

Thermo. Titr. Application Note No. H-077

Title: Determination of Sodium in Brines by Aluminium Titration

Scope: Determination of sodium in sea water and similar brines. This procedure is suitable for the analysis of sodium in sea water contaminated with sodium aluminate solutions emanating from alumina refineries, and sea water which has been used for the neutralization of alumina refinery waste („red mud“) slurries.

Principle: Titration with a standardized solution of aluminium containing a stoichiometric excess of potassium ions in the presence of ammonium hydrogen difluoride at ~pH3 to give an exothermic reaction, forming insoluble NaK_2AlF_6 .

$$\text{Al}^{3+} + \text{Na}^+ + 2\text{K}^+ + 6\text{F}^- \leftrightarrow \text{NaK}_2\text{AlF}_6 \downarrow$$

The titrant is standardized against a solution prepared from anhydrous sodium sulfate

Reagents: *Titrant:* Mixed 0.5mol/L $\text{Al}(\text{NO}_3)_3$, 1.1mol/L KNO_3 solution.
Conditioning reagent: 300g/L $\text{NH}_4\text{F} \cdot \text{HF}$

Method: Basic Experimental Parameters:

Titration delivery rate (mL/min.)	4
Titration pre-dose (mL)	0.5
Delay before titration commences (sec)	30
No. of exothermic endpoints	1
Data smoothing factor (DSF)	42
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.

Titration: Pipette 5mL of sea water into a titration vessel. Add 5mL 300g/L $\text{NH}_4\text{F} \cdot \text{HF}$ solution and 25mL DI water. Titrate to a single exothermic endpoint.

Blank determination: Titrate 2,3,4,5, and 6mL aliquots of a typical sea water sample. Plot mL of sea water (x-axis) against mL of titrant consumed (y-axis). The y-intercept of the resultant linear plot is the titration blank, which is to be subtracted from the titration volume before calculation of the sodium content.

Examples:		<i>Analysis of sea water collected from Moreton Bay, Queensland, Australia 25/06/2008</i>	
<p><i>The contaminant was a „spent liquor“ obtained from an alumina refinery.</i></p> <p><i>Samples were dispensed by Dosino to eliminate human error in pipetting.</i></p>	Sample	Na ⁺ g/L	
	Sea water as collected	10.70±0.026 (n=5)	
	Sea water contaminated with 2mL/L sodium aluminate solution (filtered)	10.84±0.015 (n=5)	
	Sea water contaminated with 4mL/L sodium aluminate solution (filtered)	11.26±0.004 (n=5)	
	Sea water contaminated with 10mL/L sodium aluminate solution (filtered)	12.44±0.004 (n=5)	

Calculations:

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

