Journal of Electroanalytical Chemistry 808 (2018) 14–20

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

journal homepage: www.elsevier.com/locate/jelechem

Platinum electrode regeneration and quality control method for chronopotentiometric and chronoamperometric determination of antioxidant activity of biological fluids

Khiena Z. Brainina[a,b,*], Aleksey V. Tarasov[a], Yan E. Kazakov[c], Marina B. Vidrevich[a]

[a] Ural State University of Economics, Scientific and Innovation Center for Sensory Technologies, 62/45, 8 Marta/Narodnoi Voli St., Yekaterinburg 620144, Russia
[b] Ural Federal University, Department of Fundamental and Applied Chemistry, 19, Mira St., Yekaterinburg 620002, Russia
[c] Joint Stock Company "Medical Technology", 83, Kuznechnaya St., Yekaterinburg 620075, Russia

ARTICLE INFO

Keywords:
Surface regeneration
Platinum screen-printed electrode
Chronopotentiometry
Chronoamperometry
Antioxidant activity

ABSTRACT

The state of the indicator electrode surface, its quality control and regeneration methods play a major role in electroanalysis results. It is especially important in in the analysis of biological fluids and tissue, because the adsorption of biological matrix components may distort analytical signals and results of the analysis. This article describes an integrated approach to resolving the problem, which includes the selection of regeneration and quality control methods evaluation of availability of platinum screen-printed electrodes for chronopotentiometric and chronoamperometric analysis, as well as their use for determining antioxidant activity of blood serum and ejaculate. The electrodes are treated with solvents (acetone or ethanol) or subjected to annealing. Sources of information about the availability of electrodes for measurements are chronopotentiograms, chronoamperograms and cyclic voltammograms. For chronopotentiometric and chronoamperometric analyses, the most effective regeneration method is annealing at 750 °C for 1 h. Satisfactory regenerated platinum screen-printed electrodes are used as indicator electrodes for evaluating antioxidant activity of blood serum and ejaculate with the use of chronopotentiometry and chronoamperometry. The role of indifferent electrolyte in analytical signal formation is considered. Composition of solution used for different biological fluids (blood serum/plasma, ejaculate) was optimized and unified. The obtained results demonstrate a strong correlation: $r = 0.91$ for blood serum and $r = 0.80$ for the ejaculate.

1. Introduction

Redox reactions occurring in living cells, on the one hand, ensure the life functions of the body; on the other hand, they cause oxidative stress (OS). OS is created when the production of reactive oxygen and nitrogen species and the activity of the antioxidant system of the body (antioxidant defense mechanisms) do not balance. OS is an integral part of the pathogenesis of > 100 human diseases, such as diseases of cardiovascular [1–3,5], nerve [3,5], reproductive [1,3,5], and endocrine [1–3,5] systems, cancer [1–5] and aging [1,3,5]. Supplements containing antioxidants are widely used to improve the condition of the body. Their choice, concentration and OS monitoring are essential for human health assessment and the therapy.

The indicators of OS in the human body are an increase in oxidant activity (OA) or a decrease in antioxidant activity (AOA) of biological fluids. AOA of plasma and serum is the primary measure and marker to evaluate the state of OS [6,7]. The reviews [3,8–12] describe many methods for determining AOA. Nowadays, the most commonly used methods for determining antioxidants and AOA are the methods based on the interaction between the determined substance with a specially generated radical compound and the photometric [13–15] or fluorescent [16] method of signal registration. Also popular is the colorimetric method for determining the AOA, developed by Erel [17,18]. But as OS has the "electron – donor – acceptor" nature, we believe that electrochemical methods [11–13,19,20] of OS assessment are preferred.

Over the past few years, the potentiometric method for determining antioxidants and oxidants has generated considerable research interest. In this method the source of information is the shift of the electrode potential as the result of the reaction between the determined compounds and the components of the mediator system [21–28]. The research has focused on applying this method for determining AOA of blood and its fractions [23–25], ejaculate and seminal fluid (seminal plasma) [26], follicular fluid [26] and skin [27,28]. The possibility of using potentiometry for invasive [23–25] and non-invasive [26–28]

* Corresponding author.
E-mail address: baz@usue.ru (K.Z. Brainina).

https://doi.org/10.1016/j.jelechem.2017.11.065
Received 28 July 2017; Received in revised form 23 October 2017; Accepted 25 November 2017
1572-6657/ © 2017 Elsevier B.V. All rights reserved.

monitoring of AOA has also been discussed. It shows a high correlation in results of determination of AOA of blood plasma using potentiometric and TAS Randox method with photometric signal detection [23,24]. However, such issues as the role of the surface condition of the electrodes, electrode regeneration and criteria for its quality control remain unstudied. An important factor affecting the results of electrochemical measurements is the preparation of the indicator electrode with reproducible physical, chemical, and electronic properties. The adsorption of pollutants (matrix components) and the formation of oxide layers on the electrode surface have impact on the kinetics of electrode processes and distort the analytical signal.

In potentiometry platinum screen-printed [21–28] and bulk [29] electrodes are used as indicator electrodes. While the surface of the bulk electrode can be recovered mechanically (by cutting the surface layer or part of the electrode [30] or by polishing the electrode [31,32], this is not the case with the screen-printed electrode. Moreover, to use a platinum electrode as disposable is not economically feasible. Such methods as cyclic polarization [31,32], laser [31] or ultrasonic [32] treatment require additional equipment and are not always effective, especially when indicator electrodes are used for analyzing biological fluids. Unfortunately, at present there is no clear understanding of what parameters could allow to assess the availability of the electrode for measurements. Earlier we have described [22] the regeneration and quality control of electrodes in the analysis of ozonated and chlorinated water. However, these methods are unsatisfactory for analyzing biological fluids. High quantities of protein fractions and other compounds possessing high adsorption capacity lead to rapid degradation of the electrode surface and the distortion of analytical results. The role of background electrolyte composition in analytical signal formation was not considered yet.

The aims of this study are: (i) to offer a simple and effective regeneration method for platinum screen-printed electrodes used as indicator ones in complex biological matrices analysis; (ii) to identify a set of criteria for assessing electrode availability for measurements in chronopotentiometric and chronoamperometric analysis; (iii) to evaluate the role of indifferent electrolyte concentration in analytical signal formation; (iv) to optimize and to unify analysis procedure and composition of background solutions for determining AOA of biological fluids; (v) to compare analysis results obtained with the use of chronopotentiometric and chronoamperometric methods.

2. Experimental

2.1. Apparatus

Chronopotentiometric measurements were conducted using a pH/ions meter, model TA-ION (Tomanalit, Russia). Chronoamperometric and voltammetric measurements were conducted using a stripping voltammetry analyzer, model IVA-5 (IVA, Russia). For determination AOA of blood serum and ejaculate a potentiometric analyzer, model ANTIOXIDANT (Antioxidant, Russia) was used.

2.2. Electrodes

A bulk platinum disk electrode $d = 2$ mm and $S = 3.14$ mm^2 (Metrohm, Switzerland) served as the control indicator electrode. Before the start of the experiment, the platinum bulk electrode was polished with fine powder of alumina (0.05 µm) located on the fabric moistened with deionized water. Then the electrode was subjected to cyclic polarization (10 cycles) in 0.5 M H_2SO_4 in the range of potentials between 0.04 and 1.5 V with the scan rate of 0.05 V s^{-1} [31,32]. This electrode was never immersed in a solution containing biological samples, in order to avoid irreversible adsorption of organic compounds on its surface. Platinum screen-printed electrodes $S = 15.0$–20.0 mm^2 (IVA, Russia) were investigated and used for the AOA determination. The manufacturing process of platinum screen-printed electrodes consists in applying two layers of platinum paste GP–226 (Ferro Inc., Germany) using screen printing technology and annealing of each layer at stepwise temperature increase from 100 to 800 °C and back. After having been used in biological fluids, the platinum screen-printed electrodes were regenerated in three ways: by keeping in 99% acetone for 1–24 h (1), in 96% ethanol for 1–24 h (2) or by annealing at 750 °C for 1 h (3).

A silver–silver chloride electrode EVL–1M3.1 (Ag/AgCl/3.5 M KCl) (Gomel Plant of Measuring Equipment, Belarus) was used for chronopotentiometric, chronoamperometric and voltammetric measurements. A silver–silver chloride electrode (Ag/AgCl/3.5 M KCl) supplied with the ANTIOXIDANT analyzer served as a reference electrode for measurements with the use of the instrument.

Glassy carbon rod (R&D Institute Graphite, Russia) served as an auxiliary electrode.

2.3. Reagents

The following reagents were used: $K_3[Fe(CN)_6)]$ pure for the analysis, $K_4[Fe(CN)_6]\cdot 3H_2O$ pure, H_2SO_4 95% chemically pure, acetone 99% pure for the analysis (Reachem, Russia), KCl chemically pure (Mikhailovsky Plant of Chemical Reagents, Russia), $Na_2HPO_4\cdot 12H_2O$ pure for the analysis (Chemreaktivsnab, Russia), KH_2PO_4 chemically pure (NevaReaktiv, Russia), Al_2O_3 pure (Industrial-chemical BP Group, Russia), ethanol 96% (SpirtForm, Russia), ascorbic acid chemically pure (Component-reaktiv, Russia).

2.4. Objects of investigation

The objects of the study were: 1) 75 platinum screen-printed electrodes used in biological fluids; 2) human blood serum; 3) ejaculate of a man.

Blood was venipunctured from the vein of the elbow joint into a tube containing activator of clot formation (SiO_2). Then the sample was centrifuged at a rate of 3500 rpm for 15 min. Ejaculate was obtained through natural masturbation after 2–3 days of sexual continence. Blood serum was analyzed immediately after centrifugation of blood or after its storage at − 18 °C. In the latter case, the samples were analyzed after keeping them at room temperature for at least 40 min. Ejaculate was analyzed after keeping it during 30 min at room temperature or after storage this sample at − 18 °C. In the latter case, the samples were analyzed after keeping them at room temperature for at least 40 min.

2.5. Procedure of AOA determination

For determination of AOA of blood serum and ejaculate by chronopotentiometry 1 ml of a background solution was used. After electrode potential is stabilized, an aliquot (200 µl) of blood serum or ejaculate was added to the cell and measurement was repeated. For chronoamperometric analysis the first measurement is carried out using 5 ml of a background solution (1×10^{-2} M $K_3[Fe(CN)_6]$ + 1 M KCl). The current is recorded 60 s after starting the process. Then an aliquot (400 µl) of blood serum or ejaculate is introduced into the cell and measurement is repeated. After that 400 µl of 1.24×10^{-2} M $K_4[Fe(CN)_6]$ (concentration in the cell is 8×10^{-4} M) is introduced into the cell and measurements repeated once more. AOA of the sample is calculated taking dilution into account. Its value is expressed in M–eq, that reflects impact of all antioxidants (total AOA) into found concentration.

2.6. Methods and calculations

AOA of blood serum and ejaculate was determined by two methods: chronopotentiometry and chronoamperometry. The sources of information about the availability of platinum electrodes for measurements were chronopotentiograms, chronoamperograms and cyclic voltammograms.

Download English Version:

https://daneshyari.com/en/article/6662171

Download Persian Version:

https://daneshyari.com/article/6662171

Daneshyari.com