Potentiometric sensor for chromium (VI) determination

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Abstract. The development of rapid, miniature and high-sensitivity sensors to control the environment is a topical problem of analytical chemistry. The purpose of this paper is to create an ion-selective electrode for determining the chromium (VI). The electrode was formed by sequential electrochemical assembly. Chromotropic acid was used to form a stable compound with chromate ions. In order to create a highly developed electroactive surface, a polyaniline film was previously formed on the electrode. The tetraethoxysilane film was used as a semi-permeable membrane to prevent the washing out of modifier. This work studied the mechanism of analytic signal formation and proposed a possible structure of the final complex. The electrode allows determining the chromium concentration in the range of $10^{-6}$ to $10^{-3}$ M. The method “introduced-found” and measurement data obtained by the method of spectrophotometry validate the results.

1. Introduction

Chromium is one of the most widely used metals in many industries. It most used in alloying steel for the automotive, defense, aviation and aerospace industries. Such significant part of production process as welding contributes to occurrence of a huge amount of toxic chromium in the air of the working area. The wastewater of galvanic processes contains the chromium; it discharge is extremely dangerous for flora and fauna [1]. The toxic effects of chromium (VI) are not comparable with other compounds of this metal because it is considered as carcinogenic (may causes cancers) and oxidizers (may causes hemolysis and chemical burns) [2, 3].

Nuclear adsorption and atomic emission analysis are currently the most commonly used methods for chromium determination [4, 5]. However, these methods do not provide information on individual forms of chromium, but only its full composition. The method of spectrophotometry [6, 7] makes it possible to assess the content of the chromium forms in the analysed objects, but the methods are not sensitive and require the labour-intensive sample preparation to eliminate the matrix influence. Different types of voltammetry [8] are the promising methods for determining the low concentrations of the chromium forms in different objects, but they are generally based on adsorption concentration, which reduces the repeatability of analytical signals. Therefore, a new direct, rapid and reliable method of controlling the MPC levels of Cr (VI) needs to be developed.

Ionometry is one of the most rapid and economical method of analysis. The use of ionophores (neutral or ion-genic substances that bind ions selectively) as active substances has greatly increased the potential of this method in the last decade. Sensitivity has increased, the linear ranges of analysed concentrations have been extended [9]. To create the ionoslectic electrodes the substances, which can form low-dissociative compounds with a determined ion, are used as electroactive components [10].
We propose to use chromotropic acid as a reagent for the creation of the ionosensitive electrode on Cr(VI). This acid is used for qualitative as well as spectrophotometric chromium determination [1].

2. Experimental

The working electrode was formed by the method of layered electrochemical assembly [12]. A polyaniline was applied as the first layer on the surface of the graphite-containing electrode by electrochemical polymerization under cyclic voltammetry conditions in the range of potentials –1.0 +0.8 V [13]. The second layer was formed in the similar condition from 0.001 M chromotropic acid. The third layer was made when the electrode was polarized in a potassium chromate solution at a potential of +0.8 V or also by cyclic voltammetry. Then the surface was applied by tetraethoxysilane (TEOS) composite with polyvinyl alcohol (figure 1). The formed electrode was dried at room temperature for 48 hours. Before using the electrode, it was soaked for 15 minutes in distilled water.

![Figure 1. Ion-selective electrode structure.](image)

Voltammetry studies were conducted on the TA-Lab voltammetry analyzer, IR spectra were registered on the Agilent Cary 600 FTIR Spectrometer IR 600 Series and UV spectra – on the RF-5301PC Spectrometer. The ionomer «Anion-4100» was used as the recording device.

3. Results and discussion

It is known that interaction chromate ions and chromotropic acid in the nitric acid medium induces the formation of a brightly red compound. Although the reaction is highly selective, its mechanism is still unknown. The literature is contradictory: some sources suggest that chromate oxidizes chromotropic acid [10], while other refer to the possible formation of complexes [14].

Figure 2 shows the UV spectra of chromate-ions (1), chromotropic acid (2) and their mixture (3). The presence of additional bands on the UV spectra near 255, 270 nm may indicate the formation of new bonds when reagents interact.

To determine the possible structure of this compound the IR spectra of chromotropic acid and the complex of hexavalent chromium and chromotropic acid were obtained (figure 3). In the presence of nitric acid, chromotropic acid changes to red, probably due to its dimerization. There is an intense band at 1042 nm of the spectrum, which is typical for cumulated binary bonds. The occurrence of new intensive bands near 736 and 944.8 nm in the presence of chromium may indicate its entry into the dichromotropic acid structure.
Figure 2. UV spectra: 1 – $\text{K}_2\text{CrO}_4$, 2 – chromotropic acid, 3 – $\text{K}_2\text{CrO}_4$ + chromotropic acid.

Figure 3. IR spectra: 1 – $\text{K}_2\text{CrO}_4$ + chromotropic acid, 2 – chromotropic acid + $\text{HNO}_3$, 3 – chromotropic acid.

The process of layer formation of electroactive coating of electrode is presented in figure 4. When the potential is cycling in the range from $-1.0$ to $+0.8$ V, the voltammetry curve presents an anodic peak at a potential of $+0.2$ V and cathodic peak at a potential of 0 V. Current increase for each subsequent cycle indicates an increasing the thickness of polyaniline film (figure 4-1). Subsequent cyclic change of the potential in the solution of chromotropic acid (figure 4-2) shows the anodic peak reduction of polyaniline oxidation, which may relates to the formation of a new layer. In the solution
of the chromate potassium (figure 4-3), a peak occurs on cathode branch at a potential of −0.4 V caused by the chromium (Cr(VI) + 3e → Cr(III)) recovery. The significant dissection of cathode and anode branches of the cyclic voltammetry curve is associated with the increasing the capacity of the double electrical layer.

![Figure 4. Cyclic voltammetry curves of layer-by-layer application of modifier to electrode: 1 – polyaniline, 2 – chromotropic acid, 3 – K$_2$CrO$_4$.](image)

Therefore, we can assume the following structure of the formed compound (figure 5).

![Figure 5. The possible structure of the complex of chromate ion and chromotropic acid.](image)
The electrode allows estimating the content of Cr(VI) in a concentration range from $10^{-6}$ to $10^{-1}$ M. The dependence of concentrations logarithm on the potential is linear and is described by equation $y = -26.5x + 279$ ($R^2 = 0.9939$).

Table 1 presents the results of chromium determination in model systems, natural water and wastewater from galvanic productions by ionometry and spectrophotometry. The data obtained by different methods are well consistent.

**Table 1.** The results of Cr(VI) determination in different samples of water by spectrophotometry and potentiometry ($n = 5$, $P = 0.95$).

| Sample of water       | Nominal concentration of Cr(VI) [mg/l] | Concentration of Cr(VI) [mg/l] | Potentiometric determination by modified electrode |
|-----------------------|---------------------------------------|--------------------------------|---------------------------------------------------|
| Wastewater            | 82.6                                  | 83.4 ± 10                      | 82.0 ± 10                                         |
| Natural water         | 53.3                                  | 52.1 ± 7                       | 53.0 ± 6.5                                        |
| Model system          | 125.9                                 | 128 ± 21                       | 125.5 ± 17                                       |

The validation of the methodology was evaluated by “introduced-found” method and the calculation of the discovery rate $R$ as shown in table 2. The values of $R$ are close to 100 %, indicating that there is no significant systematic error.

**Table 2.** The validation of the methodology by “introduced-found” method.

| Sample number | Concentration in sample [mg/kg] | Introduced [mg/kg] | Found [mg/kg] | $\Delta$ [mg/kg] | $R$ [%] |
|---------------|---------------------------------|--------------------|---------------|------------------|--------|
| 1             | 1.00                            | 1.0                | 1.98±0.28     | 0.98             | 98     |
|               | 1.00                            | 2.0                | 2.95±0.32     | 1.95             | 97.5   |
|               | 1.00                            | 3.0                | 3.02±0.39     | 3.02             | 100.7  |
|               | 2.20                            | 1.0                | 3.18±0.37     | 0.98             | 98     |
| 2             | 2.20                            | 2.0                | 4.23±0.41     | 2.03             | 101.5  |
|               | 2.20                            | 3.0                | 5.16±0.44     | 2.96             | 98.6   |

4. Conclusion
Optimum conditions for modified electrode formation according to multi-layered technology for chromium (VI) determination were selected. The process of sensor formation is based on layer-by-layer assembly technology. The ionic layer is proposed to be a chromium compound with chromotropic acid specific to chromium (VI). The optimal conditions for chromium determination in the concentration range from $10^{-6}$ to $10^{-1}$ mol/dm$^3$ were selected. A possible mechanism for analytical signal formation is proposed.

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