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## Investigation of Iron-based Nanoparticles Action by Solid-Phase Voltammetry

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### Abstract

The electrochemical conversion of Fe<sub>2</sub>O<sub>3</sub> nano-particles from the surface of carbon paste electrode was investigated by solid-phase voltammetry. Cyclic voltammetric curves of Fe<sub>2</sub>O<sub>3</sub> nanoparticles transformations were recorded in direct current (first derivative) mode with a potential change at the speed of 80-90 mV/s in the potential range from -1.2 to +1.0 V. The dependence of the anodic peak of Fe<sub>2</sub>O<sub>3</sub> nanoparticles on exposure time in a background electrolyte was researched and the method for identifying and quantification of solid-phase nanoparticles of Fe<sub>2</sub>O<sub>3</sub> was developed. The results of determination were tested by a standard addition method.

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### 1. Introduction

Increasing interest in metal nanoparticles (including Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>2</sub>O<sub>3</sub>) is induced by the discovery of their unique physical and chemical properties, especially a biological action, which often differs from the properties of these substances in a macrodispersed form. It allows using it in various industries including medicine and agriculture. Nanomaterials are frequently used either for targeted delivery of drugs into the pathological organism hearth or as magnetically sorbent toxins. In this case, quite aggressive environment may be present, for example, in a digestive

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tract (saliva, gastric and intestinal juice). There arises a question of possible degradation of nanoparticles with the release of ions which can be toxic to the body. Therefore, there is an acute problem of determining both the nanoparticles and the products of their chemical interactions with the environment in which they are placed.

To determine the size, structure, shape, surface roughness and degree of agglomeration of nanoparticles the methods of scanning and transmission electron microscopy have been used<sup>1,2</sup>. To investigate physical and chemical characteristics of nanoparticles based on iron chromatographic methods (absorption, sieve, hydrodynamic, gas chromatography), with which there is a possibility to determine the shape and size of nanoparticles have also been used. These methods enable to research the interaction of nanoparticles with a matrix<sup>3,4</sup>.

Mossbauer spectroscopy is a research method of physical and chemical properties of iron nanoparticles, based on a determination of resonant absorption of recoil-Y-monochromatic radiation emitted by a radioactive source<sup>5,6</sup>. The provided research<sup>5</sup> allowed obtaining information on the properties of nanoparticles: restructuring of changing their size and temperature; magnetic state; action of an ensemble of particles in a liquid.

A promising method to identify and quantify substances is solid-phase voltammetry which is used with a carbon paste electrode (voltammetry of immobilized particles). It has been quite widely applied in the phase analysis of semiconductors, materials possessing superconductivity and other substances<sup>7-12</sup>.

For example, the authors in the research<sup>9</sup> conducted their own phase analysis of the oxide semiconductor of type  $A^{III}B^V$ . That method was used to identify superconducting properties of high-temperature ceramic superconductors based on Y-Ba-Cu-O<sup>12</sup>. It is based on a balance between analytical signals of cathodic currents on current-voltage curves of superconductors from a carbon paste electrode (SEA). The voltammetric method for the quantitative determination of iron in solution (III) by an anodic oxidation peak value of a Trilon complex of iron (II) on a gold graphite electrode is well-known<sup>13</sup>. However, published data on the determination of nanoparticles by voltammetric methods are not available.

The target of exploration is to research an electrochemical action of  $Fe_2O_3$  nanoparticles by solid-phase voltammetry and to develop a voltammetric method for identification and quantitative determination of solid-phase  $Fe_2O_3$  nanoparticles, procedures for their determination in various objects including biological ones.

## 2. Experimental

A voltammetric analytical measurement complex STA TU 4215-001-20694097-98 (Tomsk, Russia, "ITM"), which is a compact device consisting of an electronic unit and a measuring unit with three electrochemical cells was used. Data processing was carried out using installed "STA" programs. As an indicator electrode a carbon-paste electrode (CPE) which is a graphite rod with a diameter of 1.5-2.0 mm, pressed into a fluoroplastic holder with a diameter of 2.0 mm so that the length of a protruding part was 2-3 mm, was used. An electrode contact with the instrument was carried out using a metal electrical power supply and a standard connector. For manufacturing of CPE powder of spectral grade graphite C-4 with a particle size of 100-200 microns was mixed with silicone oil (1 g of powder and 0.5 ml of oil) and introduced into protruding part of the holder. As a reference electrode a saturated silver-chloride electrode was used. All studies were performed in the background electrolyte of 0.02 M Trilon B solution (pH 3-4).

## 3. Results and Discussion

Electrochemical conversion of  $Fe_2O_3$  nanoparticles from CPE surface and their cathodic and anodic polarization were studied.

Cyclic voltammetric curves of electrotransformation of  $Fe_2O_3$  nanoparticles were recorded in direct current (first derivative) mode with potential change from -1.2 to +1.0 V (anodic scan) or from 1.0 to -1.2 V (cathodic scan) (Fig. 1, 2) at the speed of 80-90mV/s.

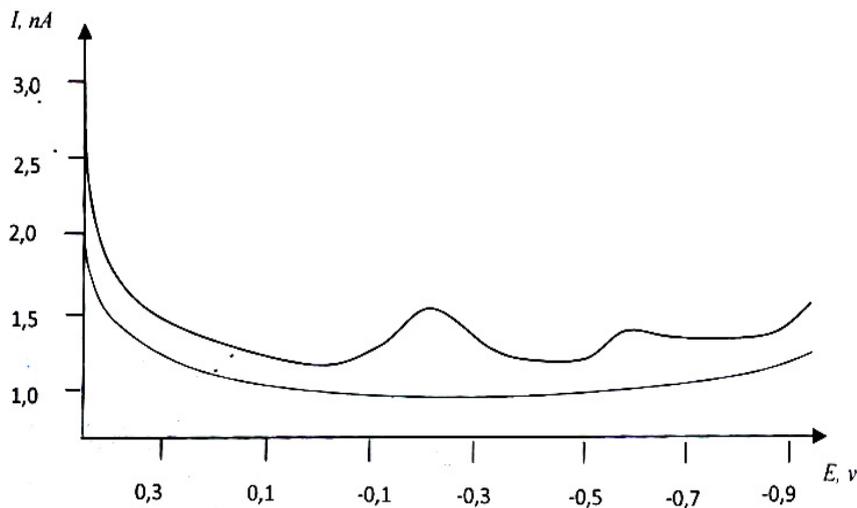


Figure 1: Cathodic voltammogram of  $\text{Fe}_2\text{O}_3$  nanoparticles from CPE in background electrolyte of 0.02M Trilon B, pH 3-4

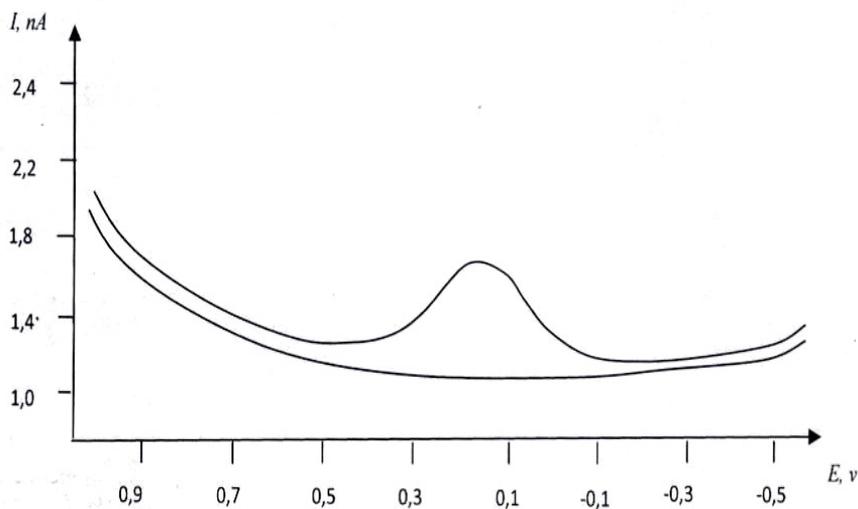


Figure 2: Anodic voltammogram of  $\text{Fe}_2\text{O}_3$  nanoparticles from CPE in background electrolyte of 0.02M Trilon B, pH 3-4

In the cathodic voltammogram the following signals were observed: the first peak at  $E = -0.26$  V and the second peak at  $E = -0.55$  V (Fig.1). However, the linear dependence, linear increase of cathode current peaks on the content of nanoparticles in the CPE, was not observed.

In the anodic voltammogram (Fig. 2), a highly reproducible peak ( $E_p = -0.12$  V), the value of which increased linearly with increasing amounts (mass fraction %) of nanoparticles in CPE (Fig. 3) is observed. An anodic peak potential value remained practically unchanged increasing the content of nanoparticles in CPE. Therefore, as an analytical signal for identification and quantitative determination of solid- $\text{Fe}_2\text{O}_3$  nanoparticles the peak at a potential  $(-0.12 \pm 0.01)$  V, which was recorded in an anodic mode after cathodic polarization of the electrode, was selected. The anodic peak is likely associated with oxidation of Fe(II) from the CPE surface to Fe(III). The formation of Fe(II), obviously, is due to reducing of  $\text{Fe}_2\text{O}_3$  during the cathodic polarization of the electrode.

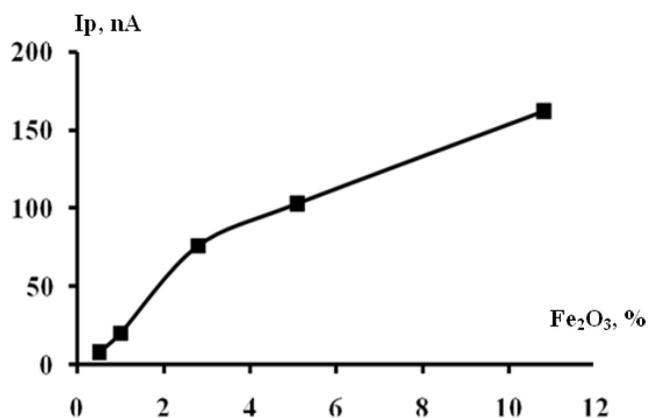


Figure 3. Anodic peak of nanoparticles is depended on mass fraction of Fe<sub>2</sub>O<sub>3</sub> on CPE

To explore the influence of the type of a supporting electrolyte on voltammetric curves of Fe<sub>2</sub>O<sub>3</sub> nanoparticles maintaining of CPE with different content of Fe<sub>2</sub>O<sub>3</sub> nanoparticles in the background electrolyte without polarization was carried out for various times (1 to 20 min). The results of the investigation are presented in Table 1.

Table 1. Dependence of the anodic peak of Fe<sub>2</sub>O<sub>3</sub> nanoparticles on the exposure time in the background electrolyte at their different content on CPE

Curing time	The magnitude of the anodic peak current of nanoparticles Fe <sub>2</sub> O <sub>3</sub> , nA		
	m(Fe <sub>2</sub> O <sub>3</sub> ) = 28 mg	m(Fe <sub>2</sub> O <sub>3</sub> ) = 51 mg	m(Fe <sub>2</sub> O <sub>3</sub> ) = 108 mg
2 min	76±11	103±15	162±20
10 min	75±10	101±14	147±20
20 min	66±9	92±12	132±19

After investigation of CPE with Fe<sub>2</sub>O<sub>3</sub> nanoparticles in the background electrolyte, the anode current-voltage curves form remained practically unchanged with a constant value of anodic peak potential. The maximum size of the anode current with increasing exposure time of CPE with Fe<sub>2</sub>O<sub>3</sub> nanoparticles in the background solution hardly decreased (decrease, if observed, did not exceed the method error i.e. 10-15%). This fact indicates the absence of chemical dissolution (degradation) of Fe<sub>2</sub>O<sub>3</sub> nanoparticles from CPE surface in the background electrolyte, and confirms the fact that the analytical signal is connected directly to electroconversion of Fe<sub>2</sub>O<sub>3</sub> from CPE, but not electroconversion of iron ions from the solution by chemical dissolution of Fe<sub>2</sub>O<sub>3</sub> from CPE in the background electrolyte.

As the form of current-voltage curves at different exposure time of CPE with Fe<sub>2</sub>O<sub>3</sub> nanoparticles did not change (no additional signals), it may indicate a lack of formation of any new electroactive compounds on CPE in the investigated range of potentials.

As a real object of the analysis an emulsion, which was used as a dispersed phase in magnetic fluids, and almost harmless for a human body, and used for a drug delivery, was investigated.

Evaluation was carried out correctly by a standard addition method on model and real samples. Data are presented in Table 2.

Table 2. Contents of Fe<sub>2</sub>O<sub>3</sub> nanoparticles in various objects

Sample	Contents of Fe <sub>2</sub> O <sub>3</sub> nanoparticles, mg		
	Test	Added	Obtained
Model solution	< 0.6	2.0±0.1	2.0±0.3
Emulsion	< 0.6	5.0±0.3	5.1±0.9

#### 4. Conclusion

The quantitative content of Fe<sub>2</sub>O<sub>3</sub> nanoparticles in the samples of the emulsion by solid-phase voltammetry using the calibration curve constructed for the mass fraction of Fe<sub>2</sub>O<sub>3</sub> nanoparticles prepared in carbon paste in the range of 0.05-12% was assessed. The nanoparticles content in the emulsion was changed to 2-fold increase (decrease).

The proposed method is simple and does not require large amounts of reagents and labor, and may be acceptable in any chemical laboratory, especially now, when domestic and foreign electrical equipment is launched with the control and management of data processing (STA, TA analyzers, etc.). The proposed method can be used in pharmaceutical research, process control in the production of nanomaterials.

Conclusion: electrochemical action of Fe<sub>2</sub>O<sub>3</sub> nanoparticles by solid-phase voltammetry was studied; a voltammetric method for identification and quantitative determination of solid-phase Fe<sub>2</sub>O<sub>3</sub> nanoparticles and a technique of their determination in real objects have been developed..

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#### References

- Shtansky DV. Transmission electron microscopy of high resolution in nanotechnology research. *Ros. chem. Well. (Russian J. of General Chemistry)* 2002; **XLVI**: 5-81-88.
- Chebanov VA Mironchenko SI. Methods and evaluation nanoparticle characterization in pharmaceutical. *The success of modern science*. 2014; **6**: 111-112.
- Belyakov, LD, Larionov OG, Revina AA Kolomic LN. Chromatography in the study of surface properties of nanomaterials, metal nanoparticles and nanocomposites. *Modern problems of physical chemistry of nanomaterials: Collection*. 2008:513-531.
- Chen Yao, Yu Xin-wei, Liu Jian-ping, Zhao Guo-peng, Peng Yuan-fang. Methods for determination of nanoparticles in composite coatings SiO. *Diandu yu tushi = Electroplat. and Finish* 2005; **24**: 4-27-29
- Shipilin AM Mossbauer spectroscopy of iron oxide nanoparticles. Author's abstract of dis. doctor of physical and mathematical sciences. Yaroslavl, 2000, p 37.
- TsurinVA., Ermakov AE., Uimin MA., Mysik AA., Schegoleva NN., Gaviko VS., Mike V. Investigation of structure and magnetic properties of nanocomposites based on iron and nickel encapsulated in carbon. *Fizika tverdogo tela* 2014; **56**:2-287-300
- Brainina HZ. Inversionnaya voltamperometriya tverdikh faz. Moskva: "Khimia", 1972
- Brainina K., Neyman E. Electroanalytical Stripping Methods. USA J. Wiley & Sons, 1993.
- Zakharchuk NF, Smirnov TP, Fedorov VN. Voltammetry solid phases in the diagnosis of solid materials. *Journal of Structural Chemistry* 2010; **51**:71-177.
- Scholz F., Meyer B. Voltammetry of Solid Microparticles Immobilized on Electrode Surface In: *Electroanalytical Chemistry, a Series of Advances / Eds. A, J. Bard, I, Rubinstein*. -New York: Dekker, 1998.
- Zakcharchuk NF, Meyer B., Henning H. et al. *J. of Electroanalytical Chem.* 1995.; **398**-23.
- Kaplin AA., Svishchenko NM Dubova NM, Slepchenko GB, Karbainov YA, Ivanov GF Identification of the superconducting properties YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6.5</sub> + X by voltammetry of solid phases. *J. of Analyt. Chemistry* 1991; **46**:5-976-980.
- Slepchenko GB, Gindullina TM, Cerempei EG, Hlusov IA, Shchukina TI, Feduschak TA. Development of voltammetric determination of iron and silver to assess the degree of degradation of nanoparticles based on them. *Bulletin of the Tomsk Polytechnic University*, **2011**; 318:346-49.