Calcium carbonate and ca2+ ions

Environment, Water

Experiment. EDTA Titration of Ca^{2+} in an unknown solution Experiment. EDTA Titration of Ca^{2+} in an unknown water sample Modified 9/2012 Objective: The most common multivalent metal ions in natural waters are Ca^{2+} and Mg^{2+}. In this experiment, you will find the total concentration of calcium ions that can react with EDTA with the assumptions that EDTA reacts 1: 1 with metal (Ca^{2+}) ions. Equipment 250-mL Erlenmeyer flask (3) 50-mL Buret Ring-stand and hardware Desiccator 400-mL Beaker 500-mL Vol. flask 250-mL Vol. flask 1. 0-mL Vol Pipette 100-mL Grad cylinder Hot plate Safety and Waste Disposal

Chemicals Buffer (pH 10): Add 142 mL of 28 wt % aqueous NH_3 to 17. 5 g of NH_4Cl and dilute to 250 mL with water. Eriochrome black T indicator: Dissolve 0. 2 g of the solid indicator in 15 mL of triethanolamine plus 5 mL of absolute ethanol. 50 wt % NaOH: Dissolve 100 g of NaOH in 100 g of H_2O in a 250-mL plastic bottle. Store tightly capped. When you remove solution with a pipet, try not to disturb the solid Na_2CO_3 precipitate. Discussion: Hard water is due to metal ions (minerals) that are dissolved in the ground water. These minerals include Ca^{2+}, Mg^{2+}, Fe^{3+}, SO_4^{2-}, and HCO_3^-.

Generally hard water arises because rainwater moves through limestone, $CaCO_3$ underground that occurs in our area to the aquifer. This is why we measure hardness in terms of $CaCO_3$. The concentration of the Ca^{2+} ions is greater than the concentration of any other metal ion in our water. The determination of water hardness is routinely used to measure the quality of water that the general public uses. Originally, water hardness was defined as the measure of the capacity of the water to precipitate soap. Hard water is not ahealthhazard since the main chemical in hard water is calcium.

People regularly take calcium supplements. In fact, hard water can be a source of necessary minerals (calcium and magnesium) that is necessary for good health. Indeed, the National Academy ofSciencego so far as stating that that consuming extremely hard water could be a major contributor of calcium and magnesium to the diet. The problem with hard water is that it cause soap scum, clog pipes and clog boilers. Soap scum is formed when the calcium ion binds with the soap. This causes an insoluble compound that precipitates to form the scum you see.

Soap actually softens hard water by removing the Ca^{2+} ions from the water. When hard water is heated, $CaCO_3$ precipitates out, which then clogs pipes and industrial boilers. This leads to malfunction or damage and is expensive to remove. There are two types of water hardness, temporary and permanent. Temporary hardness is due to the bicarbonate ion, HCO_3^-, being present in the water. This type of hardness can be removed by boiling the water to expel the CO_2, as indicated by the following equation: HCO_3^- (aq) ? H_2O (l) + CO_2 (g). Because bicarbonate can be removed it is classified as temporary hardness.

Permanent hardness is due to the presence of the ions Ca^{2+}, Mg^{+2}, Fe^{3+} and SO_4^{-2}. Because boiling cannot eliminate this type of hardness, the water is said to be permanently hard. The table below shows the degree of hardness of the water in terms of its calcium carbonate concentration in ppm and grains. Hardness rating Soft Medium Hard Hard Very Hard Concentration of Calcium Carbonate (mg/L or ppm) 0 < 75 75 to < 150 150 to < 300 300 and greater Concentration of Calcium Carbonate (grains/US gallon) 0 to < 5. 2 5. 2 to < 10. 5 10. 5 to < 21 21 and greater

Permanent hardness is usually determined by titrating it with a standard solution of ethylenediamminetetraacetic acid, EDTA. The EDTA is a complexing, or chelating agent used to capture the metal ions. This causes water to soften, but the metal ions however, are not removed from the water. EDTA simply binds the metal ions so that the ions do not precipitate to form soap scum. EDTA is a versatile chelating agent. A chelating agent is a substance whose molecules can form several bonds to a single metal ion. Chelating agents are multidentate ligands.

A ligand is a substance that binds with a metal ion to form a complex ion. Multi-dentate ligands are many clawed, holding onto the metal ion to form a very stable complex. EDTA can form four or six bonds with a metal ion. It is frequently used in soaps and detergents because it forms complexes with calcium and magnesium ions. The ions in hard water are bound to the EDTA and cannot interfere with the cleaning action of the soap or detergent. EDTA is also used in foods. Certain enzymes are responsible forfoodspoilage. EDTA is used to remove metal ions from these enzymes.

It is used to promote color retention in dried bananas, beans, chick peas, canned clams, pecan pie filling, frozen potatoes and canned shrimp. It is used to improve flavor retention in canned carbonated beverages, beer, salad dressings, mayonnaise, margarine, and sauces. It inhibits rancidity in salad dressings, mayonnaise, sauces and salad spreads. In this lab you will be asked to determine the total permanent hardness. EDTA grabs all the metal ions in the water, not just the Ca2+ ions. This gives us a value that is not truly the concentration of Ca2+ ions.

This causes an experimental error of about 1%, which is acceptable due to the " fuzzy" endpoints in this type of titration. Erio-T indicator or Eriochrome Black-T indicator is used in this titration. When it is chelated or acidifies, it produces a Pink-Red solution. When it is not chelated and under basic conditions it is Blue. The three pictures show the end point in this titration. There is a 1-drop difference of 0. 01 M EDTA between the first and second pictures and between the second and third pictures. Two or three seconds were allowed for colors in the second and third pictures to develop after adding the additional drop.

In each case the solution was thoroughly mixed. This color change from wine red to violet to blue is due to the compact nature of the complex. Experiment. EDTA Titration of Ca2+ in an unknown solution PROCEDURE Modified 9/2012

Dry Na2H2EDTA. 2H2O (FM 372. 24) at 80° C for 1 h and cool in the desiccator. Accurately weigh out ~ 0. 6 g and dissolve it with heating in 400 mL of water in a beaker. Cool to room temperature pour into a 500-mL volumetric flask. , mix and dilute to the mark. 2. You should practice finding the end point several times by adding a little tap water in a clean beaker and titrating with EDTA.

Save a solution at the end point to use as a color comparison for other titrations. Pipet a 1-mL sample of unknown into a 250-mL flask and fill to the mark with deionized water. Mix thoroughly. From this 250-mL stock solution draw 4, 50mL aliquot samples and place each aliquot in 250mL Erlenmeyer flasks. To each sample, add 3 mL of pH 10 buffer and 6 drops of Eriochrome black T indicator. To the first 50-ml solution, titrate with EDTA from a 50-mL buret and note when the color changes from wine red to blue. 4. Repeat the titration with the next three samples to find an accurate value of the total Ca2+ concentration.

Perform a blank titration with 50 mL of distilled water and subtract the value of the blank from each result. 5. Upon completion of the experiment, discard all solution in a chemical waste bottle and wash out the glassware. Be sure to dry your buret in the upside down position.

Calculations – Analysis: Analyte Ca2+

Report the mean, medium, standard deviations (s), relative standard deviation (RSD), variance (s2) and the 95% confidence interval for your results. 2. 3. 4. Apply the student’s t test at the 95% confidence interval Apply a Q-test to any suspected result. Confidence interval = x + ts n 5. Compare the results of this experiment to the previous experiment, Gravimetric determination of Ca. Apply the Comparison of Means with Student’s t, Case2 (p76) Comparing Replicate Measurements. Do the two methods agree within the 95% confidence interval? € Test for Outlier Apply a Grubb’s Test and Q-Test for any suspected outliers at 95 % level. See page 83 of text for critical values for 95% confidence.

If your results show an anomalous data then use the Q-test to determine if the result should be rejected. Q= (Suspected Value - Nearest Value) (Suspected Value - Furthest Value) G calc = | Questionable value - x| s Table of Data, Results and Statistical Analysis: Calcium Raw Data 1. Unknown number 2 Mass of EDTA used 3 Concentration of EDTA 4 Volume of Unknown Ca2+ Solution 5 Volume EDTA during titration 6 Volume EDTA for blank trials

7 Q-Test (95%) of any outlier Analysis and Results 8 Mass of calcium in 1-mL aliquot (Average) 9 Mass of calcium in 1-L solution (Average) 10 Conc. of calcium, %, ppm (m: v) and Molarity (Average) 11 Mass of calcium carbonate in 1-L (Average) Statistical Analysis 12 Averages and Standard deviations of all results 13 Variance, RSD and CV of all results 14 95% Confidence interval 15 ttable and tcalc for replicate measurements

Discussion

The goal of this experiment was to determine the “ hardness” of the unknown sample by calculating the concentration of calcium ions in an analyte solution. Correcting for dilution factors, the concentration of calcium in the unknown in g/L is to be determined and compared to analysis for calcium by EDTA titration. Statistical analysis is applied to the results. A discussion of this experiment should include the accuracy and precision of this experiment compared to the EDTA titration method. An analysis of a comparison of replicated measurement is performed and discussed. Table of results should include Include in your summary table the following: i) Moles of Ca2+ in the unknown and the average equivalent value. ii) Concentration of [Ca2+] in the unknown in molarity, ppm and g/L iv) Mean, standard deviations, RSD and CV for each of the above concentration units. v) Student’s t at the 95% confidence interval vi) Application of a G and Q-test to any suspected result at the 95% level. vii) ttable, tcalc, Conclusion on comparison of replicated measurements.

Experiment. EDTA Titration of Ca2+ in an unknown solution Modified 9/2012 Sample data table. Sample Unknown # ______ Mass Na2EDTA, (g) Molarity Na2EDTA, (M) Vol. unknown, (ml) Buret Volinitial, (ml) Buret Volfinal, (ml)

Volume EDTA used, (ml) Vol EDTA for blank, (ml) Corrected Col EDTA, (ml) Trial 1 Mass Ca2+ in 1 ml aliquot (g) Mass Ca2+ in 1-L solution (g) Concentration Ca (%) Concentration Ca (ppm) Molarity Ca2+, unknown (M) Mass calcium carbonate in 1L Q and G Test for Outliner CaCO3 (g/L), unknown Trial 2 Trial 3 Trial 4 Average Std dev Variance RSD , CV 95% CL Trial 1 Trial 2 Trial 3 Trial 4 Blank Student's t Analysis: Comparing replicate measurements Analysis A: CaCO3 (g/L) 1 2 3 4 Trial 1 Trial 2 Trial 3 Trial 4 Avg Avg X1bar - X2bar Sqrt ((n1*n2)/(n1+n2)) (xi-x1)^2 deg freedom Spooled Expt 2 Expt 3 Ex2 (Xi-Xbar)^2 Ex3 (Xi-Xbar)^2 T calc t table Conclusion T calc ? T table, at 95%, two result are (not) considered to be different EDTA Titration of Ca2+ in an unknown solution. # 1 2 CRITERIA (Tentative point distribution - may change depending on experiment) Quiz / Homework [NONE} Introduction and Procedures

Introduction

- Objective of Expt.
- Background information.
- Math relationship used in study.

Procedures

- Outline of procedures in Expt.
- Flow chart pictorial of procedures. Procedural changes.
- Information (data) to be recorded during experiment. (to be presented in Table form.)
- Safety and disposal information. This portion of the report should be turned in before the start of lab class (prelab discussion). Data, Observe. , Results and Calc.

Data and Observation

- Data in table form. & detailed observations written in the table. All data entry should contain the proper number of significant figures and units. Data should always be recorded in an organize fashion.
- Balance chemical equations; all chemical reaction which occurred during an experiment should be written in this section. Then it should also be written in the discussion portion of the report. This portion of the report should be turned in before you leave the laboratory.

Calculations & Results

Calculations

- Sample calculation shown with Excel spreadsheet available with formulas shown
- Statistical analysis of data and result. Avg, Std dev, RSD, CV

Results

- Summary of Result(s) in table form. In this section accuracy of results is very important as well as detailed calculation showing how the result was obtain. " Unknown" will also be included in this section. Discussion / Conclusions and Post-Lab Questions

Discussion (Talking points)

- What is your final result in this experiment. Are the four trials consistent with each other? If not what would account for the inconsistencies? How did the results in this experimental result compare to the result in experiment 2? Is your result for the amount of calcium carbonate in your unknown within the range of 10 – 25 g/L? Elaborate on this. What is the average amount of calcium in tap water, how much more higher is this unknown compared to the average content in tap water (express in %).

Conclusion

- Summary of the goal of the experiment and how that goal was achieved in the experiment. H. Post-lab questions or Editorial comment
- What did you learn in this experiment? What skills in lab practice did you develop through this expt? This portion (Calculation and Discussion) is turned in at the beginning of class of the due-date Overall Presentation (of lab notebook)
- Lab technique during experiment; example are, class preparation, safety glasses precautions and leaving the laboratory clean.
- Report presentation: examples are the headings of each report that includes name, title, lab partner, date and section #, witness signature. Legibility of report. Is the report easy to read or is important information jotted down by small print in the corners of the lab report. The overall impression is important. Lab Technique
- Safety: wear goggles, handle chemicals with caution, proper handling of lab equipment
- Leave lab clean and tidy