AQUACOUNTER Application Sheet	COM series	DATA No. H3	1st edition

Paper and Pulp — Quantification of trace chlorine ion in sodium hydroxide

1. Measurement outline

Trace amount of chlorine ion exists as an impurity included in sodium hydroxide besides sodium carbonate. The most typical quantification method of chlorine ion is potentiometric titration method with silver nitrate titrant. However, the potential change for titration curve near the end point tends to be extremely small when the concentration of chlorine ion is about 50ppm. In addition, the concentration of salts contained in the titrated solution is extremely high and the tendency for potential change near the end point to decrease is further promoted. This section introduces a measurement example applying potentiometric titration method using standard addition method for quantification of trace chlorine ion contained in 48% sodium hydroxide.

(1) Approximately 7g of sample is weighed precisely.
(2) To neutralize sodium hydroxide, 20mL sulfuric acid (1+1) is added. Then 50mL mixture solution of 2-propanol + purified water (1+1).
(3) 1mL standard 0.05mol/L hydrochloric acid solution is added.
(4) It is titrated with 0.01mol/L silver nitrate titrant.

$$Cl^- + AgNO_3 \rightarrow AgCl + NO_3^- \quad \text{---------- (1)}$$

(5) Measurement operations from (2) to (4) are conducted without adding the sample to calculate the titration value for standard 1mL of 0.05mol/L hydrochloric acid solution.
(6) Titration value for the sample is calculated by subtracting the titration value in section (5) (1mL standard hydrochloric acid) from the titration value in section (4) (1mL sample + 1mL standard hydrochloric acid solution).

2. Reagents and Electrodes

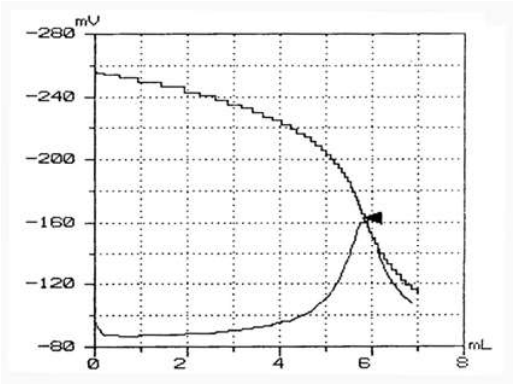
(1) Reagents	Titrant	0.01mol/L silver nitrate titrant
	Standard solution	0.05mol/L standard hydrochloric acid solution
	Loading buffer	50mL 2-propanol + purified water (1+1) mixture solution
(2) Electrodes	Indicator electrode	Silver indicator electrode AG-312 to IE jack (P/N D231259-A for titration in organic solvent)
	Reference electrode	Silver reference electrode MS-231 to RE jack (P/N D231243-A)

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

Master File No.1 Condition file: 1	
Method	AUTO
Amp No.	2
Buret No.	1
Meas Unit	mV
S-Timer	30 sec
CP	0 mL
DP	0 mL
End Sens	100
Over mL	2 mL
Max Vol	7 mL
Mode No.	20
Unit	ppm
Blank	Blank result value
Factor	Titer of the titrant
Molarity	0.01
K	58.44
Formula	(D-B)×K×F×M×1000 /S

Mode No.20	
Pre Int	0 sec
Del K	5
Del Sens	0 mV
Int Time	10 sec
Int Sens	3 mV
Brt Speed	2
Pulse	10

4. Measurement example



Measurement results on trace chlorine ion in NaOH

Sample No.	Measure-ment count	Sample volume (g)	Titration value (mL)	Concentra-tion (ppm)
Blank	1	1mL	5.040	
	2	〃	5.060	
Sample	1	7.4963	5.813	59.90
	2	7.4801	5.802	59.16
	3	7.4960	5.810	59.67
	Avg.			**59.58 ppm(NaCl)**
	Std. Dev.			**0.38 ppm**
	C.V.			**0.06 %**

5. Outline

About addition of organic solvent

In this measurement, 2-propanol was added to the titrated solution to conduct titration. In general, precipitation titration is ruled by solubility product constant for the formed precipitate. The smaller the solubility product constant is, the easier the end point detection becomes (potential change at end point becomes larger). In titrations in which precipitates with large solubility product constants, detection of titration end point becomes easier by reducing the solubility product constant for the formed precipitate with addition of non-aqueous solvent. As the non-aqueous solvent, alcohols and acetone that are mixed at any optional ratio with water are often used. The following provides the solubility product constants for various precipitates that are used in precipitation titration for reference.

Precipitate	Solubility product constant (K_{SP})	25℃
Ag2S	5.7×10^{-51}	
Ag(CN)2	1.8×10^{-19}	
AgI	1.5×10^{-16}	
AgCN	1.6×10^{-14}	
AgBr	5.2×1^{-13}	
AgCNS	1.2×10^{-12}	
AgCl	1.78×10^{-10}	
BaSO4	$1.1 - 2.0\times10^{-10}$	
PbSO4	1.1×10^{-8} (18℃)	
AgCNO	2.3×10^{-7}	

Key words

Quantification of trace chlorine ion in sodium hydroxide, precipitation titration, non-aqueous titration

Hitachi High-Technologies Corporation
Head Office 1-24-14, Nishishinbashi,Minato-Ku,Tokyo 105-8717, Japan
Tel : 81-3-3504-7239 Fax : 81-3-3835-7302
http://www.hitachi-hitech.com

Hiranuma Sangyo Co.,Ltd.
1739, Motoyoshidacho, Mito-City, Ibaraki 310-0836, Japan
Tel : 81-29-247-6411 Fax : 81-29-247-6942
http://www.hiranuma.com