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Quantitative Assay of Peracetic Acid in Disinfectant “Delakson” by Cathodic Voltammetry

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Abstract

Objective: The electrochemical behavior of peracetic acid (PAA) in disinfectant “Delakson” has been studied. **Materials and Methods:** “Delakson” disinfectant is a sample preparation, which was used for the analysis. A new voltammetric method for the quantitative determination of PAA in “Delakson” disinfectant at the carbosital rotating electrode (CE) in the interval of potential +1.0...–1.0 V (the reference electrode Ag, AgCl/KCl [sat]) ($E_p = +0.15$ V) was proposed. **Results:** It has been experimentally proved that height of PAA reduction peak decreases and the reduction peak potential is shifted toward more electronegative values with the background electrolyte pH increasing from 2.15 to 4.78. The optimum pH for analysis is approximately 3.6. The linear relationship has been observed in the PAA concentration range $3.12\text{--}12.50 \times 10^{-5}$ mol/L, the calibration curve equation was $I_p = (3.78 \pm 0.46) \times 10^3 c$ ($r = 0.995$). Determining PAA in the work solution with the relative standard deviation (RSDs) were 0.035–0.022 ($\delta = +0.30\text{...} +0.90\%$); limit of detection = 1.19×10^{-6} mol/L, and limit of quantification = 3.97×10^{-5} mol/L. Determining PAA in the test solution of “Delakson” disinfectant with the concentrations of 0.1% the RSD was 0.024 ($\delta = +0.9\%$). **Conclusions:** Thus, new voltammetric method of PAA determination in “Delakson” disinfectant at CE has been developed and the possibility of its quantitative determination has been shown.

Key words: Carbosital electrode, disinfectant, peracetic acid, voltammetry

INTRODUCTION

Peracetic acid (PAA, CAS Number 79-21-0) was introduced as an antibacterial agent in 1955. It has a broad spectrum of activity, including bacteria, spores, molds, yeasts, algae, and viruses.^[1-4] PAA, a possibly safe oxidizing agent, has been increasingly used, especially as a high-level disinfectant in hospital establishments.^[5,6]

The usage of PAA for sterilization attracts high attention so as the problems of infectious agents spreading in the environment are intensified and the necessity in so-called cold sterilization has increased. PAA displays a wide spectrum of attack against microbes. In addition, PAA offers the advantages of being sporicidal at low temperature, even lower than room temperature, and of leaving only nontoxic residues. Due to these PAA disinfectant advantages, it has been widely used in food industry and health-care industry as effective sterilizer.^[3]

PAA has been widely used as a disinfectant and bleaching agent^[1,2] in recent years. Furthermore, PAA does not form toxic wastes and its decomposition products (acetate acid, water, and hydrogen peroxide) are environmentally friendly.^[3] PAA is also used as an active ingredient in certain disinfectants such as “Delakson” (“Delana,” Kyiv, Ukraine), “Nukdez” (“Inter Chemical group,” Ukraine), “Dezynfektor,” “Septacid,” and “Steridial W” (Impuls, Gdańsk, Poland), and “Sterioks” and “Sterisyl” (Baltiachemi, Estonia). It shows bactericidal, tuberculocidal, virucidal, sporicidal, and fungicidal properties^[4] and intended for the final, flow-line, and preventive object disinfection in health-care institutions and nidus of intestinal and respiratory infections of bacterial and viral etiology, tuberculosis, dermatophytes, and Siberian

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plague, as well as for the sterilization of medical products^[5] (including rigid and flexible endoscopes)^[6] and suture material.

Various methods have been used for the determination of PAA. The most widely used methods for analyzing solutions containing PAA and H₂O₂ are modifications of the initial D'Ans-Frey and Greenspan-Mckellar methods^[7,8]. It is obvious that two stepped titration method is not suitable for the continuous monitoring of PAA because it is very time-consuming. As the alternative techniques for the determination of PAA, electrochemical measurements^[9-16], chromatographic methods^[17-19], fluorescence^[20,21] and spectroscopic methods^[22-25] have been used. Conductivity measurements are rapid and convenient, but their common disadvantage is their low selectivity. Spectroscopic methods have often been used for direct determination of a few species in aqueous solutions. Near-infrared spectroscopy has recently been of keen interest as a practical technique for a variety of water and aqueous solution analyses. So far, a ultraviolet (UV) spectroscopic method for the direct determination of PAA has not been reported probably because its UV absorption maximum is located at a very short wavelength (<180 nm) and the extinction coefficients, obtained by ordinary UV-visible spectrometer, are very low. However, all these methods are not sufficiently sensitive and furthermore require conducting of many chemicals, complicated cleaning, and extraction procedures, and the use of cumbersome equipment may interfere the whole procedure.

Nowadays, selective amperometric and potentiometric methods, which allow to perform simultaneous PAA and H₂O₂ determination at the compatible presence in water solutions, have been proposed.^[10-17] H₂O₂ presence in PAA solutions is imminent according to several reasons so as the synthesis of PAA is carried out by HP reaction and acetate acid that is why the hydrogen peroxide is a constant technological admixture, and also, due to the course of hydrolysis reaction, in aqueous solutions, there is a continuous unilaterally hydrolytic decomposition of PAA into HP and acetate acid.

Extensive literature survey reveals that, due to the well-known selectivity and sufficiently high sensitivity, the most common method of the peroxide compounds analysis is a voltammetry methods with variety indicator electrodes.^[26,27] Along with dropping mercury, platinum, and gold electrodes, the electrodes based on carbon materials such as glassy carbon, pyrographite, and carbositall are used. These electrodes offer new feasibility of the peroxide analytical determinations which virtually impossibly carry with mercury electrodes, although it does not have constantly updating surface properties and not so easy to use, because they require a lot of effort for their preparation and service. Carbositall is the material from pyrographite, but unlike it, due to its specific structure, has isotropic properties, requires no special orientation in the electrode device, has a high electrical conductivity, and is practically

non-porous so that there are small residual current. It has a low resistivity, practically impermeable to gases and resistant to oxidation by atmospheric oxygen. It is less fragile, easily to mechanical polishing, and relatively cheap than glassy carbon. A low rate of electrode processes are characteristic of the carbositall electrode (probably due to poor oxygen adsorption capacity). It should be noted that carbositall electrode can successfully replace mercury (negative potential region) and platinum (positive potential area) electrodes in the analysis of peroxide compounds complex mixtures by voltammetry.

The usage of carbositall electrode for electrochemical determination of some peroxides in preparations has been studied in our previous works.^[28-31]

“Delakson” (“Delana,” Kyiv, Ukraine) is a complex disinfectant in the form of granulated water-soluble powder, which contains PAA (5–15%), hydrogen peroxide (10–22%), acetate acid (22–26%), and stabilizing agents.

The preparation is used in the form of water working solutions in concentration from 0.05% to 1.2%. The water working solution is prepared straight before the usage. It is allowed to store unused working solution for 5 days after producing in a container with a tightly closed lid at room temperature. The solution is used for disinfection during the day. The daily necessity of working solution concentration control, containing PAA, is evident. The determination (mass fraction) of PAA in “Delakson” disinfectant is carried out by redox titration.^[32]

The aim of the present work is to determine the feasibility of PAA quantitative determination in “Delakson” disinfectant by cathodic voltammetry using carbositall rotation electrode (CE) as indicating electrode.

MATERIALS AND METHODS

“Delakson” disinfectant is a sample preparation, which was used for the analysis. A new voltammetric method for quantitative determination of PAA in “Delakson” disinfectant at the CE in the interval of potential +1.0...–1.0 V (the reference electrode Ag and AgCl/KCl [sat]) ($E_p = +0.15$ V) was proposed.

The stock solution of PAA

Commercial preparation of PAA solution (Sigma-Aldrich Chemie GmbH, Steinheim, Germany) was used in the experiment. The stock solution was prepared by accurately commercial preparation diluting, and it is standardized by the recommended procedure^[32]. 10.00 mL of obtained PAA solution was diluted in 100 mL volumetric flask with double-distilled water to obtain 1.56×10^{-3} mol/L solution of PAA.

The solution of acetate buffer (pH = 3.6) was prepared by diluting 425 mL of 1.00 mol/L solution of acetic acid and 50.0 mL of 1.00 mol/L solution of NaOH in 500 mL volumetric flask with double-distilled water at 20°C.

The solution of ice acetic acid, 17.5 mol/L (AA), was prepared by diluting of 28.6 mL of concentrated (ice) solution of acetic acid in 500 mL volumetric flask with double-distilled water at 20°C.

The solution of sodium sulfate, 1 mol/L (Na_2SO_4), was prepared by dissolving of 142.0 g of Na_2SO_4 in 1000 mL volumetric flask by double-distilled water.

The background solution consists of a mixture of the acetate buffer solution background (pH 3.6) and 0.1 mol/L Na_2SO_4 .

The sample preparation which was subjected to the analytical procedures for the analysis of PAA was “Delakson” disinfectant (“Delana,” Kyiv, Ukraine).

The test solution of “Delakson” disinfectant, 0.1%, was prepared by dissolving of 1.0 g of preparation in 1000 mL volumetric flask by double-distilled water.^[32]

The pH was measured using an ionmeter of I-160M type (Belarus) with a glass electrode of ESL-43-07 type paired with Ag and AgCl/KCl (sat) electrode.

The electrochemical measurements have been carried out in AVS-1.1 Analyzer (Volta, St. Petersburg) with a three-electrode scheme by alternating the current mode with a square wave modulation in the potential range of +1.0...-1.0 V, $W = 1000$ rpm, the amplitude of 40 mV, $\nu = 65$ Hz. The values of potential peaks directly at the maximum have been measured by the electrochemical sensor “Module EM-04” with the accuracy of ± 5 mV. The CE has been used as a working and auxiliary electrode and Ag and AgCl/KCl(sat) electrode type EVL-1M4 as a reference electrode.

RESULTS AND DISCUSSION

Effect of nature and pH of background solution

The effect of pH on the reduction process has been investigated by recording voltammograms of PAA at 3.12×10^{-5} mol/L concentration at several pH values ranging from 2.15 to 4.78. A mixture of 1 mol/L Na_2SO_4 with acetate buffer solution has been used as background solution, and the pH of the solution has been changed gradually by adding NaOH 0.2 mol/L. As it can be seen from the graph [Figure 1], the height of PAA reduction peak decreases and the reduction peak potential is shifted toward more electronegative values with the background electrolyte increasing pH from 2.15 to 4.78. The two well-separated peaks (I_p) are observed at

pH approximately 2.5–3.7, and at pH, about 4.78 analytical signal almost disappears. The effect of pH on the peak potential (E_p) shows the following: When pH value increases in the interval from 3 to 4, E_p remains almost constant, but E_p decreases markedly to the negative value with pH increasing over 4 [Figure 1]. That is why, the optimum pH for analysis is approximately 3.6.

The procedure of obtaining results for the calibration graph

Working solutions have been prepared by diluting different volumes of PAA stock solution (1.00–4.00 mL) and 5 mL of 1 mol/L Na_2SO_4 in 50 mL volumetric flask by acetate buffer solution. 25 mL of the working solution was transferred to the cell. The voltammograms have been recorded by scanning the potential toward the negative direction in the potential range from +1.0 V to -1.0 V (vs. Ag and AgCl/KCl [sat]).

The graph was positioned in the following coordinates: The height of peaks I_p in μA at $E_p = +0.15$ V on the ordinate axis and corresponding concentration of PAA, c in mol/L on the abscissa axis [Figure 2]. The graph equation coefficients have been calculated by least square method.

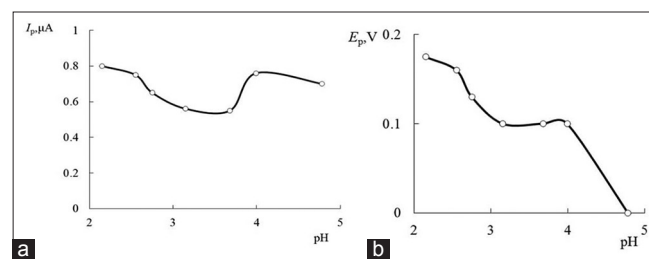


Figure 1: The influence of pH on the current peak intensity (a) and peak potential (b) of peracetic acid reduction process at the carboxital rotating electrode (vs. Ag and AgCl/KCl[sat])

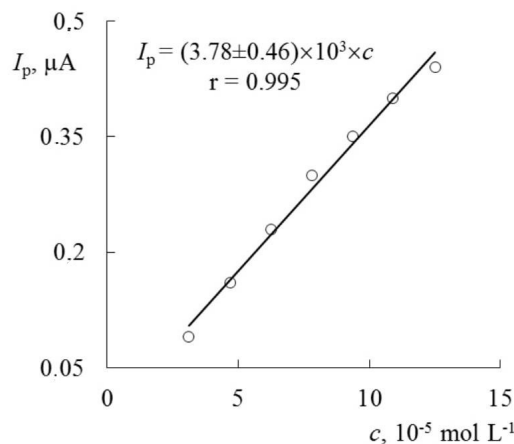


Figure 2: The calibration graph of the peracetic acid reduction current peak versus concentration ($c = 4.0 \times 10^{-3}$ mol/L); $E_p = +0.15$ V

Analytical characteristics of the calibration graph of the PAA voltammetric determination procedure are given in Table 1.

The procedure of PAA quantitative determination in “Delakson” disinfectant

Working solutions have been prepared by diluting different volumes (10.00–15.00 mL) of the test solution and 5 mL of 1 mol/L Na₂SO₄ in 50 mL volumetric flask by acetate buffer solution. The voltammograms have been recorded by scanning the potential toward the negative direction in the potential range from +1.0 V to –1.0 V (vs. Ag and AgCl/KCl [sat]). The concentration of the test solution C_x has been calculated by the following equation:

$$C_x = \frac{I_p - b}{a}$$

Where I_p - current peak of test solution; a and b - graph equation coefficients.

PAA mass fraction, %, in the test solution has been calculated by the following equation:

$$X, \% = \frac{C_x \cdot 76.05 \cdot 100 \cdot V_0}{m \cdot 1000 \cdot 10 \cdot V} \cdot 100\%$$

Where 76.05 - PAA molar weight; V_0 - volumetric flask capacity; V - test solution volume; m - sample weight; 10 - stock solution volume; and 100 and 100 - volumetric flask capacities.

The high sensitivity of this method is accompanied by a very good reproducibility. The reproducibility has been evaluated from five repeated electrochemical signal measurements of model solutions of “Delakson” disinfectant. The precision of the developed method in terms of the relative standard deviation (RSD) was 2.39% ($\delta = +0.90\%$), respectively. The obtained results have been summarized in Table 2.

CONCLUSION

Thus, new voltammetric method of PAA determination in “Delakson” disinfectant at CE using the method of calibration graph has been developed, and the possibility of its quantitative determination has been shown.

The linear dependence is observed in the PAA concentration range $(3.12-12.50) \times 10^{-5}$ mol/L, the calibration curve equation was $I_p = (3.78 \pm 0.46) \times 10^3 c$ ($r = 0.995$); RSD = 2.39% and $\delta = +0.90\%$ ($n = 5$; $P = 0.95\%$), limit of detection = 1.19×10^{-6} mol/L, and limit of quantification = 3.97×10^{-5} mol/L.

Table 1: Analytical characteristics of the calibration graph of PAA voltammetric determination procedure in model solutions are $y=ax+b$

| Parameters | Data |
|---------------------------------|---------------------------------------|
| Concentration ranges (mol/L) | $(3.12-12.50) \times 10^{-5}$ |
| Regression equation | $I_p = (3.78 \pm 0.46) \times 10^3 c$ |
| a | 3.78×10^3 |
| b | 0.013 |
| S_a | 0.46×10^3 |
| S_b | 0.038 |
| Δ_a | 0.18×10^3 |
| Δ_b | 0.015 |
| Correlation coefficient (r) | 0.995 |
| LOD (mol/L) | 1.19×10^{-6} |
| LOQ (mol/L) | 3.97×10^{-5} |

LOD: Limit of detection, LOQ: Limit of quantification, PAA: Peracetic acid

Table 2: The results of PAA voltammetric determination in “Delakson” disinfectant ($n=5$; $P=0.95\%$)

| Taken* (%) | Found (%) | Metrological characteristics |
|-------------|-----------|------------------------------|
| 0.100±0.015 | | $\bar{X}=0.101$ |
| | 0.100 | $S=0.0024$ |
| | 0.099 | $S_x=0.0012$ |
| | 0.105 | $\Delta\bar{X}=0.003$ |
| | 0.101 | RSD=2.39% |
| | 0.0995 | $\varepsilon=2.97\%$ |
| | | $\delta^*=+0.90\%$ |

*The calculation has been made according to the average content established by means of standard procedure.^[32] PAA: Peracetic acid, RSD: Relative standard deviation

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