Thermo. Titr. Application Note No. **H-080**

Title:	**Determination of Total Sodium in Sodium Aluminate Liquors by Aluminium Titration**

***Scope*:**	Determination of the total sodium content of sodium aluminate liquors, such as Bayer Process liquor. This method is suitable for the analysis of all sodium aluminate solutions down to at least 1g/L as Na_2CO_3. The determination may be automated by adding a 814 USB sample processor to 859 Titrotherm

***Principle*:**	It is necessary to decompose aluminate ion present in solution before the titration for sodium can take place. This is done by treating an aliquot of liquor with an excess of magnesium ions, which react with hydroxyl ions in solution. $Al(OH)_4^- \leftrightarrow Al(OH)_3 + OH^-$ $Mg^{2+} + 2OH^- \leftrightarrow Mg(OH)_2$ Magnesium ions also react with carbonate and a range of organic compunds present in the liquor to form slightly soluble magnesium salts. After this treatment, the pH of the solution is close to neutrality. The solution containing a gelatinous precipitate is then filtered or centrifuged. An aliquot of the filtrate or centrifugate is then treated with a solution of ammonium hydrogen difluoride before titration with a standardized solution of aluminium containing a stoichiometric excess of potassium ions. The exothermic formation of insoluble NaK_2AlF_6 forms the basis of the determination. $Al^{3+} + Na^+ + 2K^+ + 6F^- \leftrightarrow NaK_2AlF_6 \downarrow$ The titrant is standardized against a solution prepared from anhydrous sodium sulfate

Reagents:	*Titrant:* Mixed 0.5mol/L $Al(NO_3)_3$, 1.1mol/L KNO_3 solution. C*onditioning reagent:* 300g/L $NH_4F.HF$ *Precipitant:* 300g/L $Mg(NO_3)_2$, prepared from AR salt

Method:	*Basic Experimental Parameters:*	
	Titrant delivery rate (mL/min.)	5
	Titrant pre-dose (mL)	0.5
	Delay before titration commences (sec)	30
	No. of exothermic endpoints	1

Data smoothing factor (DSF)	70
Stirring speed (802 stirrer)	15

Titration program: The titration program is set up to pre-dose 0.5mL of titrant before the actual titration starts. A delay of 30 seconds is programmed to allow an initial precipitate seed surface upon which subsequent precipitate may grow rapidly. This improves the precision of the method considerably. The pre-dose volume is added to the titrant volume at the endpoint to obtain the actual titrant consumption.

Sample preparation: Pipette 5mL of concentrated process liquor into a 500mL volumetric flask. Add 100mL of water, then add 50mL 300g/L $Mg(NO_3)_2$ solution. Make to volume with DI water and mix well. Allow the solution to stand for 30 minutes to permit full reaction to take place. *(Note: other aliquots of liquor may be used according to the strength of the liquor, and other size volumetric flasks may also be used. A ratio of 1mL of liquor to 10mL of $Mg(NO_3)_2$ solution was found to be satisfactory in the experiments reported here)*. Filter through a dry filter paper suitable for coarse gelatinous precipitates, or centrifuge to obtain a clear centrifugate. Pipette a 30mL aliquot of filtrate or centrifugate into a titration beaker. This aliquot is equivalent to 0.3mL of original liquor. Add 5mL 300g/L $NH_4F.HF$ solution, swirl to mix, and allow the solution to rest for an hour, or at least until a clear interface is visible above the white precipitate. It is important to allow the solution to “age” properly before titrating, otherwise high results will be obtained.

Titration: Titrate to a single exothermic endpoint.

Blank determination: Prepare a 1:10 dilution of concentrated Bayer liquor. Pipette aliquots of 5, 10, 15, 20 and 25mL of the diluted solution into 250mL volumetric flasks. Add 100mL of DI water, swirl to mix, and pipette 25mL of 300g/L $Mg(NO_3)_2$ solution into each flask. Make the flasks to volume with DI water and mix well. Filter or centrifuge each solution as above, and take a 30mL aliquot of the filtrate or centrifugate. Add 5mL 300g/L $NH_4F.HF$ solution, swirl to mix, and allow the solution to rest for an hour. Titrate each solution, and plot mL of liquor (x-axis) against titration volume (y-axis). The y-axis intercept is the titration blank. This is subtracted from the titration volume in the calculation. *Note: a **negative** blank value must therefore be **added** to the titration volume*.

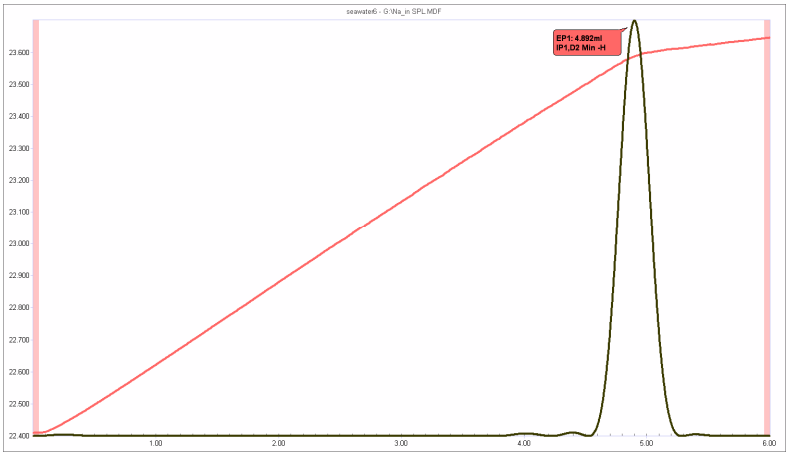
Example:	*Analysis of alumina refinery spent liquor:*	
	Calculated as:	**Result**
	Na^+ g/L	223.3±0.5
	Na_2O g/L	301.0±0.7
	Na_2CO_3 g/L	514.6±1.2

Calculations:

$$Na^+ \text{ g/L} = \frac{((\text{Titre, mL} + \text{pre} - \text{dose, mL} - \text{blank, mL}) \times \text{Al mol/L} \times 22.9877)}{\text{aliquot, mL}}$$

Thermometric Titration Plot:

Legend:
Red = solution temperature curve
Black =second derivative curve (for endpoints)



Determination of Titration Blank:

y-intercept = -0.2423mL = titration blank