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A simple and sensitive methodology for voltammetric determination of valproic acid in human blood plasma samples using 3-aminopropyletriethoxy silane coated magnetic nanoparticles modified pencil graphite electrode

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Abstract

In this work, we have prepared a nano-material modified pencil graphite electrode for the sensing of Valproic Acid (VA) by immobilization 3-aminopropyletriethoxy silane coated magnetic nanoparticles (APTES-MNPs) on the pencil graphite surface (PGE). Electrochemical studies indicated that the APTES-MNPs efficiently increased the electron transfer kinetics between VA and the electrode and the free NH₂ groups of the APTES on the outer surface of magnetic nanoparticles can interact with carboxyl groups of VA. Based on this, we have proposed a sensitive, rapid and convenient electrochemical method for VA determination. Under the optimized conditions, the reduction peak current of VA is found to be proportional to its concentration in the range of 1.0 (±0.2) to 100.0 (±0.3) ppm with a detection limit of 0.4 (±0.1) ppm. The whole sensor fabrication process was characterized by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) methods with using [Fe(CN)₆]³⁻/⁴⁻ as an electrochemical redox indicator. The prepared modified electrode showed several advantages such as high sensitivity, selectivity, ease of preparation and good repeatability, reproducibility and stability. The proposed method was applied to determination of valproic acid in blood plasma samples and the obtained results were satisfactory accurate.

Keywords: Valproic acid, Magnetic nanoparticles, Pencil graphite electrode, Electrochemical impedance spectroscopy, Differential pulse voltammetry, Plasma
1. Introduction

Nano-materials are used in a variety of sensor and biosensor applications [1-5] because they exhibit good electro-catalytic properties, high surface-to-volume ratio, high stability, widely available, and provide fast electron transfer rates.

Magnetic nanoparticles (MNPs) are important to various biomedical applications such as magnetic separation, cell labeling, targeted drug delivery, and hyperthermia treatment of solid tumors and contrast agents for magnetic resonance imaging (MRI) [6-10]. Recently, we used functionalized magnetic nanoparticles for modification of electrode surface [11, 12]. APTES-MNPs, due to their basic groups of amino and hydroxyl anchored on the external surface, can be used in many technological applications such as in decontamination of effluents produced by industries and nuclear power plants and in various bioprocesses, molecules or drugs [13].

Due to the simple sample preparation, low-cost instrumentation, high sensitivity, selectivity, accuracy and precision of electrochemical methods, they have been used widely in biological and environmental analysis [14-23].

Valproic acid with the chemical name of 2-propylvaleric acid was first approved as an anticonvulsant in the United States in 1978. VA is used in the treatment of primary seizures, partial seizures, myoclonic seizures, bipolar disorders, prophylaxis of migraine headache, febrile convulsions, and brain tumor [24]. Other investigations have proposed to use VA in the treatment of anxiety, alcoholism, schizophrenia and borderline personality disorders [25].

After oral administration of VA, the drug is rapidly adsorbed from the gastrointestinal tract, getting maximum blood levels one to four hours and binds to human plasma proteins (90%). Mainly, metabolism occurs in the liver (95%).