Preparation of Water Hardness Colorimetric Card with Calcium Ion as Index

Qiyue Zhu, Shiyi Liu, Zitong Fang, Yi Wu, Chuyi Xie, Yinyi Xiao, Yongchun Wei*
School of Materials and Environment, Zhuhai College, Beijing Institute of Technology, Zhuhai, Guangdong, China
**Corresponding Author.*

Abstract: The aim of this study was to explore the accuracy of chrome-black T as an indicator for determination of calcium ion concentration in water. By comparing the color changes of the solution under different reaction conditions, the optimal reaction conditions were determined as follows: under the condition of pH=9, the volume of chrome black T was 0.1mL and the reaction time was 10s. The final reaction color is made into a colorimetric card for the determination of water hardness, the results show that at a pH value of 9, chromium black T forms a colored complex with calcium ions, which has good stability, sensitivity, and identification. This colorimetric method has demonstrated high precision, reproducibility, and accuracy in actual water sample testing, and is expected to be widely applied in fields such as domestic water detection and other fields.

Keywords: Chrome Black T; Calcium Ion; Color Reaction; Colorimetric Card

1. Introduction

Calcium is one of the essential trace elements for the human body, crucial for bone health and muscle contraction, among other physiological functions. The concentration of calcium ions in water is an important indicator of water quality, directly affecting the hardness of water, pH value, and other characteristics, greatly influencing the health of humans and animals and plants. Therefore, accurately determining the concentration of calcium ions in water is of great significance for protecting human health and assessing the quality of drinking water [1].

The methods for analyzing calcium ion concentration include instrumental analysis methods and chemical analysis methods [2-5], all of which require relatively professional operation requirements and large instrument equipment. For example, chemical analysis methods can accurately determine the content of calcium ions in water through titration analysis and gravimetric analysis but require strict and standardized experimental operations; instrumental analysis methods such as fluorescence spectroscopy and atomic absorption spectroscopy need expensive equipment, making it inconvenient to promote their use among the general public.

Due to the characteristics of colorimetric technology, such as low detection cost, speed, and low technical personnel requirements, it has been widely researched and applied in many fields [6-7]. This study is based on the experimental method of measuring total water hardness using the EDTA titration method. By applying the principle of EDTA complexometric titration and using Chrome Black T as an indicator, with the coloration of calcium ion standard solutions of different concentrations as a reference, color cards of different colors are made. This aims to provide a new method for the rapid detection of calcium ion concentration in domestic water.

2. Experimental Section

2.1 Reagents and Instruments

All reagents used were of analytical grade, and ultra-pure water was used for the experiments, along with an analytical balance, among others.

2.2 Experimental Principle

In water, certain metal cations and some anions combine together. During the heating process of water, due to evaporation and concentration, scale can easily form and adhere to heated surfaces, affecting heat transfer. Therefore, the total concentration of these metal ions in water is referred to as the hardness of water. The most common metal ions in natural water are calcium ions (Ca^{2+}) and magnesium ions (Mg^{2+}), which combine with anions in the water such as carbonate ions (CO_3^{2-}), bicarbonate ions (HCO_3^-), sulfate ions (SO_4^{2-}), chloride ions (Cl^-), and nitrate ions (NO_3^-) to form substances such as carbonates, bicarbonates, sulfates, chlorides, and nitrates of calcium and magnesium. Metal ions like iron, manganese, and zinc in water also affect its hardness, but since their content in natural water is very small, they are usually disregarded. Thus, the total concentration of Ca^{2+} and Mg^{2+} is generally considered as the measure of water hardness. The national sanitary standard for water quality stipulates that the total hardness of domestic drinking water should not exceed 450 (calculated as $CaCO_3$, mg/L) [8].

This experiment focuses on the research of water hardness based on the concentration of Ca^{2+} as a standard. The hardness of water indicated by calcium ion concentration is roughly divided into 7 types, as detailed in Table 1.

This experiment involves preparing standard solutions of calcium ions at different concentrations, adding an equal amount of Chrome Black T indicator for color development, to determine the relationship between color and water hardness. Chrome Black T is a commonly used metal indicator, whose coloration principle is based on the reaction between chromate and the metal surface to form a dense layer of chromium oxide. The thickness of this chromium oxide layer can be controlled by adjusting the concentration of chromate and the treatment time, thus achieving different coloration effects. For example, in determining water hardness, the content of metal ions such as Ca^{2+} and Mg^{2+}. Under the condition that the pH of the water solution is 8–10, calcium ions in water form complexes with Chrome Black T indicator. As the concentration of calcium ions decreases, the color changes from dark pink to purple, and then to sky blue.

2.3 Development of Colorimetric Cards

2.3.1 Preparation of reagents

Weigh out 600 mg of calcium carbonate standard material accurately on an analytical balance and place it in a small beaker. Add a small amount of water to moisten it, then gradually add HCl solution until completely dissolved, taking care to prevent the reaction from becoming too vigorous, which could produce CO_2 bubbles and cause the loss of $CaCO_3$ through splashing. Heat to near boiling, cool, then transfer into a 1000 ml volumetric flask, dilute to the mark, and mix well.

Table.1 Water Hardness Classification

Water Quality	Very Soft Water	Soft Water	Moderately Hard Water	Hard Water	Very Hard Water	Extremely Hard Water	Excessively Hard Water
Ca^{2+}Concentration (mg/L)	0~75	75~150	150~300	300~450	450~700	700~1000	>1000

2.3.2 Preparation of solutions

(1) Preparation of 5 mg/mL Chrome Black T Indicator:

Weigh 0.5 g of solid Chrome Black T, dissolve it in water, transfer the solution into a 100 ml volumetric flask, dilute to volume, mix well, and set aside.

(2) Preparation of Ammonium Buffer Solution: Weigh 25 g of ammonium chloride, dissolve in 100 mL of ammonia water, transfer the solution to a 1000 ml volumetric flask, dilute to the mark with water, and mix well.

(3) Preparation of 6 mol/L Hydrochloric Acid Solution: Mix equal volumes of concentrated hydrochloric acid and water to obtain a homogeneous solution.

2.3.3 Determination of color parameters

After adding the color-developing agent to the water sample, the color changes according to the concentration of calcium ions present. Photograph the test samples with a camera to create a water hardness colorimetric card indexed by calcium ion concentration. This article investigates the factors affecting color development, including the concentration gradient of the solution, pH value, type of color-developing agent, and the amount of color-developing agent used, aiming to achieve better experimental results.

3. Results and Discussion

3.1 The Effect of Preparation Conditions on Color Development

3.1.1 Type of color-developing agent

50 mL of calcium ion standard solution was taken, and under the conditions of pH=9 and a reaction time of 10 seconds, 0.1 mL of Chrome

Black T was added. The color development effects of using a calcium carboxylate indicator and Chrome Black T indicator under the same conditions were explored.

The results show that when using the calcium carboxylate indicator, there is little color difference between different water qualities, all presenting as purplish-red, which does not accurately reflect the calcium ion content in different water qualities; whereas with the Chrome Black T indicator, the color differences are significant. The water quality colors change from deep pink to purple and then to sky blue as the concentration of calcium ions varies. The small color differentiation with the calcium carboxylate indicator may be due to the pH value of the experiment's solution being in the range of 8~10. When using the calcium carboxylate indicator to measure the concentration of calcium ions in water, the pH value has a significant impact on the experimental measurements. At pH values of 12.0 and 12.5, the relative error rates reach up to 5.06% and 3.18%, respectively, and the most accurate results are obtained near a pH value of 13.0. Therefore, the Chrome Black T indicator shows a more distinct effect under these experimental conditions.

3.1.2 Amount of color-developing agent

50 mL of calcium ion standard solution was taken, and under the conditions of pH=9 and a reaction time of 10 seconds, varying volumes of Chrome Black T indicator (0.05, 0.1, and 0.15 mL, corresponding to one, two, and three drops, respectively) were used to explore the color development effect of different doses of the indicator under the same conditions.

The results showed that when using 0.05 mL of Chrome Black T indicator, the color difference among various water qualities was minimal, all presenting as light purplish-red, which does not accurately reflect the calcium ion content in different water qualities. With 0.1 mL of Chrome Black T indicator, the color differences were significant and distinct; when using 0.15 mL of Chrome Black T indicator, the coloration was also similar across different water qualities, all presenting as dark purplish-red, which does not accurately reflect the calcium ion content in different water qualities. The water quality colors changed from deep pink to purple and then to sky blue with different concentrations of calcium ions using 0.1 mL of Chrome Black T as the indicator, showing significant coloration. Therefore, 0.1 mL of Chrome Black T indicator is the optimal amount.

3.1.3 PH value

50 mL of calcium ion standard solution was taken, and under the conditions of pH=8~10 and a reaction time of 10 seconds, the pH value was adjusted using ammonium buffer solution, exploring the color development effect at different pH values (8, 9, and 10) under alkaline conditions.

The results showed that the color development effect was best at a pH value of 9. When the pH value was 8, the color development was poor, with little variation in color among water qualities with different calcium ion contents, which was not sufficiently distinct. The color development was also poor at a pH value of 10. At a pH value of 9, the color change was more pronounced after the addition of Chrome Black T across different water quality intervals. Therefore, adjusting the pH to 9 is optimal.

3.2 Preparation of the Colorimetric Card

3.2.1 Determination of color change points

Colors corresponding to calcium ion standard solutions of 500, 100, 20, 4, 0.8, and 0 mg/L (a fivefold concentration difference) were taken, and significant color differences were found. Therefore, colors of solutions at halfway points between each concentration gradient were taken next. If the color differences remained significant, colors of the solutions at halfway points between each of these new concentrations and their adjacent concentrations (i.e., quarter points of the original concentration gradient) were taken. If significant color differences still existed, the above steps were repeated, observing color changes until the color at a halfway point closely matched the color of one side of the concentration gradient. Then, this halfway (or adjacent) concentration value was selected as a color change point. Finally, colors corresponding to concentrations in order of magnitude were chosen to make the colorimetric card.

3.2.2 Preparation of the colorimetric card

Under optimal conditions determined by the single-factor experiment, namely a sample volume of 50 mL, water sample pH=9, 0.1 mL of Chrome Black T added, and a color development time of 10 seconds, the colorimetric card was created. The results are shown in Table 2. From Table 2, it can be seen that water qualities with different concentrations of calcium ions change color from deep pink to purple and then to sky blue, a phenomenon that is clear and easy to identify.

Table 2. Color Rendering Results of Different Calcium Ion Concentrations

Concentration (mg/L)	Color	Concentration (mg/L)	Color
500		17	
450		16	
300		15	
100		10	
60		5	
40		1	
20		0	

3.3 Application of the Colorimetric Card

Using the colorimetric card prepared by this experimental method, spike tests were conducted on different types of actual water samples (reservoir water, river water, groundwater, tap water). Each spiked sample was prepared in three replicates. Good identification was achieved at each concentration point within the measurement range, and the results were reproducible.

4. Conclusions

This paper has conducted a detailed study and verification on the relationship between calcium ion concentration and the color development with Chrome Black T, establishing a colorimetric method for the concentration of calcium ions in water based on the titration method with Chrome Black T. By taking a 50 mL water sample, adjusting the pH to 9, and adding 0.1 mL of Chrome Black T (5 mg/mL) for color development with a reaction time of 10 seconds, one can clearly observe the relationship between water hardness and color change, which offers high distinguishability. This method is not only easy to operate but also provides clear results without the need for expensive equipment. It is simple, straightforward, and offers a fast, environmentally friendly, and accurate way for the public to determine water hardness.

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