

Anodic oxidation of thiosulfate ions at a carbon-based electrode with deposited Au-particles

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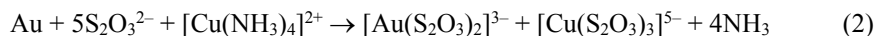
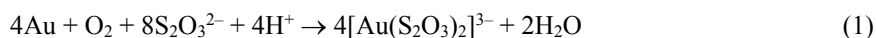
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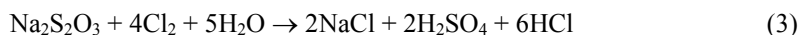
Abstract. In the present work, the anodic oxidation of thiosulfate ions in neutral electrolytes at a carbon-based composite electrode with deposited submicron gold particles was studied using the direct current voltammetry method. It is shown that the oxidation process is displayed in the voltammetric curves in the form of two peaks of anodic current, the magnitude of which depends on the experimental conditions. An explanation of the most probable mechanism of the oxidation reactions of $S_2O_3^{2-}$ ions at an anodically polarized gold-containing electrode has been proposed. It has been shown a possibility to monitor low concentrations of thiosulfate ions (0.1-10 μM) using a current peak at potentials $E > 1.0$ V (vs. Ag/AgCl/1M KCl). The accuracy parameters of the analytical procedure were verified, practical applications of the analytical method have been outlined.

1 Introduction

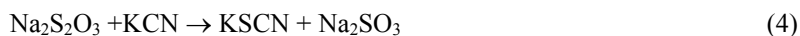
The high reducing activity of thiosulfates is used in a number of applications, among them: textile industry (removal of an excess bleach) [1], leather industry (treatment of hides) [2], water conditioning systems (dechlorination of a ballast water) [3], analytical chemistry [4]. As a complexing reagent, sodium and ammonium thiosulfates are considered as a possible replacement for highly toxic cyanides in the extraction of precious metals (gold, silver) from ores [5]:



In medicine, the reducing and complexing properties of sodium thiosulfate $Na_2S_2O_3$ have long been used in the treatment against poisoning by halogens, cyanides, heavy metal salts, to reduce intoxication during chemotherapy, as well as for curing the calcification, in the sepsis therapy [6]:



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In agriculture, ammonium, sodium, calcium, silver and other metals thiosulfates are used as environmentally low-risk reagents to control the flowering of fruits, berries and ornamental crops, during the soil fumigation, as a part of fertilizers [7]. In the production of food, sodium thiosulfate (the food additive E539) is used as an antioxidant, and as a complexing agent as well. Thus, due to the extensive list of applications of thiosulfates, the improvement of methods for monitoring the thiosulfate content in technological media, environmental objects, medicines, and food is an important task.

The electrochemical methods are the most accessible, sensitive and express ones for determining sulfur compounds, including thiosulfate ions. There are known variants of both classical (voltammetry, amperometric titration) and modern electroanalytical methods, based on electrocatalysis, for determining thiosulfates. The use of classical and alternating current polarography makes it possible to determine thiosulfate ions in mixtures with sulfides and elemental sulfur [8]. Aluminum or zinc can be used as a metal base to obtain electrodes modified with catalysts increasing the sensitivity of the analytical procedure [9]. Chemical modification of the surface of the metal substrate with gold particles or with cyanide-containing metal complexes [9, 10] makes it possible to determine thiosulfate ions in neutral solutions using the electrocatalytic oxidation currents in the potential range 0.6-0.8 V (s. c. e.) [10]. Cobalt and nickel hexacyanoferrates, nickel oxides, ferrocene derivatives, and ruthenium bipyridine complexes are used as electrocatalytically active additives in modified electrodes based on carbon-containing materials [11-15]. Analysis of the literature data has shown that the possibilities of using affordable and relatively easy-to-prepare carbon-containing electrodes modified with precious metal particles have not been sufficiently studied. In this regard, the purpose of the present work was to determine the possibility to use the values of electrooxidation current of thiosulfate ions at a carbon based composite electrode modified with gold particles (CCAu) for analytical practice.

2 Experimental section

The chemicals of the analytical purity grade were used in the work without additional purification: sodium thiosulfate pentahydrate, sodium sulfate, potassium nitrate. The 0.1 M solutions of substances were prepared by dissolving the weighed amounts of the reagents in a corresponding volume of bidistilled water. The working solutions with a lower concentration of reagents were prepared by diluting the initial solutions. A working 0.1 mM sodium thiosulfate solution was prepared immediately before the experiments by diluting the initial 0.1 M solution in pre-boiled and then cooled bidistilled water. For the voltammetric measurements, a three-electrode 20 ml quartz cell with a non-separated electrode space was used. As the working CCAu electrode, a composite electrode was used, consisting of a polyethylene tube filled by the injection molding with a mixture of polyethylene (70 wt.%) and the highly dispersed carbon (30 wt.%). The deposition of gold particles on the carbon-containing electrode surface was carried out by the cathodic reduction of a 500 mg/l hydrogen tetrachloroaurate solution at a potential -0.1 V (vs. Ag/AgCl/1M KCl) for 60 s. The reference and auxiliary electrodes were silver chloride electrodes (Ag/AgCl/1M KCl). The voltammetric analyzer TA-Lab was used to carry out the measurements in a direct current mode with linear potential sweep. Before the voltammogram registration, the dissolved oxygen was removed from the solutions by bubbling nitrogen gas of high purity. The morphology and composition of the surface layer

of the CCAu electrode were monitored using a Philips SEM 515 scanning electron microscope equipped with the EDAX analyzer.

3 Results and discussion

From the voltammetry data obtained, it follows that the anodic oxidation of thiosulfate ions at the CCAu electrode includes two processes at potentials 0.1-0.6 V (the first peak potential $E_{p,1}=0.35$ V) and at potentials 0.8-1.3 V (the second peak potential $E_{p,2}=1.1$ V) (Figure 1, *a*). The cathodic reduction processes corresponding to the both anodic currents are not distinguished, the values of the cathode current in solutions containing thiosulfate ions differ insignificantly from those for background electrolytes. Apparently, these processes are irreversible due to the formation of the thiosulfate oxidation products which do not reduce at the mentioned potentials.

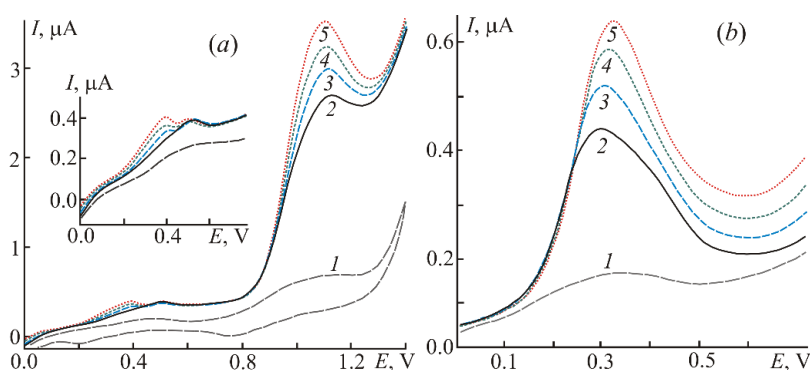


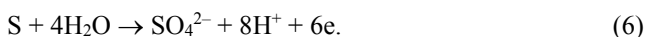
Fig. 1. Voltammetric curves registered at the carbon-based composite electrode with deposited submicron Au-particles (CCAu) in different supporting solutions contained sodium thiosulfate of different concentrations: (a) supporting electrolyte 50 mM Na_2SO_4 ; conditions: $E_{\text{initial}}=0.0$ V, $E_{\text{final}}=1.4$ V, $w=100$ mV/s, $\text{pH}=7$, solutions were deaerated by bubbling nitrogen gas; concentrations of sodium thiosulfate: 1 - blank curve, 2 - 0.2, 3 - 0.4, 4 - 0.6, 5 - 0.8 μM ; fragments of voltammertic curves in the potential range 0.0-0.6 V are shown in the insert; (b) supporting electrolyte 50 mM KNO_3 ; conditions: $E_{\text{initial}}=0.0$ V, $E_{\text{final}}=1.6$ V, $w=100$ mV/s, $\text{pH}=7$, solutions were deaerated by bubbling nitrogen gas; concentrations of sodium thiosulfate: 1 - blank curve, 2 - 2, 3 - 4, 4 - 6, 5 - 8 μM .

Within the potential range 0.3-0.4 V, the values of the first peak current, $I_{p,1}$, are much lower compared to the second anodic current maximums, $I_{p,2}$, at $E_{p,2}=1.1$ V (Figure 1, *a*). The parameters of the first anodic process ($E_{p,1}$, $I_{p,1}$) vary depending on the composition of the background electrolyte and on the concentration of thiosulfate ions in the solution. If sodium sulfate is used as a background electrolyte, the first peak of the anodic current includes two waves at potentials 0.4 and 0.5 V (Figure 1, *a*). In a solution of potassium nitrate, the first current peak does not contain a second wave (Figure 1, *b*); at concentrations of thiosulfate ions below 1 μM , this maximum is practically not observed. The study of the influence of the concentration of thiosulfate ions (*c*) on the anodic processes showed that the dependences of the peak currents on concentration $I_{p,n}=f(c)$ for the both currents $I_{p,1}$ and $I_{p,2}$ are linear within a certain concentration range: for the first peak, the $I_{p,1}$ depends linearly on a concentration in the range 1-10 μM ; for the second peak, the $I_{p,2}$ depends linearly on a concentration in a wider range of 0.1-10 μM .

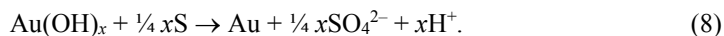
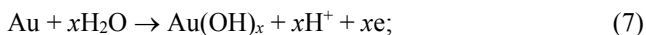
From the analysis of the electrode and chemical reactions occurring at the CCAu electrode in the potential area $E<0.6$ V, it follows that the analytical signal $I_{p,1}$ depends on a numerous difficulty-to-control factors. Firstly, it depends on the concentration and on

stability of the intermediate products of thiosulfate oxidation; secondly, the part of the active surface of gold particles, blocked by the sediment of elemental sulphur, influences the signal magnitude as well. These features are responsible for a rather narrow concentration range in which the dependence $I_{p,1}=f(c)$ is linear, as well as for a low value of the angular coefficient of such a dependence. Therefore, the use of the first anodic current $I_{p,1}$ at potentials $E < 0.6$ V is inappropriate for the determination of thiosulfate ions.

Unlike the first anodic peak, the second anodic peak $I_{p,2}$ in the potential range 0.8-1.3 V is characterized by sufficiently higher values. The dependence $I_{p,2}=f(c)$ is linear in a wide concentration range 0.1-10 μM and is characterized by a high value of the angular coefficient (Figure 2, a). According to the literature data [16], the anodic oxidation of sulfur films deposited on the gold surface leads to the formation of sulfate ions within the mentioned potential range:



A significant increase in the peak current $I_{p,2}$ at the same concentration of thiosulfate ions, as compared to $I_{p,1}$, indicates about a large quantity of sulfur accumulated at the surface of Au-particles during the potential growth. At potentials greater than 0.8 V, the formation of metastable gold (hydr)oxides as mediators [17] cause an increase in the anodic current due to the catalytic stage of the electrode process. It is obvious that the catalytic current increases significantly (Figure 1) due to the participation of nanoscale gold particles during the oxidation process:



Thus, the anodic current within the potential range 0.8-1.3 V can be used as an analytical signal to determine sufficiently low concentrations of thiosulfate ions. The sensitivity of the method increases due to the accumulation of sulfur at the surface of Au-particles. The complex of electrode and chemical reactions involves the formation of numerous intermediate products of thiosulfate ions oxidation, as well as catalytic processes with the participation of metastable gold (hydr)oxides (eqs. 7, 8).

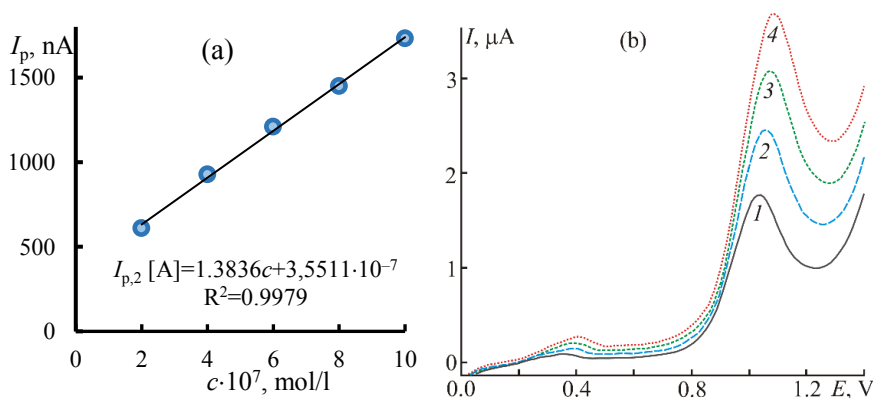


Fig. 2. (a) The dependence of anodic peak current $I_{p,2}$ at $E_{p,2}=1,1$ V (the CCAu electrode) on concentration of sodium thiosulfate in supporting electrolyte 50 mM Na_2SO_4 ; conditions: $E_{\text{initial}}=0.0$ V, $E_{\text{final}}=1.4$ V, $w=100$ mV/s, pH=7, solutions were deaerated by bubbling nitrogen gas; (b) voltammetric curves registered at the CCAu electrode in supporting solution 50 mM Na_2SO_4 contained 0.1 mM sodium thiosulfate at different potential scan rates: 1 - 40, 2 - 60, 3 - 80, 4 - 100 mV/s; the conditions were the same.

To clarify the influence of mass transfer on the anode process, the dependence of the peak current $I_{p,2}$ on the potential sweep rate (w) was examined (Figure 2, *b*). It follows from the data obtained that the dependence $I_{p,2}=f(w^{1/2})$ is linear within the scan rate interval 30-150 mV/s. According to the absence of cathode currents on the voltammograms corresponding to the mentioned anodic peaks, as well as to the linear dependence of $E_{p,2}=f(\log w)$, the electrode process is irreversible, it contains a delayed diffusion stage and is accompanied by a surface reaction. The formation of a passivating sulfur layer on the surface of Au-particles and the course of a surface chemical reaction (eq. 8) are consistent with the proposed explanation.

The working stability of the CCAu electrode was studied by repeatedly registering voltammograms in solutions 50 mM KNO₃ in the presence of 0.1 mM Na₂S₂O₃ without renewing the electrode surface. It follows from the measurements that multiple registration (1000 times) of the analytical signal leads to a decrease in the active surface of the electrode by approximately 20%, and, as a consequence, to a decrease in the anodic current value. Therefore, during the course of electrode reactions, the dispersivity of Au particles and the composition of their surface layer do not undergo significant changes; the electrode can be repeatedly used to register a signal for a certain time without a substantial error in the results.

The accuracy of the results of determining the concentration of thiosulfate ions in accordance with the proposed method was evaluated using the standard addition method. To do this, a voltammogram was initially recorded for the CCAu electrode immersed in a 20 ml deaerated solution of a background electrolyte (50 mM Na₂SO₄ or KNO₃), then an aliquot of 0.1 mM Na₂S₂O₃ solution was injected into the cell using a micro-dispenser, and the analytical signal was measured again. The measurements were repeated three times for each concentration. The Keiser method was used to calculate the detection limit c_d (0.05 μM) and the quantitation limit c_q (0.12 μM) for the proposed analytical procedure; these two values were found using the dependence of standard deviation s_r on the analyte concentration [18]. The results of the determination of thiosulfate concentrations are shown in Table 1.

Table 1. The results of determining thiosulfate ions in the model solutions using the proposed voltammetric procedure (supporting electrolyte 50 mM KNO₃; conditions: $E_{initial}=0.0$ V, $E_{final}=1.6$ V, $w=100$ mV/s, pH=7, solutions were deaerated by bubbling nitrogen gas).

Thiosulfate added, μM	Thiosulfate found, μM
0.20	0.20±0.03
0.40	0.40±0.03
0.60	0.60±0.02
0.80	0.81±0.02
1.00	1.05±0.02

The results obtained indicate that the measurement quality is satisfactory. The error of determination of the lowest specified concentrations of thiosulfate ions does not exceed 15% (Table 1). It is known that the most common contaminant compounds in thiosulfate-containing solutions are sulfides and sulfites [4]. When developing a method for the determination of thiosulfate based on the results of the present work, precipitating and/or masking reagents can be used to eliminate the interfering effect of those compounds (for example, sulfite ions are masked by adding formaldehyde into a sample) [4].

4 Conclusions

Anodic oxidation of thiosulfate ions at a carbon-based composite electrode modified with gold submicron particles (CCAu) proceeds in two potential intervals 0.2-0.6 V and 0.8-1.3 V (vs. Ag/AgCl/KCl) displaying two anodic current peaks at $E_{p,1}=0.35$ V and $E_{p,2}=1.1$ V under conditions of direct current voltammetry with linear potential sweep in background electrolytes 50 mM KNO₃ or Na₂SO₄. The value of the anode current $I_{p,2}$ is an order of magnitude higher than the value $I_{p,1}$ at the same analyte concentration. The concentration dependences of the current peaks $I_{p,1}$ and $I_{p,2}$ are linear within the intervals of thiosulfate ions concentration 2-8 μ M and 0.1-10 μ M, respectively. The possibility of using the value $I_{p,2}$ to determine low concentrations of thiosulfate ions has been shown.

The conditions for the voltammetric determination of thiosulfate ions at the CCAu electrode have been established, as follows: the mode of registration of the analytical signal is DC voltammetry with linear sweep of potentials, the potential scan rate $w=100$ mV/s; a neutral background electrolyte 50 μ M KNO₃ (Na₂SO₄) deaerated by bubbling an inert gas; the potential range of the analytical signal registration: $E_{\text{initial}}=0.0$ V, $E_{\text{final}}=1.4$ V (vs. Ag/AgCl/KCl); the nature of the analytical signal: anodic current peak $I_{p,2}$ within the potential range 0.8-1.3 V, $E_{p,2}=1.1$ V; the linearity of the concentration dependence of the analytical signal is observed in the range of thiosulfate ions concentrations 0.1-10 μ M; the detection limit of $c_d=0.05$ μ M (7.9 μ g/l), the quantitation limit $c_q=0.12$ μ M. The proposed method can be adapted to determine low concentrations of thiosulfate ions in technological solutions, wastewater, and food products using appropriate methods of masking interfering compounds.

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