Thermo. Titr. Application Note No. H-066

Title: Carbonate and bicarbonate in solution

***Scope*:**	Determination of bicarbonate and carbonate in a mixture by sequential thermometric titrations

***Principle*:**	Titration of HCO_3^- with OH^-, followed by titration of total CO_3^{2-} with Ba^{2+} $HCO_3^- + OH^- \leftrightarrow CO_3^{2-} + H_2O$ $CO_3^{2-} + Ba^{2+} \leftrightarrow BaCO_3 \downarrow$

Reagents:	1. Standard 1mol/L sodium hydroxide 2. Standard 1mol/L barium acetate ($Ba(OAc)_2$) 3. A.R. potassium hydrogen phthalate (for standardization of NaOH titrant) 4. A.R. anhydrous sodium carbonate (for standardization of $Ba(OAc)_2$)

Method:	Basic Experimental Parameters: Titrant delivery rate (mL/min.) 5 Data smoothing factor NaOH titration 70 Data smoothing factor $Ba(OAc)_2$ titration 55 Stirring rates: NaOH titration 11 $Ba(OAc)_2$ titration 12 Procedure: The titration is setup so that the NaOH titration of HCO_3^- is performed first. The succeeding $Ba(OAc)_2$ titration for the total carbonate content is “daisy-chained” to the first titration, so that it starts automatically following completion of the HCO_3^- titration. It is only necessary to click “Start” for the HCO_3^- titration for the entire sequence to be completed automatically. The example illustrated here is a solution of sodium hydrogen carbonate and sodium carbonate, with a total carbonate concentration of approximately 10g/L Na_2CO_3. A 50mL aliquot is pipetted into a titration vessel, and the titration sequence commenced without further sample preparation.

Standardization of titrants:

1. NaOH titrant is standardized against potassium hydrogen phthalate (KHPhth). Quantitities of KHPhth corresponding to approximately 1,2, 3, 4 and 5 mmole are weighed accurately into titration vessels and allowed to dissolve in 30mL of DI water before titrating at 5mL/min against the NaOH titrant. The results are plotted, mmole KHPhth on the x-axis, mL NaOH titrant consumed on the y-axis. The molarity of the titrant is calculated from the reciprocal of the gradient, as computed by regression analysis.

2. $Ba(OAc)_2$ titrant is standardized against a 0.1mol/L Na_2CO_3 solution prepared from anhydrous A.R. Na_2CO_3. Aliquots are prepared according to the following table:

mL 0.1mol/L Na_2CO_3	mL DI water	mmole Na_2CO_3
50	0	5
40	10	4
30	20	3
20	30	2
10	40	1

Solutions are titrated at 5mL/min, the results being plotted with mmole Na_2CO_3 on the x-axis, mL $Ba(OAc)_2$ titrant consumed on the y-axis. The molarity of the titrant is calculated from the reciprocal of the gradient, as computed by regression analysis.

Results:

Solution comprising $NaHCO_3$ and Na_2CO_3 with mole ratio of ~2:1, and with total carbonate concentration ~0.1mol/L as Na_2CO_3

$NaHCO_3$ =5.38±0.014 g/L, n=10
Na_2CO_3 = 7.42±0.015 g/L, n=10
Total carbonate (as Na_2CO_3) = 10.81±0.012, n=10

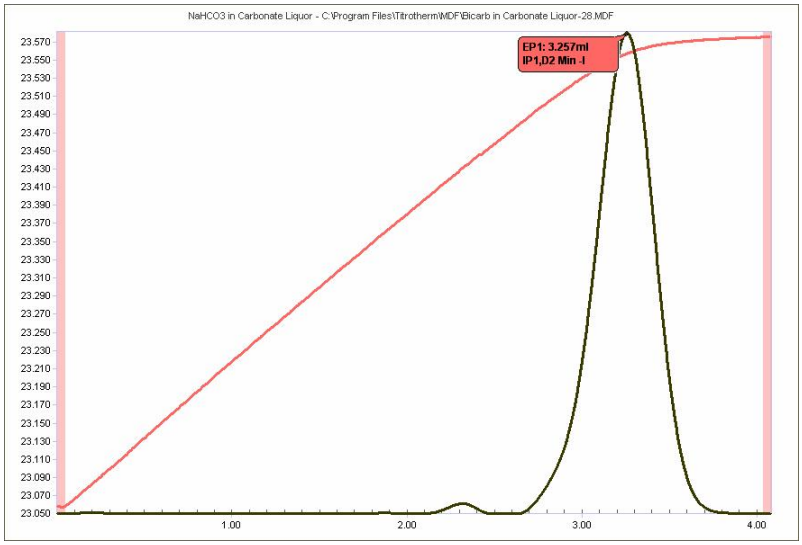
Calculation formulae:

$$NaHCO_3\ g/L = \frac{((mL\ NaOH - mL\ blank) \times 84.01 \times M\ NaOH)}{mL\ sample}$$

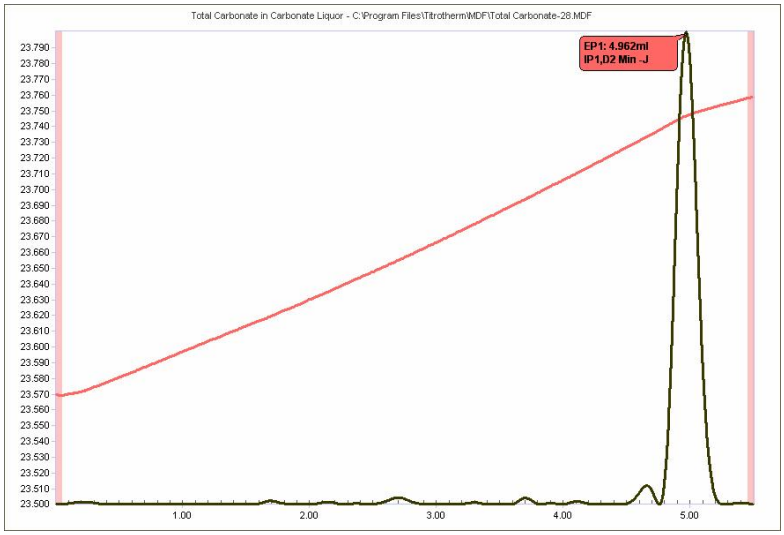
$$\text{Total Carbonate } g/L = \frac{(mL\ Ba(OAc)_2 - mL\ blank) \times 105.99 \times M\ Ba(OAc)_2}{mL\ sample}$$

$$Na_2CO_3\ g/L = \text{Total Carbonate } g/L - \frac{NaHCO_3\ g/L \times 105.99}{2 \times 84.01}$$

Thermometric Titration Plots:



Titration of $NaHCO_3$ component with NaOH



Sequential titration of "total carbonate" with $Ba(OAc)_2$

Legend:

Red = solution temperature curve

Black = second derivative curve

Example of titrant calibration: $Ba(OAc)_2$

Molarity =1/gradient = 1/0.95201 = 1.0504

Blank = y-intercept = 0.112mL