	2	0.5458	0.9935	2.6202	3.00	36.7371	60.86	37.7501	1.11
	3	0.5286	0.9935	2.5370	3.00	35.6176	60.93	36.5301	1.03
	Mean(wt%)	-	-	-	3.00	-	60.90	-	1.08
	S.D.(wt%)	-	-	-	0.01	-	0.04	-	0.04
	R.S.D.(%)	-	-	-	0.46	-	0.06	-	3.94
	MAX-MIN(wt%)	-	-	-	0.02	-	0.07	-	0.08

9. Summary

Measurement result of nitric acid concentration was obtained with good accuracy. However, measurement result of phosphoric acid and acetic acid tends to be larger deviation when these concentrations are higher. Therefore, the accuracy of these acids became worse than nitric acids. However, the difference between the maximum and minimum is only at most about 0.7 wt%, therefore, it is considered that these results are also obtained with sufficient accuracy.

This method is effective and easy method to determine the concentration of each acids without any requirement of complicated preparation process. However, the detection limit and accuracy depend on the concentration. In case that sample testing is necessary to verify if this method is effective, please contact us.