HIRANUMA APPLICATION DATA	Automatic Titrator	Data No.	H6	Apr. 5, 2019
SODA PULP INDUSTRY	**Determination of sodium chloride in sodium hypochlorite**			

1. Abstract

Sodium hypochlorite is produced by having sodium hydroxide absorb chlorine gas. Produced sodium hypochlorite contains residual alkali (sodium hydroxide, sodium carbonate) and sodium chloride generated by the degradation of hypochlorous acid. The residual alkali is determined by neutralization titration, and sodium chloride is determined by precipitation titration. This report introduces an example of the determination for sodium chloride in the sodium hypochlorite with potentiometric titration as the following procedure: the titration for the total chlorine component (sodium hypochlorite + sodium chloride) is performed first. After that, sodium hypochlorite (available chlorine) is titrated by another method. Finally, sodium chloride is determined by the subtraction of sodium hypochlorite from the total chloride component.

The total sodium chloride (total chloride component) is determined according to the following formula (1) and (2): add hydrogen peroxide into a sample to degrade sodium hypochlorite, and generate sodium chloride as described in formula (1). Titrate with nitric acid standard solution until the pH goes down to 2 ~ 3. After the solution is acidified, determine the total sodium chloride with silver nitrate standard solution by precipitation titration as formula (2).

$$NaClO + H_2O_2 \rightarrow NaCl + H_2O + O_2 \quad \cdots\cdots\cdots \quad (1)$$

$$NaCl + AgNO_3 \rightarrow AgCl + NaNO_3 \quad \cdots\cdots\cdots\cdots\cdots \quad (2)$$

Regarding the determination of available chlorine, free iodine generated by the addition of potassium iodide as described in formula (3) is determined with sodium thiosulfate standard solution by redox titration as shown in formula (4).

$$NaClO + 2\,KI + H_2O \rightarrow I_2 + NaCl + 2KOH \quad \cdots\cdots\cdots \quad (3)$$

$$I_2 + 2\,Na_2S_2O_3 \rightarrow 2NaI + Na_2S_4O_6 \quad \cdots\cdots\cdots\cdots\cdots \quad (4)$$

2. Configuration of instruments and reagents

(1) Configuration

Main unit : Hiranuma Automatic Titrator COM series

Option : One buret, one buret head

Electrodes : <For total sodium chloride>

Glass electrode	GE-101B
Silver combination electrode	AGR-811Z (Double junction type)

<For available chlorine>

Platinum electrode	PT-301
Reference electrode	RE-201Z

(2) Reagents

<For total sodium chloride>

Titrant : 0.2 mol/L Silver nitrate standard solution,
0.1 mol/L Nitric acid standard solution

Additive : 3 % Hydrogen peroxide solution

<For available chlorine >

Titrant : 0.2 mol/L Sodium thiosulfate standard solution

Additive : 10 % Potassium iodide solution
2 mol/L Acetic acid solution

3. Measurement procedure

(1) Measurement for total sodium chloride

(i) Dispense 0.5 mL of sample into a 100 mL beaker with micropipette.

(ii) Add 50 mL of DI water.

(iii) Add 5 mL of 3 % hydrogen peroxide solution and degrade sodium hypochlorite.

(iv) Immerse the electrodes (GE-101B/AGR-811Z) into sample solution.
Titrate with 0.1 mol/L nitric acid standard solution and adjust the pH to 2 ~ 3.

(v) Titrate with 0.2 mol/L silver nitrate standard solution.

(2) Measurement for available chlorine

(i) Dispense 0.5 mL of sample into a 100 mL beaker with micropipette.

(ii) Add 50 mL of DI water.

(iii) Add 1 mL of 10 % potassium iodide solution.

(iv) Add 10 mL of 2 mol/L acetic acid solution.

(v) Immerse electrodes (PT-301/RE-201Z) and titrate with 0.2 mol/L sodium thiosulfate standard solution.

4. Measurement conditions and results

Examples of titration conditions

(1) Measurement for total sodium chloride

(i)Titration with 0.1 mol/L nitric acid standard solution

Cndt No.	1							
Method	Set		ConstantNo.	1		Mode No.	4	
Buret No.	1		Size	0.5	mL	Pre Int	0	sec
Amp No.	1		Blank	0	mL	Del K	9	
D. Unit	pH		Molarity	0.1	mol/L	Del Sens	0	mV
S-Timer	5	sec	Factor	1.004		Int Time	3	sec
C.P. mL	0	mL	K	0.00		Int Sens	3	mV
Direction	↓		L	0.000		Brt Speed	2	
T Timer	0	sec				Pulse	40	
D.P. mL	0	mL	Unit	mL				
End Point	3.0	pH	Formula	D				
Over mL	0.0	mL	Decimal Places	3				
Max.Vol.	20	mL	Auto In Pram.		Non			

(ii) Titration with 0.2 mol/L silver nitrate standard solution

Cndt No.	2							
Method	Auto		ConstantNo.	2		Mode No.	8	
Buret No.	2		Size	0.5	mL	Pre Int	0	sec
Amp No.	2		Blank	0	mL	Del K	5	
D. Unit	mV		Molarity	0.2	mol/L	Del Sens	0	mV
S-Timer	5	sec	Factor	1.000		Int Time	5	sec
C.P. mL	0	mL	K	58.44		Int Sens	3	mV
T Timer	0	sec	L	0.000		Brt Speed	2	
D.P. mL	0	mL				Pulse	40	
End Sens	100		Unit	%				
Over mL	0.2	mL	Formula	(D-B)*K*F*M/(S*10)				
Max.Vol.	20	mL	Decimal Places	4				
			Auto In Pram.		Non			

(2) Measurement for available chlorine (Calculation of sodium chloride concentration)

(i)Titration with 0.2 mol/L sodium thiosulfate standard solution

Cndt No.	3							
Method	Auto		ConstantNo.	3		Mode No.	5	
Buret No.	1		Size	0.5	mL	Pre Int	0	sec
Amp No.	2		Blank	0	mL	Del K	5	
D. Unit	mV		Molarity	0.2	mol/L	Del Sens	0	mV
S-Timer	5	sec	Factor	1.002		Int Time	3	sec
C.P. mL	0	mL	K	35.45		Int Sens	3	mV
T Timer	0	sec	L	0.000		Brt Speed	2	
D.P. mL	0	mL				Pulse	40	
End Sens	200		Unit	%				
Over mL	0.3	mL	Formula	(D-B)*K*F*M/(S*10)				
Max.Vol.	20	mL	Decimal Places	4				
			Auto In Pram.		Non			

(ii) Calculation of sodium chloride concentration

Cndt No.	4			
Method	Calc	ConstantNo.	4	
		Size	0.5	mL
		Blank	0	mL
		Molarity	0.2	mol/L
		Factor	0	
		K	14.80	※1
		L	0.8243	※2
		Unit	%	
		Formula	K-CA*L	
		Decimal Places	4	
		Auto In Pram.		Non

※1 Input the result of total sodium chloride.

※2 Conversion coefficient from available chlorine to sodium chloride (58.44(NaCl)/70.9(Cl_2))

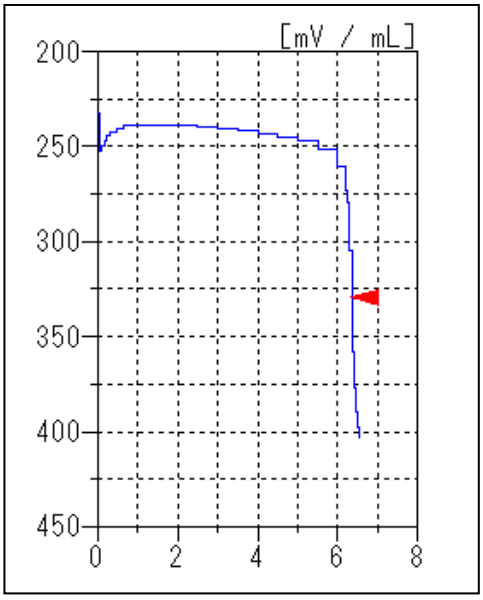
Measurement results

(1) Results of total sodium chloride

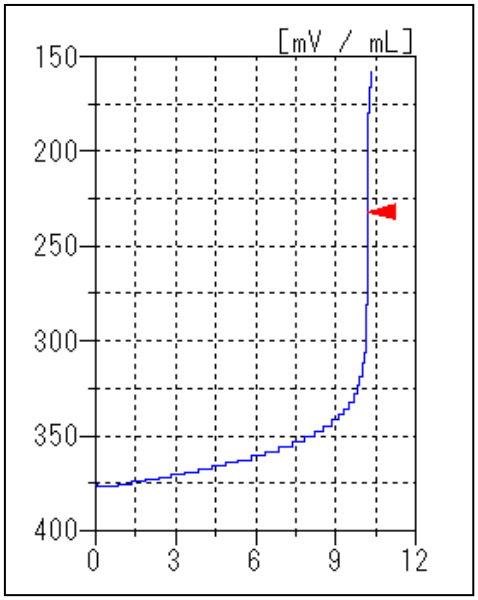
Number of Measurement	Size (mL)	Titrant Volume (mL)	Total sodium chloride Concentration (%)
1	0.5	6.329	14.795
2	0.5	6.324	14.783
3	0.5	6.339	14.818
Statistic calculation		Avg.	14.80 %
		SD	0.02 %
		RSD	0.12 %

(2) Results of available chlorine (Calculated results of sodium chloride concentration)

Number of Measurement	Size (mL)	Titrant Volume (mL)	Available chlorine Concentration (%)	Sodium chloride Concentration (%)
1	0.5	10.174	14.456	2.884
2	0.5	10.223	14.525	2.827
3	0.5	10.276	14.601	2.765
Statistic calculation	Average		14.52 %	2.83 %
	Standard deviation		0.07 %	0.06 %
	Coefficient of variation		0.50 %	2.11 %



Measurement for total sodium chloride



Measurement for available chlorine

Examples of titration curves

5. Note

1) Measurement for total sodium chloride

Residual sodium hypochlorite could cause measurement error. Addition of excess hydrogen peroxide is required to degrade sodium hypochlorite completely.

2) Measurement for available chlorine

The following tips can improve measurement accuracy.

i) Weigh a sample size quickly because available chlorine is unstable.

ii) Titrate free iodine immediately because the iodine generated by addition of potassium iodide is easy to volatilize. Addition of plenty potassium iodide is required because the volatilization of iodine depends on the concentration of added potassium iodide.

Keywords: Sodium hypochlorite, Sodium chloride, Residual alkali, Available chlorine, Precipitation titration

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