HIRANUMA APPLICATION DATA	Automatic Titrator	Data No.	K7	Feb. 10, 2021
Organic acid	**Fractional determination of acetic acid and ammonium acetate**			

1. Abstract

The mixed solution of acetic acid and ammonium acetate is used as washing solution on the production process of semiconductor. There are some determination methods for the fractional determination of a weak acid and a salt of a weak acid. The formaldehyde addition method which is the most typical determination method is introduced in this report.

First, the neutralization titration is performed for acetic acid with sodium hydroxide (formula (1)). After that, acetic acid and hexamethylenetetramine equivalent to ammonium acetate are generated by adding formaldehyde (formula (2)). Finally, the generated acetic acid is continuously titrated with sodium hydroxide to determine the ammonium acetate.

$$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O \quad \cdots (1)$$

$$4CH_3COONH_4 + 6HCHO \rightarrow 4CH_3COOH + \underline{C_6H_{12}N_4} + 6H_2O \quad \cdots (2)$$

Hexamethylenetetramine

2. Configuration of instruments and reagents

(1) Configuration

Main unit : Automatic Titrator COM series

Option : One buret

Electrode : Glass electrode GE-101B

: Reference electrode RE-201Z

*Instead of above electrodes, the following combination electrodes are usable.

・GR-501BZ (Fixed sleeve type)

・GR-511BZ (Flexible sleeve type)

(2) Reagents

Titrant : 0.1 mol/L Sodium hydroxide standard solution

Additive : 35 % Formaldehyde

3. Measurement procedure

(1) Take 1 mL of sample into a 100 mL beaker with a volumetric pipette.

(2) Add about 50 mL of DI water.

(3) Immerse the electrodes to start titration. The titration with 0.1 mol/L sodium hydroxide for acetic acid, dispensing formaldehyde by an optional buret, and the titration with 0.1 mol/L sodium hydroxide for ammonium acetate are sequentially performed.

4. Measurement conditions and results

Examples of titration conditions

(1) Titration for acetic acid

Cndt No.	1							
Method	Auto		Constant No.	1		Mode No.	5	
Buret No.	1		Size	1	mL	Pre Int	0	sec
Amp No.	1		Blank	0	mL	Del K	5	
D. Unit	pH		Molarity	0.1	mol/L	Del Sens	0	mV
S-Timer	5	sec	Factor	1.006		Int Time	3	sec
C.P. mL	0	mL	K	60.05		Int Sens	3	mV
T Timer	0	sec	L			Brt Speed	2	
D.P. mL	0	mL	Unit	%		Pulse	40	
End Sens	300		Formula					
Over mL	0	mL	(D-B)*K*F*M/(S*10)					
Max Vol.	20	mL	Decimal places	3				
			Auto input parameter		None			

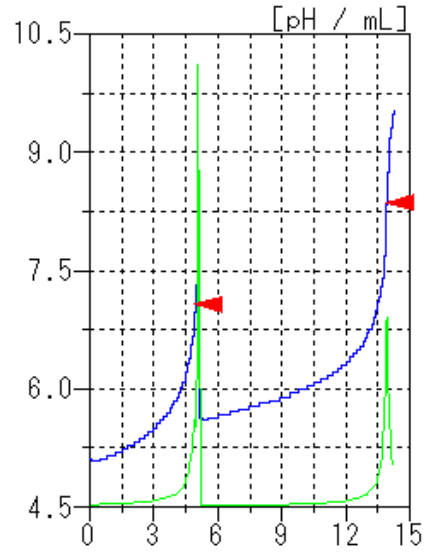
(2) Dispense formaldehyde.

Cndt No.	2	
Method	Disp	
Buret No.	2	
S-Timer	0	sec
Disp Vol.	5	mL

(3) Titration for ammonium acetate

Cndt No.	3							
Method	Auto		Constant No.	3		Mode No.	5	
Buret No.	1		Size	1	mL	Pre Int	0	sec
Amp No.	1		Blank	0	mL	Del K	5	
D. Unit	pH		Molarity	0.1	mol/L	Del Sens	0	mV
S-Timer	15	sec	Factor	1.006		Int Time	3	sec
C.P. mL	0	mL	K	77.08		Int Sens	3	mV
T Timer	0	sec	L	0		Brt Speed	2	
D.P. mL	0.3	mL	Unit	%		Pulse	40	
End Sens	500		Formula					
Over mL	0.3	mL	(D-B)*K*F*M/(S*10)					
Max Vol.	20	mL	Decimal places	3				
			Auto input parameter		None			

Measurement results



Example of titration curve

Measurement results of acetic acid

Number of Measurement	Size (mL)	Titrant Volume (mL)	Acetic acid Concentration (%)
1	1	4.928	2.977
2	1	4.920	2.972
3	1	4.916	2.970
Statistic calculation		Average	2.973 %
		Standard deviation	0.0036 %
		Coefficient of variation	0.121 %

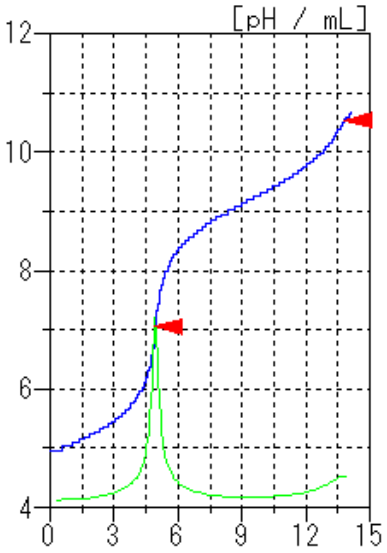
Measurement results of ammonium acetate

Number of Measurement	Size (mL)	Titrant Volume (mL)	Ammonium acetate Concentration (%)
1	1	8.976	6.960
2	1	8.965	6.952
3	1	8.957	6.945
Statistic calculation		Average	6.952 %
		Standard deviation	0.0075 %
		Coefficient of variation	0.108 %

5. Note

Another method for successive titration

There is a method without adding formaldehyde for fractional determination other than the method described in this report. The sample is titrated with sodium hydroxide standard solution in this method; the first inflection point indicates the end point for acetic acid, and the second inflection point is obtained as the end point for ammonium acetate. The advantage of this method is that the addition of formaldehyde is not required. On the other hand, the second end point of ammonium acetate sometimes gets unclear inflection point depending on the concentration of the ammonium acetate. The right figure shows an example of titration curve on this method.



Keywords: Acetic acid, Ammonium acetate, Sodium hydroxide, Formaldehyde, Neutralization titration

*Some measurement would not be possible depending on optional configuration of system.

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