A Study Focusing on the Preparation and Application of New-mode Electrode Materials for Water Hardness Measurement

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Abstract—This paper aimed to study the calcium ion selective electrode, based on using PVC as the electrode carrier and didecyl calcium phosphate which was synthesized from decanol, phosphorus oxytrichloride, pyridine and calcium chloride as the electroactive substance. This paper mainly focused on the study and the fabrication process of both the electrode diaphragm and electrode, with conducting the performance test of the newly developed electrode. The results showed that the response time of the developed water hardness sensor was 2-5 s, which had good response characteristics and was suitable for fast and portable testing of water hardness in environmental testing. There was no significant difference between this water hardness sensor method and the national standard method. When the water temperature varies between 10 and 60 Centigrade, the influence of temperature on the data of the water hardness sensor was very small, and the water hardness sensor had good stability to test the temperature change.

1. Introduction
Water hardness is an important factor of water quality, which refers to the levels of soluble calcium and magnesium ions in water. Long-term intake of over-hard water for human beings is prone to result in a symptom of getting kidney stones and cholecystitis and further health deterioration. If the hardness of the water used in the boiler has been detected as excessive, the heat transmitting efficiency will be greatly reduced by the scaling problem without longer being conducive to energy saving. What is more, asymmetric temperature distribution during the process of heating may even trigger boiler explosion [1]. On the other side, if the hardness in food processing water is comparatively higher as well, trouble like turbidity, precipitation, flavor change, reduced water retention (meat), hardening (meat, soy products) and other related problems are undoubtedly going to appear automatically [2].

Water hardness measurement currently is widely used in food processing, environmental monitoring and other aspects, whose measuring methods mainly include EDTA complexation titration method[3], colorimetric method[4], and the electrode method[5]. Generally speaking, the EDTA complexation titration method serves as the national standard method to measure the total hardness of water quality. Nevertheless, this method has great uncertainty in endpoint judgment and fails to meet the requirements of field measurement. Colorimetric method, on the other hand, is a means that is capable of conducting qualitative and quantitative analysis by using the spectrophotometer. This method has simple operation conditions and highly reliable, but the only shortcoming is that it usually needs to be operated in the laboratory, with numerous consumable materials and high maintenance costs. Electrode method, based on a particular kind of electrode with selective response to a particular...
ion, possesses the characteristics of good selectivity, convenient operation and simple requirements of devices. [6]. The electrodes for measuring water quality hardness mainly constitute the electrode film with PVC as the carrier, and calcium phosphate as the electroactive material[7]. At present, the mostly applied calcium phosphate salts are calcium diocphenyl phosphate as well as double [4- (1,1,3,3-tetramethylbutyl) phenyl] calcium phosphate[8]. However, the extraction methods in the whole procedure of the above phosphate calcium are rather complicated and not many formal recommendations are provided here. There are also calcium ion selective electrodes with thioacetamide / bump stone complex as the carrier[9], yet the production procedure is even more sophisticated. This paper tries to conduct further research on producing an electroactive material with a relatively simple preparation method and explore a calcium ion selective electrode on that basis, aiming to provide rigorous technical support for the promotion and application of the above-mentioned selective electrode.

2. Materials and methods

2.1. Instruments and reagents

Acetic ether (C\textsubscript{4}H\textsubscript{10}O, AR), pyridine (C\textsubscript{5}H\textsubscript{5}N, AR), phosphorus oxychloride (POCl\textsubscript{3}, AR), decanol (C\textsubscript{10}H\textsubscript{22}O, AR), calcium chloride (CaCl\textsubscript{2}, AR), reflux device, tetrahydrofuran (C\textsubscript{4}H\textsubscript{8}O, AR), tributyl phosphate (C\textsubscript{12}H\textsubscript{27}O\textsubscript{4}P, AR), PVC powder, hydrochloric acid (HCl, AR), potassium chloride (KCl, AR), 0.5 mm silver wire, circular plastic mold (10 mm diameter), millivoltmeter, 1.5V battery, tube (10 mm PVC pipe diameter, electric heater).

2.2. The synthesis of didecyl calcium phosphate [11]

Add 50 mL POCl\textsubscript{3} into the round bottom flask, connecting to the reflux device with adding and stirring 500 mL of ether. In the stirring state, dropping a certain amount of decyl ether solution into the drip funnel in a slow pace at the controlling rate of 30-40 drops per minute. Then a certain amount of pyridyl ether solution should be poured slowly into the flask, with controlling the speed at 60 drops per point. After the stage is completed, let the reflux reaction continue for 1 hour at room temperature. The above mixed reaction system solutions later are poured into a 500 mL split funnel, washed with one volume of water acidified by hydrochloric acid for many times. In the next step, the organic phase (colorless transparent upper liquid) must be added into a vacuum distillation device (gram flask), firstly distilled at 449 mm Hg column under the temperature of 40°C for 1 hour long and then distilled again at 0-5 mm Hg column under 70°C until the liquid became a yellow brown viscous liquid, which is the so called didecyl phosphate. This composite material should continue to be mixed with saturated CaCl\textsubscript{2} that has a ten-time volume under the condition of 40°C. Having undergone full vibration and stratification, the water phase is abandoned. After repeating for several times, there is only slightly yellow liquid left. Having been placed for a moment to coagulate into milky white, didecyl calcium phosphate is eventually acquired.

The above-mentioned compounding reaction mechanism is as follows:

\[
2C_{10}H_{23}OH + POCl\textsubscript{3} \rightarrow (C_{10}H_{23}O)\textsubscript{2}POCl \text{ (C_{10}H_{23}O)\textsubscript{2}POCl} \rightarrow (C_{10}H_{23}O)_{2}POOH \\
2[(C_{10}H_{23}O)_{2}POOH] + CaCl\textsubscript{2} \rightarrow [(C_{10}H_{23}O)_{2}POO \text{]}\text{Ca} + 2HCl
\]

2.3. The manufacturing of the water hardness sensor

2.3.1 Preparation of electrode film

Mix 4-5 mL tetrahydrofuran with PVC powder (per 0.5 g) and grind in the mortar until the PVC powder is completely dissolved. One to five drops of tributyl phosphate should be added, waiting to be grinded and blended for a while. Later on, 0.1-0.2 g didecyl calcium phosphate is added and grounded as well until the solution dissolves and becomes slightly sticky. As soon as the grinding process stops, absorb the solution into the prepared round plastic mold by using a dropper. (The mold
should be placed on clean glass plate) The electrode film is completed after the liquid solution is entirely covered with the mold bottom and generates with a certain thickness. The electrode film should be dust-free and natural-dry for 8 hours before use.

2.3.2 The production of silver chloride electrode filaments
Select the battery with low current and good electrode stability and weld two silver wires with the length of about 12CM and the width of 0.5mm respectively onto both the positive and negative poles of a 1.5V battery. Later on, the battery is about to be placed in the center of a beaker containing 0.1mol/L HCl solution. Dip the two silver wires into the beaker reaching the depth of 8-9cm for electroplating on the condition that the surface of the two wires is cleaned thoroughly. The stage takes about 100 minutes till the positive silver - silver chloride wires are fetched out for later use. During the production process, there are bubbles generated from the negative electrode. After two silver wires were immersed in the 0.1mol/L HCl solution, the immersed part of the positive silver wires first turns into gray and then becomes blackened, forming an even silver chloride electroplating layer.

2.3.3 Production of the reference electrodes
Weight 1.5g AGAR and put it into the prepared 100mL saturated KCl solution, ready to heat the mixture in an electric heater. During the heating procedure, a glass rod should be used to stir continuously to prevent AGAR from excessive burning. Remember to remove the beaker when it reaches the boiling point. Block the electrode tube using cotton, and mix the hot saturated KCl - AGAR solution through the other side, reaching the height of 9-10 cm. In the process of dumping, please ensure that the electrode tube does not generate any air bubbles in the solution. Then quickly insert a piece of silver chloride electrode tube into it until the black part fully emerges into the electrode tube solution. Apply a rubber plug through the uncovering silver wires, and try to plug the end of the electrode tube with connecting the remaining silver wires with a conductor wire as the electrode wire. The whole course of making the reference electrode (immersed in water and stored for later use) is finished.

2.3.4 Production of the indicator electrodes
Completely seal one side of the electrode tube using ready-made electrode film and pour the 0.01mol/L CaCl$_2$ solution into the electrode tube for the depth about 9-10cm. One silver-silver chloride wire should be selected and inserted into the electrode tube until the black part completely emerges into the solution of the electrode tube. Use a rubber plug to pass through the remaining silver wire to fix this end of the electrode tube, and connect the remaining silver wire as the electrode wire. The indicator electrodes then are made well.

The electrode film shall completely seal one side of the electrode tube in case of the outflow of the CaCl$_2$ Solution. The situation that no bubbles in the electrode tube solution must be ensured, as the concentration of the CaCl$_2$ Solution is going to affect four orders of magnitude among the measurement range. (The hardness range of 0.01mol/L CaCl$_2$ Solution is measured to be between the range from 0.1mmol/L to 100mmol/L)

2.3.5 Fabrication of the water-quality hardness measurement sensor
Connect the electrode line of the reference electrode to the “reference electrode” interface of the millivolt meter, and the indicating electrode to the “indicator electrode” interface of the display watch which should be turned on. Place the reference electrode and the indicator electrode into the ready-to-be-measured solution and read the number of mV displayed.

2.4 The functional test of water-quality hardness measurement sensor
In order to test the performance of the newly-developed water hardness measuring electrode, the following three methods are selected in this paper.
(1) The Response test of different detected concentrations
Under the same conditions, several water quality samples with different hardness of 0.1, 1, 10 and 100mmol/L are measured by the newly-developed electrode sensor in order to get their response curves.

(2) The influence test of temperature on electrode performance
Under the conditions of 10℃, 20℃, 30℃, 40℃, 50℃ and 60℃ respectively, use the water hardness sensor made by the water-quality hardness measurement sensor to determine the hardness of 0.1, 1, 10 and 100mmol/L standard water quality samples.

(3) The comparison test of national standard methods
Under the same conditions, use the above-mentioned water hardness sensor and national standard methods (total determination EDTA titration GB7477-87of water quality calcium and magnesium) to determine water samples separately.

3. Results and Discussions
Analysis of electrode performance test results of water hardness measurement sensor

3.1 Analysis of water samples with different levels of hardness [12]
Prepare standard solutions with 4 gradients of hardness namely 0.1, 1, 10 and 100mmol/L, respectively. The newly-developed water hardness determination electrode is inserted into the solution for determination, and the display watch showed that the millivolts are 70, 102, 131 and 156mV. Take the hardness of water as the horizontal axis, the corresponding display watch millivolt reading as the ordinate to draw hardness response curves.

The data is shown in Fig.1.

![Hardness response curve of water quality](image)

Fig.1 Hardness response curve of water quality

As can be seen from the hardness response curve in Fig. 1, the water hardness between 0.1, 1, 10 and 100mmol/L is in an exponential relationship with the millivolt reading of the hardness measurement sensor, which is in line with the Nernst equation of thermodynamics. Water hardness can be determined by simply measuring the electromotive force based on the relationship between electromotive force and the liquid density. Within this range, the water hardness sensor can accurately measure the level of water hardness.

3.2. Analysis about the test results of temperature influence on water hardness electrode [13]
Under the given conditions of 10℃, 20℃, 30℃, 40℃, 50℃ and 60℃, the newly-developed water hardness sensor can be used to measure the hardness of 0.1, 1, 10, and 100mmol/L standard water samples, and the determination results are shown in Fig.2.
It can be seen from Fig. 2 that, when the measurement temperature varies between 10℃ and 60℃, the measurement results of the ready-made electrode sensor for different concentrations of water samples do not have great change. That is to say, the electrode sensor has better stability towards the temperature variation.

3.3. Compared with national standard methods
In order to conduct the comparison test thoroughly, both the manufactured water-quality hardness sensor and national standard methods[14](Total determination EDTA titration GB7477-87 of water quality calcium and magnesium) are used to measure the tap water samples and standard samples. Table.1 clearly shows the comparison results of the hardness of the water samples. (Unit: mmol/L).

| Water hardness sensor (mV) | 10 | 20 | 30 | 40 | 50 | 60 |
|---------------------------|----|----|----|----|----|----|
| 0.1mmol/L                 | 150| 150| 150| 150| 150| 150|
| 1mmol/L                   | 140| 140| 140| 140| 140| 140|
| 10mmol/L                  | 130| 130| 130| 130| 130| 130|
| 100mmol/L                 | 120| 120| 120| 120| 120| 120|

Table.1 Comparison of sensor and GB method

|               | 1   | 2   | 3   | 4   | 5   | 6   | Σ   |
|---------------|-----|-----|-----|-----|-----|-----|-----|
| National      | 1.42| 1.43| 1.41| 1.42| 1.40| 1.43| --  |
| standard      |     |     |     |     |     |     |     |
| Measurement   |     |     |     |     |     |     |     |
| Sensor        | 1.41| 1.42| 1.41| 1.40| 1.42| 1.44| --  |
| Measurement   |     |     |     |     |     |     |     |
| Difference    | 0.01| 0.01| 0   | 0.02| -0.02| -0.01| 0.03|
| number di     |     |     |     |     |     |     |     |
| d i^2         | 0.0001| 0.0001| 0 | 0.0004| 0.0004| 0.0001| 0.0011|

For results in Table.1, the selected significance level, α = 0.05, is calculated as follows:

\[
\bar{d} = \frac{\sum d_i}{6} = 0.005 \quad s = \sqrt{\frac{\sum_{i=1}^{6} d_i^2}{n-1}} = 0.0015 \quad t = \frac{|\bar{d} - d_0|}{S/\sqrt{n}} = 1.34
\]

Check the distribution table of t (t_{0.05,6} = 2.57, t < t_{0.05,6}) and it can be known from the calculation results that, there is no significant difference about the hardness of tap water measured by the two different methods, which has satisfying comparability [15].

The comparison results of the hardness of standard samples are shown in Table.2.
Table 2: Determination of standard solution with sensors

| Sensor Hardness (mmol/L) | Standard hardness (mmol/L) | Relative error |
|--------------------------|-----------------------------|----------------|
| Water sample 1 0.1003 | 0.1000 | +0.30% |
| Water sample 2 0.4979 | 0.5000 | -0.42% |
| Water sample 3 1.004 | 1.000 | +0.40% |
| Water sample 4 5.020 | 5.000 | +0.40% |
| Water sample 5 10.05 | 10.00 | +0.50% |
| Water sample 6 40.11 | 40.00 | +0.28% |
| Water sample 7 70.16 | 70.00 | +0.23% |
| Water sample 8 99.86 | 100.0 | -0.14% |

We can see immediately from Table 2 that, the relative error of standard sample hardness measured by water-quality hardness measurement sensor is within ±0.50%, having high accuracy.

4. Conclusion

Using decyl alcohol, phosphorus oxytrichloride, pyridine and calcium chloride as the main raw materials through a series of reaction processes can obtain the substance of didecyl calcium phosphate. As a kind of electroactive substance, the synthesized didecyl calcium phosphate can be loaded on PVC to produce the electrode, which serves as the core element in successfully manufacturing the water hardness sensor. The results show that this newly-developed instrument has a good response curve and a good comparison result with the national standard method while testing its performance. When the temperature of the water sample changes between 10°C-60°C, the temperature is proved to have little influence on the reading of the water hardness sensor, which means that, the water hardness sensor has a comparatively better stability towards the temperature change.

Acknowledgments

This work was financially supported by the Major Scientific Research Projects of Beijing Polytechnic(2020Z003-KXZ).

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