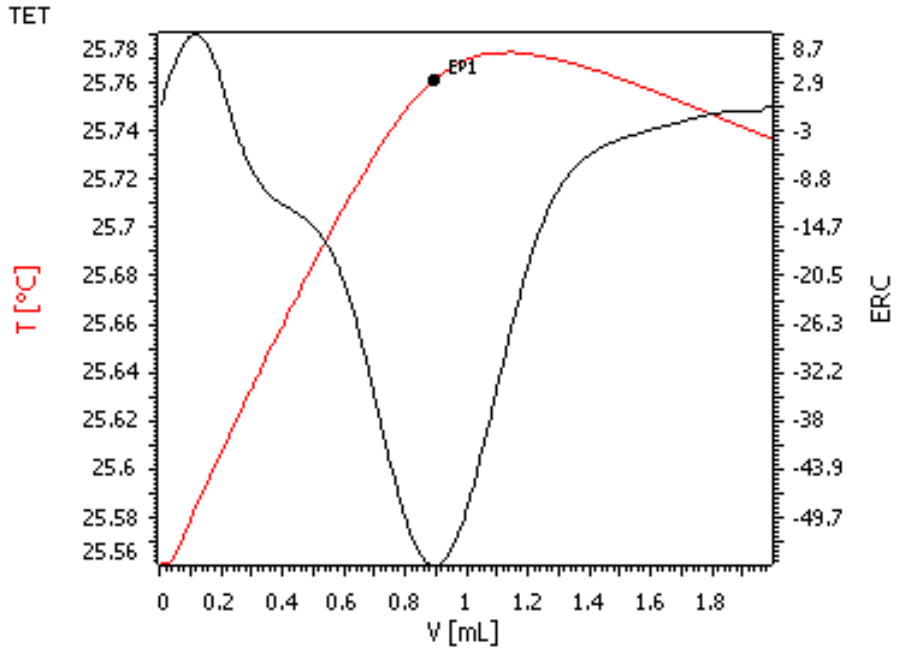
Titration Application Note H–117

Rapid determination of caustic and alumina in aluminate liquors



This Application Note looks at the determination of free caustic, total caustic, and alumina in Bayer process and other aluminate liquors. The method is not subject to interference by carbonate. An aliquot of sodium aluminate liquor is titrated with standard potassium hydrogen carbonate solution to yield the free hydroxyl ion («free caustic») content of the liquor.

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Method description

Summary

An aliquot of sodium aluminate liquor is titrated with standard potassium hydrogen carbonate solution to yield the free hydroxyl ion («free caustic») content of the liquor.

$HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O$

The titration solution is then treated automatically with a measured volume of concentrated sodium potassium tartrate solution, which complexes the aluminate ion, releasing 1 mol hydroxyl ion per mol aluminate ion present. A second titration with standard potassium hydrogen carbonate solution then proceeds automatically to react with the released hydroxyl ion.

$[Al(OH)_4]^- + (C_4H_4O_6)^{2-} \rightarrow Al(OH)_3(C_4H_4O_6)^{2-} + OH^-$

The total volume of titrant consumed to the endpoint in the second titration is used to calculate the «total caustic» content of the liquor.

The alumina content of the liquor is calculated from the difference in titrant volumes of the two endpoints.

Sample

Bayer process or sodium aluminate liquor

Sample preparation

No sample preparation required

Solutions

Titrant	1 mol/L $KHCO_3$, stabilized with 1 g/L anhydrous Na_2CO_3
In situations where high consumption of titrant is anticipated, it is recommended that large volumes (at least 20 L) are made up and standardized. It may be transferred to smaller containers, and stored under refrigeration to extend shelf life.	
Complexant	614 g/L sodium potassium tartrate or 500 g/L disodium tartrate
Standard solution	0.2 mol/L NaOH for standardizing $KHCO_3$ titrant
Standardizing substance	potassium hydrogen phthalate AR for the 0.2 mol/L NaOH

Analysis

Basic Procedure

A 1 mL aliquot of Bayer process or sodium aluminate liquor is diluted to approx. 25–30 mL, depending on the type of titration vessel used. It is titrated to an exothermic endpoint with 1 mol/L $KHCO_3$, and stopped automatically approx. 0.5 mL after the endpoint. The endpoint volume (EP1) and the final volume (EVT) are recorded by *tiamo*™.

5 mL of sodium potassium tartrate is then dosed automatically, and the hydroxyl ions thereby released by complexation of aluminate are titrated with 1 mol/L $KHCO_3$ to an exothermic endpoint (EP2).

Note: for more concentrated liquors, especially those with high aluminate contents, it may be necessary to use 10 mL of tartrate solution.

Determination of blanks

The systematic errors («blanks») for the «free caustic» and «total caustic» determinations should be determined following the establishment of optimal parameters by the analyst. Further determination of the blanks is not required unless either the titrant dose rate or digital smoothing filter factor is altered.

Dilute 20 mL of a typical process liquor to 500 mL with dist. water. Note: allow at least 5 minutes for the pipette to drain, as the liquor is very viscous. For determination of the blank value for «free caustic», titrate aliquots of 5, 10, 15, 20, 25, and 30 mL of the diluted liquor, after making to approx. 25–30 mL with dist. water.

For determination of the blank value for «total caustic», titrate aliquots of 5, 10, 15, 20, 25, and 30 mL of sodium potassium tartrate solution and making to approx. 25–30 mL with dist. water. Store the blank values as Common Variables.

Standardization of 1 mol/L $KHCO_3$ solution

Prepare a 20 or 50 mL Dosino with 0.2 mol/L NaOH solution, and supply with a guard tube filled with fresh soda-lime granules. Using the dedicated *tiamo*™ method, titrate aliquots of 5, 10, 15, 20, 25, and 30 mL 0.2 mol/L NaOH, making the volume in each titration vessel to approx.. 25–30 mL with dist. water. The *tiamo*™ program will compute the molarity of the $KHCO_3$ solution.

Basic experimental parameters

Titrant delivery rate mL/min	4
Data smoothing («filter factor»)	40

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Method description

Calculations

g/L free caustic	=	((EP1– blank1) × C01 × C02)/(2C00)
g/L total caustic	=	((EVT + EP2 – blank2) × C01 × C02)/(2C00)
g/L alumina	=	(TC – FC) × C03/C02

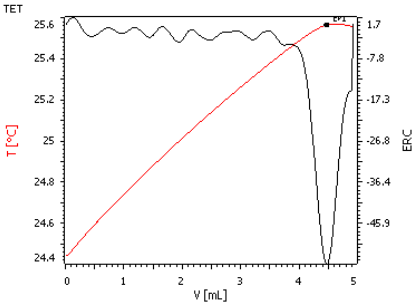
FC	=	free caustic
TC	=	total caustic
EP1	=	endpoint in mL for **free** caustic titration
EP2	=	endpoint in mL for **total** caustic titration
EVT	=	volume of titrant to automatically stopped end of free caustic titration
C00	=	sample weight in mL
C01	=	concentration of titrant in mol/L
C02	=	molecular weight of Na_2O (61.97894 g/mol)
C03	=	molecular weight of Al_2O_3 (101.96128 g/mol)
2	=	stoichiometric factor
blank1	=	blank for free caustic titration in mL
blank2	=	blank for total caustic titration in mL

Results

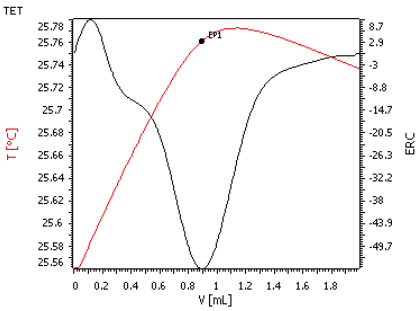
	Bicarbonate method		Customer method	
	Mean	Std.Dev	Spec.	Tolerance
Free Caustic Na_2O g/L	139.0 (n = 11)	0.2	140.4	-
Total Caustic Na_2O g/L	183.0 (n = 11)	0.1	184.8	2
Alumina Al_2O_3 g/L	72.5 (n = 11)	0.3	73.1	1
Molar ratio Na_2O/Al_2O_3	4.15 (n = 11)	0.02	4.16	

Results are from analysis of a customer-supplied standard check liquor which has been extensively analyzed in an interlaboratory round-robin exercise by the customer's standard method. Results are statistically within the customer's tolerances.

Thermometric titration plots



Titration of «free caustic» with 1 mol/L $KHCO_3$



Titration of «total caustic»/«alumina» with 1 mol/L $KOCO_3$ after addition of sodium potassium tartrate on completion of «free caustic» titration.

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