

## ACID-BASE TITRATION 2:

### Standardization of HCl and Analysis of Accuracy and Precision

In this experiment you will compare the concentration of hydrochloric acid obtained by two different methods (both titrations). Hopefully they will be the same or only slightly different. You will do a statistical analysis of your data to determine whether the two concentrations are distinguishable within your experimental uncertainty. You could regard this as a check on your lab technique – this would sometimes be called an inter-comparison experiment. In a sense, this can also provide a one-sided check on accuracy since two statistically distinguishable results cannot both be correct, meaning one (or both) can have a systematic error.

### Standardization of Hydrochloric Acid Solution by back titration

In the first step you will standardize the diluted HCl stock solution against primary standard sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) using sodium hydroxide in a back titration. In a back titration, an excess of a reagent to be standardized (in this case HCl) is added to completely react with the primary standard (sodium carbonate) leaving some of the reagent behind, which is then determined in a titration with the previously standardized second reagent (here NaOH). Keep in mind that the stoichiometry for  $\text{HCl} + \text{Na}_2\text{CO}_3$  is 2:1 while  $\text{HCl} + \text{NaOH}$  is 1:1 and that the "knowns" in the final calculation will be the mass (and thus moles) of the sodium carbonate and the volume (and hence moles) of NaOH as well as the volume of HCl used. *Doing this one by hand before incorporating it into the prelab spreadsheet is generally easier.*

### Solutions to Prepare

As before with the NaOH, the solution in your lab's carboy is nominally 1.0 M HCl, so you will need to make ten-fold dilutions of both the NaOH and HCl for this experiment using your calibrated glassware. Dilute the NaOH first and store it in your brown plastic bottle with the cap on tight to minimize absorption of atmospheric  $\text{CO}_2$ . Then you can make and store your diluted HCl in the 250 mL volumetric flask. Rinse your volumetric flask with DI before making the diluted HCl to avoid contamination and loss of HCl.

### Back Titration of HCl with Standard NaOH

Using the analytical balance, weigh out three samples (nominally about 0.13 g, but weighed to 0.1 mg accuracy) of primary standard sodium carbonate into 250-mL Erlenmeyer flasks. As with the KHP in the preceding experiment, the  $\text{Na}_2\text{CO}_3$  should be in the oven and should be transferred to the desiccator to cool before weighing. Add about 25 mL of water to dissolve the solid. Add 5 drops of phenolphthalein to each.

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Pre-calculation: Calculate the volume of HCl required to neutralize the sodium carbonate and leave enough hydronium ions to require about 15 - 30 mL of your standardized NaOH to titrate back to an equivalence point. {Note that this procedure would cost you some accuracy and precision if the amount doesn't correspond to a volume you can add with a calibrated volumetric pipet. (Note1)}

Add the 50-mL of HCl to the three flasks containing the carbonate solution. Then put the mixtures on a hot plate and heat them until they are about to boil (Note 2) (the solutions should remain colorless). This will drive off the carbonate as gaseous CO<sub>2</sub>. Remove from the hot plate and allow the solutions to cool to room temperature. Finally back titrate the HCl with NaOH to the phenolphthalein endpoint as in the previous experiment.

### Titration of HCl with Standard NaOH (a.k.a. Direct Titration)

Standardize the diluted HCl solution against the NaOH solution that you standardized in the last experiment. This will be taken as an independent measurement of the concentration of the HCl. Pipet 25.00 mL of HCl into three 250-mL Erlenmeyer flasks and add 5 drops of the phenolphthalein indicator. Titrate to an endpoint with NaOH as before. (Note 3 and Note 4)

Before proceeding check to make sure your RSD for each set of replicates is reasonable and that there is some level of agreement between the results for the two different methods. If not, check to see if there is a clear outlier (a data point that looks questionable) in either of your titration datasets.

### The t-Test

A common approach for checking the accuracy of a measurement is to measure the same quantity by two different methods, especially if one method is known to work well. For example, one might analyze for iron in an ore by a gravimetric method and then compare the result with a volumetric method. Because of experimental uncertainties different methods rarely give exactly the same result. One must then ask whether the different results are in agreement within experimental uncertainty or whether the difference is real. That is, is any difference observed between the mean results obtained by the two methods significant? If so, this could demonstrate a systematic error in the less well characterized method.

Statistics provides a tool called the t-test that can help answer the question. The t-test compares a critical value of the t statistic to one calculated from the data (t is obtained by dividing the absolute value of the difference between the means of the two sets of data by the pooled standard deviation of the mean). In this experiment, you can take an average of the two standard deviations to derive a pooled standard deviation and divide this by  $\{N_1N_2/(N_1+N_2)\}^{1/2}$  to obtain the pooled standard deviation of the mean. {Properly speaking, you wouldn't do this unless you verified that the standard deviations of the two sets were not statistically

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distinguishable using an F-test, but with only three points in each set, you can rarely demonstrate a difference.} If the computed value for the t statistic is larger than the critical value, you will be able to reject the null hypothesis and conclude with some stated confidence level that there is a difference between the means of the two data sets.

### REQUIRED MEASUREMENTS

The PreLab calculation spreadsheet – with correct answers – must be submitted before you can begin work on the experiment. You must present the results for both standardizations of the HCl (based on the stock solution concentration) and your statistical analysis of the two data sets to your lab TA before leaving. As usual, results include the mean and relative standard deviation (‰) of your replicate determinations of the concentrations of the solutions. You should also present the results of the statistical analysis and your conclusion of whether the two methods give the same answer for [HCl] in the carboy. If not, be sure to suggest a possible interpretation.

**Sample Results Table**

	Concentration (carboy)	Stdev	RSD (‰)
HCl (carbonate)			
HCl (direct)			

### NOTES

- 1) The only piece of glassware with the requisite accuracy is your volumetric pipet, so you can only choose multiples of 25-mL, implying that 50-mL (two x 25 mL) is the "right" answer.
- 2) The solution just has to reach boiling – the solubility of gases plummets right at the boiling point. If you really boil it, you risk losing HCl (which is a gas). Look for the appearance of condensation/ water vapor on the neck of Erlenmeyer flasks as an indication of boiling.
- 3) If the liquid level inside the buret is changed rapidly allow a minute for drainage of the upper wall before making a reading.
- 4) Absorption of atmospheric carbon dioxide causes the color to fade over several minutes time.