

## Take-Home Assignment #7

1. Solutions of perchloric acid,  $\text{HClO}_4$ , may be standardized by titrating against a primary standard of sodium carbonate,  $\text{Na}_2\text{CO}_3$ . Typically, the titration is carried out to the carbonate ion's second endpoint. Suggest a mass of  $\text{Na}_2\text{CO}_3$  to use if you are standardizing a solution of  $\text{HClO}_4$  whose concentration is within the range of 0.145 M to 0.155 M and you wish to use between 35 mL and 45 mL of titrant.

The reaction between  $\text{HClO}_4$  and  $\text{Na}_2\text{CO}_3$  will be



The lower limit for the mass of  $\text{Na}_2\text{CO}_3$  will be with 35 mL of 0.145 M  $\text{HClO}_4$  and the upper limit will be with 45 mL of 0.155 M  $\text{HClO}_4$ . For the lower limit

$$0.145 \text{ M HClO}_4 \times 0.035 \text{ L HClO}_4 \times \frac{1 \text{ mol Na}_2\text{CO}_3}{2 \text{ mol HClO}_4} \times \frac{105.99 \text{ g Na}_2\text{CO}_3}{\text{mol Na}_2\text{CO}_3} = 0.27 \text{ g Na}_2\text{CO}_3$$

A similar calculation for the upper limit gives 0.37 g  $\text{Na}_2\text{CO}_3$ .

2. A 50.00-mL sample of white grape juice requires 21.48 mL of 0.03776 M NaOH to achieve a visual endpoint. Express the acidity of the grape juice as grams of tartaric acid,  $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$ , per 100 mL. Assume that both of tartaric acid's acidic protons are titrated at the titration's endpoint.

The titration reaction is

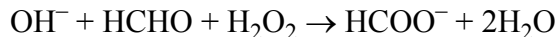


Letting  $\text{H}_2\text{A}$  represent tartaric acid we have

$$0.03776 \text{ M NaOH} \times 0.02148 \text{ L NaOH} \times \frac{1 \text{ mol H}_2\text{A}}{2 \text{ mol NaOH}} \times \frac{150.09 \text{ g H}_2\text{A}}{\text{mol H}_2\text{A}} = 0.06087 \text{ g H}_2\text{A}$$

Since this is for the analysis of a 50.00-mL sample of the juice, there are 0.1217 g of tartaric acid per 100 mL of juice.

3. The formaldehyde,  $\text{HCHO}$ , content of a pesticide preparation was determined by weighing 0.3124 g of the liquid sample into a flask containing 50.0 mL of 0.0996 M NaOH and 50 mL of 3%  $\text{H}_2\text{O}_2$ . Upon heating, the following reaction takes place:



After cooling, the excess NaOH was titrated with 23.3 mL of 0.05252 M H<sub>2</sub>SO<sub>4</sub>. Calculate the % w/w HCHO in the sample of pesticide.

This is a back-titration in which the NaOH first reacts with the HCHO, as shown above, and then with sulfuric acid



The total moles of NaOH are

$$\text{moles NaOH}_{\text{tot}} = 0.0996 \text{ M} \times 0.0500 \text{ L} = 0.00498 \text{ mol}$$

The moles reacting with the H<sub>2</sub>SO<sub>4</sub> are

$$0.05252 \text{ M H}_2\text{SO}_4 \times 0.0233 \text{ L H}_2\text{SO}_4 \times \frac{2 \text{ mol NaOH}}{\text{mol H}_2\text{SO}_4} = 0.00245 \text{ mol NaOH}$$

The moles reacting with the HCHO, therefore is 0.00253 mol NaOH. The mass of HCHO in the sample is

$$0.00253 \text{ mol NaOH} \times \frac{1 \text{ mol HCHO}}{\text{mol NaOH}} \times \frac{30.03 \text{ g HCHO}}{\text{mol HCHO}} = 0.0761 \text{ g HCHO}$$

The %w/w HCHO in the 0.3124 g sample, therefore, is 24.3%.

4. Suggest an appropriate molarity of HCl if you wish to titrate 25-mL samples of nominally 0.055 M Na<sub>3</sub>PO<sub>4</sub> to the bromocresol green endpoint using between 25 mL and 35 mL of titrant.

The pK<sub>a</sub> values for phosphate are pK<sub>a1</sub> = 2.148, pK<sub>a2</sub> = 7.199 and pK<sub>3</sub> = 12.35. BG serves as an indicator at pH levels of 3.8-5.4. The equivalence points for a titration of PO<sub>4</sub><sup>3-</sup> will be between 12.35 and 7.199, between 7.199 and 2.148 and below a pH of 2 (this one actually isn't visible). The titration, therefore, must go to the second equivalence point and the reaction is



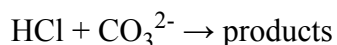
To find appropriate volumes, we begin with

$$0.055 \text{ M Na}_3\text{PO}_4 \times V \times \frac{2 \text{ mol HCl}}{\text{mol Na}_3\text{PO}_4} \times \frac{1}{[\text{HCl}]}$$

and substitute 0.025 L and 0.035 L in for V and solve for the concentration of HCl, obtaining values of 0.110 M and 0.0786 M. Any concentration within these limits will work.

5. The alkalinity of natural waters is assumed to arise from a combination of NaOH, Na<sub>2</sub>CO<sub>3</sub>, and NaHCO<sub>3</sub>. Possible combinations include NaOH alone, NaOH and Na<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub> alone, Na<sub>2</sub>CO<sub>3</sub> and NaHCO<sub>3</sub>, or NaHCO<sub>3</sub> alone. Suppose you titrate a 25.00-mL sample of water with 0.1202 M HCl and find that it takes 29.64 mL to titrate to the phenolphthalein endpoint and 34.62 mL to titrate to the bromocresol green endpoint. What compound(s) is (are) responsible for the sample's alkalinity and what is (are) its (there) concentration(s)?

Because V<sub>bg</sub> is more than V<sub>p</sub>, but not twice as large or more than twice as large, we know that the sample contains OH<sup>-</sup> and CO<sub>3</sub><sup>2-</sup>. The difference between the two volumes is the volume of HCl needed to titrate the CO<sub>3</sub><sup>2-</sup> to the phenolphthalein endpoint (and from the phenolphthalein endpoint to the bromocresol green endpoint as well), where the reaction is



Thus,

$$0.1202 \text{ M HCl} \times (0.03462 \text{ L} - 0.02964 \text{ L}) \times \frac{1 \text{ mol CO}_3^{2-}}{\text{mol HCl}} \times \frac{1}{0.025 \text{ L}} = 0.02394 \text{ M CO}_3^{2-}$$

Since 4.98 mL of the HCl needed to titrate the sample to the phenolphthalein endpoint went to the titration of carbonate, the volume needed to titrate the OH<sup>-</sup> to the phenolphthalein endpoint is 24.66 mL; thus

$$0.1202 \text{ M HCl} \times (0.02466 \text{ L}) \times \frac{1 \text{ mol OH}^-}{\text{mol HCl}} \times \frac{1}{0.025 \text{ L}} = 0.1186 \text{ M OH}^-$$