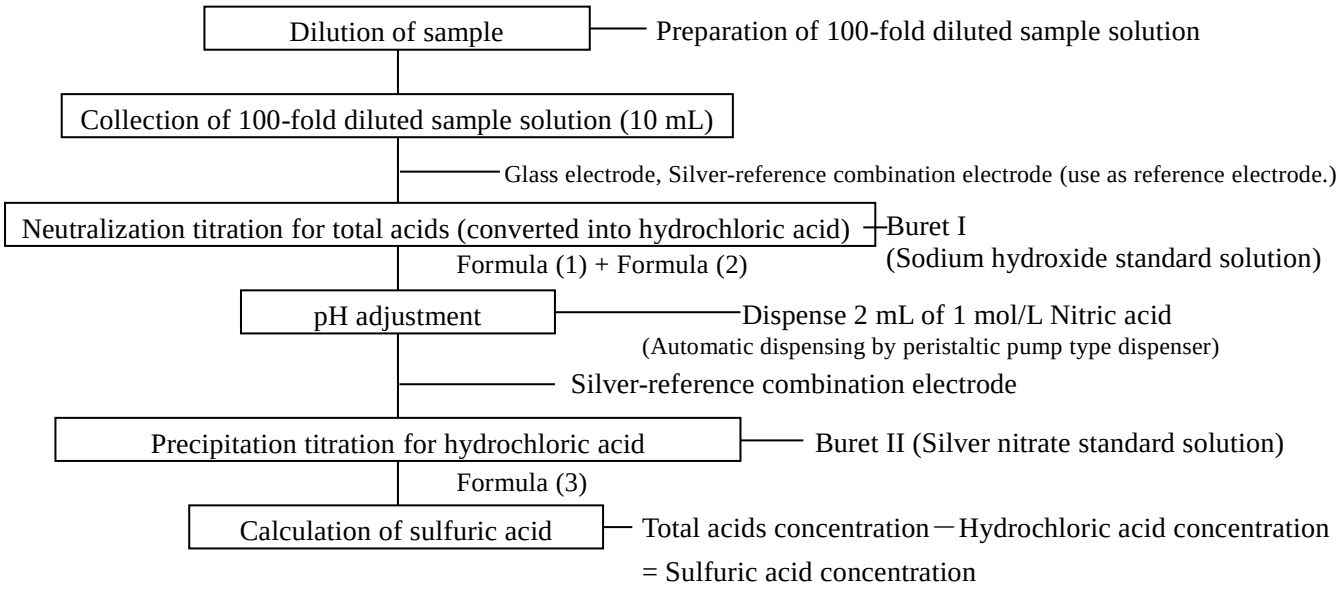
HIRANUMA APPLICATION DATA	Automatic Titrator	Data No.	J5	Apr. 5, 2019
Inorganic acids & Mixed acids	**Fractional determination of hydrochloric acid and sulfuric acid**			

1. Abstract

The mixed solution of hydrochloric acid and sulfuric acid works as strong acid, and also has the strong oxidizability and solvency. It is used as the surface treatment solution for metals, glass products, and semiconductors. Hydrochloric acid and sulfuric acid are strong acids, therefore the fractional determination by neutralization titration is difficult.

The total acids of hydrochloric acid and sulfuric acid in the mixed solution are determined first by neutralization titration in this report. Nitric acid is added to the sample solution continuously to adjust the pH. Finally, the concentration of hydrochloric acid is determined by precipitation titration, the concentration of sulfuric acid is calculated by subtracting the concentration of hydrochloric from the total acids concentration.

The example of fractional determination for hydrochloric acid and sulfuric acid with additional burets are introduced in this report.



$$H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + H_2O \quad \cdots (1)$$

$$HCl + NaOH \rightarrow NaCl + H_2O \quad \cdots (2)$$

$$HCl + AgNO_3 \rightarrow AgCl + HNO_3 \quad \cdots (3)$$

2. Configuration of instruments and reagents

(1) Configuration of instruments

Main unit : Hiranuma Automatic Titrator COM series

Options : One buret, Peristaltic pump type dispenser

Electrodes : Glass electrode GE-101B for total acids measurement
Connect to IE-1.
Silver -reference electrode AGR-811Z for hydrochloric acid measurement
(Double junction type) Connect to IE-2 and RE-2.

(2) Reagents

Titrant	:	0.1 mol/L Sodium hydroxide standard solution for total acids measurement
		0.1 mol/L Silver nitrate for hydrochloric acid measurement
Additive solution	:	2 mL of 1 mol/L Nitric acid solution for pH adjustment

3. Measurement procedure

(1) Dispense 1 mL of sample into 30 mL DI water in a volumetric flask with volumetric pipette. Cool it to room temperature and dilute to 100 mL with DI water.

(2) Dispense 10 mL of diluted sample solution into a 100 mL beaker with volumetric pipette.

(3) Add 40 mL of DI water.

(4) Immerse electrodes and start titration with 0.1 mol/L sodium hydroxide standard solution.

(5) After the procedure (4), 2 mL of 1 mol/L nitric acid is automatically dispensed by optional dispenser.

(6) Titrate with 0.1 mol/L silver nitrate standard solution with optional buret.

4. Measurement conditions and results

Examples of titration conditions

(1) Titration for total acids with sodium hydroxide standard solution (converted into hydrochloric acid)

Cndt No.	1							
Method	Auto		ConstantNo.	1		Mode No.	20	
Buret No.	1		Size	10.000	mL	Pre Int	0	sec
Amp No.	1		Blank	0	mL	Del K	9	
D. Unit	pH		Molarity	0.100	mol/L	Del Sens	0	mV
S-Timer	5	sec	Factor	1.004		Int Time	2	sec
C.P. mL	0	mL	K	1.000		Int Sens	3	mV
T Timer	0	sec	L	0.010		Brt Speed	2	
D.P. mL	0	mL	Unit	mol/L		Pulse	40	
End Sens	1000		Formula					
Over mL	0	mL		(D-B)*K*F*M/(S*L)				
Max.Vol.	20	mL	Decimal Places	3				
			Auto In Pram.	Non				

K: Equivalent of NaOH to HCl L: Dilution ratio

(2) Dispense 1 mol/L nitric acid

Cndt No.	2	
Method	Disp	
Buret No.	3	
S-Timer	0	sec
Disp Vol.	2	mL

(3) Titration for hydrochloric acid with silver nitrate standard solution

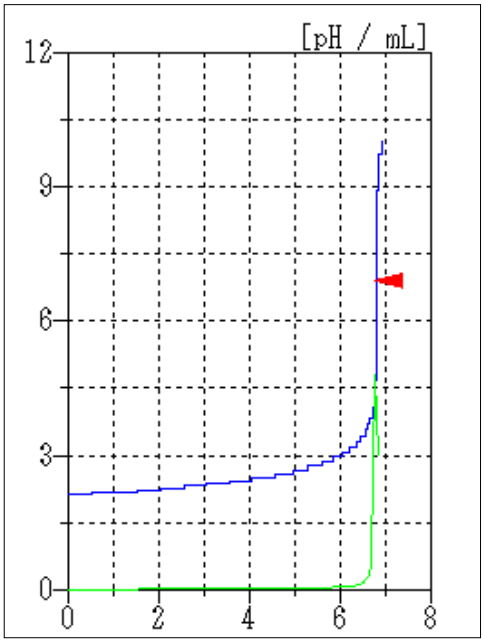
Cndt No.	3							
Method	Auto		ConstantNo.	3		Mode No.	6	
Buret No.	2		Size	10.000	mL	Pre Int	0	sec
Amp No.	2		Blank	0.0000	mL	Del K	2	
D. Unit	mV		Molarity	0.100	mol/L	Del Sens	0	mV
S-Timer	5	sec	Factor	1.005		Int Time	3	sec
C.P. mL	0	mL	K	1.000		Int Sens	3	mV
T Timer	0	sec	L	0.010		Brt Speed	2	
D.P. mL	0	mL	Unit	mol/L		Pulse	40	
End Sens	300		Formula					
Over mL	0.2	mL		(D-B)*K*F*M/(S*L)				
Max.Vol.	20	mL	Decimal Places	4				
			Auto In Pram.	Non				

(4) Calculation for sulfuric acid concentration

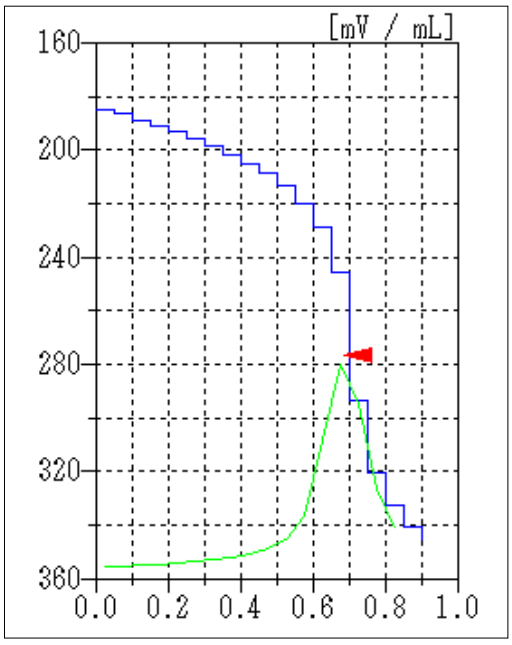
Cndt No.	4			
Method	Calc			
		ConstantNo.	4	
		Size	10.000	mL
		Blank	0.000	mL
		Molarity	0.100	mol/L
		Factor	1.000	
		K	1.000	
		L	0.01	
		Unit	mol/L	
		Formula		
			(CA-CB)/2	
		Decimal Places	4	
		Auto In Pram.	Non	

Measurement results

Number of Measurement	Size (mL)	Dilution ratio	NaOH Titrant Volume (mL)	Total acids (mol/L) (converted into hydrochloric acid)	$AgNO_3$ Titrant Volume (mL)	Hydrochloric acid Conc. (mol/L)	Sulfuric acid Conc. (mol/L)
1			6.777	6.8041	0.683	0.6864	3.0589
2	10	1/100	6.776	6.8031	0.680	0.6834	3.0599
3			6.779	6.8061	0.682	0.6854	3.0603
Statistic calculation		Avg.		6.804 mol/L		0.685 mol/L	3.060 mol/L
		SD		0.002 mol/L		0.002 mol/L	0.001 mol/L
		RSD		0.022 %		0.223 %	0.02 %



Measurement of total acids



Measurement of hydrochloric acid

Examples of titration curves

5. Note

(1) Fractional determination of hydrochloric acid and sulfuric acid

The concentration of hydrochloric acid is measured by the determination of chloride ion in this method. This method cannot be applied to the sample containing chloride ion from other than hydrochloric acid.

(2) Control of titrant

The carbon dioxide gas absorber (soda lime) on reagent bottle has to be regularly exchanged because sodium hydroxide used for total acids determination readily absorbs carbon dioxide gas in the air.

Keywords: Fractional determination of hydrochloric acid and sulfuric acid, Neutralization titration, Precipitation titration