AQUA COUNTER

AQUACOUNTER Application Sheet	COM series	DATA No. H9	1st edition
Paper and Pulp	**Quantification of NaOH, Na₂S and Na₂CO₃ in pulp cooking solution**		

1. Measurement outline

Among the chemical solutions used in pulp industry, concentration control on pulp cooking solution that mainly contains NaOH, Na$_2$S and Na$_2$CO$_3$ is an important process in control of pulp quality. The analysis method introduced in this section is called the SCAN method (Scandinavia method: Pulp, paper and hardboard testing committee). This section introduces a measurement example in which barium chloride is added to precipitate carbonate salt to titrate sodium hydroxide and sodium sulfide with hydrochloric acid and then formaldehyde is added to titrate the alkali hydroxide formed by its reaction with sulfide with hydrochloric acid. Titration is continued to titrate the carbonate salt successively in this section.

(1) Titration of sodium hydroxide (NaOH) and sodium sulfide

Barium chloride is added to the sample to precipitate and mask the carbonate salt.

$BaCl_2$ + CO_3^{--} → $BaCO_3$ + $2Cl^-$ ------------------------ (1)
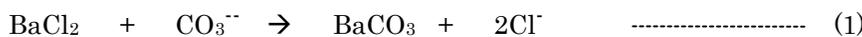
Sodium hydroxide and sodium sulfide are titrated with hydrochloric acid until pH is around 9.5. NaOH + 1/2 Na$_2$S is titrated (a mL).

$NaOH$ + HCl → $NaCl$ + H_2O ----------------------- (2)

Na_2S + HCl → $NaHS$ + $NaCl$ ------------------------ (3)
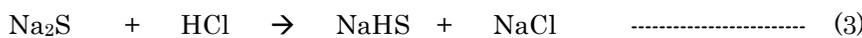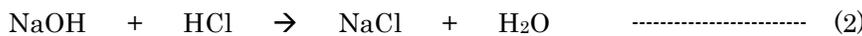
(2) Titration of sulfides (NaHS) and sulfur content

Titration is conducted successively to the previous titration of sodium hydroxide. When titration of sodium hydroxide is completed, formalin is added to react with NaHS and sulfur content and form sodium hydroxide. Titration is then continued with hydrochloric acid until pH is around 8.0. S^{--} + 1/2 Na$_2$S is titrated (b mL).

$HCHO$ + Na_2S + $2H_2O$ → $HOCH_2SH$ + $2NaOH$ ------------- (4)

$HCHO$ + $NaHS$ + H_2O → $HOCH_2SH$ + $NaOH$ ------------- (5)

(3) Measurement of carbonate salt (Na$_2$CO$_3$)

Successively to the previous titration of sulfides, the barium carbonate formed in Formula (1) is titrated with hydrochloric acid (C mL).

$BaCO_3$ + $2HCl$ → $BaCl_2$ + CO_2 + H_2O ------------- (6)
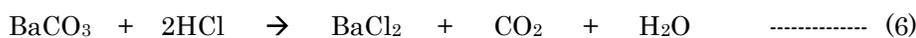
Na$_2$O conversion value of each alkaline component is calculated from the titration values a, b and c from the first to the third inflection points above.

NaOH = $62 / 2 \times (2a - b) f / S$ f : Titer for titrant

Na$_2$S = $62 / 2 \times 2 (a - b) f / S$ S : Sample collection volume (mL)

Na$_2$CO$_3$ = $62 / 2 \times (c - b) f / S$

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2. Reagents and Electrodes

(1) Reagents	Titrant	1mol/L hydrochloric acid titrant
	Added reagent solution	-10mL 15% $BaCl_2$ aqueous solution used for 1 measurement -5mL 38% HCHO used for 1 measurement
(2) Electrodes *standard accessories	Indicator electrode	*Glass electrode GE-101B
	Reference electrode	*Reference electrode RE-201

3. Measurement conditions example (for COM-1600S + 2 units of Buret B-2000-20)

Master File No.1

   Condition file: 1 + 2 + 3 + 4 + 5

Condition file.1 (For Disp. $BaCl_2$)		Condition file.3 (For Disp. HCHO)		Condition file.5 (For 3rd End point)		
Method	Disp	Method	Disp	Method	AUTO	
Buret No.	1	Buret No.	3	Amp No.	1	
S Timer	0 sec	S Timer	0 sec	Buret No.	2	
Disp volume	10 mL	Disp volume	5 mL	Meas Unit	pH	
				S Timer	60 sec	
Condition file.2 (For 1st End point)		Condition file.4 (For 2nd End point)		CP	0 mL	
Method	AUTO	Method	AUTO	DP	0 mL	
Amp No.	1	Amp No.	1	End Sens	100	
Buret No.	2	Buret No.	2	Over mL	0.5 mL	
Meas Unit	pH	Meas Unit	pH	Max. Vol.	40 mL	
S Timer	60 sec	S Timer	60 sec	Mode No.	9	
CP	0 mL	CP	0 mL	Unit	g/L	
DP	0 mL	DP	0 mL	Formula	z×6.2	
End Sens	100	End Sens	100	Blank	0	
Over mL	0 mL	Over mL	0 mL	Factor	Titer of titrant	
Max. Vol.	40 mL	Max. Vol.	40 mL	Molarity	1	
Mode No.	4	Mode No.	4			
Unit	g/L	Unit	g/L	**Mode. No.**	4	9
Formula	(x-y)×K	Formula	2×y×6.2	Pre Int	0	0
Blank	0	Blank	0	Del K	9	2
Factor	Titer of titrant	Factor	Titer of titrant	Del Sens	0	0
Molarity	1	Molarity	1	Int Time	3	5
K	6.2	K	6.2	Int Sens	3	3
				Brt Speed	2	2
				Pulse	40	40

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4. Measurement example

Measurement results on NaOH

Sample No.	Sample volume (mL)	Titration value (mL)	Concentration (%)
1	5	14.792	79.5894
2	5	14.822	79.7816
3	5	14.824	79.7940
Avg.			79.8 %
Std. Dev.			0.13 %
C.V.			0.17 %

Measurement results on Na₂S

Sample No.	Sample volume (mL)	Titration value (mL)	Concentration (%)
1	5	1.955	24.2420
2	5	1.954	24.2296
3	5	1.954	24.2296
Avg.			24.3 %
Std. Dev.			0.066 %
C.V.			0.27 %

Measurement results on Na₂CO₃

Sample No.	Sample volume (g)	Titration value (mL)	Concentration (%)
1	5	4.247	26.3314
2	5	4.264	26.4368
3	5	4.346	26.9452
Avg.			26.6 %
Std. Dev.			0.27 %
C.V.			1.0 %

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5. Outline

About automation of titration

Since this measurement is a successive titration with 3 inflection points and reagent dispensing operation is implemented at the beginning of titration as well as in the middle, it comprises of complex titration operations. It also applies to concentration calculation. It is possible to be freed from these complex measurement operations and calculations by utilizing the COM series. The titration sequence for this measurement will be dispensing + titration (first inflection point) + dispensing + titration (second inflection point) + titration (third inflection point). With COM series, such measurement sequence can be easily prepared and executed by connecting the condition files.

Key words

Scandinavia method, sodium hydroxide, sodium sulfide, sodium carbonate, neutralization titration, successive titration