



Original article

Development of new potentiometric sensors for the determination of proguanil hydrochloride in serum and urine



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ABSTRACT

Potentiometric electrodes were developed for the rapid determination of proguanil hydrochloride in pure samples, pharmaceutical preparations and spiked serum and urine samples using PVC membrane, screen printed (SPE), coated wired (CWE), carbon paste (CPE) and modified carbon paste (MCPE) electrodes based on the ion-exchanger of proguanil with phosphotungstic acid (Pr-PT) as a chemical modifier. The prepared electrodes showed Nernstian slopes of 59.7, 58.1, 58.5, 58.5 and 57.0 for the PVC, SPE, CWE, CPE and MCPE for the proguanil ions in a wide concentration range of 1.0×10^{-5} – 1.0×10^{-2} mol L⁻¹ at 25 °C with detection limits of 7.94×10^{-6} , 1.0×10^{-5} , 1.0×10^{-6} , 7.07×10^{-6} and 2.5×10^{-6} mol L⁻¹, respectively. The prepared electrodes exhibited high proguanil selectivity in relation to several inorganic ions and sugars and they could be successfully utilized for its determination in pure solutions, pharmaceutical preparations and serum and urine samples using the direct potentiometry and standard addition methods with very good recovery values.

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1. Introduction

Proguanil, (1-(*p*-chlorophenyl)-5-isopropylbiguanidehydrochloride) (C₁₁H₁₇Cl₂N₅, MW 290.19), is a prophylactic antimalarial [1,2] with the structure given in Fig. 1.

It has been used for malarial prophylaxis in children with sickle cell disease living in malaria-endemic areas for many years [3]. Proguanil is usually taken in combination with another antimalarial drug, such as Atonil [4]. The active metabolite of the proguanil is cycloguanil, which binds to the dihydrofolatereductase (DHFR) enzyme of the parasite and inhibits the folic acid metabolism. The mechanism for the cyclisation of the proguanil to cycloguanil has been recently explored by Bharatam [5]. Due to the pharmacological effect and importance of proguanil, it was quantified by several methods such as high performance liquid chromatography in Tablet dosage form and in biological fluid [6,7], however, these methods are expensive and not suitable for routine work. Thus, there is a critical need for the development of selective and inexpensive analytical tool for the determination of this drug. Analytical methods based on potentiometric ion-selective electrodes (ISEs) are suitable alternative for this purpose. They have the

longest history and probably the largest number of applications [8]. The most important advantages of this technique are high speed, which is good for routine analysis, portability of the device, on-line monitoring, low cost, and wide application concentration range [9–13]. Also, ISEs were found effective in analysis of pharmaceutical formulations [7,9,14–17] for their attractive properties mentioned before in addition to simplicity of construction, high selectivity, short response time, applicability to colored and turbid solutions and possible interfacing with automated and computerized systems [17]. PVC membrane electrodes are one of the subdivisions of potentiometric sensors. Although they are widely used, they do not have adequate mechanical stability for long-term usage. In contrast, carbon paste electrodes (CPEs) are another category of potentiometric sensors that are mechanically strong. In addition, CPEs have attracted attention more than membrane electrodes because of their advantages such as renewability by changing the electrode surface, low Ohmic resistance and the absence of the internal solutions [18,19]. Recently, for improvement of the CPEs response, pastes can be modified by different modifiers such as carbon nano-tubes (CNTs) [20–23] to form MCPE, or with PVC gel to form SPE. CNTs have interesting physicochemical properties, as the ordered structure with a high aspect ratio, high electrical and thermal conductivity, ultra-light weight, high mechanical strength and high surface area [24,25]. The combination of these characteristics makes CNTs

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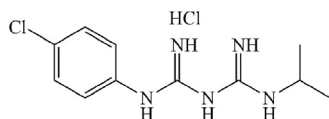


Fig. 1. Structure of proguanil hydrochloride.

unique materials with the potential for various applications. SPEs have the advantages of both the PVC and CPEs. The most important advantages of the coated wire electrodes (CWEs) are the absence of the filling solution and no need for long time soaking before first measurement. There is only one published method for proguanil hydrochloride (PrCl) determination using electrochemical methods [26]. Although the reported method showed a lower detection limit, it suffered from the very small concentration range of application and also the use of more sophisticated method, voltammetry. Here, five kinds of potentiometric sensor were introduced, namely PVC membrane electrode, CPE, MCPE using MWCNTs, CWEs and SPEs, prepared by embedding the ion-pair proguanilium-phosphotungstate (Pr-PT) in the different matrices. The electrodes are used for the determination of proguanil hydrochloride in pure samples, Tablets and spiked serum and urine samples.

2. Experimental

2.1. Reagents

All chemicals were of analytical grade and were used without any further purification. Stock solutions were prepared with doubly distilled water. High-molecular weight poly(vinyl-chloride) (PVC), phosphotungstic acid (PTA), dioctyl phthalate (DOP), tricresyl phosphate (TCP), tetrahydrofuran (THF), graphite and multi-walled carbon nanotubes (MWCNTs) were purchased from Sigma–Aldrich. Acetone, glucose, maltose, lactose, glycerin, L-alanine, sucrose, sodium hydroxide, hydrochloric acid, and chloride salts of sodium, ammonium, ferric, aluminum and potassium were purchased from ADWIC (Cairo, Egypt). Proguanil hydrochloride as a pure sample and its pharmaceutical formulation (Atonil 100 mg coated Tablet) were obtained from October pharma for pharmaceutical preparation (6th of October city, Giza, Egypt).

2.2. Preparation of solutions and ion-exchangers

Stock solutions (10^{-2} mol L $^{-1}$) of PrCl and PTA were prepared by dissolving accurately weighed amount of these materials in distilled water. Lower concentration solutions were prepared by appropriate dilution of the stock solutions. The ion-pair Pr-PT was prepared by mixing 150 mL of 10^{-2} mol L $^{-1}$ PrCl with 50 mL of 10^{-2} mol L $^{-1}$ of PTA. The resulting yellowish white precipitate was then filtered, washed with water and dried at room temperature and ground to fine powders. The composition was assisted by elemental analysis and potentiometric titration.

For sampling of tablets (Atonil[®]), five tablets were accurately weighed and powdered in a mortar; the required amount from the tablet powder was dissolved in about 30 mL of distilled water, filtered in a 100 mL measuring flask and the volume was completed with distilled water. The content of the measuring flask was subjected to potentiometric determination and standard additions method. Different amount of PrCl and 1 mL of plasma or 5 mL of urine of a healthy person were transferred to a 25 mL measuring flask and completed to the mark with water [14]; then these solutions were subjected to the potentiometric determination and standard additions method.

2.3. Preparation of the electrodes

2.3.1. PVC membrane electrode

Membranes of different compositions were prepared as described elsewhere [27]. Briefly, the required amount of PVC, plasticizer and the ion-pair of total weight of 0.30 g were dissolved in a 5.0 cm (diameter) Petri dish containing 5 mL of THF. To obtain homogenous and uniform thickness, the membrane was left to dry freely in air (no less than 24 h). The membrane was divided into four parts, and one part was taken and glued to the polished end of a rubbery tube using a PVC/THF slurry and the tube was left for 10 min and then filled with the inner solution, which contained 10^{-3} mol L $^{-1}$ of PrCl and 10^{-1} mol L $^{-1}$ of NaCl. The sensor was finally conditioned for 0.5 h by soaking in a 10^{-3} mol L $^{-1}$ PrCl solution.

2.3.2. CPEs and MCPE

In case of CPE [19], The required amount of the plasticizer and ion-pair was weighed and mixed using an agate pestle in an agate mortar for complete homogenization then graphite (and MWCNTs for MCPE) was added and mixing continued for about 10 min until the paste was homogeneous. A Teflon holder (12.0 cm, length) with a hole at one end (7.0 mm diameter, 3.5 mm deep) for the carbon paste filling served as the electrode body. Electrical contact is made through a stainless steel rod through the center of the holder. This rod can move up and down by screw movement to press the paste down when renewal of the electrode surface is needed. The paste is then packed into the hole of the electrode body. The carbon paste was smoothed onto a paper until it had a shiny appearance. A fresh electrode surface could be obtained by squeezing out a small amount of paste and removing the excess against a conventional paper then polishing the electrode on a smooth paper to obtain a shiny appearance. Electrode can be used directly for potentiometric measurements without soaking.

2.3.3. SPE

SPEs (5 mm × 35 mm) were printed using homemade carbon ink [28]. This ink is prepared by mixing 0.04 g of Pr-PT, 0.5 g of graphite powder, 0.31 g of TCP, 0.9 g of PVC (8% in cyclohexanone–acetone mixture 1:1) until complete homogeneity and the ink was printed on a PVC substrate (insulator), leaving a rectangular part (5 mm × 5 mm) at both ends of the electrode for working area and electrical contact. The prepared SPEs were used in potentiometric measurements without preconditioning.

2.3.4. CWE

A pure stainless steel rod of 12.0 cm length that has 7.0 mm at one end for the coating and 0.5 cm at the other end for connection. The coating solutions were prepared by dissolving various amount of PVC, TCP and the ion-exchanger in a minimum amount of THF. The stainless steel rod was coated by quickly dipping it into the coating solutions several times and allowing the film adhering the wire to dryness in about 3 minutes [8]. The process was repeated until a plastic membrane was formed. Then the prepared electrode was soaked for 0.5 h in a 10^{-3} mol L $^{-1}$ PrCl solution.

2.4. EMF measurements

The potentiometric measurements were carried out using a JENWAY 3310 pH-meter, where pH measurements were carried out using a Jenway pH-conductivity meter 4310. A saturated calomel electrode (SCE) (Hanna-Italy) was used as the external reference electrode. The electrochemical system may be represented as follows:

SCE/sample/workingelectrode

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