EXPERIMENT: DETERMINATION OF SODA ASH (pH)

INTRODUCTION
The measurement of soda ash in industrial samples is important. In this experiment, an HCl solution is prepared and standardized with dried sodium carbonate. The standardized HCl is then used to analyze a dried soda ash sample. In the following procedures both indicator and pH meter methods (potentiometric titration) will be used.

PROCEDURE:
Indicator Method
Prepare 500 mL of a 0.1 M HCl (conc. HCl stock is approx. 12.1 M) solution by diluting the appropriate quantity of conc. HCl with distilled water. Fill your burette with the HCl solution and standardize it against sodium carbonate as follows.

Weigh accurately two samples of 0.1g pure, dried sodium carbonate (by difference) into two 250ml Erlenmeyer flasks. Add 50mL distilled water and 2 drops phenolphthalein indicator. Titrate slowly (0.5mL/sec) until the pink color disappears. This is a slight excess for half the volume of acid required for total neutralization. Add 2 drops of methyl orange indicator and continue titrating until the color changes from straw to pale orange to pink. Calculate the molarity of the HCl solution, which is standardized.

Now weigh accurately two 0.2 to 0.3g samples of the dried unknown soda ash and titrate with the standardized acid in duplicate with indicators as above. (Note: At the start of the experiment on the unknown, the student should run a quick, approximate titration using the indicators to establish the approximate location of the end points and the color changes to be expected. With this information, the student should be able to estimate the required HCl for the particular end-point, and then carefully add the remaining 10% of the HCl slowly so that an accurate endpoint is obtained.)

pH Meter Titration (Note: the important data are the pH readings; the indicators are added only for reference purposes.)
Weigh accurately 0.1-0.2g pure, dried sodium carbonate (by difference) into a 400mL beaker provided with a magnetic stirring bar. Add 50mL water, dissolve, and add 2 drops of phenolphthalein indicator. Insert a glass and calomel electrode into the solution (Note: Avoid it contact with the stirring bar). Add titrant and record readings until the phenolphthalein indicator changes color (Note: It is best to take points at 2-3mL intervals between the end points, and at 0.2mL increments near the end points). Add 2 drops of methyl orange indicator and continue the titration until the color changes again. Record the end points. Exceed the final equivalent volume with and additional 10ml of titrant. Do this titration rapidly, because the pH will tend to drift as CO\textsubscript{2} escapes from the solution.

E.g. If the end point occurs around 14 mL, add the following mL increments:
3, . . . 3, . . . 2, . . . 2, . . . 0.5, . . . 0.2, . . . 0.1, . . . 0.05, . . . 0.05, . . . 0.05, . . . 0.05, . . . 0.05, . . . 0.1, . . . 0.2, . . . 0.5, . . . 2, . . . 2, . . . 3, . . . 3...Exceed the end point by about 10 mLs.

Now weigh accurately 0.2 to 0.3 g of the dried soda ash unknown. Titrate, following the above procedure using the pH meter. For each pH meter titration, plot a curve of pH versus volume of titrant, and the Grand plot. Calculate your results based on the total volume to the second end point* as if the soda ash unknown were sodium carbonate and contained no sodium bicarbonate. Report the results as % sodium carbonate (Na\textsubscript{2}CO\textsubscript{3}) and as % sodium oxide (Na\textsubscript{2}O).
Possible Sources of Determinate Errors.
If you compare the pH at the first end point with the pH at which you observed the phenolphthalein end point, you may find that the indicator color changes, not at the end point, but by as much as 3% to 5% of the volume of titrant after the endpoint. (For example, the equivalence point may occur at pH 8.4, whereas the red color may disappear at pH 8.0). This has some interesting consequences. One is that, with indicator, the ratio of the volumes of acid at the second to the first end point is not exactly ‘2’ but about 1.9 (check your indicator data in the textbook to see whether the discrepancy occurs and if it agrees with this discussion). Another major difference between the two end points is that of precision. Refer to your data obtained from the pH meter titrations. The main factor influencing precision will be the ratio of changes in pH to changes in volume of added titrant at the first and second end points. To see this, examine the pH vs. Vol. of HCl graph. At each end point, measure the Vol. of HCl at $(pH + 0.5)$ and at $(pH - 0.5)$. From these, calculate Vol. of HCl needed to change the pH by $\pm 0.5$ for the first and second end points.

*Calculate your results based on a Gran Plot (see Section 12-5 of your textbook for further discussion of the theory). The Gran Plot is based on the following equation:

$$V_a \cdot 10^{pH} = \left\{(1/K_a)(\gamma_B/\gamma_{BH+})\right\} (V_e - V_a)$$

$$= -\left\{(1/K_a)(\gamma_B/\gamma_{BH+})\right\} V_a + \left\{(1/K_a)(\gamma_B/\gamma_{BH+})\right\} V_e$$

$$\Rightarrow \quad y = m \cdot x + b$$

where $V_a$ = is the volume of strong acid added, pH = is the pH meter reading, $K_a$ = acid dissociation constant of the acid form of the base, $BH^+$, $B$ is the weak base being titrated, and $V_e$ = equivalence point. Note that the above equation resembles that for a straight line: $y = mx + b$, for regions not very near the equivalence point. The variables are $V_a \cdot 10^{pH}$ for the ordinate (y-axis) and $V_a$ for the abscissa (x-axis). It is not necessary to know the actual values of the other parameters, $K_a$, $\gamma_B$, $\gamma_{BH+}$ and $V_e$. By extrapolating the straight line portion of the graph to obtain the x-intercept, one can determine the value of $V_e$ more accurately than by a first derivative curve.

The above equation simplifies to: $y = mx + b$ by equating $y = V_a \cdot 10^{pH}$, $m$ (the slope) = $-\left\{(1/K_a)(\gamma_B/\gamma_{BH+})\right\}$, $x = V_a$ and $b = \left\{(1/K_a)(\gamma_B/\gamma_{BH+})\right\} V_e$. The x-intercept occurs when $y=0$. That occurs when $V_a = V_e$. It is not necessary to know the slope. ***Submit a copy of your graph with the informal results for this experiment.

Waste Disposal: Discard all waste in appropriate bottles as instructed. If you have any questions, please see your instructor or teaching assistant before disposing of waste.
Informal report: 

Experiment: Determination of Soda Ash

Name: __________________________

Values obtained:

(1) ________ %

Locker # _______________ (indicator method)

(2) ________ %

(Gran plot)

(3) ________ %

Average value = ________ %

(if applicable) Standard deviation= ________ %

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I (indicator) II (indicator) III (pH meter)

g dried Na₂CO₃ used for standard solution: ___________ ___________ ___________ g

Standardization titration:

mLs of HCl added to reach 1ˢᵗ end point ___________ ___________ ___________ mL

mLs of HCl added to reach 2ⁿᵈ end point ___________ ___________ ___________ mL

Molarity of the HCl standard: _______________ M

Sample calculation: $M_{HCl} =$

Unknown titration:

I (indicator) II (indicator) III (pH meter)

g dried unknown sample: ___________ ___________ ___________ g

mLs of HCl added to reach 1ˢᵗ end point ___________ ___________ ___________ mL

mLs of HCl added to reach 2ⁿᵈ end point ___________ ___________ ___________ mL

% Na₂CO₃ in unknown: % ___________ ___________

Sample calculation: At the 2ⁿᵈ equivalence point, milliequivalents, mEq of titrant, A = mEq analyte, B at 2ⁿᵈ end point: mEq HCl = mEq Na₂CO₃; #mols HCl = 2 x (#mols Na₂CO₃);

$M_{HCl} V_{HCl} = 2(g \text{ Na}_2\text{CO}_3)/(\text{FW of Na}_2\text{CO}_3)$ => $g \text{ Na}_2\text{CO}_3 = (M_{HCl} V_{HCl})(\text{FW of Na}_2\text{CO}_3)/2$

% Na₂CO₃ = $(g \text{ Na}_2\text{CO}_3)(100%)/(g \text{ of unknown sample})$

FW of Na₂CO₃ = 105.99 g/mol; FW of Na₂O = 61.98 g/mol;