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# Determination of Chloride Ion in Selenium(IV) System with Silver-Diethyldithocarbamate Modified Electrode

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The silver-diethyldithocarbamate (DDTC Ag) modified electrode was constructed and a new method for the determination of chloride ion has been established at the modified electrode. The results indicated that a well-defined stripping peak were obtained at DDTC Ag modified electrode by the anodic stripping voltammetry technique and the addition of Se(IV) can further increase the sensitivity. In addition, the experiment parameters such as buffer pH, the concentration of Se(IV), accumulation potential and accumulation time were optimized. Under the selected conditions, the oxidation peak currents were in linear with concentration of chloride ion in the range of $1 \times 10^{-4} - 8 \times 10^{-3}$ mol $L^{-1}$ (R = 0.9992). Detection limit of it reached $2 \times 10^{-5}$ mol $L^{-1}$. The method could obtain better result when it applied to the determination of chloride ion in soy.

**Key Words: Silver-diethyldithocarbamate, Modified electrode, Chloride ion, Anodic stripping voltammetry.**

## INTRODUCTION

It is necessary to determine the content of chloride ion in medicine, food, geology and entironment[1-4]. A variety of methods have been used for chloride ion determination, including capacity method[5], ion selective electrode method[6], potentiometric titration[7], ion chromatography[8] and spectrophotometry[9]. The chemically modified electrodes (CMEs) is one of the popular techniques to be studied in analytical field, it has many advantages such as good stability and reproducibility, higher sensitivity and alternative and modified it more flexible.

However, the reports about the determination of chloride ion by CMEs are comparatively less. We describe herein a simple and rapid method to prepare the DDTC Ag modified electrode and a new method for the determination of chloride ion has been established at the modified electrode. The results indicated this electrode not only prepared simply but also had higher sensitivity and alternative in detecting chloride ion. The proposed method has been applied to the determination of chloride ion in soy with satisfactory result.

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## EXPERIMENTAL

The anodic stripping voltammetry measurements were carried out using an AD-300 multi-function electrochemical analyzer (Tianjin Aida Instrument Int., China). All the anodic stripping voltammograms were made using a three-electrode system with a glassy carbon electrode as a working electrode, an Ag/AgCl (saturated with KCl) as a reference electrode and a platinum wire electrode as a counter electrode. The KQ218 ultrasonic instrument (Kunshan Ultrasonic Instrument Factory, China) was used.

Stock solutions (1 mol $L^{-1}$) of KCl and stock solutions (1000 m g $L^{-1}$) of Se(IV) were prepared in pure water and diluted appropriately before use. Other reagents were of analytical-reagent grade and all other chemical reagents were used without further purification. 0.05 mol $L^{-1}$ $H_3PO_4$ + 0.05 mol $L^{-1}$ $CH_3COOH$ + 0.05 mol $L^{-1}$ $H_3BO_3$-0.2 mol $L^{-1}$ NaOH buffer solutions of various pHs were prepared by mixing two stock solutions. All solutions were prepared with double-distilled water.

**Preparation of the silver-diethyldithocarbamate modified electrode:** Glass carbon electrodes were polished first with emery paper, alumina (0.1 mm) and then cleaned in an ultrasonic bath in (1:1) $HNO_3$, (1:1) $CH_3CH_2OH$ and water in turn. After rinsing with water, the electrodes were cyclically scanned in 0.5 mol $L^{-1}$ $H_2SO_4$ (from -0.8 to 1.2 V) until a reproducible voltammogram was obtained. The GCE was coated by casting 10 μL dispersion of DDTC Ag (0.1 g DDTC Ag dissolved in 2 mL $CCl_4$ at a brown volume) and dried at room temperature. The freshly prepared DDTC Ag modified electrode was activated in pH 2.21 (0.05 mol $L^{-1}$ $H_3PO_4$ + 0.05 mol $L^{-1}$ $CH_3COOH$ + 0.05 mol $L^{-1}$ $H_3BO_3$-0.2 mol $L^{-1}$ NaOH) buffer solution. By using successive cyclic scans from-0.8 to 1.0 V. The electrode was thoroughly washed with doubly distilled water before use.

**Procedure:** The anodic stripping voltammetry experiments for the examination of chloride ion was carried out in buffer solutions containing $1 \times 10^{-4}$ g $L^{-1}$ Se(IV). The deposition step lasted 40 s at -1.0 V whilst the solution was rotated with a magnetic stirrer. After a 5 s quiescent time the stripping step was initiated at -0.8 V and ended at 0.6 V. The scan rate was 100 mV/s. At the same time note down the anodic stripping voltammograms for investigating the voltammetric behaviors of chloride ion on DDTC Ag modified electrode. The experiential results were obtained at room temperature.

## RESULTS AND DISCUSSION

**Anodic stripping voltammograms:** Fig. 1 showed the anodic stripping voltammograms of $1.0 \times 10^{-3}$ mol $L^{-1}$ KCl at different electrodes in the pH 2.21 buffer solution (containing $1 \times 10^{-4}$ g $L^{-1}$ Se(IV)). The sensitive oxidation peak was observed at the DDTC Ag modified electrode (Fig. 1b), the oxidation peak potential (EPa) was 0.01 V. There was no response at the bare glassy carbon electrode (Fig. 1a).

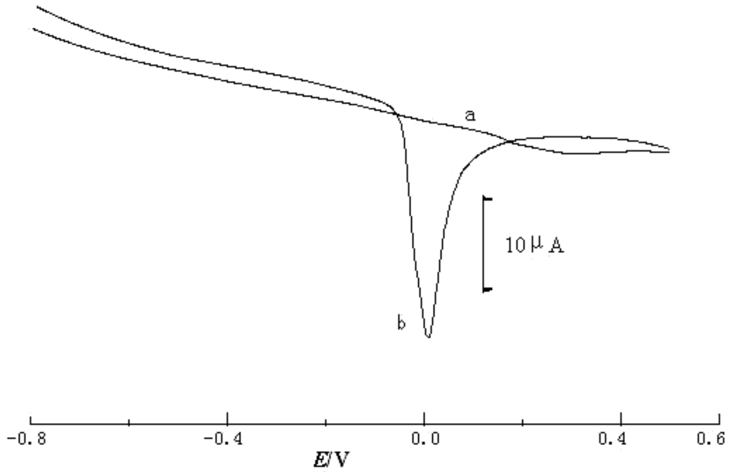

Fig. 1. Stripping voltammograms (a) bare glassy carbon electrode, (b) DDTC Ag modified electrode

Fig. 2 showed the anodic stripping voltammograms of DDTC Ag modified electrode in different solution (pH 2.21). Fig. 2c showed the stripping voltammograms of DDTC Ag modified electrode in 1.0 × $10^{-3}$ mol $L^{-1}$ KCl solutions, an oxidation peak was observed at the stripping curve, the oxidation peak potential ($E_{Pa}$) was 0.09 V. There had the same electrochemical behaviour when KCl was changed by NaCl under the same condition, there was no response when there was no $Cl^-$ in the solution (Fig. 2a), the experiment indicated that the oxidation peak was present because of $Cl^-$ could produce reaction on the electrode surface. The mechanism may be that AgCl due to $Ag^+$ in modified layer react to $Cl^-$ would deposit on electrode, then the AgCl could produce reversible oxidation and reduction reaction under the electrochemical action. The electrode process showed as below:

$$AgCl + e^- \rightleftharpoons Ag + Cl^-$$

The oxidation peak current increased notably if 1 × $10^{-4}$ g $L^{-1}$ Se(IV) was added to the above solution (Fig. 2d), but there was a very small peak at the curve when Se(IV) was added alone (Fig. 2b). It indicated that there was no distinct response of Se(IV) at the DDTC Ag modified electrode directly, it would accelerate the reaction of $Cl^-$ on the DDTC Ag modified electrode, therefore, the oxidation peak current of $Cl^-$ would increase notably.

Furthermore, the effect of the scan rate on the oxidation peek of $Cl^{-1}$ was investigated in 1.0 × $10^{-3}$ mol $L^{-1}$ KCl solutions. The oxidation peak potential positive shifted slightly with increasing scan rate and the oxidation peak current ($i_{Pa}$) was proportional to the scan rate at the scan rate (50-400 mV $s^{-1}$). The linear regression equation was $i_{Pa}$ (μA) = 5.7349 + 0.0493ν (mV $s^{-1}$), with a correlation coefficient of R = 0.9935. It followed Langmuir adsorption isotherm: $i_P = n^2F^2A\Gamma_T V/4RT$, it indicated that electrode process was controlled by adsorption.

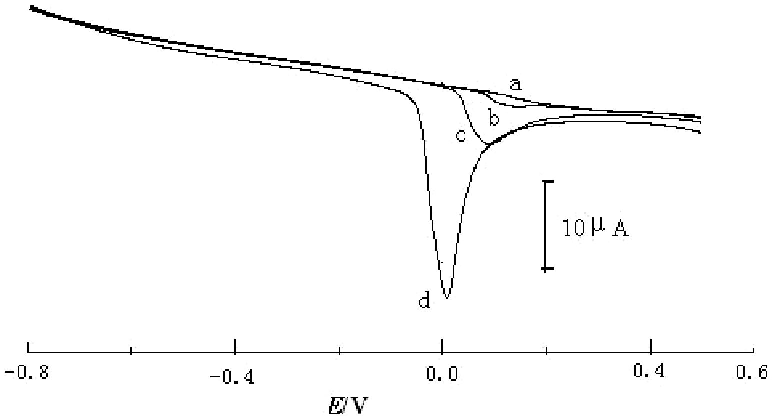

Fig. 2. Stripping voltammograms at DDTC Ag modified electrode. (a) the blank solution, (b) a + 1 × $10^{-4}$ g $L^{-1}$ Se(IV), (c) a + 1.0 × $10^{-3}$ mol $L^{-1}$ KCl, (d) a + 1 × $10^{-4}$ g $L^{-1}$ Se(IV) + 1.0 × $10^{-3}$ mol $L^{-1}$ KCl

## Optimization of experimental conditions

**Effect of the background solution and it's pH value on the voltammetric responses:** The effect of the background solution and it's pH value on the response of $Cl^-$ were studied in KHPh-NaOH, AcOH-NaOAc, HCl, KCl and $H_3PO_4$ + $CH_3COOH$ + $H_3BO_3$-NaOH buffer solutions. The experiment indicated that the oxidation peak was the most sensitive in pH 2.21 (0.05 mol $L^{-1}$ $H_3PO_4$ + 0.05 mol $L^{-1}$ $CH_3COOH$ + 0.05 mol $L^{-1}$ $H_3BO_3$-0.2 mol $L^{-1}$ NaOH) buffer solution. The oxidation peak potential (Ep) had no obviously change with increasing pH value. Fig. 3 showed the relationship between the oxidation peak current and pH value of solution, the oxidation peak current increased in the range of pH 1.81-2.09, the oxidation peak current was the biggest when pH 2.21 and it decreased with increasing solution pH in the pH 2.21-4.56. Considered as a whole, pH 2.21 (0.05 mol $L^{-1}$ $H_3PO_4$ + 0.05 mol $L^{-1}$ $CH_3COOH$ + 0.05 mol $L^{-1}$ $H_3BO_3$-0.2 mol $L^{-1}$ NaOH) buffer solution was chosen for the support electrolyte in the electrochemical detection.

**Effect of Se(IV):** The effect of the different concentration of Se(IV) on the oxidation peek was investigated in 1.0 × $10^{-3}$ mol $L^{-1}$ KCl solution (pH 2.21). The oxidation peak current increased with increasing the Se(IV) concentration, the peak current increased little when the Se(IV) concentration was above 1 × $10^{-4}$ g $L^{-1}$, therefore, 1 × $10^{-4}$ g $L^{-1}$ Se(IV) was chosen under the experimental condition.

**Effects of accumulation time and potential:** The effects of accumulation times on the peak currents of $Cl^-$ were investigated for the determination of 1 × $10^{-3}$ mol $L^{-1}$ $Cl^-$ by stripping scanning. The accumulation time has a certain influence on the electrocatalytic behaviour of $Cl^-$. It could be seen that the peak currents increased with increasing accumulation time in the range of 10.40 s and the peak currents remained almost constant when further increasing the accumulation time. There

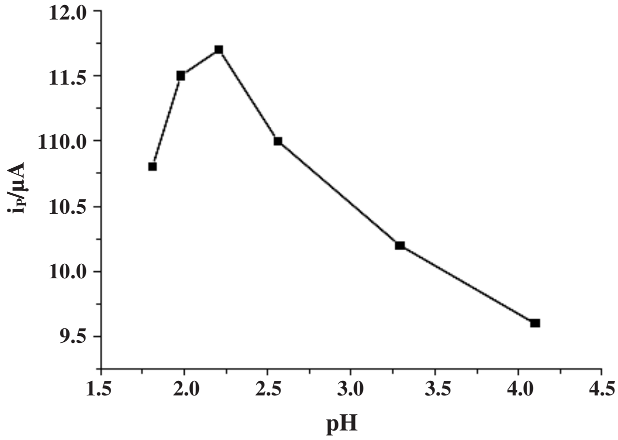

Fig. 3. Relationship between pH and the peak current

had no stripping peak at the voltammograms when the accumulation potential was above -0.6 V, the peak currents increased with decreasing the accumulation potential in the range of -0.6-1.0 V, the peak current was stronger with better reproducibility when the accumulation potential was -1.0 V. Considered as a whole, 40 s accumulation time and -1.0 V accumulation potential were used.

**Relationship between peek current and concentration:** Determination of $Cl^-$ by the stripping voltammetry under the optimum conditions. The oxidation peak of $Cl^-$ is linear with its concentration from $1 \times 10^{-4}$ mol $L^{-1}$ to $8 \times 10^{-3}$ mol $L^{-1}$ with the linear regression equation was $i_{Pa}$ (µL) = 0.4269 + 1.1387c (R = 0.9992), detect limit of it reached $2 \times 10^{-5}$ mol $L^{-1}$.

**Interference tests:** Under the selection condition, the interference tests for some materials that probably coexisted with $Cl^-$ have been conducted in pH 2.21 buffer solution containning $2 \times 10^{-3}$ mol $L^{-1}$ $Cl^-$. The experiment showed: 50-fold of $Pb^{2+}$, $Cd^{2+}$, $Zn^{2+}$, $Fe^{3+}$ did not interfere with the determination, 10-fold of $Hg^{2+}$ had not influence on the determination too, but $I^-$, $Br^-$ had important influence on the determination.

**Sample analysis:** The $Cl^-$ concentration in soy was analyzed by using above method. The sample were diluted with above electrolyte solution ($1 \times 10^{-4}$ g $L^{-1}$ Se(IV)). The results were that the $Cl^-$ concentration was 2.61 mol $L^{-1}$ with RSD of 0.54 for 6 times measurements. The recovery experiment of adding standard had been done at the same time. The determination results were shown in Table-1.

TABLE-1
DETERMINATION RESULTS OF RECOVERY

| $Cl^-$ concentration in sample (mol $L^{-1}$) | 2.61 | 2.61 | 2.61 | 2.61 |
|---|---|---|---|---|
| Added (mol $L^{-1}$) | 1.00 | 1.50 | 2.00 | 2.50 |
| Found of total (mol $L^{-1}$) | 3.60 | 4.10 | 4.57 | 5.05 |
| Recovery of adding (%) | 99.0 | 99.3 | 98.0 | 97.6 |

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