A Microscale Spectrophotometric Determination of Water Hardness

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There is continuing concern for instruction in water analysis and treatment, in particular water hardness, for both science and non-science majors (*1*). Traditionally, water hardness is determined by performing a titration; however, it is relatively easy to add too much titrant and pass the end point. One well-tested method for alleviating this problem is a spectrophotometric titration because it allows data taken away from the end point to determine the end point (*2–4*). In this procedure a microscale titration of a water sample was performed using EDTA as the titrant and calmagite as the indicator (*5*). The absorbance data were collected using a Texas Instruments (TI-83) calculator interfaced through a TI Calculator-Based Laboratory system to a Vernier colorimeter. One of the colorimeter's available wavelengths, 635 nm, was found to be ideal for this experiment. Students in our quantitative analysis course perform this spectrophotometric titration and compare the result with that from the traditional titration.

Procedure

The EDTA solution was first standardized using solutions of 0.01030 g/L calcium carbonate. Traditional titrations were performed on 50.0-mL samples of tap water from the laboratory using the standardized EDTA solution. The solutions were buffered to pH 10 using a NH_4OH/NH_4Cl buffer and 5 drops of 0.1% calmagite were added as the indicator. The titrations were carried out until the blue end point was reached. While another similar chelating indicator, Eriochrome Black T, can be used for this titration, calmagite was chosen for its color change and its greater stability in aqueous solutions (*6*).
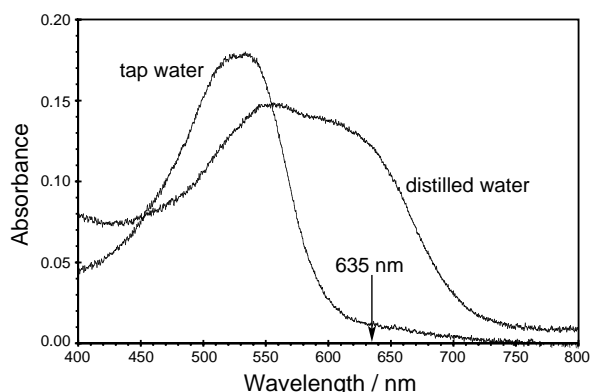

Figure 1. Absorbance spectra for solutions of tap water (containing Ca^{2+} and/or Mg^{2+}) and distilled water (containing neither Ca^{2+} nor Mg^{2+}).

For the spectrophotometric titration, the reaction vessel was a plastic square 1-cm cuvette. Into the cuvette were added 2 mL of tap water, 0.5 mL of pH 10 buffer, and 0.10 mL of calmagite. A small, 0.5-cm, stir bar was placed into the cuvette. To expedite the experiment, approximately 75% of the expected volume of EDTA was added to the cuvette before any absorbance data were collected. The EDTA was added using an adjustable-volume 100-μL pipetter that had been calibrated prior to use.

Absorbance measurements were recorded for each addition of 5 μL of the EDTA. After each addition, the cuvette was placed on a magnetic stir plate for about 10 seconds. The total time for the experiment was about 15 minutes.

Absorbance spectra were collected for distilled water and tap water containing buffer and calmagite indicator. The spectra were collected using an Ocean Optics CHEM2000 UV–vis spectrometer.

Hazards

Except when using the concentrated acids and bases in solution preparation, there are no significant hazards associated with this experiment.

Results and Discussion

Initial absorbance spectra were obtained for tap water and distilled water buffered to pH 10 and containing calmagite. These spectra were necessary for determining if one of the colorimeter settings would be appropriate for detecting the change in color of the calmagite as the end point of the titration was reached. As seen in Figure 1, at 635 nm the distilled water having no magnesium or calcium present had a significant absorbance (0.122), whereas the sample of tap water containing magnesium and/or calcium had a relatively low absorbance (0.012). From these data, it was concluded that using the colorimeter detecting at 635 nm would work well in determining the end point for the spectrophotometric titration. Any spectrometer with variable wavelength selection could be used for this experiment. If possible the wavelength of 610 nm would preferably be used to give the maximum absorbance difference and greatest sensitivity.

Standard solutions of 0.01030 g/L $CaCO_3$ were used to determine the concentration of the EDTA. The average concentration (of three samples) of the EDTA was 0.005365 M. Traditional titrations for water hardness using this standardized EDTA solution were performed on three samples of laboratory tap water. The average concentration of $CaCO_3$ in tap water was 122.3 ± 0.3 ppm.

A representative graph for the results of a spectrophotometric titration can be seen in Figure 2. As predicted from the absorbance spectra, the initial additions of EDTA produced virtually no change in absorbance. Upon reaching the end point the absorbance increased to a maximum value. Two best-fit lines were constructed from the data and the volume of their intersection was calculated. For this set of data, the intersection volume was calculated to be 452 mL. Using this volume and the concentration of the standardized EDTA, the concentration of $CaCO_3$ was determined to be 121 ppm. For two experimental samples, the average concentration was 123 ± 3 ppm.

Conclusion

The results of the spectrophotometric titration nicely match those of the traditional titration. The exercise allows students to become familiar with the technique of spectrophotometric detection and to hone skills in statistical analysis and linear regression.

Acknowledgments

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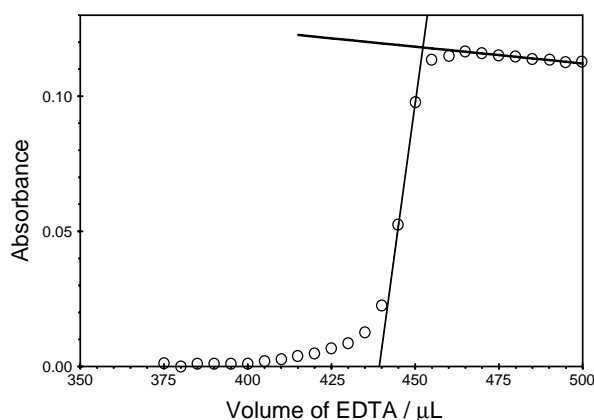

Figure 2. Absorbance curve for a spectrophotometric titration of tap water using 0.00537 M EDTA as the titrant and calmagite as the indicator.

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