Crude sodium carbonate, Na\(_2\)CO\(_3\), is commonly called soda ash. It is frequently used as a commercial neutralizing agent. Besides the carbonate small amounts of sodium hydroxide, NaOH, and sodium hydrogen carbonate, NaHCO\(_3\), may also be present. Titrating with standard acid, usually HCl, makes it possible to determine the total alkalinity of the soda ash. It is common practice to report the total alkalinity as percent sodium carbonate or sodium oxide, Na\(_2\)O. Since samples are frequently non-homogeneous, the method of aliquot portions is usually employed. Instead of weighing out three separate samples of soda ash, one accurately weighs out a larger amount. This is then transferred into a volumetric flask, dissolved in water and then diluted to an accurately known volume. From this solution are then taken samples or aliquots on which the titration is carried out.

**DISCUSSION**

The titration involved in the determination of the carbonate content is an example of a weak base being titrated with a strong acid. The two weak bases involved are \( CO_3^{2-} \) with \( K_{b1} = 2.1 \times 10^{4} \) and \( HCO_3^- \) with \( K_{b2} = 2.4 \times 10^{-8} \). The reactions involved are:

\[
\text{(1)} \quad CO_3^{2-} + H_3O^+ \rightleftharpoons HCO_3^- + H_2O
\]

and

\[
\text{(2)} \quad HCO_3^- + H_3O^+ \rightleftharpoons H_2CO_3 + H_2O
\]

The equivalence point pH for reaction \( \text{(1)} \) occurs at a pH of about 8.3, hence a suitable and commonly used indicator is phenolphthalein. The equivalence point for reaction \( \text{(2)} \) occurs at a pH of roughly 4.0. Indicators that have been used are methyl red, methyl orange, methyl purple and bromocresol green. Bromocresol green will be used in the analysis that you will perform. At the beginning of the titration, CO\(_3^{2-}\) exists to the practical exclusion of the other carbonate species. When one equivalent of acid has been added, almost all of the CO\(_3^{2-}\) has been changed into HCO\(_3^-\). Addition of a further equivalent of acid changes practically all hydrogen carbonate into carbonic acid, H\(_2\)CO\(_3\). The latter is in equilibrium with water and CO\(_2\). The steep portions of the titration curve near the two equivalence points are not so steep and do not extend over so large a pH range as is required for a titration accuracy of 0.1 relative percent.

Near the HCO\(_3^-\) equivalence point pH of 8.3 the change in pH caused by adding 1.0 mL of acid is only about 0.3 units and 10 mL are needed for a pH change of 1 unit. The situation near the second equivalence point at pH 4.0 is somewhat more favorable. About 4 mL of acid are needed for a pH change of 1 unit. The accuracy of the titration can be improved considerably by removal of the CO\(_2\) just before the second equivalence point has been reached. An accuracy of better than 0.1 relative percent may be obtained by the experimental procedure outlined below.

Phenolphthalein indicator is added to the carbonate solution which is then titrated with HCl until the pink color has just disappeared, which will occur at an approximate pH of 8. Since the equivalence point is at pH 8.4 an amount of acid somewhat in excess of one equivalent is used, and the titration gives only a rough measure of the carbonate content of the original solution. Next bromocresol green indicator is added, which will turn the solution blue. When the titration is continued the solution will gradually turn from blue to green and will then approach yellow. Just before the solution turns completely yellow the solution is boiled to remove the dissolved CO\(_2\). This will change the pH back to somewhere
between 8 and 9 and the indicator color back to blue. The solution is then cooled in an ice bath and the titration is continued until the solution becomes yellow-green. Removal of the CO$_2$ changes the aspects of this last part of the titration to one of a strong base titrated with a strong acid, which explains the accuracy of better than 0.1% that can be obtained by this method.

The complete equation for this reaction, and the one on which you will base your calculations, both for the standardization of HCl and the determination of the mass % Na$_2$CO$_3$ in soda ash is

\[
\text{Na}_2\text{CO}_3(\text{aq}) + 2\text{HCl} \rightarrow \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) + 2\text{NaCl}(\text{aq})
\]

Since anhydrous sodium carbonate of high purity can readily be obtained, it is often used as a primary standard for the standardization of strong acids. You will use this reagent for your standardization, however, be certain that you are using the anhydrous reagent and not the decahydrate.

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**EXPERIMENTAL**

**Preparation and Standardization of 0.10 M HCl**

Dry about 2.0 g of primary standard, anhydrous Na$_2$CO$_3$, in a weighing bottle for 2 hours at 105-110°C, then cool and store in a desiccator.

Rinse your 1-quart glass bottle with distilled water. Add distilled water just up to the beginning of the gentle curve near the top, leaving a little air between the water surface and the neck. Using an appropriate graduated cylinder, measure and add 17 mL 6M HCl. Then add a little water to the graduated cylinder, swirl gently and add the mixture to the bottle. Stopper the bottle and invert several times to achieve a homogeneous mixture. One quart is 946 mL, almost one liter. Seventeen mL of 6M acid when diluted with 946 mL water gives a solution equal nearly to 0.1M concentration:

\[
\frac{17\,\text{mL}}{946\,\text{mL} + 17\,\text{mL}} \times 6\,\text{M} = 0.11\,\text{M}
\]

This solution is to be standardized using anhydrous Na$_2$CO$_3$ so there is no need to attend to analytical precision in this procedure. The concentration of commercial HCl isn't assayed with a precision greater than ±0.2 M (it is routinely assayed at 36.5-38.0%, close to 12 M) so even if the 17 mL were measured to ±0.001 mL the molarity still couldn't be determined with a precision sufficient for this experiment. To achieve the necessary precision the solution must be standardized with measured samples of anhydrous sodium carbonate.

Accurately weigh out three 0.20 to 0.25 g samples of dried, anhydrous Na$_2$CO$_3$ directly into separate, clean and dry 250 mL Erlenmeyer flasks. Add 50 mL of distilled water to dissolve the carbonate, then cover the flasks with paraffilm. Rinse your clean 50 mL buret with small portions of your HCl solution and then fill it with the acid solution. Record the initial reading (which does not have to be exactly 0.00 mL) to the nearest hundredth of a mL. Anhydrous sodium carbonate absorbs both water and carbon dioxide from the atmosphere, so your samples will likely show a slow increase in weight. It is not unusual to observe an increase of 0.0001 g every 5 to 10 seconds. You musn't dilly dally in trying to make the mass equal to 0.2000 g or 0.2500 g or some other specific number, or the gradual increase in mass will produce a significant systematic error in your results. Transfer the reagent until the observed mass is between 0.2 and 0.25 g, close the doors
of the balance, take a reading when the mass stabilizes to ±0.0001 g and be done with it. One other warning: crystals of anhydrous sodium carbonate don't stick together on your flat spatula. They tend to fall off so during your transfers don't try to make large mounds of the reagent on your spatula tip or you'll lose some. The places where you don't want to lose any is down the side of the flask wall, on the lip of the flask or on the pan outside the flask. You want all of it to go into the mouth of the flask.

The titration which is described below involves a blue-to-green color transition. The subtlety of the change is not easily seen by some people. Blue-green color blindness is common in our population and there are many people who are unaware that they suffer a slight impairment. To be sure that you can determine a reproducible end point, prepare 100 mL of 0.05 M NaCl in a 250 mL Erlenmeyer flask by diluting 5 mL 1.00 M NaCl to 100 mL with distilled water. Add 3 drops bromocresol green indicator and 3 drops phenolphthalein indicator, boil briefly, cool and titrate to the end point where the green color just changes to yellow-green. Take care, as the volume required will be quite small, possibly as little as one drop. This volume is called the "indicator correction", "blank correction" or "titration error"; it ought to be subtracted from your other titration volumes (because the volume is that which is required to reach the end point for a sample containing no Na$_2$CO$_3$).

Keep this titration as a guide to repeatability for all future titrations. It gives you a reference color for your end point. Bringing all future titrations to that final color and then subtracting the indicator correction from your final volumes ought to improve your results. At the end of every lab period throw out your indicator correction titration and make up a new one at the beginning of the next lab period.

Add 3 drops of phenolphthalein indicator to one carbonate sample and titrate it with the acid, as described above in the discussion section. Place a piece of white paper under the flask which is to be titrated so that you can see easily any subtle color changes. At the first equivalence point the color will fade quite slowly, therefore do not expect a sudden change from pink to colorless. Use your best judgment. Phenolphthalein is colorless in acid solutions and vivid pink in basic solutions. The first equivalence point of CO$_3^{2-}$ is reached when the solution has changed from pink almost to colorless but still has a ghostly hint of pink left in it. After the first equivalence point, add 3 drops of bromocresol green indicator; the solution will turn blue. Titrate with HCl until the solution just begins to change from blue to green. If it turns yellow you have gone too far. Your solution must be discarded and you must start over with your second sample. A new "first" sample can be reweighed after the last two have been completed successfully. Add acid while continually swirling the flask. When the blue color begins to fade into the green, heat the solution to boiling on a hot plate to expel the CO$_2$ formed during the titration. Cool to room temperature with the aid of an ice bath. The solution should again be green, possibly even blue. Complete the titration by adding acid dropwise until the solution changes to the color of the blank prepared previously. Record the buret reading and calculate the total amount of acid used from the beginning of the titration to the bromocresol green end point after boiling. Correct the volume of acid used with the aid of the buret calibration graph prepared earlier and subtract your end point error, or blank correction. Now repeat the same procedure with the other two samples one at a time. From the acid volume and the mass of Na$_2$CO$_3$ used calculate the molarity of the HCl solution. The average deviation from the mean molarity ought not to be greater than 0.2% of the mean.

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**Titration of a Soda Ash Sample**

Dry your unknown sample in an oven for 1 hour at 110°C and cool in a desiccator. Using a weighing bottle, accurately weigh out 2.5 g to an accuracy of ±0.0001 g. Using your wash bottle add a small amount of distilled water to the weighing
bottle and then transfer the dissolved material into a clean 250 mL volumetric flask using your wide-stem funnel and water washes. Add additional distilled water to the volumetric flask and make up to the calibration mark. While adding water be sure to mix the contents of the flask well by agitating it. However, do not invert the flask at this stage. Only after filling to the mark can you invert it. When filling to the calibration mark use your eye-dropper to add the last few drops. The next step will include the use of a 25 mL volumetric pipet. Click here to receive some helpful hints on the use of a volumetric pipet. When using a rubber bulb to draw liquid into the pipet do not force the bulb over the end of the pipet. If necessary ask your instructor for help. Once you feel that you are proficient in the use of pipets, use a 25 mL pipet to transfer three 50 mL aliquots of the unknown solution into three separate 250 mL Erlenmeyer flasks. Using a 25 mL pipet to measure out these aliquots is considerably easier than using a 50 mL pipet which, because of its size, is difficult to handle. Titrate each sample, one at a time, as in the procedure for the standardization of the acid.

**Report**

From your experimental data calculate, for each aliquot taken, the percentage of Na\(_2\)CO\(_3\) in the unknown. Your report must include the following data.

1. Unknown number
2. The mass of each sample anhydrous sodium carbonate
3. Volume of HCl for each sample of anhydrous sodium carbonate
4. Average molarity of the HCl used
5. The mass of your unknown sample.
6. Aliquot volume of unknown solution to be titrated
7. For each aliquot taken give the net volume of acid used to the bromocresol green endpoint (the corrected volume which will be used to calculate the percent sodium carbonate).
8. Percentage of Na\(_2\)CO\(_3\) in the soda ash for each aliquot titrated
9. Average percentage of Na\(_2\)CO\(_3\) in the soda ash
10. Average deviation from the mean of the individual values of percent Na\(_2\)CO\(_3\).
11. Pages in your lab notebook containing the pertinent data

**Questions on the Carbonate Content of Soda Ash**

1. Why is the solution boiled just before reaching the second equivalence point?
2. The soda ash in your analysis was assumed to be pure Na\(_2\)CO\(_3\). If some of the Na\(_2\)CO\(_3\) is replaced by an equal number of formula weights of NaHCO\(_3\), how would the volume of acid change from (a) the starting point to the phenolphthalein end point? (b) the phenolphthalein end point to the bromocresol green end point? (c) the starting point to the bromocresol green end point?
3. Referring to question 2. above, how would the volumes change if some of the Na\(_2\)CO\(_3\) were replaced with an equal number of formula weights of NaOH?
4. Why does the pink color at the first equivalence point fade only gradually?
5. What is the primary standard which is used for the standardization of the HCl?
6. What is meant by the “aliquot portion method”? Why is it used in this analysis?
Contributors

• Ulrich de la Camp and Oliver Seely (California State University, Dominguez Hills).