Determination of Calcium Content in *"Wahaha AD calcium milk"* by Potassium Permanganate Titration

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DESIGN EXPERIMENT REPORT

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Section 4 Group 2

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Dear Dr. Hamade:

VC211 course is approaching to an end. I started to memorize your efforts on devising your own straightforward method, and this helps me to understand some complex concepts. Therefore, I feel confident to do this design report and gain a lot during this process.

The guideline of design the report is to apply the knowledge I have learned in this course. For example, I apply titration in Experiment 1, buffer solution calculation and properties in Experiment 2, methods to boost the reaction in Experiment 4 and separate a particular ion by precipitation in Experiment 5. Only by applying knowledge I have learn can I create something new.

I also try to search different methods to determine the calcium content. By comparing the essay, I decide to choose the method of potassium permanganate titration. The difficulties I meet with are that I want to create some new method, but it turns out to be difficult since my limited knowledge. Hence, I place the key part of the experiment in improving the experiment in many small parts. All these improvement may give a more accurate result. Some of the improvements are refer by the lab manual of this course, and the other are refer to other essays.

The whole design report is complete and involve almost all parts. Since the page number is limited, some details might not be explained well. If there is any question about the report, feel free to contact with me. My email address is yifan_ding@sjtu.edu.cn.

By the course of designing the experiment, I have learned a lot of advanced knowledge and notice that I can apply the method of searching information when we become real engineers. I also learn how to write the report in a professional way. I really appreciate Dr. Hamade's efforts in my progress. Thank you for giving me a chance to act in a way that professional engineers usually do.

Yours Sincerely,

Ding Yifan
April 10, 2014

Abstract

The design experiment will determine the calcium content in "Wahaha AD calcium milk" and judge whether it satisfy the standard value printed on the bottle. The experiment conduct the potassium permanganate titration method to determine the calcium content. The method use $(NH_4)_2C_2O_4$ to selective precipitate Ca^{2+} in milk, and then filter and wash by dilute H_2SO_4 to dissolve CaC_2O_4. Then use $KMnO_4$ standard solution to titrate at a certain temperature with $MnSO_4$ as catalyst. The highlights of the report is considering various interference factors and the environmental protection issues.

Keyword: Calcium Content; Determination; Potassium Permanganate Titration

1. Introduction

As the most abundant mineral in your body, calcium is essential for our body's overall nutrition and health. Almost every cell in our body uses calcium in some way, such as nervous system, muscles, heart and bone. Our bones store calcium in addition to providing support for our bodies. As we age, we absorb less and less calcium from our diet, and less of calcium easily cause or contribute to osteoporosis.

One important way to get calcium is by drinking milk. "*Wahaha AD calcium milk*" is a commercial product which is popular among the young in their daily life. The experiment will determine the calcium content in this kind of milk and judge whether it satisfy the standard printed on the bottle. The experiment conduct the potassium permanganate titration method to determine the calcium content.

Potassium permanganate oxidation-reduction titration method is an important titration analysis method, which can be used to determine the content of oxidizing or reducing substances in water. Permanganate index of water quality monitoring is an important indicator which can reflect the degree of organic pollution in water.

2. Theory

a) Separate Ca^{2+}

EDTA, or ethylenediaminetetraacetic acid, is a polyprotic acid, which binds a total of 6 places on an ion in solution, containing four carboxylic acid groups (acidic hydrogens are red) and two amine groups with lone pair electrons (green dots). Molecules that bind at multiple points in a coordination complex are said to be chelated. The classic structural formula is given below (Figure 1).

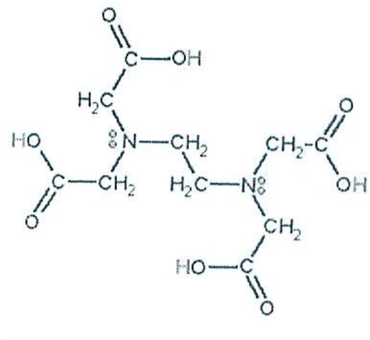

Figure 1 The classic structural formula of EDTA

The main purpose of adding EDTA solution in this experiment is to separate Ca^{2+} and avoid influence by other ions, such as Mg^{2+}, Ba^{2+}, Pb^{2+}, Cr^{2+}, Cu^{2+}, Zn^{2+}. These ions will lead to precipitation with $C_2O_4^{2-}$.By using EDTA solution, only Ca^{2+} will precipitate with $C_2O_4^{2-}$. The ion reaction is as follow.

$$Ca^{2+}(aq)+C_2O_4^{2-}(aq)\longrightarrow CaC_2O_4(s)$$

By adding diluted H_2SO_4 solution, the CaC_2O_4 will dissolve. The reactant will be $H_2C_2O_4$ and Ca^{2+}. The ion reaction is as follow.

$$CaC_2O_4(s)+2H^+(aq)\longrightarrow Ca^{2+}(aq)+H_2C_2O_4(aq)$$

The mole ratio of the reaction is exactly 1:1, and thus Ca^{2+} can be determined indirectly by testing the moles of $H_2C_2O_4$. The method to test the moles of $H_2C_2O_4$ is potassium permanganate titration, which will be introduced below.

b) Potassium Permanganate Titration

The main theory in this experiment is potassium permanganate titration. Potassium permanganate, $KMnO_4$, is a strong oxidizing agent. Permanganate, MnO_4^-, is an intense dark purple color. Reduction of purple permanganate ion to the colorless Mn^{2+} ion, the solution will turn from dark purple to a faint pink color at the equivalence point. The reduction of permanganate requires strong acidic conditions. This reaction requires 5 electrons and 8 hydrogen ions. The ion reaction is as follow.

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$

In this experiment, permanganate will be reduced by oxalate, $C_2O_4^{2-}$ in acidic conditions. Oxalate reacts very slowly at room temperature so the solutions are titrated hot to make the procedure practical.

The potassium permanganate is previously standardized against sodium oxalate in acid solution (Not included in this experiment. In this experiment, standard solution has already be prepared). Potassium permanganate acts as its own indicator both in the standardization and in the calcium determination. The ion reaction is as follow.

$$2MnO_4^-(aq) + 5H_2C_2O_4(aq) + 6H^+(aq) \longrightarrow 2Mn^{2+}(aq) + 10CO_2(g) + 8H_2O(l)$$

3. Experimental setup

Chemical used:

Wahaha AD calcium milk;

De-ionized water;

$0.02\,mol/L$	$KMnO_4$ solution;
1 g/L	Methyl orange indicator;
pH = 4	HAc-NH_4Ac buffer solution;
200 g/L	Ethylene Diamine Tetraacetic Acid (EDTA) $C_{10}H_{16}N_2O_8$ solution;
$1\,mol/L$	$MnSO_4$ solution;
$3\,mol/L$	H_2SO_4 solution;
$0.25\,mol/L$	$(NH_4)_2C_2O_4$ solution;
$3\,mol/L$	Aqueous ammonia;

Material used:

Pipette; Buret; Buret Clamp; 100 mL beaker (1); 250 mL Erlenmeyer flask (2); Analytical Balance; Weighing paper; Ring stand; Water bath heating device; Hot plate or Bunsen burne; Rubber Stopper; Watch glass.

4. Procedure

> **Caution**
>
> $KMnO_4$ solution and H_2SO_4 solution are caustic acids. Wear gloves and googles at all times when working in the laboratory! If any is spilled on your skin, immediately rinse with running water and inform your laboratory instructor. Pay attention to dispose of $KMnO_4$ waste according to instructor's directions.

a) Use pipette transfer 10.0 mL "*Wahaha AD calcium milk*" in the 100 mL beaker. Add 20 mL de-ionized water and 4 mL 200 g/L EDTA to the same beaker. Shake up the solution;

b) Add two drops 1 g/L Methyl orange indicator. Add several drops of 6 mol/L HCl solution until the color of solution change to red.
c) Use pipette transfer 6.0 mL 0.25 mol/L $(NH_4)_2C_2O_4$ solution slowly. Add 3 mol/L aqueous ammonia to the beaker slowly until the color of solution change to orange-yellow.
d) Use pipette transfer 10.0 mL pH = 4 HAc-NH_4Ac buffer solution to control the pH within 3.5 to 4.5.
e) Put the watch glass above the beaker. Heating the beaker in water bath at the temperature of 80 ℃. Keep heating for 30 minutes. Cool down and filtrate the precipitate.
f) Put the precipitation in the 250 mL Erlenmeyer flask completely. Label the flask as #1. Wash the precipitate in case of the interfere ions. Use pipette transfer 10.0 mL 3 mol/L H_2SO_4 solution into the same Erlenmeyer flask. Add 2 drops of 1 mol/L $MnSO_4$ solution as catalyst. Add de-ionized water to the tick mark.
g) Heat the Erlenmeyer flask in water bath at the temperature of 80 ℃. Rinse and fill the buret with the $KMnO_4$ solution. Use $KMnO_4$ solution to titrate immediately. The end point of titration is the solution turns faint pink and stay faint pink in 30s.
h) Record the initial volume V_0 of $KMnO_4$ solution. Record the final volume V_1 of $KMnO_4$ solution. Calculate ΔV by $(V_0 - V_1)$.
i) Label the other 250 mL Erlenmeyer flask as #2. Pour the water the experiment use until water reach the tick mark. Repeat step f to h and compare the result.
j) Repeat the step a to i above twice. The volume of $KMnO_4$ solution used should agree with the previous titration within 0.20 mL.
k) Wash hands. Treat the chemical wastes safely. Calculate the calcium content of "*Wahaha AD calcium milk*".

5. Data and Calculation

a) Data Record Table

Vol. (mL) \ Trail	#1	#2	#3
V_0			
V_1			
ΔV			
Average V			

b) Formula and Calculation

$$c_{Ca^{2+}}(mg/mL) = \frac{c_{KMnO_4}(mol/L)\cdot V_{KMnO_4}(mL)\cdot M_{Ca^{2+}}(g/mol)\cdot \frac{n_{Ca^{2+}}}{n_{KMnO_4}}\cdot\frac{1L}{1000mL}\cdot\frac{1000mg}{1g}}{V_{milk}(mL)}$$

$c_{Ca^{2+}}$ is the calcium content of the milk sample;

V_{KMnO_4} is the average V in the data table, and it is the only variable in this equation;

All the followings are constant in this experiment:

$$c_{KMnO_4} = 0.02mol/L\,;\,M_{Ca^{2+}} = 40.08g/mol\,;\;\frac{n_{Ca^{2+}}}{n_{KMnO_4}} = \frac{5}{2};\;V_{milk} = 10.0mL\,.$$

Plunge in all these constant in to the formula, a simple equation is as follow.

$$c_{Ca^{2+}}(mg/mL) = 0.2004(mg \cdot mL^{-2}) \cdot V_{KMnO_4}(mL)\,.$$

Compare the calculation result with the value printed on the bottle. The calcium content printed on the bottle of "*Wahaha AD calcium milk*" is 60 mg/mL.

The absolute error = $\left|c_{Ca^{2+}std} - c_{Ca^{2+}test}\right|$.

The relative error = $\dfrac{\left|c_{Ca^{2+}std} - c_{Ca^{2+}test}\right|}{c_{Ca^{2+}std}} \times 100\%$.

6. **Discussion**

a) Determination of the Solution Acidity

CaC_2O_4 weak acid precipitate, the solubility will increase with the larger acidity. When pH is equal 4, almost all of the CaC_2O_4 precipitate will be transfer to $C_2O_4^{2-}$ and Ca^{2+}, and the loss of CaC_2O_4 in dissolution is negligible. I use the pH=4 HAc-NH_4Ac buffer solution to control the acidity, which apply the knowledge in Experiment 2.

b) Washing the precipitate of CaC_2O_4

If the excess 0.25 mol/L $(NH_4)_2C_2O_4$ solution cannot be wash clean, the result will be unexpected high. Hence, I wash the CaC_2O_4 by using aqueous ammonia, and I ensure that every time the washing solution is little amount and wash several times. When I wash the CaC_2O_4, I will pay attention to wash the precipitate along the edge in case of the precipitate concentrated in the central and cause the error.

c) Elimination of the Interfering Ions

When pH is equal 4 and is in the ammonia solution, Ca^{2+} and $C_2O_4^{2-}$ will produce white precipitate. However, some heavy metal ions and rare earth elements will also react with $C_2O_4^{2-}$ and produce white precipitate. To avoid the interfering ions, I used EDTA solution to separate Ca^{2+}, and control the pH condition within 3.5 to 4.5.

d) Control of the Precipitation Condition

According to the textbook of analytical chemistry printed by East China University of Science, Ca^{2+} and $C_2O_4^{2-}$ will only be 1:1 if and only if I control the precipitation condition. CaC_2O_4 mainly exist as $HC_2O_4^-$ in acidic solution, and thus I control the pH is equal to 4. In that way, I will finally get the precipitate of CaC_2O_4 instead of $Ca(OH)_2$ and $(CaOH)_2C_2O_4$.

e) Temperature and Control of Titration

The reaction temperature should be between 75℃ to 85℃. If the reaction temperature lower than 75℃, the reaction rate will be low according to Experiment 4. If the reaction temperature is higher than 85℃, the reaction formula is as follow.

$$H_2C_2O_4(aq) \xrightarrow{>85℃} CO(g) + CO_2(g) + H_2O(l)$$

f) Test of Blank Solution

The experiment should test the blank solution in case of the Ca^{2+} in the water interfere with the result. If there is Ca^{2+} in the water, it will lead to a higher result in the determination of calcium.

7. Question

a) Pre-lab question

i. What is the basic requirement of oxidation-reduction titration?

Answer: Reaction stoichiometry required under a certain relationship; React fast and no side reaction occur; Reaction must have the appropriate method to determine the end point of titration.

ii. How to fast the chemical reaction?

Answer: Increasing reactant concentrations and increase acidity; Increase temperature; Add a catalyst.

iii. What are the commonly used redox titration method?

Answer: Potassium permanganate, iodimetry and sodium nitrite method.

b) Post-lab question

i. Why should the experiment keep the pH = 4 during the reaction?

Answer: The oxidation of $KMnO_4$ is related to the acidity of solution.

In strong acidic solution, the oxidation of $KMnO_4$ is the strongest. It is able to gain 5 electrons to form Mn^{2+}, which can be dissolved in water;

In slight acidic, neutral or base solution, $KMnO_4$ is able to obtain 3 electrons. It will reduce to MnO_2 and form brown precipitate;

In strong base solution, $KMnO_4$ is able to obtain only an electron and generate MnO_4^-.

ii. When using $KMnO_4$ to determine the calcium content, can we use HNO_3 or H_2SO_4 to control the acidity?

Answer: Nitric acid has oxidation, and hydrochloric acid has reducibility. Using these two chemicals will easily occur side reactions.

iii. What effects is the $MnSO_4$ in the reaction?

Answer: $MnSO_4$ is a catalyst and will boost the reaction rate.

8. Conclusion

Through this design experiment, I learned how to design an experiment by my own. I apply knowledge which I have learned in this course such as buffer solution, titration and filtration into this experiment, which cover almost most part of the course. I also searched the advanced knowledge of potassium permanganate titrant. I learned many ways to determine calcium content in the commercial products. It is very important to compare different methods and try to analyze the advantages and disadvantages in these separate methods. I noticed how to control the titration process and experimental conditions. The choice of appropriate methods can accelerate the speed of reaction. The most important thing is that the experiment I designed should be safe and consider the environmental awareness. Although the VC211 course is approaching to an end, I will use the method I learned in my future study.

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Excellent!