AQUACOUNTER Application Sheet	COM series	DATA No. J4	1st edition

Inorganic Acid

Fractionation quantification of nitric acid and hydrofluoric acid

1. Measurement outline

The mixture solution of nitric acid and hydrofluoric acid has strong oxidizing power as well as dissolving power in addition to its effect as a strong acid, and is used as the surface treatment solution for metals, glass products and semiconductors.

This section introduces an example in which the mixture solution of nitric acid and hydrofluoric acid was measured by non-aqueous titration (methanol solvent and acetone solvent) with potassium hydroxide titrant (alcoholic).

$HNO_3 + KOH \rightarrow KNO_3 + H_2O$ ---------- (1)

$HF + KOH \rightarrow KF + H_2O$ ---------- (2)

2. Reagents and Electrodes

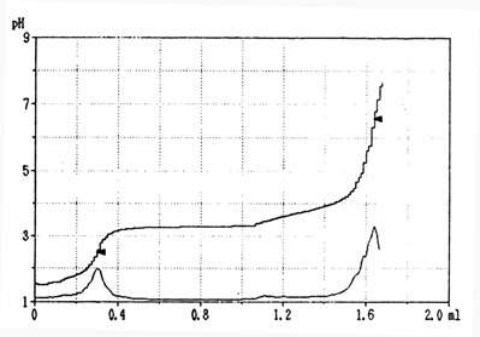
(1) Reagents	Titrant	0.1mol/L potassium hydroxide (alcoholic)
	Titration solvent	Methanol and acetone, approximately 50mL used for 1 measurement
(2) Electrodes *standard accessories	Indicator electrode	*Glass electrode GE-101B to IE jack
	Reference electrode	*Reference electrode RE-201 to RE jack

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

Master file 1 **Condition file 1 + 2** (for methanol solvent)		**Master file 2** **Condition file 1 + 2 + 3** (for acetone solvent)			
Condition file 1 (For HNO_3) / 2 (for HF)		**Condition file 1** (For HNO_3) / 2,3 (For HF)		**Mode No.**	6
Method	Auto	Method	Auto	Pre Int	0 sec
Amp No.	1	Amp No.	1	Del K	2
Buret No.	1	Buret No.	1	Del Sens	0 mV
Meas Unit	pH	Meas Unit	PH	Int Time	3 sec
S Timer	5 sec / 0	S Timer	5 sec / 0 / 0	Int Sens	3 mV
CP	0 mL	CP	0 mL	Brt Speed	2
DP	0.1 mL	DP	0.1 mL	Pulse	40
End Sens	5000	End Sens	5000 / 5000 / 1000		
Over mL	0	Over mL	0		
Max. Vol	20 mL	Max. Vol	20 mL / 20 / 1		
Unit	%	Unit	%		
Formula	(D-B)×K×F×M/(S×10)	Formula	(D-B)×K×F×M/(S×10)		
Blank	0	Blank	0		
Molarity	0.1	Molarity	0.1		
Factor	Titer of titrant	Factor	Titer of titrant		
K	63.01 / 40.02	K	63.01 / 40.02 / 40.02		

4. Measurement example

(1) Methanol solvent



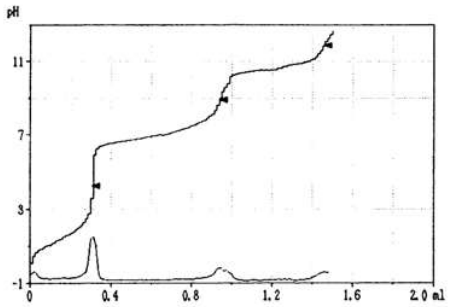
Measurement results on nitric acid

Sample No.	Sample volume (g)	Titration value (mL)	Concentration (%)
1	0.0520	0.304	3.555
2	0.0516	0.287	3.327
3	0.0515	0.296	3.457
	Avg.		3.446 %
	Std. Dev.		0.11 %
	C.V.		3.3 %

Measurement results on hydrofluoric acid

Sample No.	Sample volume (g)	Titration value (mL)	Concentration (%)
1	0.0520	1.357	5.229
2	0.0516	1.282	4.908
3	0.0515	1.337	5.151
	Avg.		5.117 %
	Std. Dev.		0.19 %
	C.V.		3.8 %

(2) Acetone solvent



Measurement results on nitric acid

Sample No.	Sample volume (g)	Titration value (mL)	Concentration (%)
1	0.0514	0.302	3.695
2	0.0522	0.315	3.795
3	0.0514	0.300	3.671
	Avg.		3.446 %
	Std. Dev.		0.11 %
	C.V.		3.3 %

Measurement results on hydrofluoric acid

Sample No.	Sample volume (g)	Titration value (mL)	Concentration (%)
1	0.0514	0.633	4.919
2	0.0522	0.611	4.675
3	0.0514	0.662	5.145
	Avg.		4.913 %
	Std. Dev.		0.24 %
	C.V.		4.8 %

5. Outline

(1) About fractionation titration of nitric acid and hydrofluoric acid

Since both nitric acid and hydrofluoric acid are strong acids, fractionation titration of these two is difficult using potentiometric titration in aqueous solution. Their titration curve shows 1 inflection point that indicates the total of nitric acid and hydrofluoric acid. It is possible to conduct fractionation quantification using the successive titration method by non-aqueous titration introduced in this section in which the titration curve for nitric acid and hydrofluoric acid shows 2 clear inflection points.

The titration curve when acetone solvent is used shows 3 inflection points as seen in the titration curve shown above. The first step indicates the end point for nitric acid, and the second and third steps indicate the end point for hydrofluoric acid. The second step indicates the end point by formation of KHF_2 (Formula 3) and the third step indicates the titration end point for KHF_2. Though the second step shows a clear end point, the third step has unclear end point and thus it is not practical.

$$2HF + KOH \rightarrow KHF_2 + H_2O \quad \text{——} \quad (3)$$

$$KHF_2 + KOH \rightarrow 2KF + H_2O \quad \text{——} \quad (4)$$

(2) About control on the titrant

Alcoholic KOH titrant is used as the titrant for this measurement. Since KOH tends to absorb carbon dioxide gas in air, it is important that the carbon dioxide gas absorbent (soda lime) on the reagent bottle cap be replaced regularly. In addition, alcoholic KOH tends to form crystals, and it is recommended that the titrant in burette cylinder be removed for storage if it is not to be used for a long period.

Key words

Nitric acid, hydrofluoric acid, fractionation titration of nitric acid and hydrofluoric acid, neutralization titration

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