Proceedings of The National Conference
On Undergraduate Research (NCUR) 2015
Eastern Washington University, Cheney, WA
April 16-18, 2015

The Analysis of Carbonate, Magnesium, and Copper by Three Separate Titrations: Weak Base, Metal-Ligand Complex, and Oxidation-Reduction Titrations

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Abstract

Many titrations depend upon an observable physical change, such as a change in color, for their endpoint to signify an equivalence point has been reached. There are a number of points during a titration where analysts can be misled prior to, at, or after an equivalence point has been reached without a visual aid for comparison. To that end, the analysis of carbonate by a weak base titration, magnesium by a metal-ligand complex titration, and copper by an oxidation-reduction titration were explored. Percent relative standard deviation (%RSD) and percent relative error (%RE) values were calculated for replicate measurements of the quality control (QC) standards. In addition, all three titration procedures were replicated with high-resolution color photographic documentation in an effort to attenuate the misdirection analysts often face due to the gradations of the observed changes near the endpoint. Generally, these gradations include how the analyte solution color appears before titration has begun, before the equivalence point, at the equivalence point, and after too much titrant has been added. Lastly, changes to the amount and type of water used in the metal-ligand complex titration of magnesium were also explored. By using 18 MΩ•cm at 25 °C deionized water instead of distilled water for every step of the procedure, there was a significant improvement in the clarity of the observed endpoint color change. This allowed for a significant increase in the precision and accuracy (in terms of %RSD and %RE) for the procedure when compared to the use of distilled water. This experiment is designed and is appropriate for an undergraduate quantitative analysis course.

Keywords: Weak Base, Metal-Ligand, Oxidation-Reduction, Titration

1. Introduction

Titrations are an essential classical wet analytical technique that demands a fastidious work ethic in order to produce viable results. Applications of titrations in general extend from the standardization of primary standard solutions to the determination of concentrations of unknown target compounds and QC standards. Here a weak base,[1-5] a metal-ligand complex,[6-10] and an oxidation-reduction titration[11-15] are investigated. In the past, the use of distilled water for the aforementioned metal-ligand complex procedure yielded poor results due to impurities that can be present in the water. "Hard water" refers to water with the presence of alkaline earth metals, such as Ca^{2+} of Mg^{2+}, that can interfere with the analysis of these particular reagents. The Mg^{2+} present in the water will react with H_2EDTA^{2-}, forming a metal ligand, and thus causing severe inaccuracies in the analysis of the standards. It was thought that the use of deionized water for every step (diluting the titrant, preparation of "unknown" samples and QC standards) would allow for sharper endpoints to be seen in this procedure. Previously, the full titration could not be accurately replicated using distilled water, and was therefore limited to a half titration in order to yield accurate and precise results. The size of the aliquots used for this analysis was increased from 20.0 mL to 50.0 mL, allowing analysts to perform the full

titration. This also severely limited the number of unknown replicates that could be performed, encouraging attention to detail and precision. The mechanism for the metal ligand titration is as follows:

$$2OH^-_{(aq)} + Mg^{2+}_{(aq)} + H_2EDTA^{2-}_{(aq)} \rightleftharpoons MgEDTA^{2-}_{(aq)} + 2H_2O_{(aq)}$$

$$Mg^{2+}_{(aq)} + In^{2-}_{(aq)}\ (blue) \rightleftharpoons MgIn_{(aq)}\ (pink)$$

Since the $MgEDTA^{2-}$ complex has no color, a Calmagite indicator is used to determine the end point color. No changes were made to the weak base titration since accurate results are attainable using distilled water. The procedures for each titration were replicated three times to assure accurate results. In order to determine the efficacy of these titrations, the %RE was calculated for the QC standards significantly before, slightly before, at, slightly after, and significantly after the equivalence points for the metal ligand (using deionized water) and the weak base titrations. As for the oxidation-reduction titration, purely qualitative analysis was performed with photographic documentation and/or pictures taken. Due to the various complexities involved in this back titration, it would have been irrational to analyze this titration in a similar manner as the previous titrations. The rapid change signifying the endpoint was irrefutable, and was therefore not analyzed quantitatively. As such, no changes were made to the procedure. The pictures at each of these various points for all three types of titrations will allow analysts to accurately determine if they have correctly reached the respective endpoints. This will also show analysts how slight errors in the observations of the endpoint can lead to poor results.

2. Methodology

2.1. Metal-Ligand: Magnesium With EDTA Titrant

For the metal ligand titration, the entire procedure was performed once using distilled water for all sample preparation, and once using deionized water. The ~0.01 EDTA titrant was made by dissolving 1.8614g and 1.8612g (for distilled water and deionized water procedures, respectively) $Na_2H_2EDTA{\cdot}2H_2O$ in a 500 mL volumetric flask with the appropriate type of water. The stock solution to be used for standardization of the titrant were made by transferring 20.00mL of 1000ppm Mg^{2+} primary standard into a 250 mL volumetric flask, and again diluting with the appropriate type of water, to yield a final concentration of 80 ppm. The QC (Mg^{2+}) samples were diluted from the 80 ppm Mg^{2+} standard by transferring 50.00 mL aliquots into separate Erlenmeyer flasks. Immediately before titration, each sample was mixed with 3mL of NH_3/NH_4^+ pH 10 buffer and 4-5 drops of Calmagite indicator. After correctly determining the endpoint due to the color change, photographs were taken before, at, and after the equivalence point (Figures 1.a-1.e). The photographs were taken at points in the titration where the analyst may have decided the endpoint matched the description of "the moment it turns blue." This process was used to determine the true concentration of EDTA (see tables 1.a-1.b for the distilled water standardization and 2.a-2.b for the deionized water standardization). The procedure was performed in triplicate to ensure accurate results, and a %RSD of ≤0.1% RSD was desirable. To ensure the appropriate accuracy when attempting to determine the concentration of a sample using a standardized titrant, a new QC stock solution was made. This solution was prepared by transferring 15.00mL of 1000 ppm Mg^{2+}primary standard into a 250 mL volumetric flask, and was diluted with the appropriate type of water for a final concentration of 60 ppm. As before, 50.00 mL aliquots were transferred to individual Erlenmeyer flasks, to which 3 mL of NH_3/NH_4^+ pH 10 buffer and 4-5 drops of freshly made Calmagite indicator were added immediately before titration. Using the volume delivered of the previously calibrated EDTA titrant, the concentration (in terms of ppm) of each of the QC samples could be determined (see tables 1.c and 2.c for the distilled water and deionized water experimental procedure results, respectively). To ensure accuracy, the samples were analyzed in triplicate with a desired %RSD of ≤0.1.

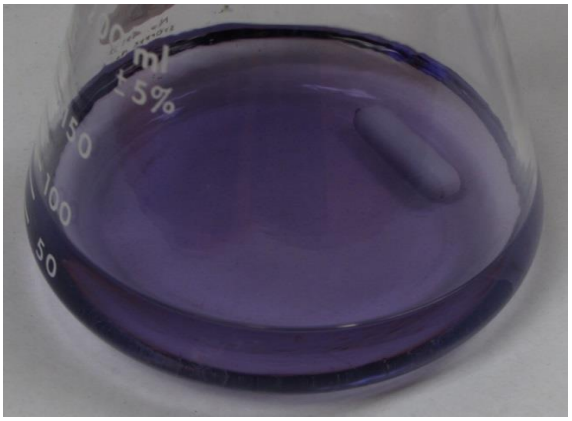

Figure 1.a 0.17 mL before equivalence point (EDTA).

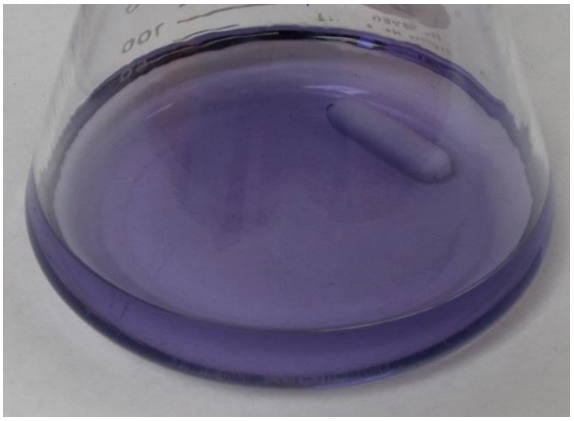

Figure 1.b 0.12 mL before equivalence point (EDTA).

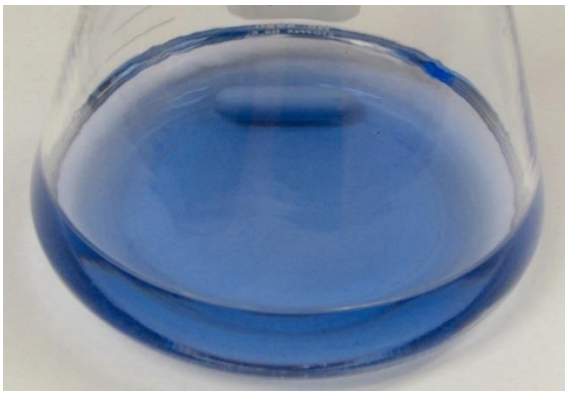

Figure 1.c Desired color at equivalence point (EDTA).

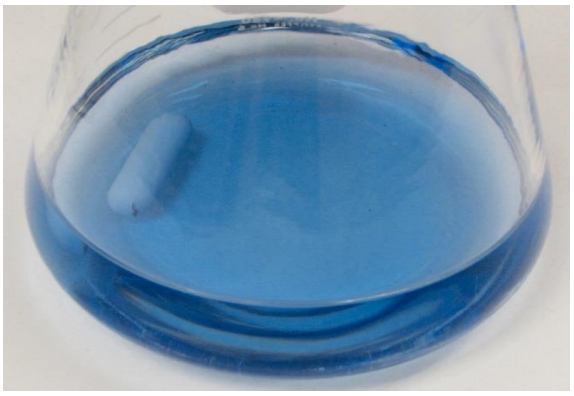

Figure 1.d 0.13 mL after equivalence point (EDTA).

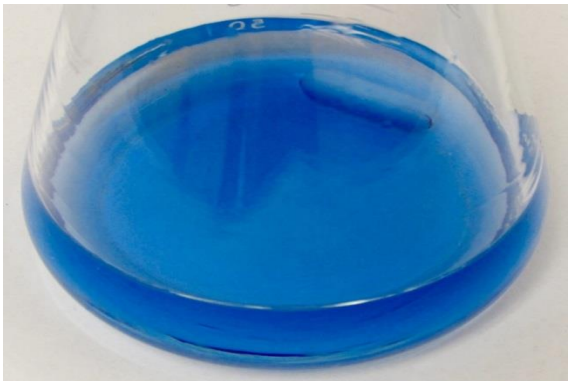

Figure 1.e 0.23 mL after equivalence point (EDTA).

Table 1.a EDTA titrant standardization (distilled water) for the Metal-Ligand: Magnesium procedure.

Replicate	EDTA titrated (mL)	EDTA (M)
1	17.30	0.009514
2	16.80	0.009798
3	17.40	0.009460

Table 1.b Data analysis of distilled water EDTA titrant using standard procedure.

Mean EDTA (M)	0.009591
Standard Deviation	0.00018
%RSD	1.89%

Table 1.c Data using standard experimental procedure (distilled water).

Replicate	EDTA Titrated (mL)	Mg^{2+} (ppm)	%RE
1	12.28	57.25	4.58%
2	12.30	57.34	4.43%
3	12.30	57.34	4.43%

Table 2.a EDTA titrant standardization (deionized water) for the Metal-Ligand: Magnesium procedure.

Replicate	EDTA titrated (mL)	EDTA (M)
1	16.35	0.01006
2	16.35	0.01006
3	16.35	0.01006

Table 2.b Data analysis of deionized water EDTA titrant using standard procedure.

Mean EDTA (M)	0.01006
Standard Deviation	0.00000
%RSD	0.00%

Table 2.c Data using modified experimental procedure (deionized water).

Replicate	EDTA Titrated (mL)	Mg^{2+} (ppm)	%RE
1	12.27	60.00	0.00%
2	12.26	59.95	0.08%
3	12.27	60.00	0.00%

2.2. Weak Base: Carbonate With HCl Titrant

For the weak base titration, reagent-grade anhydrous Na_2CO_3 were dried in a 120°C oven overnight, cooled in a desiccator, weighed into separate aliquots (0.1735g, 0.1835g, and 0.1993g), placed individually into 400 mL flasks and dissolved in 50 mL of distilled water. A 0.1M HCl solution was prepared by mixing 9.0 mL of concentrated HCl into a 1000 mL volumetric flask. Before titration, the approximated 2^{nd} equivalence point volume (V_e) was calculated. The flask contained a stir bar, and was placed on top of a magnetic stirrer. A pH meter was placed inside the flask, the 0.1M HCl solution was in the class-A buret, and titration began. The pH was noted approximately every 1.0 mL of titrant added to monitor the progress of the standardization titration, and the volume was recorded to the nearest 0.01 mL. When the volume titrated was approximately within 5.0 mL of the 2^{nd} V_e, the titration was stopped. The pH meter was removed from the carbonate solution, which was subsequently brought to a gentle boil to expel CO_2 gas. The carbonate solution was cooled in an ice bath back to room temperature. The pH meter was rinsed with distilled water and placed back in the carbonate solution, which had risen significantly in pH, and the titration could resume. The volume of titrant was added in 0.1 mL increments (approximately 2 drops as a time) until a sharp drop in pH was

observed. Generally, this sharp drop consisted of a change in pH of about 0.7 or greater. Using the volume of HCl titrated, along with the known amount of Na_2CO_3, the true concentration of the HCl titrant could be determined. This titration was repeated in triplicate to ensure accuracy, and the desired %RSD was ≤0.1%. At this point, the solutions remained clear for all steps in the analysis, so no photographs were taken for the calibration of the titrant. For the analysis of the QC standards, the previously-dried Na_2CO_3 was weighed into separate aliquots (0.1786g, 0.1780g, and 0.1801g), individually placed in 250 mL Erlenmeyer flasks, and dissolved in 50 mL of distilled water. For this stage of the titration, 4-5 drops of a methyl red indicator was added to each solution before titration. Initially, the solution is a pale yellow color. Upon titration, the solution turns orange as the analyte solution becomes more acidic. After the solution turned to a pink-orange color, the sample was gently boiled for about 5 minutes, and cooled in an ice bath until it was room temperature. This process caused the solution to turn back to the original pale yellow, due to the expulsion of CO_2 gas. The titration with the HCl titrant continued until the solution began to change colors once again, and photographs were taken before the 2^{nd} V_e (see figures 2.a-2.b). The volume of HCl titrant added was noted for each photograph, until the end point was reached. The 2^{nd} V_e was found at the very moment the solution turned from pink-orange to a faint solid pink (see figure 2.c). The volume of standardized HCl titrant delivered into the carbonate was used to determine the amount of carbonate in the sample. For photographic representation of how the solution appears when too much titrant has been added, extra titrant was added to turn the solution a darker pink, and the volume added was noted (see figures 2.d-2.e). The %RE for each of the samples was calculated. To ensure the results were accurate, the procedure was replicated in triplicate.

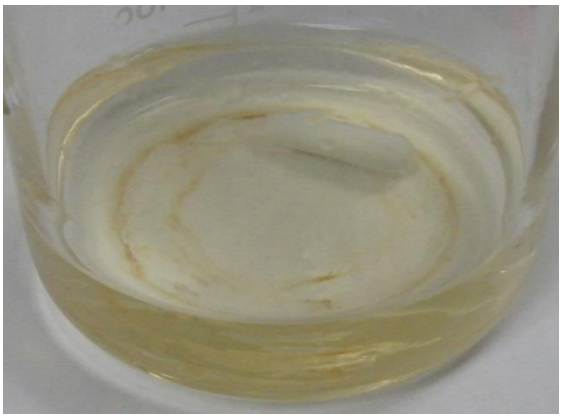

Figure 2.a 0.13 mL before equivalence point (Carbonate).

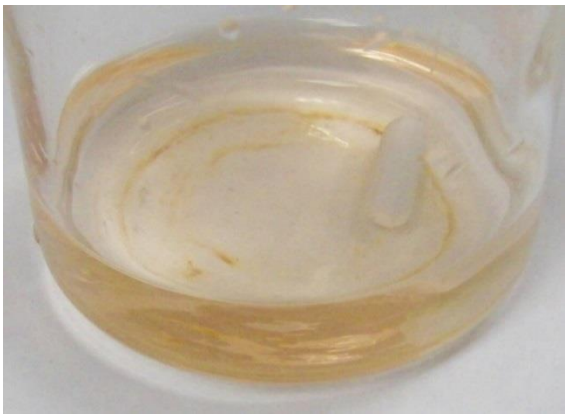

Figure 2.b 0.05 mL before equivalence point (Carbonate).

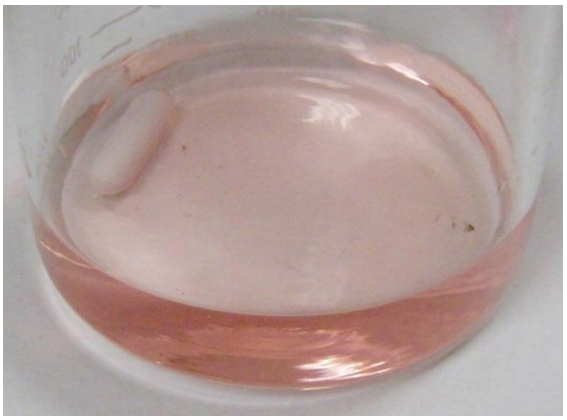

Figure 2.c Desired color at equivalence point (Carbonate).

Figure 2.d 0.11 mL after equivalence point (Carbonate).

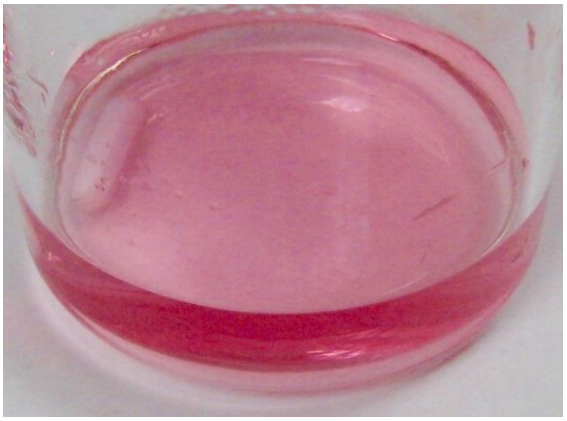

Figure 2.e 0.27 mL after equivalence point (Carbonate).

2.3 Oxidation-Reduction: Copper With $Na_2S_2O_3 \cdot 5H_2O$ Titrant

For the oxidation-reduction titration, about 1.2 L of distilled water was boiled with boiling stones to remove dissolved oxygen and microorganisms. When the water was cooled, about 25 g of reagent grade $Na_2S_2O_3 \cdot 5H_2O$ and 0.10 g of Na_2CO_3 were dissolved in a 1 L volumetric flask using the previously boiled water to make a titrant solution that is approximately 0.1M $Na_2S_2O_3$. To standardize the titrant, primary standard KIO_3 was dried in a 120°C oven overnight, stored in a desiccator, weighed into approximately 0.12 g aliquots, placed into a labeled 250 mL Erlenmeyer flask, and dissolved in 75 mL of distilled water. Before titrating a sample, approximately 2.00 g of KI and 10 mL of 1M HCl were added to the flask, making the solution a dark scarlet color (see figure 3.a). Titration began, which eventually turns the solution to a pale yellow (see figure 3.b). At this point, 5 mL of starch indicator was added to turn the solution a dark red-black color (see figure 3.c). Titration continued until the red-black I_2 solution disappeared, yielding a clear-white solution and thus the endpoint (see figure 3.d). The volume of titrant delivered and the mass of KIO_3 can be used to standardize the titrant solution. To replicate analysis of an unknown sample, a QC sample was processed to show the various steps involved. A 3x3 cm square of pure copper foil (approximated mass between 0.20 and 0.25 g) was placed in a 250 mL Erlenmeyer flask and was dissolved in 5 mL of 6 M HNO_3 over a *warm* hotplate until dissolution was complete. After the copper was dissolved, about 25 mL of distilled water and 10 mL of 5% urea were added, and the solution was brought to a gentle boil. This process makes the solution a bright blue color (see figure 3.e). The solution was cooled and placed in an ice bath, where 0.5 to 1.0 mL increments of concentrated NH_3 were added until the solution turned a dark blue due to the formation of the $[Cu(NH_3)_4]^{2+}$ complex (see figure 3.f). The concentrated NH_3 had to be added slowly because the highly exothermic reaction may result in splattering if the reagent is added in too large of volumes. Then, 3M H_2SO_4 was added drop wise until the solution returned to a similar bright blue as in the previous step (see figure 3.g). To lower the pH to around 3.5, about 2.0 mL of concentrated H_3PO_4 was added. Once this was completed, titration with the previously standardized $Na_2S_2O_3$ solution could begin. Approximately 4.0 g of KI was dissolved in the QC standard, turning the solution a dark brown (see figure 3.h), and the solution was immediately titrated until the solution turned to a yellow-brown color (see figure 3.i). At this step, 1.0 mL of 1% starch indicator was added to turn the solution a dark blue-green. Titration continued until the solution turned a light gray-purple (see figure 3.j). Then, 2.0 g of KSCN were added and the solution was swirled for about 30 seconds, turning the solution a dark grey purple (see figure 3.k). Titration slowly continued until the solution turned a milky white color, indicating the endpoint (see figure 3.l). Using the volume of the standardized titrant delivered, the concentration of a sample could be assessed.

Figure 3.a Titrant standardization, before any titrant has been added.

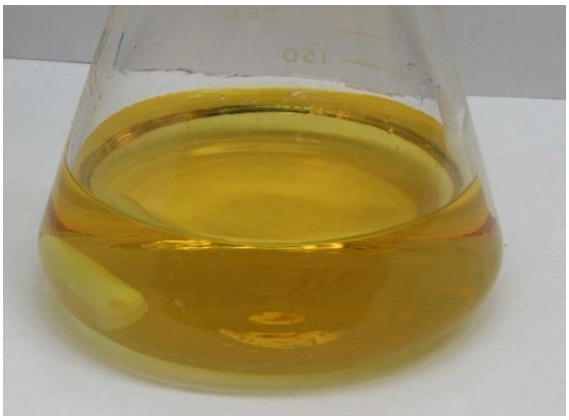

Figure 3.b Titrant standardization, after some titrant has been added but before starch indicator.

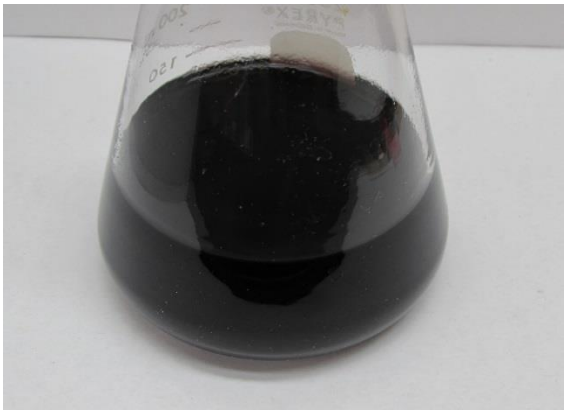

Figure 3.c Titrant standardization, after starch indicator.

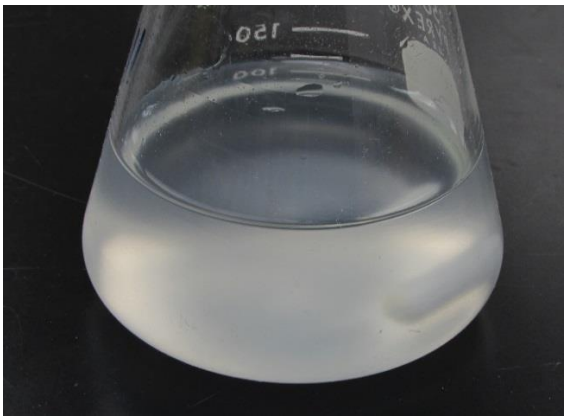

Figure 3.d Titrant standardization equivalence point.

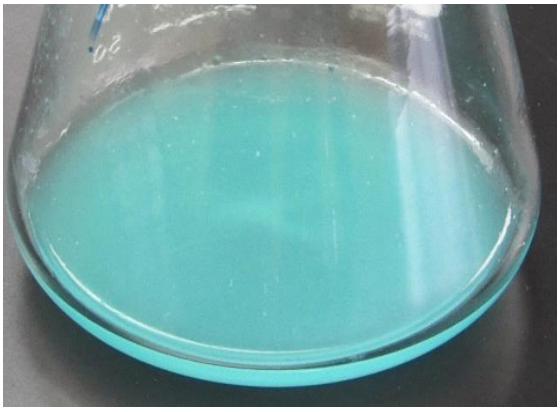

Figure 3.e QC preparation, copper foil dissolved, no NH_3 added.

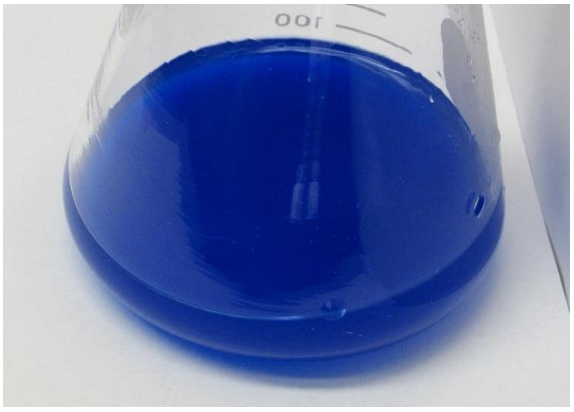

Figure 3.f QC preparation, after NH_3 was added.

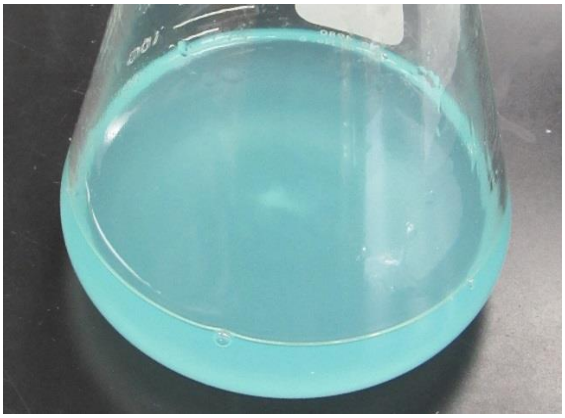

Figure 3.g QC preparation, after 3M H_2SO_4 added.

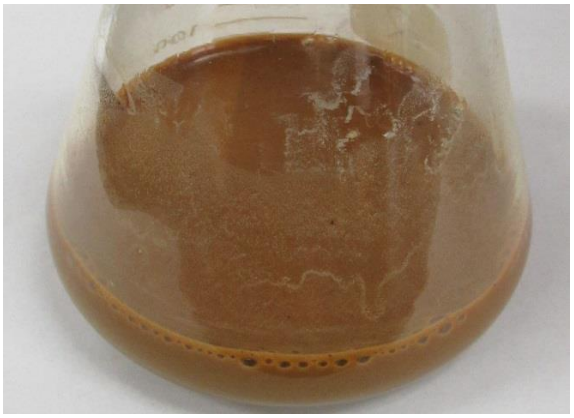

Figure 3.h QC analysis, before titration.

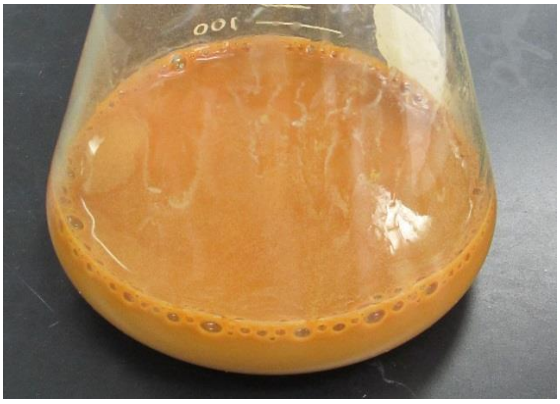

Figure 3.i QC analysis, after titrant has been added But before starch indicator.

Figure 3.j QC analysis, after starch indicator with additional titrant added.

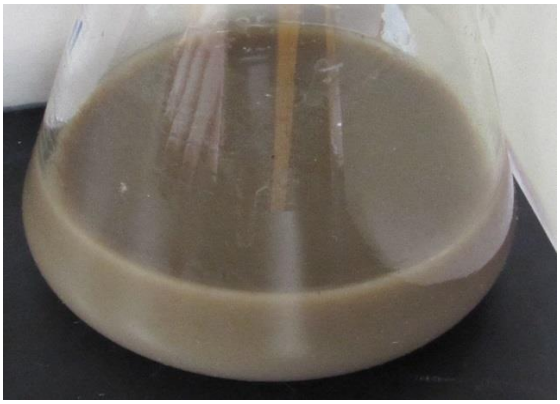

Figure 3.k QC analysis, after KSCN was added.

Figure 3.l QC analysis, at equivalence point.

3. Results

For the metal-ligand complex titration of magnesium, table 1.a shows the results for the standardization of the EDTA solution using distilled water, while table 1.b shows their accuracy. For the distilled water method, the mean EDTA concentration was determined to be 0.009591M, with a %RSD of 1.89%. The data that resulted from using the distilled-water experimental procedure for determining the concentration of Mg^{2+} in the QC standard, along with the %RE for each replicate, is shown in table 1.c. The %RE values were 4.58%, and two values at 4.43%. The results for the EDTA standardization using deionized water instead of distilled water for each step in the procedure is show in table 2.a, and the accuracy of the standardization is shown in table 2.b. For the deionized water method, the mean EDTA concentration was determined to be 0.01006M, with a %RE of 0.00%. The data obtained in the experimental procedure of determining the Mg^{2+} concentration in the QC standards using deionized water is shown in table 2.c, along with the %RE for each replicate. One replicate had a %RE of 0.08%, while two replicates had a %RE of 0.00%. Table 3 shows the %RE for each photograph, which corresponds to a particular volume of EDTA titrant deviating from the true equivalence point. Additionally, for the weak base titration of carbonate Table 4.a shows the results of the analysis of the HCl standardization, while table 4.b shows their accuracy. The average concentration of HCl in the titrant solution was determined to be 0.1034_5M, with a %RSD of 0.087%. Table 5 shows the %RE for each photograph, which corresponds to a particular volume of HCl titrant deviating from the true 2^{nd} V_e.

Table 3 %RE associated with the most commonly misinterpreted endpoints for the Metal-Ligand: EDTA titration.

Metal-Ligand: Magnesium	
Replicate	%RE
Figure 1.a	1.38%
Figure 1.b	0.97%
Figure 1.c	0.00%
Figure 1.d	-1.06%
Figure 1.e	-1.88%

Table 4.a HCl standardization for the Weak Base: Carbonate procedure.

Replicate	Mass Na_2CO_3 (g)	HCl delivered for 2^{nd} V_e (mL)	HCl (M)
1	0.1735	31.62	0.1035
2	0.1835	33.50	0.1034
3	0.1993	36.35	0.1035

Table 4.b Data analysis of HCl standardization.

Mean HCl (M)	0.1035
Standard Deviation	$9.018x10^{-5}$
%RSD	0.087%

Table 5 %RE associated with the most commonly misinterpreted endpoints for the Weak Base: Carbonate titration.

Weak Base: Carbonate	
Replicate	%RE
Figure 2.a	0.40%
Figure 2.b	0.16%
Figure 2.c	-0.08%
Figure 2.d	-0.36%
Figure 2.e	-0.87%

4. Conclusion

Standardizing the distilled water EDTA titrant solution for the metal-ligand magnesium titration was challenging, and a %RSD of 1.89% is not accurate enough for viable results. The quality controls were replicated in triplicate to ensure accuracy and precision. With the lowest %RE at 4.43%, the accuracy of the procedure using distilled water is unacceptable. The egregious incongruities stem from the slow gradation of color near the endpoint, making it very difficult to determine. The gradation transition in color from the purple-blue color (near the end point) and the faint blue color (at the end point) was very slow. Since the gradation was not immediate or obvious, the true determination of the end point was unsatisfactory. The presence of alkaline earth metals (especially Ca^{2+} and Mg^{2+}) in the distilled water interfered with the formation of the EDTA-metal ligand complexes. In contrast, the deionized water gave excellent results. Since two of the %RE values were 0.00%, it is easy to see how useful the deionized water is in determining the clarity of the endpoint. The high degree of accuracy and precision is due to how rapidly the endpoint appears using deionized water. The solution had little gradation in color, and almost immediately changed from a dark purple to the faint blue. Since there was no misinterpretation in the accuracy of the endpoint, the results were precise and accurate.

The pictures for this experiment show analysts how various colors that deviate from the endpoint can be misinterpreted as the true endpoint, along with the corresponding %RE. The %RE values were determined by noting the total volume of standardized titrant delivered into the solution at that false endpoint, and a picture was taken. When the true endpoint was reached, the volume was noted, and the %RE for the previously noted false endpoint could be calculated. After the endpoint, the amount of standardized titrant added after the endpoint was noted, and the %RE could be determined. The pictures were chosen based on colors that an analyst may inaccurately believe to be the endpoint. The colors before the endpoint are obviously a different color from the endpoint, but the colors immediately after the endpoint are less obvious. This is why analysts must understand the endpoint must be determined *immediately* when the solution turns the faint blue color. After the endpoint, the solution turns a darker blue. Hopefully, analysts will see the true color of the endpoint and understand how easily this procedure can be misinterpreted. Also, this shows how a small error in the determination of the endpoint can lead to extreme deviations in accuracy. It can be seen in table 3 that a deviation of 0.23 mL over the endpoint (which corresponds to approximately 4 drops from a class-A buret) leads to a %RE of -1.88%. Since there was significant improvement in the procedure when deionized water was used, this change was implemented in the procedure. In addition, the volume of QC analyzed was changed from 20.00 mL to 50.00 mL due to satisfactory results. Various pictures were implemented into the procedure as well in order to show analysts the inaccuracies of certain endpoints.

Standardization of the HCl titrant solution for the weak base carbonate titration lab was not difficult, but it was tedious. In this procedure, multiple samples were analyzed at the same time. For example, while replicate 1 was boiling, replicate 2 was being titrated. When replicate 1 was finished boiling and was placed in the ice bath, replicate 2 was boiled and replicate 3 was titrated. This method of rotating the replicates is the most efficient way to analyze the replicates, because waiting for the boiling and cooling can waste time. There was usually a significant rise in pH after the boiling occurred, and the endpoint was determined by the volume of HCl delivered and the moles of Na_2CO_3 in the solution. The desired %RE was to be $\leq$0.10%, and mean concentration of the solution was determined to be 0.1034_5M with a %RE of 0.087%. It should be noted that the setup for the standardization of the HCl titrant involved a pH meter, a stir bar, and a magnetic stir plate. Great care was taken to ensure the pH meter was never struck by the stir bar to prevent any deviations in results or damage to the pH meter.

The pictures in this experiment show analysts how various colors that deviate from the endpoint can be misinterpreted as the true endpoint, along with the %RE. The %RE was determined in the same manner as the EDTA titration (see above), where a picture was taken before the 2^{nd} V_e (with the volume delivered noted), and the %RE was determined after the true 2^{nd} V_e was found. The colors were chosen based on the shades that analysts commonly mistake as the endpoint, with the corresponding %RE. Although the endpoint is more obvious than that of the EDTA titration, generally analysts go beyond the endpoint to find a darker, more saturated pink. As can be seen in table 5, if an analyst goes 0.27 mL beyond the endpoint (approximately 5 drops in a class-A buret), the respective %RE is -0.87%. In order to achieve %RE $\leq$0.10%, the analyst must add the amount of titrant where the solution *immediately* turns the faintest shade of pink, and stays pink. As can be seen with these results, the procedure is satisfactory in its accuracy. Because of this, no changes were made to the original procedure except for the addition of various pictures. This shows analysts the true shade if pink that can be used to find the correct endpoint.

5. Future Work

One interesting component of the metal-ligand: magnesium titration was the use of *fresh* Calmagite indicator. Generally, the Calmagite was never more than 3 days old before a new indicator was made. The use of Calmagite that is several days old should be explored to determine precisely when the Calmagite should not be used. For example, a daily titration of QC samples performed in triplicate over the span of several weeks would show exactly when the indicator could no longer be used. The weak base: carbonate procedure involves the tedious use of utility grade pH meters. LabQuest has released an all-in-one instrument that can be used to accurately measure the pH to the hundredths decimal place. The use of the LabQuest instruments in this procedure could be explored in order to achieve more accurate results in the standardization of the HCl titrant.

6. Acknowledgements

The authors would like to acknowledge the contributions of the departmental laboratory personnel Dr. Frederick Joslin and Derick Trial for their support and for taking their time in working on this experiment. This work was supported in part by Eastern Washington University, the College of Science, Technology, Engineering, and Mathematics, Department of Chemistry and Biochemistry.

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