

## Analysis of Bayer Aluminate Liquors with 859 Titrotherm

Of interest to:

Alumina refinery process control laboratories, laboratories carrying out R&D in the alumina industry

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### Summary

The purpose of this manual is to assist the analyst engaged in the determination of sodium aluminate liquor to quickly set up the 859 Titrotherm titration system to perform this task. While every effort has been made to make this easy, it is not possible to provide for every situation. The analyst must be prepared to make modifications to the procedures where appropriate.

The two complexant method described in this manual is based on the procedure originally developed by Watts and Utley<sup>1</sup>, and modified for use in thermometric titrimetry by VanDalen and Ward<sup>2</sup>. It is arguably the fastest and most reliable determination for the analysis of Bayer Process liquor. This manual is dedicated to an explanation of the application of the VanDalen-Ward method to the 859 Titrotherm titration system. However, the method as presented has a considerable number of refinements and improvements over VanDalen and Ward's original work; not the least in the ability to measure the carbonate content of the liquor. This method has been designated as the "Bayer Classic" method, in reference to the origins of the analytical chemistry involved.

This manual is a component of a package of files which assists the analyst in rapidly setting up Titrotherm to perform analyses on Bayer liquors. The other components of this package comprise:

- Pre-optimized titration files which can be converted to titration methods.
- An Excel worksheet template which is linked to the titration methods, and automatically calculates results for caustic, alumina and carbonate in both American and European alumina refining conventions.

### Apparatus and accessories

#### Recommended basic equipment list:

2.136.0010	859 Titrotherm
2.800.0010	3 x 800 Dosino
6.3032.220	Dosing unit (1.5 mol/L HCl)
6.3032.220	Dosing unit (614 g/L potassium sodium tartrate-solution)
6.3032.220	Dosing unit (620 g/L KF-solution)
2.804.0010	804 Titration stand
2.802.0040	802 Rod stirrer
6.1415.220	10 x Titration vessel
6.1414.010	Titration vessel lid
6.1543.210	3-way stopper with antidiffusion valve
6.1446.000	3 x SGJ stoppers
6.2061.010	Reagent organizer



## Reagents

○ **Hydrochloric acid titrant, 1.5 mol/L.**

The reagent may be standardized by thermometric titration against A.R. anhydrous sodium carbonate or another appropriate primary standard. Because of the high usage rate in modern alumina refineries, it is recommended that a large volume (at least 100L) be prepared to reduce the frequency of standardization. However, it should be noted that practical experience has shown that strong hydrochloric acid solutions undergo layering in large containers where there is a substantial head space. After a time, a concentration gradient is established, with lower concentrations at the top of the container. This can result in "drift" of results. It is strongly recommended that after preparation, the well mixed solution is bottled off into convenient sized (say 2.5L) containers, and kept sealed until use.

○ **Potassium sodium tartrate solution,** nearly saturated, approximately 614 g/L. It is recommended that a large volume (at least 100L) be prepared and bottled off into 2.5L containers until needed for use. To avoid the need for frequent titration blank determinations, it is recommended that a large quantity from the same manufacturer's batch be purchased at a time. 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.

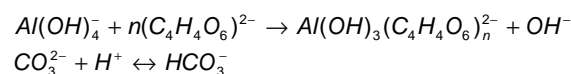
○ **Potassium Fluoride,** nearly saturated, 620 g/L. It is recommended that a large volume (at least 100L) be prepared and bottled off into 2.5L containers until needed for use. To avoid the need for frequent titration blank determinations, it is recommended that a large quantity from the same manufacturer's batch be purchased at a time.

**Note on storage and use of tartrate and fluoride solutions.** These high concentration solutions have been found to be quite stable when stored in conditions above 22°C, however, if stored at lower temperatures they should be periodically checked for signs of crystallization.

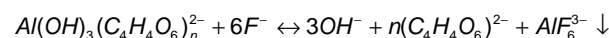
To prevent blockage of reagent delivery tubes, it is recommended that a titration vessel with sufficient water to cover the tips of the delivery tubes should be attached between titration runs. The Thermoprobe can be removed and stored dry at this time.

### Method Overview.

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 content is 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 aluminium 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 is carried out automatically.

Practically, these titrations are carried out by two separate methods which are chained or linked together in the software. The method used to determine Total Caustic and Total Carbonate is referred to as Bayer Left, and that to determine the alumina content is referred to as Bayer Right.

#### 4. Creating the Titration Methods.

##### 4.1. Setting up the computer screen and creating methods from supplied titration files.

Install Titrotherm software on the computer as detailed in the Instruction Manual. Copy the files Bayer\_Left.MDF and Bayer\_Right.MDF to the folder C:\Program Files\Titrotherm\MDF. Copy the results template file Bayer Classic.XLS to the folder C:\Program Files\Multitrate\Templates.

Start the software by clicking on the Titrotherm icon. Now, on the floating menu bar click File>New Window. This will create a new titration screen. Click Window>Tile Vertical. Adjust the display so the two method windows occupy the top half of the screen. The display should be similar to that illustrated in Figure 2.

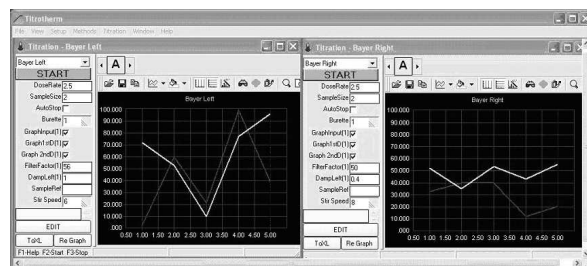


Fig. 2. Setup of titration screens.

You can now fill the Dosino reagent bottles and set up the Dosinos. Click "Re-Scan Dosinos" after entering reagent names. See Figure 3.



Fig. 3. Dosino set up

It is now necessary to create methods from the two files which have been supplied so that new titrations will be conducted under the same conditions that were originally used. Click on the left hand screen. Go to File>Open, and open the file Click on the "Edit" button, and select the Setup

form. You will notice the title is "Bayer Left". Go to Method>Save As in the main menu bar, and write this title in the space. Save the method. Now click on the right hand titration screen, and repeat the process to create the method "Bayer Right". Your computer screen should now look similar to this:

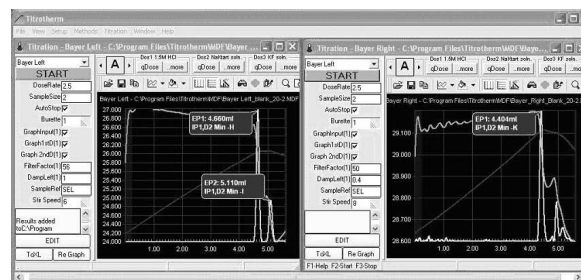


Fig. 4. Setup of methods using supplied titration files.

Assuming that the hardware has been set up correctly, you are now ready to commence a titration. For your first titration, you might consider using a strong digestion feed liquor. Prepare the sample by taking a 1mL aliquot of this liquor, and diluting with 20mL of water. Note that the sample volume at the start of the titration should be approximately 30mL (after 10mL of potassium sodium tartrate solution has been added). Click on the "START" button on the Bayer Left screen, and the titration sequence will commence. The potassium sodium tartrate solution will be added, the stirrer will start, and after a short delay of a few seconds, the titration will commence. The caustic (and any carbonate present) will be titrated. After the titration stops, the calculation spreadsheet will be automatically loaded, and the Total Caustic and Total Soda values will be computed.

If the titration has stopped properly, the chained method "Bayer Right" will automatically start after the Dosinos have refilled. The alumina titration will commence automatically after the potassium fluoride reagent has been added.

*Please note that when entering sample data (sample size, description, and time of sampling), you must do this on the Bayer Right form.*

#### 4.2. Making adjustments.

You have already set up the methods required for analysis of aluminate liquor. However, some minor adjustments may be required to account for different liquor concentrations. The following information has been provided to assist in a deeper understanding how the software has been set up for Bayer liquor analysis. It is important to have previously read the Instruction Manual. Reference is made to the various Method Edit forms, which are accessed by clicking on “Edit” at the main titration screen.

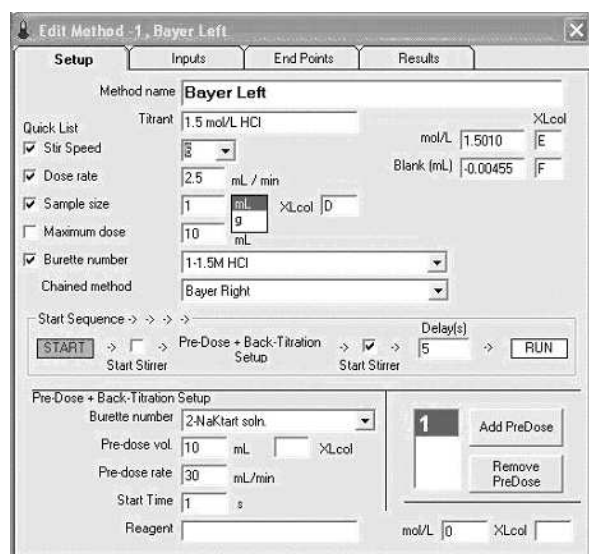


Fig. 5a. Method Edit>Setup Form for Bayer Classic Left Method

**Notes:**

- A titrant dose rate of 2.5mL/min is used for both titrations.
- So that the second half of the titration sequence Bayer Right will start automatically after Bayer Left is complete, the two methods are “chained” or linked together.
- Note that the stirrer starts after the tartrate reagent has been added.

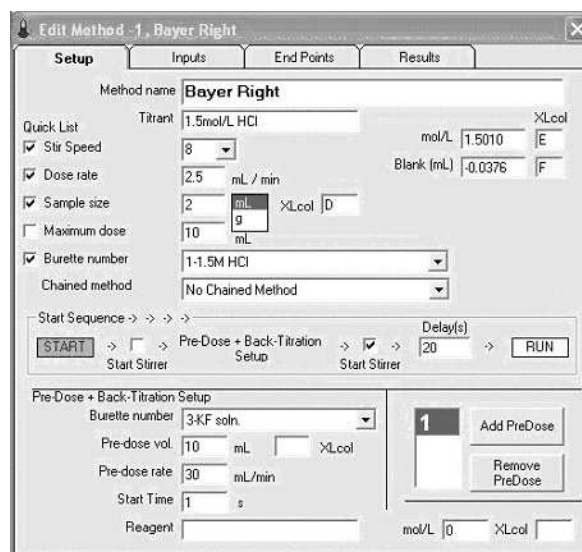


Fig. 5b. Method Edit>Setup Form for Bayer Classic Right Method.

**Notes:**

- The sample size is inserted by the analyst. This number is sent to the spreadsheet, and used in the calculations.
- It is necessary to pre-dose KF solution prior to the start of the alumina titration. This is dispensed from burette 2. The amount dosed is set at 10mL, delivered at a dose rate of 30mL/min. For high alumina concentrations in the liquor sample, this volume can be increased to 15mL. The KF is permitted to react with the sample for 20 seconds, prior to the titration commencing.

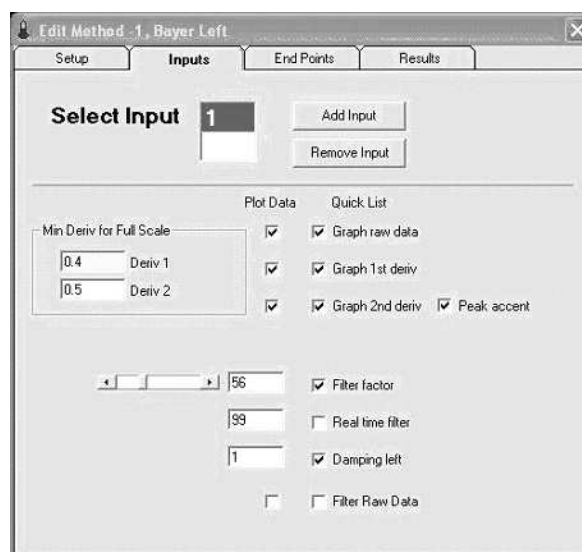


Fig. 6a. Method Edit>Input Form for Bayer Left Method

Notes:

- A *Final factor* (digital signal filter) setting of 55 has been chosen to give the best precision for the total caustic and carbonate endpoints. The *Real time filter* has been set to give a smooth display while the titration is in progress. Optimization of the digital filter setting is described in on-line “Help”.
- Damping Left. The second derivative signal has been damped for the first 1mL of the titration, to prevent a “spike” at the start of the titration from being chosen as an endpoint.

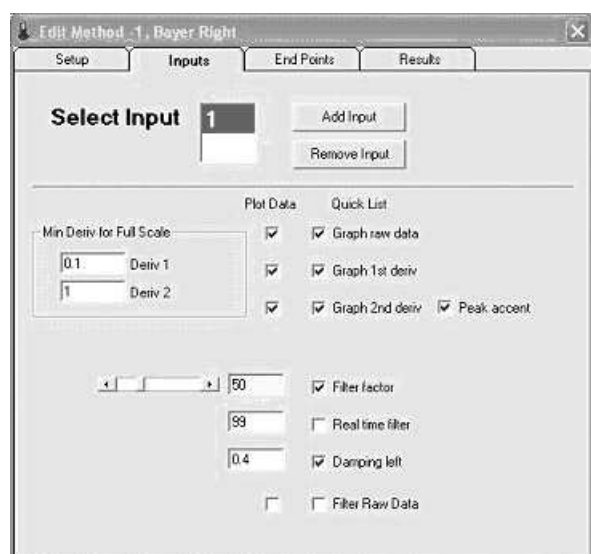


Fig. 6b. Method Edit>Input Form for Bayer Right Method.

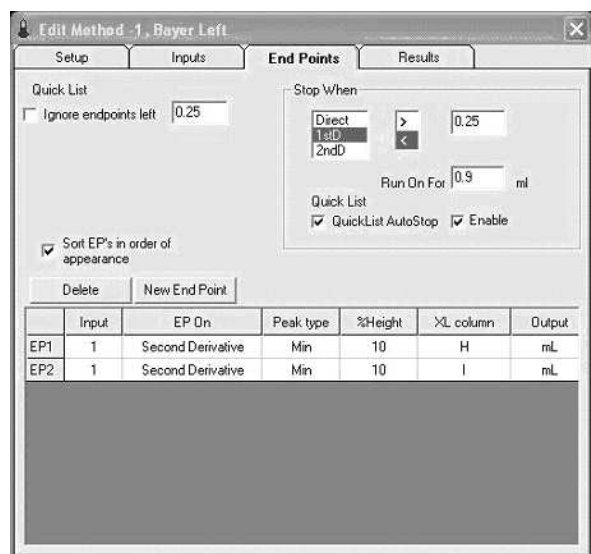


Fig. 7a. Method Edit>End Points Form for Bayer Left Method.

Notes:

- Any spike or noise for the first 0.5mL of the titration will not be selected as an endpoint.
- The titration has to be automatically cut off after the carbonate endpoint has been reached. The automatic cutoff is based on the first derivative (green curve). A value is chosen by trial and error. In this case, the titration will be shut off when the first derivative value is less than 0.25. To allow for a certain degree of error in this value, the titration is allowed to run on for another 0.9mL after this value has been reached. See the online **Help** for information on how to optimize the automatic cutoff parameter.
- Two endpoints have to be found. The endpoint is found from the second derivative, and the peak type is a “min” for an exothermic reaction. The titre for the first (Total Caustic) endpoint will be sent to column H in the Excel spreadsheet. The Total Caustic+Carbonate endpoint titre will be sent to column I. If the liquor contains little or no measurable carbonate, then the methods and the Excel template will require modification.

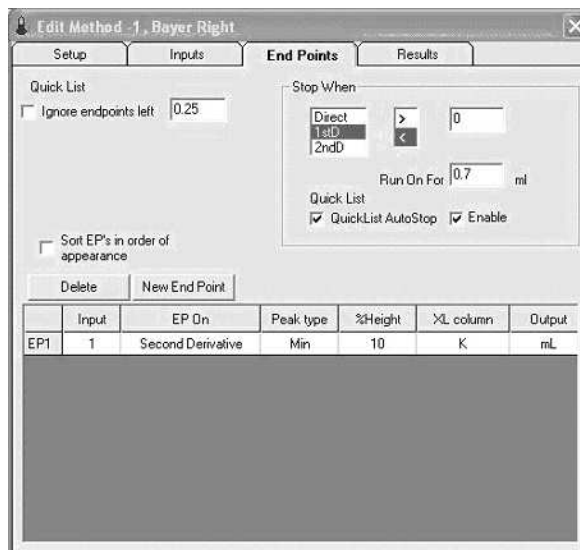


Fig. 7b. Method Edit>End Points Form for Bayer Right Method.

Notes:

- The automatic cutoff parameter has been optimized for the alumina titration. See the online **Help** for information on how to optimize the automatic cutoff parameter.
- Only one endpoint has been selected (for titration of the 3 hydroxyl ions equivalent to alumina). The titre volume for this endpoint will be transmitted to column K of the spreadsheet. The other endpoint may not be

used for calculation of the carbonate content, since it has been suggested that the presence of fluoride may cause interference from the silica content of the liquor.

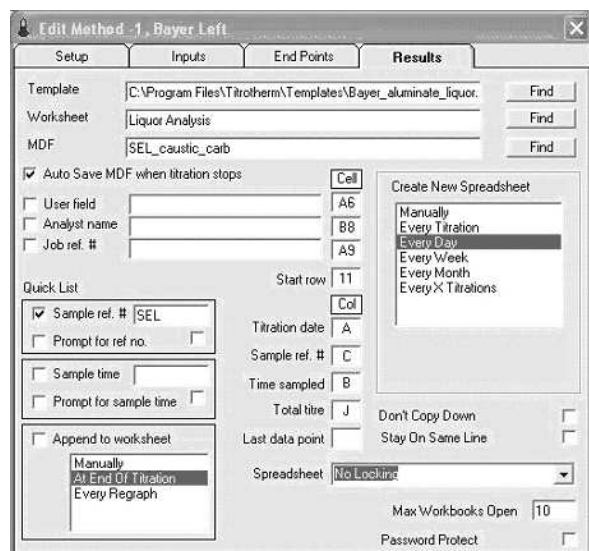


Fig. 8a. Method Edit>Results Form for Bayer Left Method

Notes:

- The spreadsheet template for calculation and reporting results is *Bayer\_aluminate\_liquor.xls*, and is located in the default folder of *C:\Program Files\Titrotherm\Templates*.
- When the results are sent to MS Excel, a workbook called "Liquor Analysis" is created from the template. The workbook is automatically saved in *C:\Program Files\Titrotherm\Results*. When the spreadsheet is created with this name, it bears a suffix which is actually a date stamp, Note that any name can be given to the workbook, it doesn't have to be the same as the template.
- Because "Every Day" has been chosen, a new workbook will be created automatically every 24 hours. A new suffix according to the date will denote the new workbook.
- Column J has been designated for the total volume delivered for this titration, since this data is required for calculation of the alumina concentration.

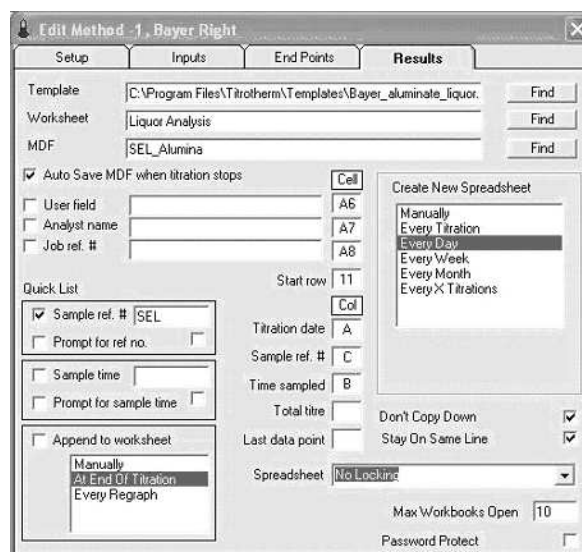


Fig. 8b. Method Edit>Results Form for Bayer Right Method

Notes:

- The same spreadsheet template is chosen as for the *Bayer Left* method, since the alumina results must be sent to the same line as the total caustic and carbonate titres, and since computation of the alumina concentration requires data from the *Bayer Left* titration.
- Sample description ("Ref No") and Sample Time should always be written in the *Bayer Right* method. If written in the *Bayer Left* method, anything in the corresponding cells in Excel will be overwritten by values in the corresponding *Bayer Right* boxes. The total volume titrated is not required, and no Excel column need be designated.
- Because it is required that data from this titration must be sent to the same line as the *Bayer Left* titration, it is necessary to suppress the automatic function to copy down data and formulae in the Excel spreadsheet, and for the Bayer Right data to stay on the same line. Therefore, these two boxes are checked.

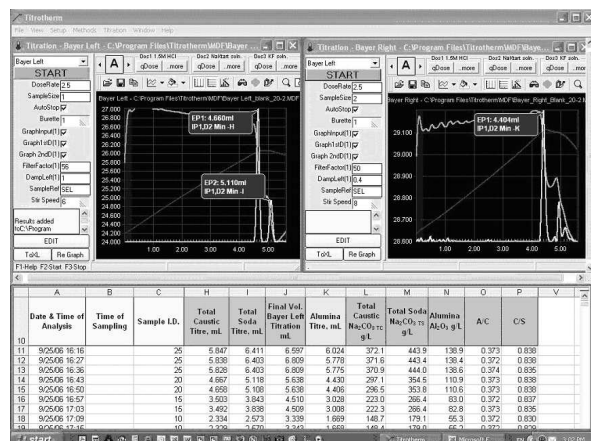


Fig. 9. Suggested Layout of Desktop for Multititrator Bayer Classic Liquor Analysis.

### 5. Theory and Calculations

The basis for calculating results is illustrated and explained below. For a detailed explanation on the nature and determination of titration system “blanks” please refer to Section 6 below.

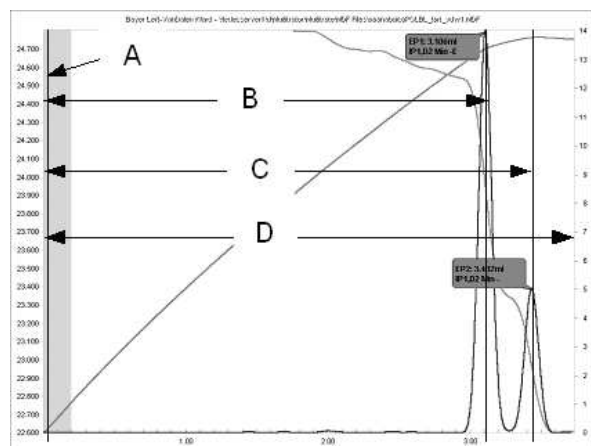


Figure 8a. Titration volumes in Bayer Left titration

- A = Bayer Left titration blank volume, mL
- B = Total caustic titre volume, mL
- C = Total caustic + bicarbonate titre, mL
- D = Total volume dispensed, mL

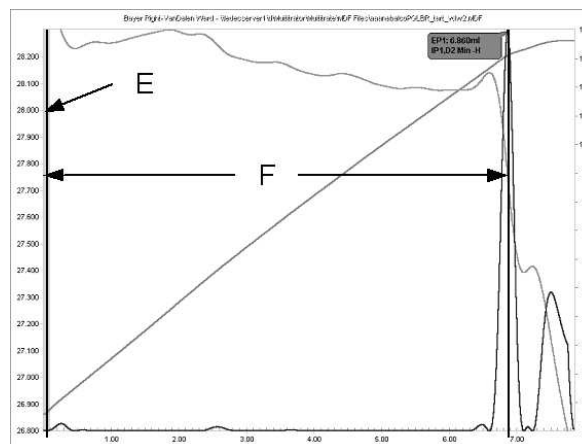
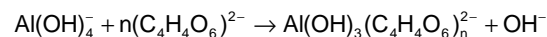


Figure 8b. Titration volumes in Bayer right titration.

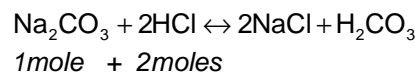
- E = Bayer Right titration blank volume, mL
- F = Alumina titre, mL

#### 5.1. Determination of Total Caustic

Total Caustic is defined as the total hydroxyl content of the liquor comprising “free” (unassociated) hydroxyl ions, and one hydroxyl of the four comprising the aluminate  $Al(OH)_4^-$  anion. By adding a suitable complexant such as tartrate to the aluminate, this single hydroxyl is released into solution to be titrated:



In the American convention, hydroxyl in Bayer liquor is referred to in terms of sodium carbonate. Thus 2 mole  $NaOH$  is equivalent to 1 mole  $Na_2CO_3$ , and for the purposes of calculation the following stoichiometric relationship can be imagined:



Thus in referring to Figure 8:

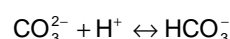
$$\text{Total Caustic "TC" } Na_2CO_3 \text{ g/L} = \frac{((B - A) \times MHCl \times 105.99)}{\text{Aliquot, mL} \times 2}$$

In the European convention, hydroxyl in Bayer liquor is referred to in terms of sodium oxide,  $Na_2O$ . Thus in European terms:

$$\text{Total Caustic "TC" } Na_2O \text{ g/L} = \frac{((B - A) \times MHCl \times 61.979)}{\text{Aliquot, mL} \times 2}$$

### 5.2. Determination of Total Soda.

Total Soda is defined as the total of the Total Caustic content of the liquor (defined above) plus the carbonate content of the liquor. The carbonate content is determined from the second endpoint in the Bayer Classic Left titration. To achieve this endpoint, 1 mole of hydrogen ion reacts with 1 mole of carbonate to form 1 mole of bicarbonate (the second endpoint due to protonation of the bicarbonate anion is not seen thermometrically in this titration):



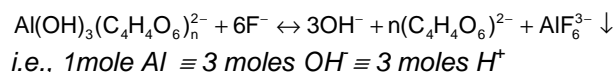
Therefore 1 mole of sodium carbonate is equivalent to 1 mole HCl. Thus in referring to Figure 8a:

$$\text{Total Soda "TS" Na}_2\text{CO}_3 \text{ g/L} = \frac{((C - B) \times \text{MHCl} \times 105.99)}{\text{Aliquot, mL}} + \text{TC}$$

where "TC" is defined above as Total Caustic.

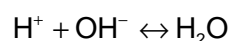
### 5.3. Determination of Alumina.

The addition of potassium fluoride breaks the alumino-tartrate complex to form the insoluble  $\text{NaK}_2\text{AlF}_6$  with the release of three hydroxyl ions. In ionic form, this reaction may be expressed as:



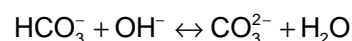
Thus to compute aluminium as  $\text{Al}_2\text{O}_3$  (which contains 2 moles Al),  $(3 \times 2) = 6$  moles  $\text{H}^+ \equiv 1$  mole  $\text{Al}_2\text{O}_3$ .

In order to employ the correct volume of acid titrated in the calculation of the "alumina" content of the liquor, it is not only necessary to use the corrected titre (titre – blank) in the Bayer Right titration (i.e., after the potassium fluoride has been added to liberate the hydroxyl ions in the alumino-tartrate complex), but also the amount of acid consumed in "overshooting" the endpoints in the Bayer Left titration. In the first, Bayer Left 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.,  $\text{H}^+$  ions. When the potassium fluoride is added, some of the liberated  $\text{OH}^-$  ions are consumed in neutralizing these free  $\text{H}^+$  ions:



Not only do the liberated hydroxyl ions react with

any free  $\text{H}^+$ , they also react with any bicarbonate ions,  $\text{HCO}_3^-$  which have been formed in the Bayer Classic Left titration



Thus (in referring to Figure 8) the volume of HCl which may be taken to be "overshot" in the Bayer Classic Left titration maybe computed by subtracting volume B from the total volume D. Therefore the "alumina" content of the liquor can be computed from:

$$\text{Al}_2\text{O}_3 \text{ "A" g/L} = \frac{(((F - E) + (D - B)) \times \text{MHCl} \times 101.96)}{(\text{Aliquot, mL} \times 6)}$$

### 6. Determination of Titration Blanks.

Thermometric titrations are conducted under conditions of a constant titrant addition rate. In this respect they differ from potentiometric titrations, where the titrant addition rate may be varied during the titration according to the electrode response. In thermometric titrations, a constant addition rate of titrant equates to a constant amount of heat being given out or consumed, and hence a more or less constant temperature change up to the endpoint. Ideally, the temperature of the solution should be transmitted to the computer and processed instantaneously throughout the titration. Practically this is not the case, and it takes a finite time before a change in temperature of the solution is received, computed and recorded. Since titrant is added at a constant rate, this time delay in the passage and processing of temperature information is expressed as a volume of titrant. These delays can be considered to be a summation of delays from various sources, including:

- Inefficiencies in the mixing of the titration solution
- Reaction kinetics (in the case of non-ionic titrations)
- Heat transfer delays across the thermistor cladding and in the thermistor bead itself
- Electronic and software processing delays.

Further, the shape of the inflection or breakpoint at the endpoint of the titration and the slopes of the temperature curve prior to and post the endpoint all have an impact on the optimum location of the endpoint as determined by the second derivative curve, and this has to be considered along with time delays in determining the actual amount of titrant consumed to the endpoint.

For given sets of titration conditions, these errors are constant and can be quantified as a single parameter – the titration method blank. This parameter is stored along with the other method parameters, and is subtracted from all titres recorded for this particular determination.

In addition to the factors described above, residual acidity or alkalinity in the tartrate and fluoride reagents used in this determination can contribute to the respective magnitude of the blanks for both Bayer Left and Bayer Right titrations.

For practical purposes, determination of titration blanks need only be done when one or more of the following parameters are changed:

- Change in HCl titrant dose rate
- Significant change in Filter Factor (only if the filter factor significantly alters the result)
- Significant change HCl molarity
- Change to a new batch of tartrate or fluoride solution, or change in manufacturer from either of these reagents

**6.1. Preparation of solution for determination of titrant blanks.**

6.1.1. Dilute 25mL strong digestion feed liquor to 500mL with water in a volumetric flask.

6.1.2. Prepare titrating solutions from this solution according to the table below:

Aliquot of diluted liquor, mL	(Effective aliquot of undiluted liquor, mL)	Water added, mL
25	(1.25)	0
20	(1.00)	0
15	(0.75)	5
10	(0.50)	10
5	(0.25)	15

6.1.3. Titrate according to the 859 Titrotherm Bayer liquor analysis method (this as-

sumes that 10mL the potassium sodium tartrate solution is added automatically – if not, add 10mL to each solution before titration). Note that with liquors containing little carbonate, it may be necessary to reduce the Filter Factor (say to 30) to get a clear resolution of the bicarbonate endpoint with smaller aliquots. Perform duplicate titrations at each liquor aliquot.

6.1.4. Fig. 9 is an excerpt from the results worksheet used to gather data for determination of titration blanks. Relevant data has been highlighted. The letters assigned to columns also relate to those items illustrated in Figs. 8a and 8b.

Titration Parameters				Bayer Left Titration			Bayer Right Titration
Aliquot, mL	Titrant Molarity HCl mol/L	Titration Blank Left mL [A]	Titration Blank Right mL [E]	Total Caustic Titre, mL [B]	Total Soda Titre, mL [C]	Final Vol. Bayer Left Titration mL [D]	Alumina Titre, mL [F]
1.25	1.50	0.00	-0.04	5.847	6.411	6.597	6.024
1.25	1.50	0.00	-0.04	5.838	6.403	6.609	5.778
1.25	1.50	0.00	-0.04	5.829	6.403	6.609	5.775
1.00	1.50	0.00	-0.04	4.667	5.118	5.638	4.430
1.00	1.50	0.00	-0.04	4.658	5.108	5.638	4.406
0.75	1.50	0.00	-0.04	3.503	3.843	4.510	3.028
0.75	1.50	0.00	-0.04	3.492	3.838	4.609	3.008
0.50	1.50	0.00	-0.04	2.334	2.573	3.339	1.669
0.50	1.50	0.00	-0.04	2.329	2.570	3.343	1.658
0.25	1.50	0.00	-0.04	1.165	1.277	2.215	0.283
0.25	1.50	0.00	-0.04	1.165	1.278	1.797	0.697

Figure 9. Data (highlighted columns) to be used in determination of titration blanks.

6.1.5. Use Excel to conduct linear regressions, as illustrated in Figs. 10a and 10b. To determine the Bayer Left blank, plot aliquot volumes (y-axis) against the Total Caustic Titre [B] (x-axis). To determine the Bayer Right blank, plot aliquot volumes (y-axis) against the volume [F]+[D]-[B] (x-axis). In both cases, the y-intercept values represent the titration blanks. Regardless of sign, these values are subtracted from the endpoint titres.

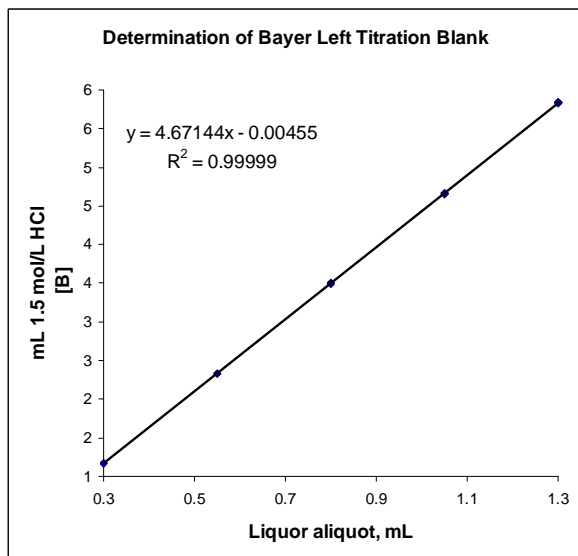


Fig. 10a. Regression analysis for Bayer Left blank determination.  
 Blank = y-intercept = -0.00455mL

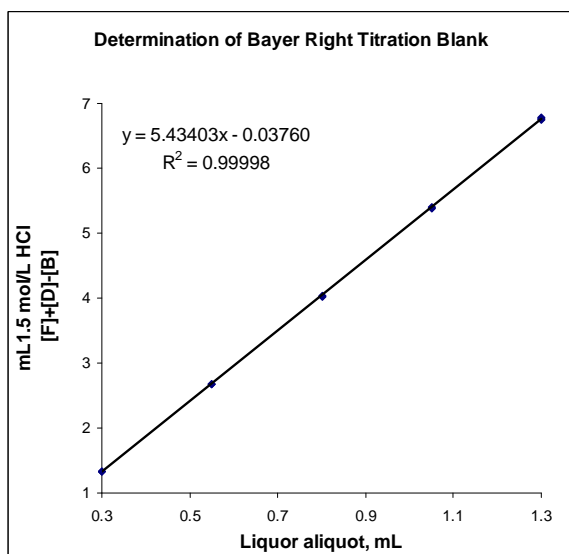
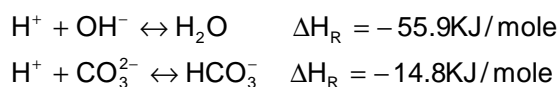


Fig. 10b. Regression analysis for Bayer Right blank determination  
 Blank = y-intercept = -0.03760mL

### 7. Determination of Carbonate.

In most aluminate liquors, the determination of carbonate is straightforward. However, special care might be necessary when the bicarbonate endpoint lies very close to the hydroxyl (“total caustic”) endpoint. This can happen when either the amount of carbonate is low (relative to the total caustic content), and/or the liquor is dilute. The reaction enthalpy for the formation of bicarbonate from carbonate is modest compared to that for the reaction of hydrogen ions with hydroxyl ions, and the endpoint can be lost if care is not taken.



Consider the case illustrated in Fig. 11a. A small aliquot (0.25mL) of a strong liquor has been titrated, and a filter factor of 55 applied. This filter factor had been found to be near optimal for larger aliquots (1 – 1.25mL) of liquor, but in the case presented here, the titration data was clearly over-smoothed. Choice of a smaller filter factor of 30 resulted in a clear delineation of the two endpoints.

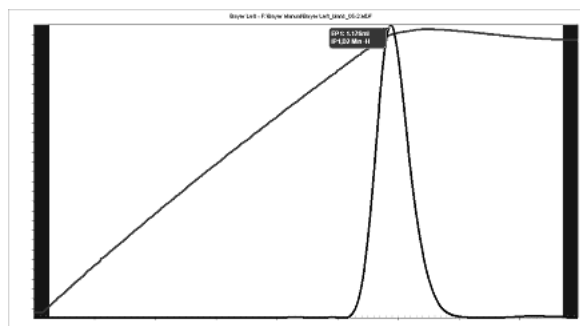


Figure 1a. Effect of filter factor on resolution of bicarbonate endpoint – 0.25mL aliquot. Filter factor = 55 EP=1.176mL.

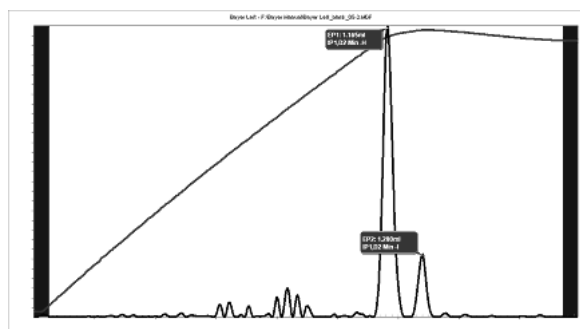


Figure 11b. Effect of filter factor on resolution of bicarbonate endpoint – 0.25mL aliquot. Filter factor=30 EP1=1.165mL, EP2=1.280mL.

Under the same experimental conditions, the amount of data smoothing required is dependent on the number of data points collected during the titration. The Titrotherm software is set to acquire a constant 50 data points per second. For a titration of the magnitude illustrated here, approximately 2000 data points would have been collected.

Compare these results with those illustrated in Figs. 12a and 12b. Here, a 1mL aliquot was titrated, generating approximately 8000 data points.

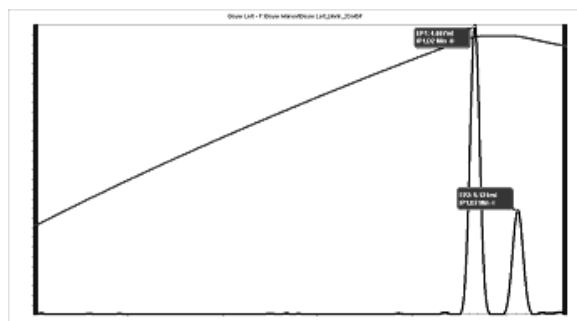


Figure 12a. Effect of filter factor on resolution of bicarbonate endpoint – 1.00mL aliquot. Filter factor = 55, EP1=4.667mL, EP2=5.121mL

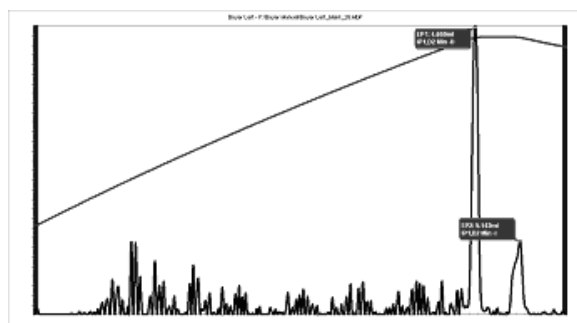


Figure 12b. Effect of filter factor on resolution of bicarbonate endpoint – 1.00mL aliquot. Filter factor =30, EP1=4.669mL, EP2=5.143mL

A filter factor of 30 is clearly inadequate, generating a noisy, asymmetric bicarbonate endpoint which is at variance with the result obtained with a filter factor of 55. In contrast, the result obtained for the Total Caustic endpoint is scarcely altered.

The question is therefore, how can we practically and easily determine the carbonate content across the wide variety of liquor concentrations present in an alumina refinery? Certainly, the easiest way is to use the large capacity of the methods database servicing the Titrotherm software. Because a method can be changed in a titration window by merely selecting it from a pull-down list, we can create individual methods optimized for a range of liquor types. In practical terms, these methods will only differ from each other in the aliquot size and the amount of data smoothing necessary to effect a smooth symmetrical bicarbonate endpoint optimally resolved from the adjacent hydroxyl endpoint. For instance, it is possible to imagine Bayer Left and Right methods divided into the following categories

Method Name	Examples of Liquor Types
High Range	Digestion feed, spent, digestion discharge, pregnant liquors
Mid Range	First and second washers, caustification, seed wash liquors
Low Range	Third and fourth washer liquors
Very Low Range	Red mud washing, plant recycle liquors

A variation on the above strategy can be considered if very low carbonate levels are encountered. Here, a larger than normal aliquot is taken in order to enhance the difference between the hydroxyl and bicarbonate endpoints. In extreme cases, a titre of say 8 - 9 mL could be contemplated. Note that because carbonate concentrations in strong liquors are not subject to rapid change, this special titration only needs to be performed perhaps once or twice per day. Since the alumina value is not required, this method should not be chained to a Bayer Right method. It might also be necessary to increase the amount of tartrate dosed, to ensure all aluminate is complexed.

It is worthwhile mentioning that the basic experimental conditions described in this manual are near optimal for the determination of carbonate as well as caustic and alumina. In particular, the fast titration rate of 2.5mL/min enhances the rate of heat output from the reactions, which is manifested by sharper inflections in the titration temperature curves. Higher titrant addition rates have been investigated (>3mL/min), but there is a degradation in precision due to increased endpoint rounding.

#### References:

- (1) H. L. Watts and D. W. Utley, *Anal. Chem.* **28**, 1731 (1956)
- (2) E. VanDalen and L. G. Ward, *Anal. Chem.* **45**, 2248 (1973)