Metrohm

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Analysis of Bayer Aluminate Liquors by thermometric titration

Branch

Metals, electroplating

Keywords

Titration; Titrotherm; TET; total caustic; total soda; alumina; carbonate; Bayer Liquors; branch 10

Summary

This Application Bulletin describes the analysis of the total caustic, total soda, and alumina in Bayer Aluminate Liquors using thermometric titration. Total caustic is defined as the total hydroxyl content of the liquor comprising unassociated hydroxyl ions, and one hydroxyl of the four in the aluminate $Al(OH)_4^-$ anion. Total soda is defined as the sum of the total caustic content plus the carbonate content of the liquor.

The method described in this bulletin is based on the procedure originally developed by Watts and Utley, and modified for use in thermometric titration by Van Dalen and Ward. It is arguably the fastest and most reliable determination for the analysis of Bayer Process liquor.

An aliquot of alumina refinery sodium aluminate liquor is treated with sodium potassium tartrate solution to complex aluminate and release one mole hydroxyl for each mole aluminate present. The total hydroxyl content of the liquor (total caustic) and the carbonate (total soda) content are determined by titration with standard hydrochloric acid.

A second titration is carried out sequentially to the first to determine the aluminate content (as "alumina") immediately thereafter. This second titration is preceded by the addition of potassium fluoride solution, which destroys the aluminotartrate complex, forming an insoluble potassium sodium aluminum fluoride and releasing three moles of hydroxyl for each mole of aluminate. This hydroxyl content is determined again by the standard hydrochloric acid titrant.

The entire two-titration sequence can be carried out automatically.

Instruments

- Thermometric Titrator
- Rod stirrer
- 10 mL buret

Electrodes

Thermoprobe HF	6.9011.040

Reagents

- Hydrochloric acid, conc., HCl, >37%
- Potassium sodium tartrate, $KNaC_4H_4O_6$
- Potassium fluoride, KF

Solutions

Titrant	$c(HCl)$ = 1.5 mol/L 147.8 g conc. HCl is weighed into a 1 L volumetric flask containing 500 mL deion. H_2O. After cooling down to room temperature, the flask is filled up to the mark with deion. H_2O.
Complexing solution 1	Nearly saturated solution of potassium sodium tartrate, $\beta(KNaC_4H_4O_6)$ = approx. 614 g/L. This highly concentrated complexing solution has been found to be quite stable when stored in conditions above 22 °C, however, if stored at lower temperatures it should be periodically checked for signs of crystallization.
Complexing solution 2	Nearly saturated solution of potassium fluoride, $\beta(KF)$ = approx. 620 g/L. This highly concentrated complexing solution has been found to be quite stable when stored in conditions above 22 °C, however, if stored at lower temperatures it should be periodically checked for signs of crystallization.

Standard

TRIS	TRIS is dried over night in a drying oven at 105 °C and allowed to cool down in a desiccator for at least 1 h.

Sample preparation

Strong digestion feed liquor is diluted previous to the titration with deion. H_2O. Each aliquot should be prepared only a few minutes prior to the titration, due to risk of absorption of atmospheric CO_2.

Analysis

Titer

0.5 – 1.2 g dried TRIS is weighed accurately into the titration vessel. 30 mL of deion. H_2O is added. After the TRIS has been dissolved the solution is titrated with c(HCl) = 1.5 mol/L until after the first exothermic endpoint.

At least 4 different initial weights of TRIS are titrated in an ascending order.

Blank

An appropriate amount of sample is pipetted into a titration vessel. The sample is then diluted to 25 mL with deionized water and 10 mL complexing solution 1 (potassium sodium tartrate) is added. After a pause of 10 s the solution is titrated with c(HCl) = 1 mol/L until after the second exothermic endpoint.

To the titrated solution 10 mL of complexing solution 2 (KF) is added and after another pause of 20 s the solution is titrated again with c(HCl) = 1 mol/L until after the first exothermic endpoint.

At least 4 different aliquots of the sample are titrated in an ascending order.

Sample

An appropriate amount of sample (see below) is pipetted into a titration vessel. The sample is then diluted to 25 mL with deionized water and 10 mL complexing solution 1 (potassium sodium tartrate) is added. After a pause of 10 s the solution is titrated with c(HCl) = 1 mol/L until after the second exothermic endpoint (determination of total caustic and total soda content).

To the titrated solution 10 mL of complexing solution 2 (KF) is added and after another pause of 20 s the solution is titrated again with c(HCl) = 1 mol/L until after the first exothermic endpoint (determination of aluminate).

For the normal range of Bayer process liquors from alumina refineries, an aliquot size should be chosen to give a titrant consumption of up to 5 – 6 mL of c(HCl) = 1 mol/L.

In the case of very dilute liquors (e.g., last washer overflow or red mud filtrate) an aliquot of up to 25 mL of undiluted liquor can be taken.

Parameters

Titer

Stirring rate	10
Dosing rate	4 mL/min
Filter factor	40
Damping until	0.5 mL
Stop slope	< 0.15 °C/mL
Stop slope active after	0.5 mL
Additional volume after stop	0.75 mL
Evaluation start	0.5 mL
Reaction type	Exothermic
EP criterion	-50

Blank and Sample (Total caustic and total soda)

Stirring rate	12
Dosing rate	4 mL/min
Filter factor	40
Damping until	1 mL
Stop slope	<-0.12 °C/mL
Stop slope active after	1.0 mL
Additional volume after stop	1.0 mL
Evaluation start	1 mL
Reaction type 1	Exothermic
EP criterion 1	-70
Reaction type 2	Exothermic
EP criterion 2	-50

Blank and Sample (Aluminate)

Stirring rate	15
Dosing rate	4 mL/min
Filter factor	35
Damping until	1 mL
Stop slope	< -0.05 °C/mL
Stop slope active after	1.0 mL
Additional volume after stop	0.5 mL
Evaluation start	1 mL
Reaction type	Exothermic
EP criterion	-20

Calculation

For more details on the calculation of the titer and the blank in *tiamo*™ please refer to the Application Note H-131.

Titer

A linear regression of the volume (mL) of titrant consumed versus the different volumes of standard in g is evaluated by *tiamo*™. The titer is calculated from the slope.

$$f = \frac{1000}{a \times M_{Std} \times c_{HCl}}$$

f:	Titer of the titrant
1000:	Conversion factor
a:	Slope of the linear regression (mL/g)
M_{Std}:	Molecular weight of TRIS, 121.14 g/mol
c_{HCl}:	Concentration of titrant in mol/L, here 1.5 mol/L

Blank

A linear regression of the different sample volumes (mL) against the volume (mL) of titrant consumed is evaluated by *tiamo*™. The method blank is defined as the intercept of the linear regression line with the y-axis.

For the aluminate determination the consumed titrant volume is calculated as follows:

$$V_{Al} = V_{EP1, Al} + \left(V_{End, CS} - V_{EP1, CS}\right)$$

V_{Al}:	Total consumed titrant volume for the aluminate determination in mL
$V_{EP1, Al}$:	Titrant volume consumed for the aluminate determination until the first endpoint in mL
$V_{End, CS}$:	Total volume of titrant used for the total caustic and total soda determination
$V_{EP1, CS}$:	Titrant volume consumed for the aluminate determination until the first endpoint in mL

Sample

The calculation is given according to the European convention, where the total caustic and total soda is calculated in terms of sodium oxide. For the American convention, where the results are expressed in terms of sodium carbonate the molecular mass is replaced with 105.988 g/mol.

$$\text{Total caustic} = \frac{(V_{EP1} - V_{B, C}) \times c_{HCl} \times f \times M_A}{V_S \times 2}$$

Total caustic: Total caustic content as Na_2O in g/L

V_{EP1}:	Titrant consumption until the first exothermic endpoint in mL of the first titration

$V_{B, C}$:	Method blank for the total caustic in mL
c_{HCl}:	Concentration of titrant in mol/L
f:	Titer of titrant
M_A:	Molecular weight of sodium oxide, 61.979 g/mol
V_S:	Sample size in mL
2:	Stoichiometric factor

$$\text{Total soda} = \frac{(V_{EP2} - V_{B, S}) \times c_{HCl} \times f \times M_A}{V_S \times 2}$$

Total soda:	Total soda content as Na_2O in g/L
V_{EP2}:	Titrant consumption until the second exothermic endpoint in mL
$V_{B, S}$:	Method blank for the total soda in mL
c_{HCl}:	Concentration of titrant in mol/L
f:	Titer of titrant
M_A:	Molecular weight of sodium oxide, 61.979 g/mol
V_S:	Sample size in mL
2:	Stoichiometric factor

$$Al_2O_3 = \frac{\left(\left(V_{EP1} - V_{B, Al}\right) + \left(V_{End, CS} - V_{EP1, CS}\right)\right) \times c_{HCl} \times f \times M_A}{V_S \times 6}$$

Al_2O_3:	Aluminate content as Al_2O_3 in g/L
V_{EP1}:	Titrant consumption until the first exothermic endpoint in mL of the second titration
$V_{B, Al}$:	Method blank for the aluminate in mL
$V_{End, CS}$:	Total volume of titrant used for the total caustic and total soda determination
$V_{EP1, CS}$:	Titrant volume consumed for the aluminate determination until the first endpoint in mL
c_{HCl}:	Concentration of titrant in mol/L
f:	Titer of titrant
M_A:	Molecular weight of aluminum oxide, 101.961 g/mol
V_S:	Sample size in mL
6:	Stoichiometric factor

$$\text{Ratio} = \frac{\text{Total caustic} \times M_{Al_2O_3}}{Al_2O_3 \times M_{Na_2O}}$$

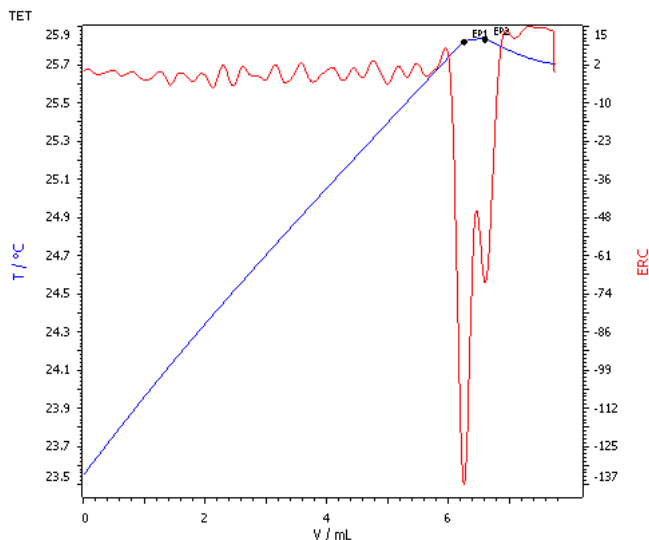|	
Ratio:	Molar ratio of sodium oxide to aluminum oxide in mol/mol
Total caustic:	Total caustic content as Na_2O in g/L
$M_{Al_2O_3}$:	Molecular weight of aluminum oxide, 101.961 g/mol
Al_2O_3:	Aluminate content as Al_2O_3 in g/L
M_{Na_2O}:	Molecular weight of sodium oxide, 61.979 g/mol

Example determination

Fig 1: Titration curve of the total caustic and total soda determination (blue = titration curve, red = ERC)
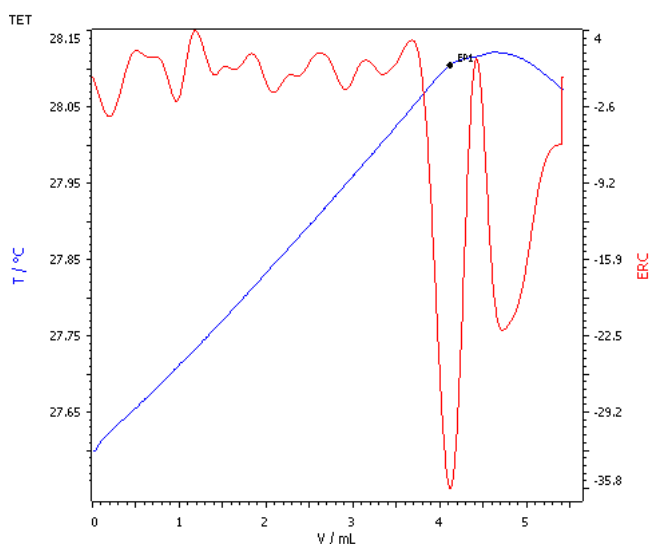

Fig. 2: Titration curve of the aluminate determination (blue = titration curve, red = ERC)

Comments

- The herein described application parameters may need to be modified depending on the sample.

- For highly concentrated liquors with low $[Na_2O]/[Al_2O_3]$ molar ratios (or high A/C ratios), it might be necessary to reduce the effective aliquot size so that the titrant consumption is 3–4 mL and increase the sodium potassium tartrate solution volume to 15 or even 20 mL (in the case of synthetic sodium aluminate liquors). This is to ensure the efficient complexation of all aluminate present in the liquor with tartrate.
  If it more than 10 mL of tartrate solution are necessary,

then it is necessary to determine titration blanks using a typical sample and the adjusted amount of tartrate solution.

- The Thermoprobe HF should be arranged in such a way in the titration vessel that is only 1 mm above the stirring propellers. The same is necessary for the buret tip.

- Potassium sodium tartrate is preferred to sodium gluconate as an aluminate complexant for thermometric titrations as it gives better resolution of the bicarbonate endpoint in the presence of hydroxyl.

- To prevent blockage of reagent delivery tubes, it is recommended that a titration vessel filled with sufficient water to cover the antidiffusion tips of the delivery tubes and is attached between titration runs. The Thermoprobe can be removed and stored dry at this time.

- In the first titration it is necessary to overshoot the bicarbonate endpoint slightly, so that this endpoint is properly resolved by the software. This leaves the solution with a slight surfeit of acid, i.e., H^+ ions. When the potassium fluoride is added, some of the liberated OH^- ions are consumed in neutralizing these free H^+ ions. Not only do the liberated hydroxyl ions react with any free H^+, they also react with any bicarbonate ions, HCO_3^- which have been formed in the Total Caustic/Total Soda titration Thus the volume of $c(HCl) = 1mol/L$ which may be taken to be "overshot" in the first titration maybe computed by subtracting the total caustic endpoint volume from the total volume of $c(HCl) = 1$ mol/L used (see *Calculation*).

References

- Watts H. L., Utley. D. W.: Sodium Gluconate as Complexing Agent in Volumetric Analysis of Aluminum Compounds, Anal. Chem., (1956) 28, 11, 1731

- Van Dalen E., Ward L. G., Thermometric titration determination of hydroxide and alumina in Bayer process solutions, Anal. Chem., (1973) 45, 13, 2248

- AN H-131
  Determination of titer and method blank for thermometric titrations using *tiamo*[TM]

- Leaflet for Thermoprobe
  8.109.8055

Author

Competence Center Titration

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