



Voltammetric vs. potentiometric sensing of dopamine: Advantages and disadvantages, novel cell designs, fundamental limitations and promising options



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ABSTRACT

Advantages and disadvantages of voltammetric vs. potentiometric sensing of dopamine are discussed. The study is focused on the measurements in small sample volumes, rather than on the selectivity to dopamine. For the potentiometric sensing, a novel flow-through tubular unit is developed. For voltammetric measurements with bare gold and platinum electrodes, miniature cylinder cells with the volume of 200 μl are developed. The CV and impedance data suggest that the dopamine diffusion to the electrode surface is the limiting stage of the whole electrode process which hinders measurements without stirring. It is shown that use of micro electrode arrays allows overpassing this limitation.

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1. Introduction

Dopamine and other neurotransmitters play a crucial role in the human neural system functioning affecting learning abilities, memory, cardiovascular systems and behavior [1–3]. The normal level of dopamine concentration in blood is about 10^{-8} M and significant deviations from this value are observed in various pathologies like schizophrenia and Parkinson's disease [4–7]. This is why reliable dopamine sensing constitutes extremely important practical task. Electrochemical sensors, in particularly voltammetric sensors, comprise the largest fraction among those aimed at dopamine quantification [8,9]. The requirements for the dopamine sensing combine low detection limit, small sample volume and sufficient selectivity over common interferences like ascorbic and uric acids.

In this work we compare the potentiometric and voltammetric modes of the dopamine measurements, with special attention to small sample volumes and to fundamental limitations.

The potentiometric sensing of dopamine relies on the protonation of the analyte, and therefore the target species constitutes a cation. This is an intrinsic advantage of the potentiometric measurement of dopamine since the main interferences: ascorbic

and uric acids are of the anionic nature. Another advantage of the potentiometric mode of sensing is virtually zero consumption of the analyte during the measurements procedure. This is especially important for small sample volumes with low concentration of the analyte. The protonated dopamine is relatively lipophilic which allows for measurements using solvent-polymeric ion-selective electrodes (ISEs) containing a simple cation-exchanger in the membrane [10]. More advanced approach implies the use of suitable neutral ionophores like crown ethers forming complexes with protonated dopamine, epinephrine and serotonin [11–13].

Voltammetric sensing of dopamine is based on the measuring of the oxidation current of this analyte. The selectivity of voltammetric sensors is achieved by measuring the current at the potentials when dopamine is oxidized, while the interferences remain in their native, unaltered forms and virtually do not contribute to the measured current. For that, the electrode surface is modified with a suitable catalytic coating which increases the dopamine oxidation rate and also shifts the dopamine oxidation potential to less positive values. Voltammetric sensors are known with the detection limits like 10^{-9} M and even lower, also in the presence of the typical interferences: ascorbic and uric acids [14–21].

It may appear therefore that voltammetric approach to the dopamine sensing is by far superior to the potentiometric one, and the task of reliable and selective dopamine quantification is actually solved. On the other hand, the very fact of publishing more and more papers devoted to the dopamine sensing implies that some problems remain unsolved.

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We believe that one of these problems is the need to measure in small sample volumes, and here some fundamental issues arise which call for special studies. Basically, potentiometry virtually does not affect the concentration of the analyte in the sample. Although at very low concentrations this is not true due to transmembrane electrolyte fluxes, recent studies in the field of ISEs revealed a number of approaches capable of the elimination of this effect and, respectively, of the large improvement of the detection limit [22–25].

On the contrary, voltammetric and amperometric sensing is intrinsically accompanied by the consumption of the analyte. In small volumes this may hinder measurements at low concentrations, and in the case of catalyzed oxidation more problems may arise due to slow transportation of the analyte from the sample bulk to the electrode surface.

Our study was focused on low concentrations, and on designs of measuring cells suitable for small sample volumes. We have developed a novel flow-through unit for the potentiometric measurements in small volumes. Among voltammetric methods we used mostly amperometry and differential pulse voltammetry. We got clear evidence in support of diffusion limitations of the dopamine oxidation process which hinders measurements in small sample volumes. We also show here that the use of microelectrode arrays may help solving this fundamental problem. The selectivity to dopamine over ascorbic and uric acid was not studied at this point.

2. Experimental

2.1. Reagents, materials and component parts

The potentiometric sensors were prepared with neutral ionophore dicyclohexyl-18-crown-6 (DCH-18-6), cation exchanger potassium tetrakis(p-Cl-phenyl)borate (KCITPB) and 2-nitrophenyloctyl ether (oNPOE) as plasticizer, all Selectophore grade from Fluka, Switzerland. The membrane matrix polymer was high molecular weight PVC S-70, Ochtalen, Russia. Volatile solvents tetrahydrofuran (THF), cyclohexanone (CH) and acetone were from Vekton, Russia, and distilled before use. Dopamine hydrochloride 99% was from Alfa Aesar, Germany. All other chemicals, as well as pH standard solutions, were of analytical grade and obtained from Reachim, Russia. Plasticized PVC tubing was from Medexport, Russia. Electrodes for voltammetric sensors were prepared using screen-printed gold planar electrodes from Gwent Electronic Materials Ltd., United Kingdom, and micro electrode array chips from Biomedical Microsensors Laboratory North Carolina State University, USA. Carbon black P-3679 was from Ochtalen, Russia; conducting glue Contactol was from Keller, Russia; silicone seal was from DoneDeal Adhesives Lab, USA.

2.2. Apparatus

Potentiometric signals were recorded with computerized 8-channel potentiometric station Ecotest, Econix, Russia. Other electrochemical measurements were made with potentiostat–galvanostat Autolab 302N with FRA2 impedance module, Metrohm, Switzerland. Membrane cocktails were prepared using ultrasonic bath Elmasonic S15H, ELMA Hans Schmidbauer GmbH, Germany. All aqueous solutions were prepared with deionized (DI) water with resistivity of 18.2 MΩ, Milli-Q Reference Water Purification System, France. The pH values of the solutions were measured with glass pH-electrode ESL-43-07, ZIP, Belarus. The reference electrode (if not specified different) was single-junction Ag/AgCl in saturated KCl, with Vikor frit. The counter electrode (if not specified different) was glassy carbon

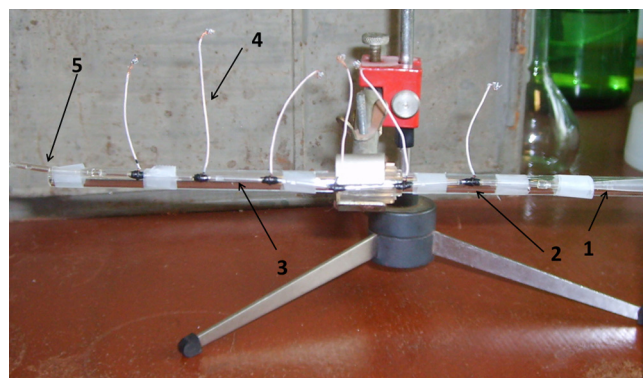


Fig. 1. Flow-through multisensor tubular unit fixed with scotch tape on a glass rod. 1 – inlet, 2 – sensor zone, 3 – insulating zone, 4 – connection wire, 5 – outlet.

rod. All measurements were performed at room temperature: 18–22 °C.

2.3. Preparation of potentiometric sensors

In order to minimize the sample volumes we prepared flow-through multisensor tubular unit shown in Fig. 1.

To obtain the sensors, PVC tubing with outer diameter of 2 mm, inner diameter of 1.5 mm and length of 15 cm was soaked sequentially in several portions of acetone to remove the native plasticizer. After that, 6 parts of the tubing were converted into sensor zones by doping with solutions of ionophores in oNPOE. The conversion was done by casting the ionophore solution on the respective parts of the PVC tubing still being swollen with acetone. After full evaporation of acetone the tubing contained 6 ion-sensitive zones separated with insulating zones: non-doped parts of the tubing. Next, the outer surface of the sensor zones was covered with electronic conductor: carbon black suspension in PVC/THF solution, and then copper wires were fixed on the sensor zones using the same slurry as conducting glue. In this way we obtained a tubular sensor unit with 6 ion-selective sensors of the coated-wire solid contact type. The tubing shrinks when the native plasticizer is removed, and the final volume of the unit was approximately 200 μl. One end of the unit (inlet) was used for injection of solutions, and the other one (outlet) was immersed into waste beaker. The reference electrode was placed into the same beaker.

2.4. Preparation of voltammetric sensors

Three kinds of voltammetric sensors were used. These were screen-printed gold planar plates, miniature cylinder cells and micro electrode arrays (MEAs) shown in Fig. 2.

The first kind of sensors was Gwent Electronic Materials Ltd. planar electrodes shown in Fig. 2a. These were square 40 mm × 40 mm ceramic plates with 6 gold spots with diameter of 4 mm, shown in Fig. 2b. The rest of the surface, including leads, was covered with an insulating layer, except of the contact pads. For the measurements, the plates were partly immersed into glass beakers so that the gold spots were within the solution and constituted working electrodes.

The second kind of sensors was miniature cylinder cells shown in Fig. 2c. Cylinders with a length of 8 mm were cut from PVC tubing with an outer diameter of 7 mm and an inner diameter of 6 mm. These cylinders were fixed on the plate concentric with the gold spots using the PVC-CH slurry. Perpendicular to the cylinders axes, in the middle of their length, the cylinders were pierced with silver wires. The inside parts of the wires were then chlorinated and served as reference electrodes. Additionally, a band-shaped mark was made on the inner side of each cylinder using carbon black

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