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The study of iron-based nanoparticles stability in biological fluids by stripping voltammetry

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Abstract

The possibility of application of voltammetric methods for evaluating the stability of nanoparticles in biological fluids has been shown for the first time. The kinetics of degradation both of uncoated nanoparticles and with different coatings in a simulated solution of gastric juice in a wide range of time has been studied. It has been shown that by using carbonaceous coatings nanoparticles resistance increases 2-4 times, and when modifying the surface with aryldiazonium salts - 5-6 times.

Keywords: Voltammetry, nanoparticles, coating, modification, gastric juice technique.

Introduction

Nanoparticles enter the body of humans and animals through the air, the gastrointestinal tract with parenteral nutrition (blood, surgery) using nanoscale and nanostructured materials (drug delivery systems, implants, heart valves, traumatology and orthopedics, dentistry, etc.). Accumulation of nanoscale objects and their products

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degradation (ions, monomers) in the tissues and fluids is fraught with a huge, still little studied, potential health hazard.

The main nanoparticles used in biology and medicine are metals accounting for 69 % of citations in scientific literature. In this regard, the stripping voltammetry related to a group of electrochemical measurement methods can be one of the leading methods of analysis of their accumulation in food, body fluids and tissues of humans, animals, fish, etc. The degradation of nano- objects, inevitably arising in fluids and tissues, results in the release of ions, which greatly increases the area of biological objects damage, and can cause multiple organ pathology.

According to the normative document [1] before the medical and biological assessment of nanomaterials and products containing them, the physical and chemical parameters that characterize the functional properties of the tested nanomaterials must be specified.

In connection with the above, the development of voltammetric control methods to assess the stability of the nano-sized objects in biological fluids is particularly important because it allows analyzing body fluids and tissues, which is important for the safety of nanotechnology in the annex to ecology, biology and medicine [2-4].

Additionally, the price/quality values of the techniques for stripping voltammetry in instrumental analysis exceed similar ones for other methods. It is essential for the creation of import substitution measurement procedures and equipment in the field of nanotechnology and nanosafety.

Methods of voltammetry (VA), including stripping (SVA), are widely used for the control of these substances on the content both of a vital trace elements and toxic contaminants. The objects in question are complex multi-component systems in which impurities are determined in different chemical forms, some of which only are electrochemically active [5,6]. The presence of highly corrosive environments (saliva, gastric and intestinal juices) in the digestive tract raises the question about a possible degradation of nanoparticles with the release of ions which might have own additional toxicity to the host organism.

Currently, in the field of nanomedicine the development of infrastructure and the methods of analysis of nanomaterials are basically focused on. According to the analysis of the leading publications, based on the compilation of Ion Channel Group Ltd. (2007) from the journals with high impact factor, about 25% of the articles are devoted to this issue.

In this regard, because of the high aggressivity of the gastric content (hydrochloric acid, the presence of enzymes and oxygen) capable of actively destroying various organic and inorganic materials, creating a model of behavior and degradation of nanoparticles in the gastric juice, followed by quantification, is very promising for nanoecotoxicology. A topical problem is a comprehensive study of the biological systems being in contact with metal nanoparticles, as well as the creation of methods of their quantitative determination.

The purpose of this research is to study the stability (degradation) of nanoparticles with different coatings in simulated solutions of gastric juice by stripping voltammetry.

Results and Discussion

We have proposed a method for studying the stability (degradation) of Fe_2O_3 nano-particles to determine the dissolved iron in the gastric juice. Figure 1 shows a differential VA curve on the background of Trilon B. An anodic signal corresponds to the iron complex oxidation on the surface of the gold-graphite electrode from the oxidation state (2+) in (3+). The iron signal is directly proportional to its concentration in the solution in the range from 0.2 to 20 mg/dm^3; the iron content may be estimated by the method of standard additions in the same solution of the prepared sample.

When studying the degradation the Fe_2O_3 nanoparticles with different coatings (coal powder, diazonium salts, and others.) were placed in a gastric juice simulated solution (0.1 M HCl) and incubated for different periods of time (from 1 to 22 hours). It was natural to assume that when making nanoparticles in the simulated solution there would be a partial chemical dissolution and transition of iron (III) in the solution. The terms of the iron (III) determination were as follow: direct current registration mode of voltammograms (1st derivative); voltage for energy accumulation Ee = -1.0 V; speed of potential sweep of 80 mV/s; electrolysis time of 30 sec; supporting electrolyte of 0.01 mol/l Trilon B; potential of analytical signal on a gold-graphite electrode (anode oxidation peak value of Trilon -Iron complex (III)), E = -0.15 [7].

The analysis of the gastric juice simulated solution after the contact with nanoparticles was performed after filtration (separation of nanoparticles from the gastric juice simulated solution) by voltammetry method using additives. The pure quartz beakers (15-20 cm^3) were used for adding 0.05 ml of a simulated solution, 1 ml of 0.2 M

Trilon B and 9 ml of bidistilled water. The voltammogram of the simulated solution was recorded with the addition of a standard iron solution $C = 0.1$ mg/dm^3 as well.

The potential of the anodic peak obtained from the studied sample solutions (in contact with nanoparticles) coincides with the anodic peak potential of the iron ions (III) and increases with the addition of the standard iron solution (III) (Figure 1) that is a kind of proof of the iron (III) presence in the test solution, i.e. chemical dissolution of Fe$_2$O$_3$ nanoparticles.
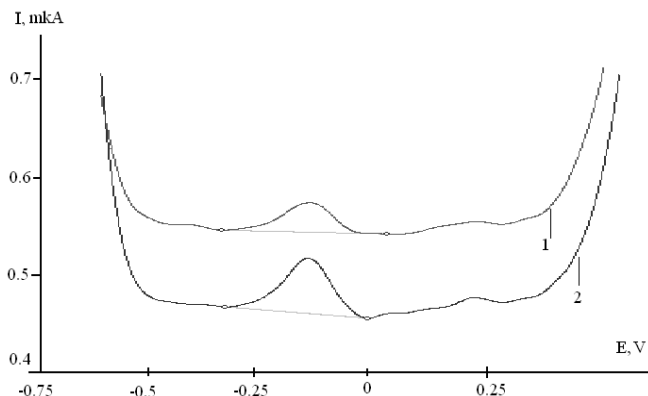

Fig.1.Differential voltammograms of a simulated solution (1) and a simulated solution with the addition of iron (III) (2).
Background - 0.01 M Trilon B, gold-graphite electrode

The kinetics of degradation both of uncoated nanoparticles and with different coatings in a simulated solution of gastric juice has been studied.

Figure 2 shows the dependence of the anodic iron current on the exposure time of nanoparticles without additional coating in 0.1 M HCl solution
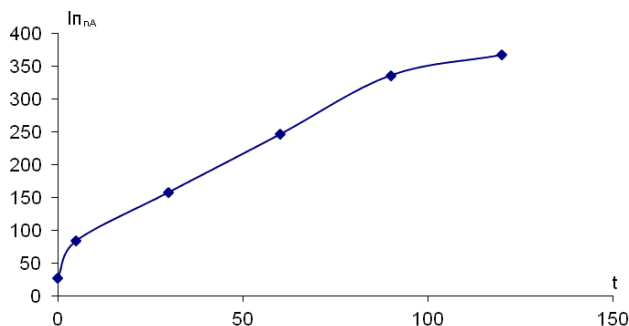

Fig.2. The dependence of the anodic current of iron on the gold-graphite electrode (background - 0.01M Trilon B) on the exposure time of nanoparticles in 0.1 M HCl solution

The studies have shown that when placing nanoparticles in the solution of 0.1M HCl without additional coating almost immediately the chemical dissolution of the nanoparticles occurs and the iron ions (III) appear. The number of ions passed into the solution of iron (III) with exposure time increasing up to 120 minutes increases approximately 10 times.

For the iron nanoparticles coated with carbon only after keeping them in the solution of 0.1 M HCl for 52 min, there was the appearance of iron (III) ions, which indicated a greater stability of the nanoparticles in the gastric juice

simulated solution compared with the iron nanoparticles without carbonaceous coating (Figure 3).
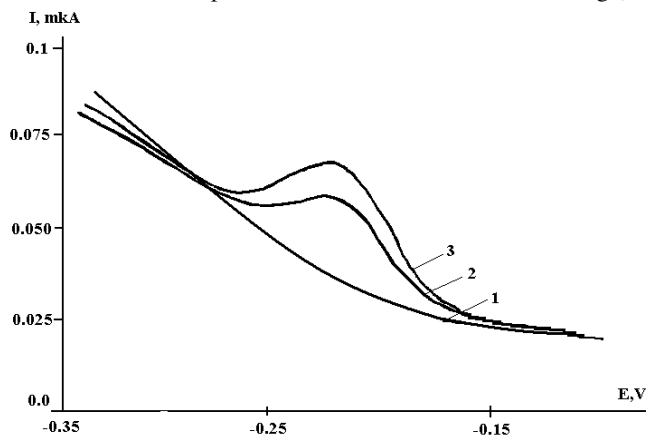

Fig.3. Differential voltammograms of the gastric juice simulated solution with the nanoparticles (1) and the same solution with the addition of gelatin (III) (2).
Terms: Background - 0.01 M Trilon B, gold-graphite electrode.
A solution of the gastric juice with carbon-coated nanoparticles: Vs-n = 10 ml, $m(Fe_2O_3)$=10 mg, $t_{exposure}$= 22h40min, C_{Fe3+} = 0.5 mg/dm^3

Aryldiazonium tosylates were used as modifiers for carbon-coated nanoparticles, which were received by the team of employees of the Department of Organic Chemistry and Organic Synthesis of the Institute of High Technology Physics of TPU [8].
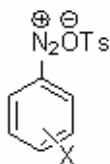
where X - COOH, NH$_2$, NO$_2$

This new class of aromatic diazonium salts with a unique-term stability and good solubility in water and organic solvents, which plays an important role in the process of surface modification. When placing the carbon-coated nanoparticles in an aqueous solution of a diazonium salt with a substituent - NH$_2$, a spontaneous release of nitrogen and Ar •free radical generation, covalently bound to the surface of carbon, occurs.

The increase of chemical stability of iron nanoparticles both carbon-coated and modified with a diazonium salt solution in the studied time interval was observed: iron (III) ions appeared in the solution after the incubation of nanoparticles in the simulated solution for 2 h 7 min; and the concentration of the iron (III) ions was reduced compared to the previous case approximately 3-5 times (Figure 4, Table 1).
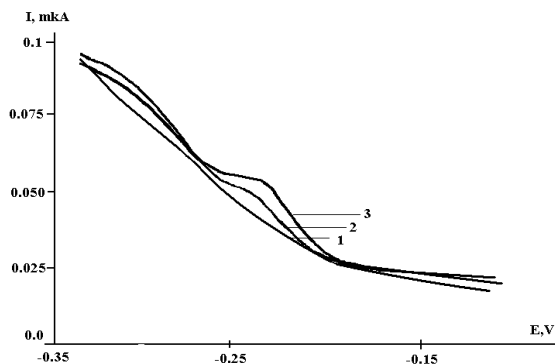

Fig.4. Differential voltammograms of the simulated solution with the nanoparticles (1) and the same solution with iron (III) (2).

Background - 0.01 M Trilon B, gold-graphite electrode nanoparticles are covered with a layer of carbon and modified with the diazonium salt solution.

$m(Fe_2O_3)$=10 mg, $t_{exposure}$= 22h40min, C_{Fe3+} = 1 mg/dm^3

Table 1. The concentration of Fe^{3+} in the simulated solution after the exposure of the coated nanoparticles for various periods of time in 0.01 M Trilon B

	Nanoparticle	Concentration of Fe^{3+}, mg/dm^3	E(B)	Nanoparticle	Concentration of Fe^{3+}, mg/dm^3	E(B)
10 min	Fe$_2$O$_3$-C	-	-	Fe$_2$O$_3$-C+R-NO$_2$	-	
52 min		1.2	-0.16		-	
2h 7 min		7.6	-0.15		0.2	-0.15
21h 40 min		36	-0.15		1.7	-0.15

Conclusion

Thus, to evaluate the stability of nanoparticles with a variety of coating the method of stripping voltammetry is used. It allows evaluating a wide range of determined contents of iron with sufficient accuracy.

The study of the stability of nanoparticles with different coating has shown that the most resistant to hostile environments (for example, gastric juice), and consequently, inflicting the least harm to the human body are carbon-coated nanoparticles and nanoparticles modified with a diazonium salt solution.

Acknowledgments

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