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## Voltammetric Determination of Manganese on Organo – Modified Electrodes

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### Abstract

The researches on the choice of aryldiazonium tosylate salts as a modifier to create an organo-modified electrode were carried out. It is shown that the best organic modifier for surface modification of a mercury-graphite electrode is aryldiazonium tosylate without a substituent. A method for producing an organo-modified electrode and the procedure for measuring the analytical signal of manganese by voltammetry was developed. The method is simple to implement and allows avoiding the use of metal mercury for forming the electrode, and making measurements without aerating of electrolyte by inert gases (nitrogen, argon) with an error (Sr) of not more than 10 %.

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*Keywords:* voltammetry, method, manganese, organo-modified electrode, aryldiazonium tosylates.

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### 1. Introduction

The global nature of today's environmental problems requires continuous monitoring of toxic substances in the environment. Manganese refers to the elements that are to be under ecoanalytical control, because its value of MPC ( $10^{-5}$  g/dm<sup>3</sup>) in natural and drinking waters is low. Although manganese is an essential element for normal development and functioning of the human body and animals, its excess affects the central nervous system, as well as has a mutagenic and teratogenic effect<sup>1</sup>. Meeting the challenges of monitoring requires the use of highly sensitive methods for the determination of standardized indicators of natural objects quality, as well as the creation of fast

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methods of operational control.

To control the manganese in the environment and in biological systems such techniques as spectrophotometry<sup>2</sup>, spectrofluorimetry<sup>3</sup>, atomic emission spectrometry with inductively coupled plasma (ICP-AES)<sup>4</sup>, atomic absorption spectrometry<sup>5,6</sup> etc. are used.

Voltammetry has a special place in the analysis of complex multicomponent systems. The method is relatively simple, characterizes by low detection limits and high selectivity of determination. Voltammetric procedures are widely used to determine  $Mn^{2+}$  in natural objects. Comparison of some voltammetric analytical procedures is given in<sup>7</sup>. Traditionally used mercury electrodes have several disadvantages in determining  $Mn^{2+}$ , such as low solubility of manganese in mercury, closeness of reduction potentials of  $Mn^{2+}$  and hydrogen ions, formation of intermetallic compounds<sup>8</sup>. Despite this, there is a fairly large number of studies on determination of  $Mn^{2+}$  on the stationary dropping mercury<sup>9-13</sup> and mercury film<sup>14-16</sup> electrodes.

The authors<sup>9</sup> developed a low-cost, rapid method for the determination of Mn(II) at the level of ppm in the medium of  $NH_4Cl-NH_4OH$  (pH 6.2), with the production of catalytic hydrogen waves with ammonium piperidine dithiocarbamate and ammonium morpholine dithiocarbamate. The methodology for determining manganese in marine waters, sediments of estuaries and mussel tissues by cathodic and anodic stripping voltammetry with a detection limit of  $1 \cdot 10^{-9}$  mol/l is described in<sup>10</sup>. The method of differential pulse stripping voltammetry was used to assess the contamination of soil with manganese<sup>11</sup>, the method of differential pulse polarography - for the analysis of industrial wastewater; linear operating range for manganese on the background of triethanolamine and KOH 1.5 -5.0 ng/ml<sup>12</sup>. A mercury film electrode is used to determine the amounts of nanomolar Mn(II) by anodic stripping voltammetry in natural<sup>13,14</sup> and drinking water<sup>15</sup>.

Currently, in voltammetry there is a trend of mercury electrodes displacement by the other ones made of non-toxic materials, mainly carbon. Although in some cases, mercury persists for modifying electrode mode «in situ», mainly based on glassy carbon electrodes, carbon-paste, graphite, including those obtained by screen-printing as well as thick film ones. For example, a mercury-graphite electrode was used for the determination of microamounts of Mn(II) in oceanic waters by cathodic stripping voltammetry<sup>16</sup>.

The use of a planar electrode of pyrolytic graphite provides a detection limit of 14.2 mmol/l in the determination of Mn in seawater by cathodic stripping voltammetry<sup>17</sup>; higher sensitivity of the determination was reached by the authors<sup>18</sup>, a technique used for the analysis of drinking water and natural water in Mn(II) concentration range of from 0.03 to 100 mg/l.

Analytical capabilities of microelectrode matrices, obtained using a screen-printing technology, are shown in the example of determination of nanomolar concentrations of  $Mn^{2+}$  by cathodic stripping voltammetry; the advantages as compared to using a standard carbon electrode are shown<sup>19</sup>.

Glassy carbon electrodes (GCE) have low adsorptivity as compared with other carbon materials that explains the relatively low sensitivity of the assay with unmodified electrodes. As modifiers of GCE metals, organic substances, biologically active substances, polymers, nanomaterials are used<sup>20</sup>. Thus, the glassy carbon electrode modified with silver amalgam is used for the analysis of samples of water and soil ( $C_{min} = 9 \cdot 10^{-8}$  mol/l) by differential pulse stripping voltammetry<sup>21</sup>. Mercury film electrode modification allowed reaching the detection limit of manganese  $6 \cdot 10^{-8}$  mol/l (differential pulse anodic inversion voltammetry) and  $8 \cdot 10^{-8}$  mol/l (square-wave inversion voltammetry)<sup>22</sup>; the detection limit of manganese on the modified bismuth film electrode was 0.001 mg/l (differential pulse voltammetry)<sup>23</sup>. GCE modified with fullerene  $C_{60}$  and  $Li^+$  ions, are used for determination of manganese at  $10^{-8}$  mol/l in seawater and blood cyclic voltammetry<sup>24</sup>.

The authors<sup>25</sup> developed a method for determination of manganese on a diamond doped with boron electrode by cathodic stripping voltammetry; the range of linearity is  $1 \cdot 10^{-11}$  -  $3 \cdot 10^{-7}$  mol/l; the technique was used in the analysis of tea samples; in later studies<sup>26</sup>, this method was used in the analysis of marine sediments and showed good selectivity and detection limit. Mercury-free thick-film graphite electrode modified with formazan was proposed to determine  $Mn^{2+}$  by cathodic stripping voltammetry. The detection limit of  $Mn^{2+}$  with that electrode was 0.04 g/l<sup>27</sup>. On the basis of formazan derivative a mercury-free voltammetric sensor, used for the analysis of drinking and natural waters, was created<sup>28</sup>.

Compared with glassy carbon electrodes carbon -paste electrodes exhibit enhanced adsorption capacity for many substances that is successfully used in voltammetry in determining inorganic ions. Introduction to a paste of the electrode or immobilization of compounds containing metal ions increases selectivity and sensitivity of the detection<sup>19</sup>. Rotating disc of the carbon-paste electrode is used for determination of manganese by differential pulse cathodic stripping voltammetry in polluted river water; the detection limit is  $4 \cdot 10^{-9}$  mol/l (0.2 mg/l)<sup>29</sup>. The authors

of<sup>30</sup> as a reagent-modifier of CPE 1-(2-pyridylazo)-2-naphthol is used; the technique of determining Mn(II) in seawater with a detection limit of  $6.9 \cdot 10^{-9}$  mol/l (0.38 ppb) by differential pulse cathodic stripping voltammetry. By cathodic square-wave adsorption voltammetry analytical characteristics of the method for determining Mn(II) was established. The method was completed with 8-hydroxyquinoline, unmodified CPE and the electrode modified with montmorillonite; the detection limits were 45 ng/l ( $8.19 \cdot 10^{-10}$  mol/l) and 1.8 ng/l ( $3.28 \cdot 10^{-11}$  mol/l), respectively. This method has been successfully applied to identify different types of manganese in water<sup>7</sup>.

Despite the success, the search for new electrode materials and reagents-modifiers providing the required level of analytical and metrological parameters of electroanalysis is still relevant. One of the classes of compounds useful for modifying the voltammetric electrodes are toluene-sulfonic acid derivatives. Examples of the methods of voltammetric determination of both organic substances and inorganic ions are known. A sensor based on GCE modified with tosylates has been developed to determine fungicides of triclosan and benzophenone<sup>30</sup>. Aryldiazonium tosylates were successfully used as reagents-modifiers electrodes for determination of organic compounds (soluble vitamins B and C, flavonoids), metals (copper, iron, nickel, etc.), nonmetals (selenium and iodine) by anodic stripping voltammetry in different types of water, food<sup>31</sup>. So it seemed promising to use organo-modified electrodes for determination of manganese.

## 2. Objective

Select the conditions for obtaining an organo-modified electrode using aryldiazonium tosylate salts as a modifier for determination of manganese and to develop the methods of measuring by voltammetry.

## 3. Experiment

Measurements were made on the voltammetric analyzer "STA" ("ITM", Tomsk) in the presence of dissolved oxygen in the background electrolyte.

Along with various backgrounds mentioned in literature, we have selected an ammonium acetate-buffer (pH 9.18), as it is widely used to determine the manganese on carbon-containing electrodes<sup>21</sup>.

Model solutions were prepared from certified mixtures that were obtained by serial dilution of base solutions in double distilled water. As the base solutions the state standard samples of aqueous solutions of  $Mn^{2+}$  with the certified value of the mass concentration of 1.0 g/dm<sup>3</sup> were used.

The aryldiazonium tosylates  $ArN_2^+OTs^-$  with different substituent groups: -COOH, -NO<sub>3</sub> and -NH<sub>2</sub> were used as modifiers<sup>19</sup>.

To determine  $Mn^{2+}$  by voltammetry the modifier was applied to the surface of graphite electrode (GE) electrochemically or by exposing the electrode in aqueous solution of tosylates aryldiazonium salt at a room temperature.

Reference electrode and supporting electrode were silver/silverchloride electrodes in the potassium chloride solution with concentration of 1.0 mol/dm<sup>3</sup> and resistance not more than 3.0 kOhm.

Mass concentration of  $Mn^{2+}$  was calculated by the method of certified mixtures addition.

## 4. Results and Discussion

Modification of GE was performed in two ways: by keeping the electrode in aqueous solution of tosylates aryldiazonium salt at a room temperature for a certain time or electrochemically at  $E_e = -1.9$  V. Then, the obtained organo-modified graphite electrode (OME) was washed with distilled water.

Unfortunately, we failed to obtain the analytical signal for  $Mn^{2+}$  on OME modified under those conditions.

Taking into account the fact that the analytical signal of  $Mn^{2+}$  depends on the amount of mercury on the surface of the electrode, the further modification of OME with mercury was carried out. That allowed obtaining the analytical signal. Experimental dependence of the  $Mn^{2+}$  peak current on the concentration of  $Hg^{2+}$  applied to the surface of OME is showed in Figure1.

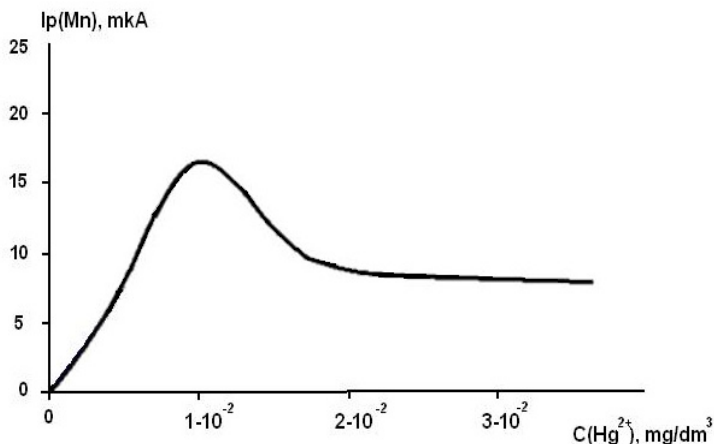


Figure.1. Dependence of peak current of manganese on the concentration of mercury in the solution. background solution - ammonium acetate-buffer (pH 9.18);  $E_c = -1.9$  V;  $C(\text{Mn}^{2+}) = 0.1$  mg/dm<sup>3</sup>;  $\tau_c = 60$ s.

As it can be seen in Fig. 1, the maximum value of the analytical signal of  $\text{Mn}^{2+}$  corresponds to the condition when the deposition of mercury from the solution with  $C(\text{Hg}^{2+}) = 1 \cdot 10^{-2}$  mol/dm<sup>3</sup> and  $\tau_c = 60$ s in mode «ex situ» is carried out. When the concentration or mercury accumulation time increase the analytical signal of  $\text{Mn}^{2+}$  decreases. Thus, for creating of OME the following conditions were selected:  $C(\text{Hg}^{2+}) = 1 \cdot 10^{-2}$  mol/dm<sup>3</sup>, in mode «ex situ».

A comparison of calibration dependences of obtained in «in situ» mode with addition of  $\text{Hg}^{2+}$  directly to the electrolytic cell at the concentration of  $2 \cdot 10^{-2}$  mol/dm<sup>3</sup> and preliminary application of  $\text{Hg}^{2+}$  in «ex situ» mode  $C = 1 \cdot 10^{-2}$  mol/dm<sup>3</sup>,  $\tau_c = 60$ c was carried out (Fig. 2).

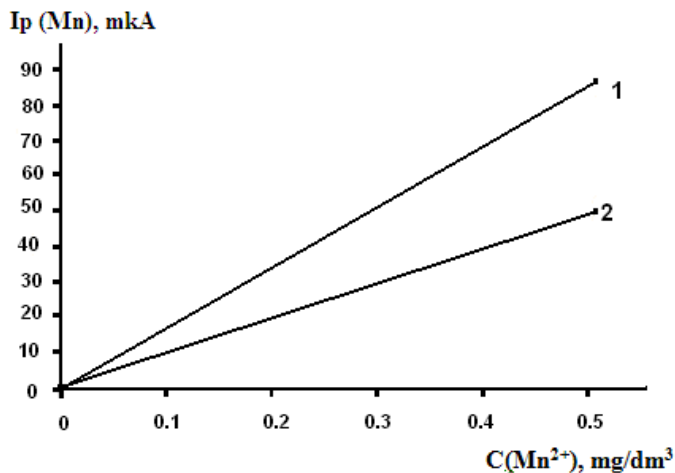


Figure.2. Calibration dependences of  $\text{Mn}^{2+}$  on OME with application of mercury in modes «ex situ» (1) and «in situ» (2).

As it can be seen from Fig. 2, the sensitivity of OME with application of mercury obtained in «ex situ» mode is about 1.5 times higher (Figure 2, Figure 1). So, for further study that mode was used.

The study on the development of the method of modifying the surface of a graphite electrode containing  $\text{Hg}^{2+}$  with tosylates aryldiazonium salts. To achieve the goal we have obtained the dependence of the  $\text{Mn}^{2+}$  peak current on the time of modification ( $\tau_m$ ) and the concentration of modifier solution ( $S_{Ar}$ ). The results are presented in Table 1.

Table 1. Dependence of  $\text{Mn}^{2+}$  peak current on the concentration of modifier in solution and the time of mercury-graphite electrode surface modification.

$\tau_M, s$	2	7	9	11	15
$C_{Ar}, \text{mg/dm}^3$	0.05	0.1	0.3	0.4	0.5
$I_p(\text{Mn}), \text{mkA}$	$0.34 \pm 0.05$	$0.58 \pm 0.9$	$0.24 \pm 0.04$	$0.18 \pm 0.03$	$0.021 \pm 0.003$

Table 1 shows that the concentration of the organic modifier of  $0.1 \text{ mol/dm}^3$  and exposure time of 7 s. are the best conditions for obtaining OME. It has been established that a further increase in the concentration of the modifier reduces the analytical signal of  $\text{Mn}^{2+}$ . This effect can be explained by the fact that with increasing the concentration of diazonium salts there occurs the formation of multilayer coatings and less durable electrode surface coating with organic fragments.

It has been found that the  $\text{Mn}^{2+}$  peak current and the range of linearity of calibration curves do not depend on the method of modification (immersion or electrochemical). Therefore, further, OME was prepared by immersing the process surface of GE in an aqueous solution of the organic modifier.

Investigations of the effect of modifier solution with various substituents in tosylates aryldiazonium salts on the analytical signal of  $\text{Mn}^{2+}$  were carried out.

Figure 3 shows the calibration curve of  $\text{Mn}^{2+}$ , obtained by OME using modifiers with various substituents (curves 1,2,4,5) and mercury film electrode (curve3), which is widely used in national standards.

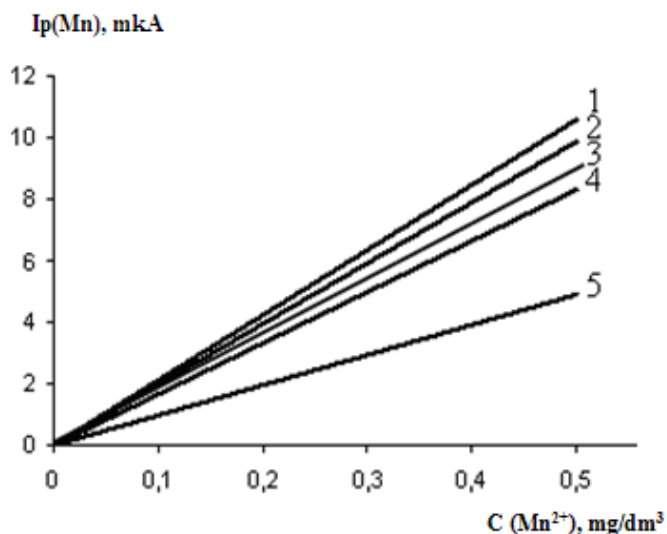


Figure.3. Calibration dependences for  $\text{Mn}^{2+}$  on OME with mercury application:  
background - ammonium-acetate buffer with pH 9.18;  $C(\text{Hg}^{2+}) = 1 \cdot 10^{-2} \text{ mol/dm}^3$ ;  $C(\text{Mn}^{2+}) = 0.1 \text{ mg/dm}^3$ ,  $\tau_c(\text{Mn}) = 120 \text{ s}$ ,  $E_p = -1.9 \text{ V}$ ;  
1 - OME without substituent ; 2 - OME – COOH; 3 - OME – MGE; 4 – OME –  $\text{NH}_2$ ; 5 – OME –  $\text{NO}_2$ .

OME, without substituent and substituted with COOH group, and MFE are within an error of 10-12% and are preferred for the use in analytical practice. Unfortunately, OME using a modifier with  $\text{NO}_2$  substituent is inferior by its sensitivity to the rest of electrodes.

A series of experiments, showing the effect on  $\text{Mn}^{2+}$  analytical signal by the sequence of diazonium salts and  $\text{Hg}^{2+}$  application to GE was carried out.

The studies have found that the prior application of  $\text{Hg}^{2+}$  to GE followed by the modification with aryldiazonium tosylate  $\text{Hg-GE-ArN}_2^+ \text{OTs}^-$  is the best option to create OME. This conclusion is based on the curves shown in Figure 4.

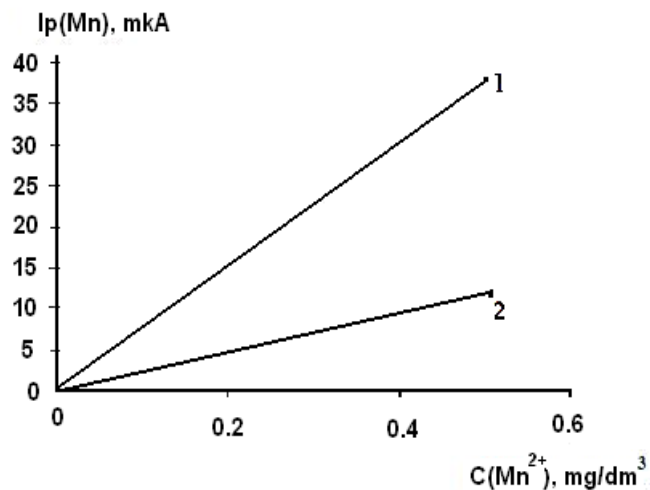


Figure. 4. Calibration dependence of  $\text{Mn}^{2+}$  on OME:

1 - Hg-ET- $\text{ArN}_2^+\text{OTs}^-$ ; 2 -  $\text{ArN}_2^+\text{OTs}^-$ -GS-Hg;

Conditions: background - ammonium acetate buffer pH = 9.18;  $C(\text{Mn}^{2+}) = 0.1 \text{ dm}^3$ ;  $\tau_c(\text{Mn}) = 120\text{s}$ ;  $E_c(\text{Mn}) = -1.9 \text{ V}$ .

As can be seen from Figure 4, the angle coefficient of dependence 1 is 1.5 times more for the electrode with the order of application of Hg-ET- $\text{ArN}_2^+\text{OTs}^-$ .

Based on these results, the method of OME obtaining and the technique of VA- measurements of  $\text{Mn}^{2+}$  were proposed.

The method for obtaining OME is as follows:

The GE surface is sanded with filter paper before modification procedure. Then, the accumulation of mercury is conducted:  $C(\text{Hg}^{2+}) = 1 \cdot 10^{-2} \text{ mol/dm}^3$  at a potential of  $-1.9 \text{ V}$  for 60 s. The prepared substrate is maintained in  $0.1 \text{ mol/dm}^3$  of a diazonium salt solution with no substituent at a room temperature for 7 s. After that the modified electrode is washed with double distilled water. Obtained under these conditions OME is stable for two days. VA-measurement technique is based on the accumulation of  $\text{Mn}^{2+}$  at electrolysis potential of  $E_c = -1.9 \text{ V}$  on the background of ammonium-acetate buffer (pH 9.18) with the subsequent registration of the anodic peak potential at a scan rate of  $50 \text{ mV/s}$ .  $\text{Mn}^{2+}$  ion concentration is determined by a certified mixture addition at the peak current in the range of potentials ( $-1.4 \div -1.5$ ) B. Figure 5 demonstrates voltammograms of  $\text{Mn}^{2+}$  obtained under these conditions.

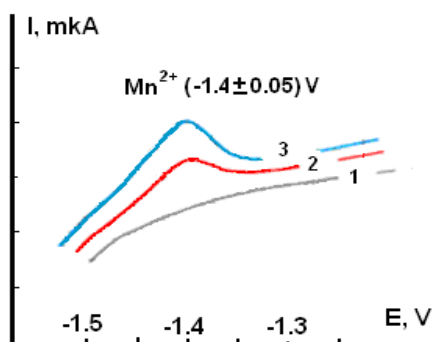


Figure.5. Voltammograms of  $\text{Mn}^{2+}$  on OME:

1 - a supporting electrolyte : ammonium acetate- buffer; pH 9.18;  
2 -  $C(\text{Mn}^{2+}) = 0.1 \text{ mg/dm}^3$ ; 3 -  $C(\text{Mn}^{2+}) = 0.2 \text{ mg/dm}^3$ ;  $E_c = -1.9 \text{ V}$ ;  $\tau_c = 120\text{s}$ .

As can be seen (Figure 5, curve 2), a well-defined analytical signal of  $\text{Mn}^{2+}$  at a potential of  $E = -1.4 \text{ V}$  is

observed on the voltammogram. When the introduction of certified mixture additives, the analytical signal of  $Mn^{2+}$  increases proportionally to introduced concentrations (Figure 4, Figure 3), that indicates the ability to quantify manganese.

It was found that accompanying elements such as Zn, Cd, Tl, Cu, etc., and several anions ( $S^{2-}$ ,  $Cl^{-}$ ) do not interfere with the analytical signal of  $Mn^{2+}$ .

The validation procedure was carried out on model solutions by the method of certified mixture additives (Table 2).

Table 2. Results of voltammetric determination of manganese on OME in model solution and potable water and their validation ( $P = 0.95$ ),  $n = 2$ .

Sample	Content of $Mn^{3+}$ , mg/dm <sup>3</sup>		
	Test	Added	Obtained
Model solution	Less than 0.05	0.40	0.38±0.07
Potable water	0.32 ±0.06	0.40	0.74±0.16

These studies provide the process of producing a new type of organo-modified electrode and the method for voltammetric determination of  $Mn^{2+}$ . The method is simple to perform and, unlike<sup>22-25</sup>, avoids the use of metallic mercury for electrode formation, as well as making measurements without aeration of electrolyte by inert gases (nitrogen, argon) with an error (Sr) of not more than 10%.

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