

Detection of Salt Content in Raw Milk on a Gold Electrode through Cyclic Voltammetry

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Abstract—The relationship model of chloride ion content and oxidation peak current was established by the study of curve obtained by using gold electrodes to test cyclic voltammetry in raw milk containing different chloride ion concentrations. The study found that with the increased of chlorine ion content, the potential of the oxidation peak was in positive correlation and the current of the peak increased dramatically. The golden matter appeared in sample liquid. In addition, we observed that corrosion in gold electrode, and the characteristic peak of Au-Cl^{-1} appeared at 269cm^{-1} by using SEM and SERS to detect the reaction electrode. The results showed that the gold electrode had the anodized dissolution because of the presence of chloride ion. The prediction model of chloride ion content with a detection limit of 0.05g/L was established by the least square method. The recovery rate and relative standard deviation of the method were respectively from 91.0% to 106.0% and from 3.4% to 4.2% . The method is suitable for rapid detection of milk mixed with salt.

Index Terms—raw milk, chloride ion, cyclic voltammetry, detection

I. INTRODUCTION

Raw milk (RM) is the source of dairy industry chain, and its quality and safety affect directly the subsequent processing of dairy products [1]. Because of the huge economic benefits, adulteration of milk has been commonplace. The most common way of adulteration is adding water [2], but with the popularization of freezing point detection in the acceptance link of raw milk, the method is no longer available. Sodium chloride (NaCl) is the high-density material that can increase the density of milk and lower the freezing point of raw milk. In order to cover up the fact that they add water to milk, dairy farmers often add salt to the raw milk. Therefore, a procedure ensuring the quality of raw milk by detecting salt before freezing point was what we aimed at.

The chloride ion content as an indicator at home and abroad reflects the concentration of salt in raw milk. Generally, the concentration of chloride ion in milk is 0.9g/L to 1.2g/L [3]. At present, the main detection technique is titrimetry which is used to detect chloride ion [4]. Titration is divided into potentiometric titration and precipitation titration. Both of them use the silver nitrate standard solution to determine the concentration of

chlorine ion in the filtrate after precipitating the protein in milk by using acid. Finally, the chlorine ion content is calculated according to the consumption of the silver nitrate standard solution. The distinction between the two methods is the end point of the titration [5]. The potentiometric titration determines titration end point by the jumping of potential and the precipitation titration determines the end point of titration by the orange precipitation which is produced by the silver chromate [6]. In addition, there are also many methods for detecting chloride ions in the laboratory. Maorong Xu [7] used capillary electrophoresis to separate and quantify chloride ion in raw milk. Chuanhui Zhang [8] determined the chloride ion in the finished product of citric acid by using spectrophotometry. Based on flow injection and turbidimetric method, Lingyun Yu [9] detected the chlorine ion in leather wastewater. However, both of these methods involve complicated operations and the samples to be pretreated, which means they are not suitable for testing on site.

Our electrochemical method functions in the way that the sensor array obtains a different signal [10]. By processing the collected data, we can carry out the analysis of the sample by measuring the electrode interface information [11]. Because the electrochemical techniques have the advantage of high sensitivity and convenience [12], the electrochemical detection method has already been applied not only to the detection of dairy, but also monitoring the source of raw milk. There have been many studies on the monitoring of cow diseases, the adulteration of raw milk, the classification of dairy products, quality control of dairy products, etc. [13]. In this paper, a method of detecting the concentration of salt in raw milk was established through the measurement loop composed in this way which we used the gold electrode as the working electrode, the platinum electrode as the auxiliary electrode, and the Ag/AgCl electrode as the reference electrode.

II. EXPERIMENTAL

A. Materials

Raw milk whose density was 1.03g/mL and chloride ion content (detected by potentiometric titration) was 1g/L was provided by Changshan Modern Organic Pasture (Nanchang, China). Urea (Ur), dextrin (Dex) and glucose (Glc) were purchased from Damao Chemical

Reagent Factory (Tianjin, China) and Sodium sulfate (Na_2SO_4), sodium nitrate (NaNO_3), sodium bromide (NaBr) and sodium chloride were made by Zhenxing Chemical Plant (Shanghai, China). All reagents are the pure analytically. First, we prepared three samples by adding respectively 584mg of sodium chloride, 849mg of sodium nitrate and nothing to 100mL of raw milk, as shown in Table I. Second, in order to keep the density of milk constant, nine samples containing different concentrations of chloride ion were prepared by adding sodium chloride and ultrapure water (UPW), as shown in Table II. Third, We prepared six samples by the method that We added respectively 3000mg of urea, dextrin, glucose, Sodium sulfate, sodium nitrate and sodium bromide to the samples in which the concentration of chloride ion was 6g/L, as shown in Table III.

TABLE I. DIFFERENT KINDS OF SODIUM SALT

Conditions of sample	
I	100mL RM
II	100mL RM+84 mg NaNO_3
III	100mL RM+584mg NaCl

TABLE II. SAMPLES OF DIFFERENT CHLORIDE ION CONTENTS

Conditions of sample	Concentration 1g/L
I	100mL RM
II	100mL RM+103mg NaCl +3.4mL UPW
III	100mL RM+214mg NaCl +7.1mL UPW
IV	100mL RM+333mg NaCl +11.1mL UPW
V	100mL RM+461mg NaCl +15.4mL UPW
VI	100mL RM+600mg NaCl +20.0mL UPW
VII	100mL RM+750mg NaCl +25.0mL UPW
VIII	100mL RM+1090mg NaCl +36.4mLUPW
X	100mL RM+1500mg NaCl +50.0mLUPW

TABLE III. SAMPLES OF ANTI-INTERFERENCE TEST

Conditions of sample	
I	100mL RM+600mg NaCl +20.0mL UPW+3000mg Ur
II	100mL RM+600mg NaCl +20.0mL UPW+3000mg Dex
III	100mL RM+600mg NaCl +20.0mL UPW+3000mg Glc
IV	100mL RM+600mg NaCl +20.0mL UPW+3000mg Na_2SO_4
V	100mL RM+600mg NaCl +20.0mL UPW+3000mg NaNO_3
VI	100mL RM+600mg NaCl +20.0mL UPW+3000mg NaBr

B. Electrode Treatment

Electrodes used in this experiment were bought from the Xianren Company (Shanghai, China). The gold electrode was hand-polished to a bright mirror finish on the wet surface of Al_2O_3 (0.05 μm), and cleaned ultrasonically by HNO_3 solution ($\text{HNO}_3:\text{H}_2\text{O} = 1:1$, V/V), absolute ethanol and ultrapure water in turn. Then it was put into the solution with 0.5mol/L H_2SO_4 for to be activated and the operation finished when we found the curves of cyclic voltammetry coincident. Finally, we tested the electrode in the solution of 0.01mol/L $[\text{Fe}(\text{CN})_6]^{3-/4-}$. If the difference of peak potential was below 80mV, the electrode conformed to the experimental requirements [14].

C. Research Methods

Electrochemical quartz crystal microbalance CHI440C was purchased from Chenghua Company (Shanghai, China). The measurement loop was composed in this way which we used the gold electrode as the working electrode, the platinum electrode as the auxiliary electrode, and the Ag/AgCl electrode as the reference electrode. Under the conditions that potential range was from 0V to 1.4V and sweep speed was 0.05V/s, the samples in Table I and Table II were swept by cyclic voltammetry to study the cyclic voltammetric behavior of raw milk in different states. The prediction model of chloride ion content was established by linear fitting of measured data in Table II. To verify the anti-interference ability of the model, the samples in Table III were scanned under the same conditions. Electrochemical determination was the same as other electrical measurement, and the measurement was often influenced by electrical noise, so all the experiments should be carried out in the shielding box.

The LabRAM HR Laser Raman Spectrometer (excitation wavelength of 632.8 nm, spectrometer focal length of 800 nm) was purchased from Jobin Yvon Company of French, with two measurement modes of high sensitivity and high resolution. The Hitachi S-3400N Scanning Electron Microscope was purchased from Hitachi High-Technologies Corporation Company of Japan. The electrode which tested the chloride ion content of 5g/L and 11g/L of raw milk was used as the reaction electrode, the electrode was washed previously with ultrapure water for 5 minutes and then dried with nitrogen. Finally, the surface properties of gold electrode was studied by SERS and SEM.

III. RESULTS AND DISCUSSION

A. Voltammetric Analysis of Milk in Different States

The CV curves of raw milk with 5g/L chloride ion is shown in Fig. 1. As shown in Fig. 1, with the number of turns increased, the current of the redox's peaks was increasing continuously. However, after the 20 circles of the scan, the current of peaks increased slowly, and the time required increased. The situation was the same as in the other samples. So we set sweep segment to 40 [15]. The CV curves of different kinds of sodium salt is shown in Fig. 2. As shown in Fig. 2, compared with the blank milk, the oxidation peak's potential of the milk added with sodium nitrate did not change, and the current increased slightly. The current and potential of milk added with sodium chloride changed obviously. These showed that the changes of oxidation peak of milk added with sodium salt were mainly caused by the electrochemical behavior of chloride ion, which was related rarely to sodion [16]. According to previous reports, the addition of sodium ions increased the conductivity of milk [17], which was the reason why the current became bigger [18]. The CV curves of samples with different chloride ion contents are shown in Fig. 3. As shown in Fig. 3, with the increase of chloride ion content, the current of the oxidation peak increased

obviously, and showed a good positive correlation with the concentration of chloride ion. It was also found in Fig. 1 and Fig. 3 that with the concentration of chloride ion and the number of scanning cycles increasing, the potential of oxidation peak shifted continuously, and even the potential of peak disappeared when the concentration of chloride ion was more than 30g/L or the number of cycles exceeded 500 cycles. In addition, the golden matter appeared in sample liquid in the process of electrochemical reaction. From the above experiment results, we speculated that the voltammetric behavior — the anodic dissolution of gold electrode in raw milk was caused by chloride ion, and the dissolution rate increased rapidly with the increase of chloride content [19]. The results of the later tests confirmed this.

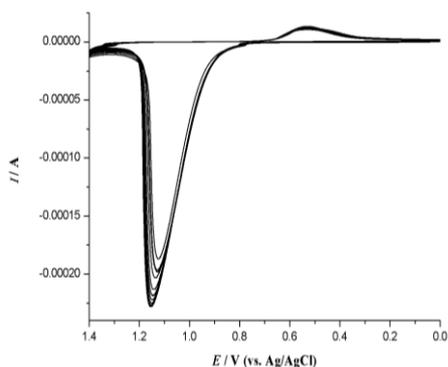


Figure 1. CV curves of raw milk with 5g/L chloride ion.

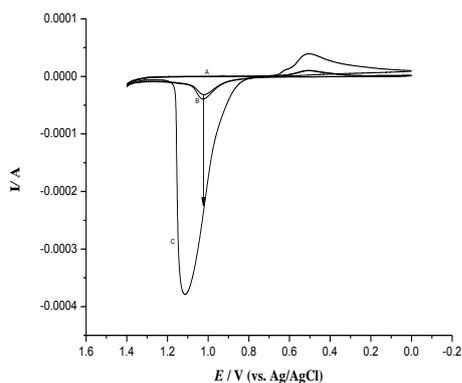


Figure 2. CV curves of different kinds of sodium salt.
A. 100 mL RM, B. 100 mL RM + 849 mg NaNO₃
C. 100 mL RM + 584 mg NaCl

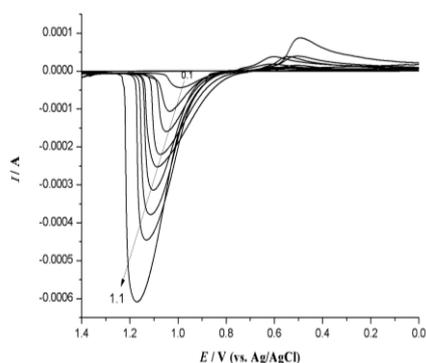


Figure 3. CV curves of raw milk with different chloride ion content.

B. Detection of SERS and SEM

It can be seen that the surface of the gold electrode was uneven from the SEM image of the reaction electrode in Fig. 4, indicating that the gold electrode was corroded. From the Raman diagram of the blank electrode and the reaction electrode in Fig. 5, it can be seen that the blank electrode had no Raman response at 100 cm⁻¹ to 400 cm⁻¹, and the Raman peaks of the two test electrodes appeared at 269 cm⁻¹, the position of the Raman peak of Au-Cl⁻ was consistent with previous research [20]. The Raman peaks of the two test electrodes differed only in the size of the response peaks, which may be related to the concentration of the test sample. The results suggested that the gold electrode had the anodic dissolution in the raw milk containing chloride ion [21]. In other words, chlorauride (Au + 3Cl⁻ → AuCl₃ + 3e⁻) was formed and Au was oxidized [22]. In addition, the dissolution rate increased rapidly with the increase of chloride ion concentration.

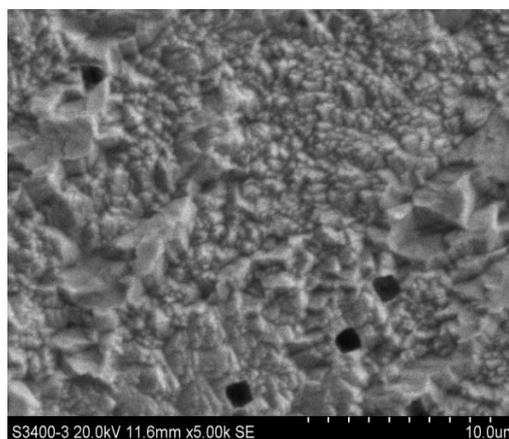


Figure 4. SEM diagram of the reaction electrode.

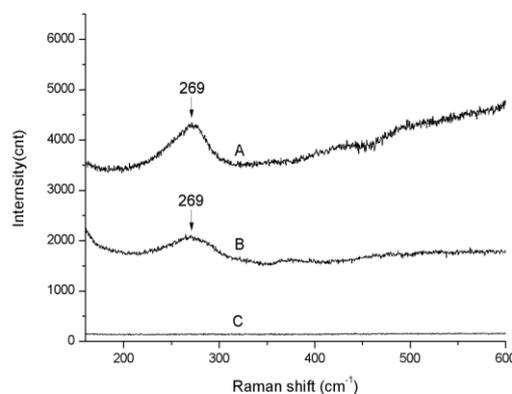


Figure 5. Raman diagram of the reaction electrode. A.11 g/L B. 5 g/L C. blank

C. The Predicting Model of Chloride Ion Content

The predicting model of chloride ion contents was shown in Fig. 6. As shown in Fig. 6, We established the model by the least square method, and the linear equation about the current of oxidation peak and the chloride ion content is $I/(10^{-4}A)=0.9691+0.4981C/(g/L)$, with a detection limit of 0.05 g/L and absolute correlation

coefficient of 0.9992. In subsequent experiments, we tested its anti-interference ability, stability and reproducibility.

D. Anti-Interference Test

The results of anti-interference ability is shown in Table IV. The results showed that urea, dextrin, and glucose didn't interfere with the detection. Sodium sulfate, sodium nitrate interfered slightly with the detection. According to previous reports, Electrical conductivity was the reason why the current became bigger or kept constant. Urea, dextrin, and glucose don't have the conductive ability but the ions could increase the conductivity of milk [17]. Bromide ion interfered seriously with the detection. The reason of interference may be that bromide ion is similar to chlorine ion [22].

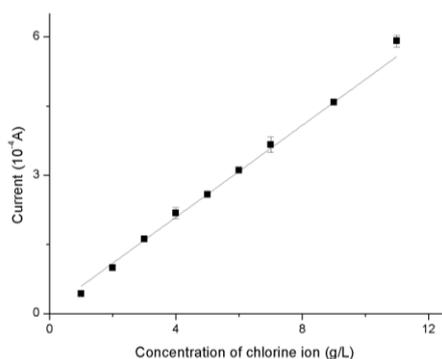


Figure 6. The predicting model of chloride ion content.

TABLE IV. RESULTS OF ANTI-INTERFERENCE TEST

The current of the oxidation peak(10 ⁻⁴ A)	
I	3.1088
II	3.1093
III	3.1105
IV	3.2451
V	3.214
VI	the oxidation peak disappeared

E. Detecting the Recovery of the Actual Sample

The samples of milk with different chloride ion contents were prepared and detected according to the predicting model of chloride ion contents. Each concentration of sample was determined 5 times. The results are shown in Table V. The recovery rate and relative standard deviation of the method were respectively from 91.0% to 106.0% and from 3.4% to 4.2%, which showed that the stability and reproducibility of this model was good.

TABLE V. RECOVERY RATES OF CHLORIDE ION IN SPIKED SAMPLES

Sample number	Concentration of chlorine ion		Recovery(%)	RSD(%)
	Amount added	Amount found		
I	1g/L	0.91g/L	91.0	4.2
II	2g/L	2.12g/L	106.0	3.4
III	2.5g/L	2.48g/L	99.2	4.1
IV	3g/L	3.12g/L	104	3.9
V	3.5g/L	3.48g/L	99.4	3.5

IV. CONCLUSIONS

We studied the cyclic voltamine of the gold electrode in the raw milk with the salt, and found that the gold electrode had the anodized dissolution. The reason is that Au was oxidized and chlorauride ($Au+3Cl^{-}\rightarrow AuCl_3^{-}+3e^{-}$) was formed. Based on this reaction, the prediction model of chloride ion content was established. The linear equation about the current of oxidation peak and the chloride ion content is $I/(10^{-4}A)=0.9691+0.4981C/(g/L)$, with a detection limit of 0.05g/L and absolute correlation coefficient of 0.9992. This model had a good anti-interference ability. The results showed that Organic matter without electrical conductivity such as urea, dextrin, and glucose didn't interfere with the detection. Inorganic salt ion which has the ability to conduct electricity such as Sodium ion, sulfate ion, nitrate ion interfered slightly with the detection. Halide ion such as bromide ion interfered seriously with the test. According to recovery rates of chloride ion in spiked samples, we know that the stability and reproducibility of this model are also good. In the subsequent studies, we will apply our experiments in this method, based on anode solution of gold electrode which is caused by the presence of chloride ion, to other fields, such as detecting chloride ion in industrial wastewater or in organic fertilizer.

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