Differential pulse voltammetry in analysis of disinfectants - 2-mercaptobenzothiazole, 4-chloro-3-methylphenol, triclosan, chloramine-T

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Abstract: The aim of this work was to study the possibility of simultaneous voltammetric determination of some disinfectants used as components in cosmetic products. The examined compounds were: triclosan (5-chloro-2-(2,4-dichlorophenoxy)phenol), chloramine-T (N-chloro-p-toluenesulfonamide sodium salt), 4-chloro-3-methylphenol and 2-mercaptobenzothiazole. Measurements were performed using glassy carbon electrode immersed in Britton-Robinson buffers which acted as supporting electrolytes. The dependence of oxidation and reduction potentials on pH was examined using cyclic voltammetry. Britton-Robinson buffer of pH 9.9 was chosen for further studies to ensure the best separation of compounds. The resultant oxidation potentials indicate the possibility to simultaneously determine some of the disinfectants. Oxidation reactions of mixtures containing two compounds (4-chloro-3-methylphenol and chloramine-T, 2-mercaptobenzothiazole and 4-chloro-3-methylphenol, 2-mercaptobenzothiazole and triclosan) were recorded as differential pulse voltammograms.

Keywords: Disinfectants • Voltammetry • Glassy carbon electrode

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1. Introduction

Disinfectants are chemical compounds regarded as water pollutants. Due to their use as components in many household products, a considerable amount of these compounds enters surface waters through urban sewage. It is then necessary to monitor the concentration of these substances in surface and drinking waters. Some of the most common disinfectants occurring in water environment are triclosan, chloramine-T, 4-chloro-3-methylphenol and 2-mercaptobenzothiazole. Triclosan is used as an ingredient in personal hygiene and household products such as soaps, antibacterial hand gels, toothpaste, mouthwash, deodorants, detergents and disinfecting lotions. Chloramine-T is used to disinfect surfaces and instruments in medicine, veterinary and food industry, as well as for water treatment. 4-chloro-3-methylphenol is an active component of disinfectant liquids, whereas 2-mercaptobenzothiazole is used as an antifungal agent.

Determination of disinfectants is usually performed by chromatographic methods, such as high performance liquid chromatography or gas chromatography. Electrochemical methods for determination of a single disinfectant have been also developed. These methods are sensitive, relatively fast and less expensive than chromatographic ones. Electrochemical oxidation of triclosan was studied using glassy carbon and diamond electrodes after microwave activation [1] and with modification of various electrodes, such as tin-doped indium oxide-coated glass electrode covered with carbon nanoparticle–poly(diallyldimethylammonium chloride) film [2], glassy carbon electrode coated with cellulose or cellulose–poly(diallyldimethylammonium chloride) [3], and pyrolytic graphite or glassy carbon electrode with immobilized tosyl-functionalized carbon nanoparticles [4]. Electrochemical reduction of triclosan was studied at glassy carbon electrode in dimethylformamid containing tetra-n-butylammonium tetrafluoroborate [5]. Amperometric sensor made of molecularly imprinted polymer electropolymerized at glassy carbon electrode was also used for detection of triclosan [6]. This compound was determined in toothpaste, mouthrinse, liquid soap and wastewater samples [7,8]. Its determination in cosmetics was performed at glassy carbon electrode in
the presence of a hydrotrope, which releases the analyte from matrices containing surfactants [9]. Electrochemical behavior of other phenolic compounds was also studied. 4-chloro-3-methylphenol was determined in fungicides and in cosmetic products at glassy carbon electrode [10]. Total concentration of different chlorophenols, including 4-chloro-3-methylphenol, in aqueous solution was estimated at boron-doped diamond electrode [11]. Determination of 2-mercaptobenzothiazole was carried out by hanging mercury drop electrode by cathodic stripping voltammetry [12].

So far, only the methods for voltammetric determination of a single disinfectant have been described. However, there are many examples of voltammetric analysis of mixtures of other chemical compounds. Differential pulse voltammetry was used for simultaneous determination of three drug ingredients, i.e., paracetamol, caffeine and ascorbic acid, at glassy carbon electrode [13]. Sulfamethoxazole and trimethoprim, drugs used in pharmaceutical products, were determined simultaneously at boron-doped diamond electrode [14]. Ni et al. used chemometrics in voltammetric analysis of mixtures of nitrobenzene and four nitrophenols. Three different methods (partial least squares, principal component regression, classical least squares) were applied to enable the determination of compounds by resolving their overlapped voltammograms [15]. Another way for simultaneous determination in case of overlapping peaks, includes neural networks. Carvalho et al. applied this method to analyze mixtures of catechol and hydroquinone by differential pulse voltammetry at carbon fibre electrode [16].

The aim of this work was to develop a method for simultaneous determination of several harmful disinfectants. The measurements were performed using glassy carbon electrode immersed in Britton-Robinson buffers which acted as supporting electrolytes. The studied compounds were: triclosan, chloramine-T, 4-chloro-3-methylphenol and 2-mercaptobenzothiazole. 2. Experimental Procedure

2.1. Reagents

Chloramine-T hydrate (N-chloro-p-toluenesulfonamide sodium salt, 98% purity), 4-chloro-3-methylphenol (99% purity) and 2-mercaptobenzothiazole (97% purity) were obtained from Aldrich (Germany). Triclosan (5-chloro-2-(2,4-dichlorophenox)phenol, Irgasan, ≥97% purity, HPLC grade) was obtained from Fluka (Germany).

Stock solutions of concentration 1 mg mL⁻¹ were prepared by dissolving appropriate amount of reagent in methanol. Britton-Robinson buffers were prepared by dissolving appropriate amounts of boric acid, acetic acid and orthophosphoric acid in water and by adjusting to their desired pH with 0.2 M sodium hydroxide.

2.2. Instrumentation

All voltammetric measurements were performed with µAUTOLAB potentiostat, type III (EcoChemie, The Netherlands) in a three-electrode system. The working electrode was a 1 mm diameter glassy carbon electrode (Cypress System, USA). Saturated Ag/AgCl electrode (Cypress System, USA) was used as a reference electrode and a platinum wire was a counter electrode. The working electrode was polished in alumina slurry and cleaned in an ultrasonic bath. The counter electrode was cleaned by heating in flame to remove all organic compounds.

2.3. Procedure

Voltammetric measurements were carried out in a glass electrochemical cell in ambient temperature. 2 mL of Britton-Robinson buffer solution was introduced into the cell and the solution was purged with nitrogen for 10 min. Then, an appropriate amount of reagent standard solution was added and the measurement was carried out. Cyclic voltammetry was performed at scan rate of 100 mV s⁻¹ in the potential range –1.4 to 1.4 V. Differential pulse voltammograms were recorded at a scan rate of 50 mV s⁻¹ in the potential range 0 to 1.4 V or 0 to 1.2 V. The measurements were repeated three times. The working electrode was cleaned before each measurement.

3. Results and Discussion

Electrochemical reactions of studied disinfectants and the dependence of their oxidation and reduction potentials on pH of supporting electrolyte were examined. Measurements were performed using cyclic voltammetry. Typical cyclic voltammograms of studied compounds in Britton-Robinson buffer at pH 9.9 are shown in Fig. 1. It can be noted that electrochemical reactions of these disinfectants are irreversible. Cyclic voltammetric studies of triclosan at glassy carbon electrode in 0.1 M phosphate buffer solution at pH 11 performed by Raghupathy et al. displayed an irreversible oxidation peak of this compound at 0.55 V as opposed to the saturated calomel electrode [9]. Knust and...