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SUMMARY

Electrochemical properties of selected preservatives and their voltammetric determination in pharmaceutical and cosmetic preparations

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The increase in demand for products with a long shelf-life requires the use of effective and, above all, safe preservatives. The most popular preservatives for pharmaceutical and cosmetic preparations are parabens, phenoxyethanol and synthetic antioxidants (BHA and BHT). The adverse impact of these preservatives on human health makes it necessary to develop and improve the methods of their determination in everyday products. The literature review presented in the doctoral dissertation shows that mainly chromatographic techniques, rarely spectrophotometric and voltammetric ones, are used for this purpose. So far, there have been no data on the use of electroanalytical methods for qualitative and quantitative analysis of phenoxyethanol, and thus its electrochemical properties are not known. The previous studies of the electrode processes involving parabens and synthetic antioxidants, as well as their determination, have been conducted in aqueous and water-organic solutions. Therefore, the dissertation based on a coherent thematic cycle of 5 scientific publications presents the use of voltammetric techniques to determine the electrochemical properties of the most popular preservatives and their determination in pharmaceutical and cosmetic preparations in acetic acid containing 20% acetonitrile (v/v).

The first stage of the undertaken actions included conducting basic studies on the electrochemical properties of selected preservatives, i.e. optimisation of the solution composition (the selection of a solvent or mixture of solvents and a supporting electrolyte), and testing its physicochemical properties affecting the course of electrode processes (viscosity, density, specific conductivity, pH), the selection of working electrode material and the operating parameters of measurement. The mechanisms of electrode processes were defined by

Jakubczyk

delineating the number of electrons exchanged, verifying the possible participation of protons in the elemental process, determining the nature and degree of reversibility of the electrode reactions, and the involvement of any possible follow-up reactions to the electrode process. The measurements were carried out using voltammetric techniques: linear sweep voltammetry (LSV), differential pulse (DPV), cyclic voltammetry (CVA), and rotating disk electrode (RDE). The experimentally selected electrode materials were: platinum, carbon fibre (as microelectrodes), and platinum and glassy carbon (as macroelectrodes).

As part of the research covered by this doctoral dissertation, the analytical signals from parabens, phenoxyethanol and synthetic antioxidants in pharmaceutical and cosmetic preparations were identified, without the need to separate them from the accompanying matrix. The use of the acetic acid-acetonitrile mixed solvent enabled the dissolution of both the basic electrolyte and the hydrophobic matrix of cosmetics and pharmaceuticals.

During the course of the study, procedures for the voltammetric determination of parabens, phenoxyethanol and synthetic antioxidants were developed and validated. In order to determine the selectivity of the proposed methods, the effect of substances most commonly included in pharmaceuticals and cosmetics on the signal of the preservatives analysed was examined. It was shown that, with the except for MP it did not exceed 4% for synthetic antioxidants and 2% for parabens and phenoxyethanol. Basic validation experiments aimed at determining the relationship between the size of the recorded signals and the concentration of analytes, as well as determining basic analytical parameters such as linearity range, the limit of detection (*LOD*) and the limit of quantification (*LOQ*). It was found that the proposed procedures were characterized by low *LOD* and *LOQ* values and one of the widest (in the case of parabens) or the widest (in the case of phenoxyethanol and synthetic antioxidants) ranges of linearity compared to the methods of their determination used so far.

Based on the standard solutions, the accuracy and precision of the developed procedures were determined. The quantitative analysis was performed using the multiple standard addition method. Its selection allowed the determination of parabens, phenoxyethanol and synthetic antioxidants in pharmaceutical and cosmetic preparations in the presence of the accompanying matrices.

In the final stage of the actions taken, the results of the quantitative analyses of analytes in cosmetics and pharmaceuticals were verified using liquid chromatography as a reference method.

The voltammetric determination of parabens, phenoxyethanol and synthetic antioxidants in pharmaceutical and cosmetic preparations presented in the doctoral dissertation is simple, fast, cost-effective, precise and accurate. It was possible to omit the separation phase from the matrices during the quantitative analysis of the preservatives due to their very good solubility

Jakubczyk

in the environments used, and the absence of interference from the accompanying substances. Limiting the sample preparation procedure only to its dissolution allows to minimize errors related to the loss of analytes, and thus shortens the time of research. In turn, the use of microelectrodes reduces both the consumption of reagents and the cost of analyses. These advantages combined with the use of environmentally safe acetic acid as the main component of the solution are important elements of the principles of green chemistry.

It should be emphasized that the method developed to determine the phenoxyethanol content in real preparations is the first development of the electroanalytical determination of this analyte. This procedure was further claimed in the form of patent No. PL417079 granted in 2019.

A practical aspect of the results obtained is the possibility to apply the developed procedures in the laboratory analyses of pharmaceutical and cosmetic industries to control the content of parabens, phenoxyethanol and synthetic antioxidants. They may, therefore, be an alternative to commonly used chromatographic methods.

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