Application Note

Fractional determination of sulfuric acid, hydrofluoric acid, and hexafluorosilicic acid

Industry	Chemicals
Instrument	Automatic potentiometric titrator
Measurement method	Potentiometric titration / Neutralization titration
Standards	

1. Scope

This Application Note introduces an example of the measurement of sulfuric, hydrofluoric and hexafluorosilicic acids present in a polishing bath solution used for glass parts, in which the respective acids were quantitated in separate analyses (8. Notes).

2. Post-measurement procedure

Combined glass electrodes should be stored as follows.

- Seal the electrolyte refill port of the combined glass electrode with a rubber stopper.
- For short-term storage (less than one month) store immersed in pure water.
- For long-term storage (longer than one month) store immersed in a solution of pH 4 standard solution and 3.3 mol/L KCl solution mixed in an equal volume ratio.

3. Apparatus

Equipment	Automatic potentiometric titrator (preamplifier STD)
Electrode	Combined glass electrode (electrolyte: 3.3 mol/L potassium chloride solution)
	Temperature compensation electrode

4. Reagents

Titrant	1mol / L and 0.2 mol/L sodium hydroxide solution
Additional reagent	Saturated potassium nitrate solution
Others	pH 7 and pH 9 standard solutions, ice chips

5. Procedure

- Titration 1 Measurement of sulfuric acid -

1) Transfer the sample to a plastic beaker and measure its mass.
2) Heat on a hot plate set at 200 ºC for 1 hour.
3) After cooling, add 100mL ion-exchanged water and titrate with 1 mol/L sodium hydroxide solution. The end point is indicated by the inflection point of the titration curve.

- Titration 2 Measurement of total hydrogen ion* -

*When measuring total hydrogen ions, the temperature needs to be less than 10°C.

1) Calibrate the glass electrode with pH7 and pH9 standard solutions.
2) Transfer the sample to a plastic beaker and measure its mass.
3) Add 20 mL of saturated potassium nitrate solution and an ice cube made from pure water.
4) After adding 80 mL of pure water, titrate with 1mol/L sodium hydroxide solution. The endpoint occurs when the sample's pH reaches 8.2.

- Titration 3 Measurement of hexafluorosilicic acid and hydrofluoric acid -

1) After measurement of total hydrogen ion content, cover the sample beaker with a watch glass.
2) Heat on a hot plate until the sample comes to a boil.
3) After the solution is cooled down to below 80 °C, titrate with 0.2 mol/L sodium hydroxide solution to obtain the endpoint (indicated by the inflection point of the titration curve).

6. Calculation

- Titration 1 -

Sulfuric acid (wt%) = (EP1 - BL1) × TF × K1 × C1 / S

EP1	Titration volume (mL)
BL1	Titration amount (mL) of Blank test = 0 (mL)
TF	Factor of Titrant = 0.9921
C1	Concentration conversion coefficient =0.04904 (g/mL)
K1	Unit Conversion coefficient = 100
S	Sample size (g)

- Titration 2 -

Total hydrogen ion (mol/kg) = (EP1 - BL1) × TF × K1 × C1 / S

EP1	Titration volume (mL)
BL1	Titration amount (mL) of Blank test = 0 (mL)
TF	Factor of Titrant = 0.9921
K1	Unit Conversion coefficient = 1000
C1	Concentration conversion coefficient = 0.001 (mol/mL)
S	Sample size (g)

- Titration 3 -

・Hexafluorosilicic acid (wt%) = (EP1 - BL1) × TF × K1 × C1 / S

EP1	Titration volume (mL)
BL1	Titration amount (mL) of Blank test = 0 (mL)
TF	Factor of Titrant = 1.0027
K1	Unit Conversion coefficient = 0.1
C1	Concentration conversion coefficient = 7.204 (mg/mL)
S	Sample size (g)

・Hydrogen ions from hexafluorosilicic acid (mol/kg) = EP1 × TF × C2 / S × K1

EP1	Titration volume (mL)
TF	Factor of Titrant = 1.0027
K2	Unit Conversion coefficient = 1000
C2	Concentration conversion coefficient = 0.0001 (mol/mL)
S	Sample size (g)

・Hydrofluoric acid (wt%) = (SMW - BSEQN × K3 - CO2) × C3 × K4

SMW	Measured total hydrogen ion (mol/kg)
SEQN	Measured concentration of sulfuric acid (%)
K3	Unit Conversion coefficient = 0.20392
CO2	Hydrogen ions from H_2SiF_6 (mg/mL)
C3	Concentration conversion coefficient = 20.01 (g/moL)
K4	Unit Conversion coefficient = 0.1

7. Example

— Parameter —

- Titration 1 Measurement of sulfuric acid -

<Titr. Mode>	Auto Int.	**<Ctrl. Para.>**	
<Titr. Form>	EP Stop	Number of EP	1
		End Sense	Auto
<Titr. Para.>		Gain	1
Max Volume	50.0 (mL)	Data Sampling	Standard
Channel/Unit (ref.)	Ch1, pH	Ctrl. Speed	Standard
Wait Time	0 (s)	Other Control	Standard
Dose Mode	None	Stirrer Speed	4

- Titration 2 Measurement of total hydrogen ion -

<Titr. Mode>	Auto Int.	**<Ctrl. Para.>**	
<Titr. Form>	EP Stop	Number of EP	1
		End Sense	Auto
<Titr. Para.>		1st EP Level	8.2 (pH)
Max Volume	40.0 (mL)	Gain	1
Channel/Unit (ref.)	Ch1, pH	Data Sampling	Standard
Wait Time	0 (s)	Ctrl. Speed	Standard
Dose Mode	None	Other Control	Standard
		Stirrer Speed	4

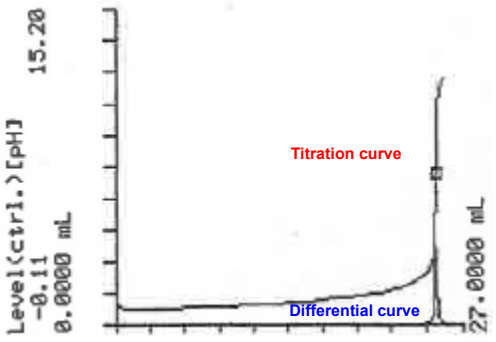
- Titration 3 Measurement of hexafluorosilicic acid and hydrofluoric acid -

<Titr. Mode>	Auto Int.	**<Ctrl. Para.>**	
<Titr. Form>	EP Stop	Number of EP	1
		End Sense	Auto
<Titr. Para.>		Gain	1
Max Volume	20.0 (mL)	Data Sampling	Standard
Channel/Unit (ref.)	Ch1, pH	Ctrl. Speed	Standard
Wait Time	0 (s)	Other Control	Standard
Dose Mode	None	Stirrer Speed	4

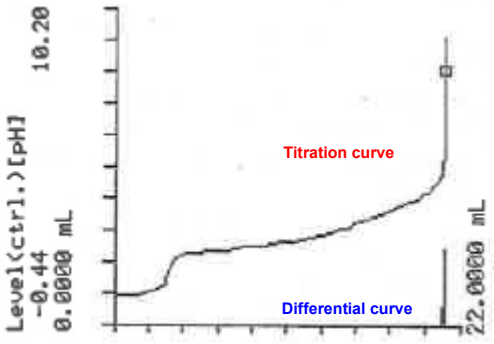
(Listed above are example settings. Availability of settings may vary by instrument model.)

— Example of Titration curve —

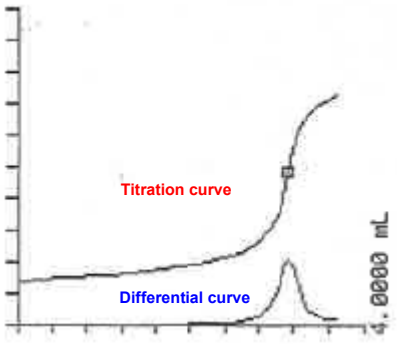
・Measurement of sulfuric acid



・Measurement of total hydrogen ion



・Measurement of hexafluorosilicic acid



— Measurement results —

Table 1 Measurement results of sulfuric acid

	Sample (g)	Titration (mL)	Sulfuric acid (%)
1	5.0537	24.8032	23.88
2	5.0239	24.7987	24.02
3	5.0059	24.6565	23.96
Mean	-	-	23.95
SD	-	-	0.07
RSD (%)	-	-	0.29

Table 2 Measurement results of Total hydrogen ion

	Sample (g)	Titration (mL)	Total hydrogen ion (mol/kg)
1	3.0530	20.8360	6.7709
2	3.0484	20.8116	6.7731
3	3.0092	20.5353	6.7703
Mean	-	-	6.7714
SD	-	-	0.0015
RSD (%)	-	-	0.0223

Table 3 Measurement results of hexafluorosilicic acid and hydrofluoric acid

	Sample (g)	Titration (mL)	Hydrofluoric acid (%)	Hexafluorosilicic acid (%)
1	3.0530	3.1027	3.57	0.73
2	3.0484	3.1066	3.58	0.74
3	3.0092	3.0818	3.57	0.74
Mean	-	-	3.57	0.74
SD	-	-	0.01	0.01
RSD (%)	-	-	0.16	1.35

8. Notes

- Titration 1 Measurement of sulfuric acid -

By heating the sample, hydrofluoric acid and hexafluorosilicic acid are volatilized and completely removed, leaving behind non-volatile sulfuric acid. The concentration of this sulfuric acid is determined by titrating with sodium hydroxide.

- Titration 2 Measurement of total hydrogen ion -

A new sample is prepared, and potassium nitrate is added in order to isolate hydrogen from the hexafluorosilicic acid and produce nitric acid (see the reaction below). This is titrated with sodium hydroxide to calculate the total hydrogen ion concentration of the sample.

$$H_2SiF_6 + 2KNO_3 \rightarrow K_2SiF_6\downarrow + 2HNO_3$$

When measuring total hydrogen ions, the temperature needs to be less than 10°C. The reason for this is to prevent the following reaction.

$$K_2SiF_6 + 2H_2O \rightarrow 2KF + SiO_2 + 4HF$$

- Titration 3 Measurement of hexafluorosilicic acid and hydrofluoric acid -

The titrated sample solution from Titration 2 (see above) is heated to generate hydrofluoric acid, and this process is shown below.

$$K_2SiF_6 + 2H_2O \rightarrow 2KF + SiO_2 + 4HF$$

Free hydrofluoric acid is then titrated with sodium hydroxide. 4 mol of hydrofluoric acid corresponds to 1 mol of hexafluorosilicic acid. The concentration of hydrofluoric acid can be calculated by subtracting the hydrogen ion concentrations of the sulfuric and hexafluorosilicic acids from the sample's total hydrogen ion concentration.

The automatic potentiometric titrator can determine the concentrations of sulfuric acid, hydrofluoric acid, and hexafluorosilicic acid.