

The Galvanostatic Reduction on Modified Platinum Electrode and Determination of Trinitrotoluene in Neutral Solution

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Received: 8 July 2012 / Accepted: 2 January 2013 / Published: 1 February 2013

The study of the electrochemical reduction on acetonitrile modified platinum electrode and determination of trinitrotoluene (TNT) in neutral solution by simple galvanostatic technique is presented here. The obtained potential-time responses on the applied constant cathodic current pulses showed two potential transitions before achieving the steady-states, referring to the multi-step reduction process of nitro groups in TNT molecule. The calibration curves of the dependence of the square root of the first transition time ($\tau^{0.5}$) on the TNT concentration were linear in the ranges 4.4 – 303.8 μM and 0.09 – 4.40 μM for applied constant current of 0.1 mA. The detection limit was 0.09 μM . The method was tested in the river water. The results indicated the sensitivity of the galvanostatic method for TNT determination in the environmental samples. From the first transition on the E-t curves the characteristics important for the understanding the mechanism of the reduction process were obtained. It was found that four electrons are involved in the reduction process of the first nitro group, indicating that the reduction product in a neutral electrolyte is hydroxylamine.

Keywords: trinitrotoluene detection; galvanostatic technique; acetonitrile modified platinum electrode

1. INTRODUCTION

Trinitrotoluene, as a nitroaromatic compound, can be reduced electrochemically due to the fact that the nitro-groups are excellent electron acceptors [1]. The reduction of TNT occurs in three steps in accordance with the three nitro-groups in the aromatic molecule [2].

The reduction of nitro compounds plays an important role in the development of organic electrochemistry. The nitro group is one of the most easily reducible groups. In aqueous solutions nitro compounds are reduced to the corresponding hydroxylamines or amines by an irreversible four- or six-electrons process that proceeds through nitroso intermediates. Nitroso intermediates are not stable on the electrode surface because their reduction potential is more positive than that of the initial nitro compounds. The reduction involves adsorption of reactants and intermediates followed by direct electron-exchange mechanism on most cathodes, except of platinum on which the reduction proceeds by an electrocatalytic hydrogenation mechanism [3]. Interesting catalytic effects were found for the reduction of aromatic nitro compounds on Pt surfaces modified by Pb, Tl and Bi UPD adlayers in aqueous solutions [4-6]. On clean platinum the reduction of nitro compounds occurs in the potential region where hydrogen is evolved and no separate well-formed reduction waves are obtained. On the Pt/M (UPD) the reduction begins at more positive potentials and diffusion-controlled limiting currents are obtained. Generally, the catalysis of the reduction of nitro compounds was attributed [4] to the change of nitro group reduction mechanism from catalytic hydrogenation on clean Pt to direct electron-transfer mechanism on Pt surface, covered by the UPD adlayers, as on metals with high hydrogen overvoltage.

During our voltametric investigation of TNT reduction on acetonitrile modified platinum electrode [7] it was observed that the hydrogen evolution reaction on platinum electrode was inhibited by the presence of acetonitrile in solution, allowing Pt electrode to be more negatively polarized in the potential region where TNT reduction occurred.

Electrochemical procedures involving various electrochemical methods [2,7-21], as well as electrode materials [2,4-12] were developed for the detection of TNT in water [7-14], soil [16] and the gaseous phase [17]. The state-of-the-art in electrochemical sensing of explosives has recently been reviewed by Wang [19].

To the best of our knowledge, the investigation of the electrochemical reduction and determination of TNT by means of galvanostatic technique has not been investigated so far.

In previous voltametric examination of TNT reduction it was shown that TNT could be successfully detected and quantitative determined by Pt electrode modified by acetonitrile which was reductively chemisorbed at Pt surface [21,22]. This electrode was prepared by cycling potential in an electrolyte which contained acetonitrile (as a solvent for TNT) [7]. Such a "chemically modified Pt electrode" exhibited electrochemically stable behavior for the TNT reduction process. Also, voltametric investigation indicated that the reduction process was irreversible and diffusion controlled.

In this study, galvanostatic technique have been applied in order to find a still simpler method for TNT determination, as well as to further clarify the electrochemical process of trinitrotoluene reduction in neutral solution on the acetonitrile modified platinum electrode. This technique provides some advantages such as high sensitivity, a wide linear range, rapid response, low cost of the instrumentation and simplicity. The application of this method for study of reduction of TNT can give new additional possibilities for understanding of the process and in the combination with existing methods (as are CV, SWV and so on) better qualitative and quantitative results can be expected. Under galvanostatic condition for an irreversible and diffusion controlled process the *Sand equation* [23] can be applied to determine the number of the electrons which take part in the reduction process (n). The

measured value of the transition time (τ) at known applied current (i), (or the values of $i\tau^{0.5}$ obtained at various currents) can also be used to determine the electrode surface area, the coefficient of diffusion and the initial concentration [23].

The results obtained in the present study were validated with HPLC [24, 25].

2. EXPERIMENTAL

All solutions were made with analytical grade chemicals and Milli-pure water. In all the experiments the supporting electrolyte was 0.5 M sodium chloride solution. Due to the limited solubility of TNT in water [26], sample solutions (50 mL) of between 0.09 – 303.8 μM TNT were prepared by adding an appropriate amount of previously prepared 1000 mgL^{-1} or 3000 mgL^{-1} solution of TNT dissolved in acetonitrile (HPLC grade) into the supporting electrolyte maintaining an approximately constant concentration of 5 vol% of acetonitrile throughout the experiments. The sample solutions were placed in a conventional 3-electrode electrochemical glass cell, with a Pt wire of 0.32 cm^2 surface area as the working electrode, a spiral Pt wire as the counter electrode and a standard Ag/AgCl (3M KCl) electrode as the reference.

The concentrations of the sample solutions were checked by HPLC analysis. The HPLC measurements were carried out with HP 1081 series HPLC system with UV detection at 254 nm. The stationary phase was an Eurospher RP-18, 250 mm x 4.6mm i.d. cartridge packed with 5 μm particles (Fa. Knauer, Berlin, Germany). The column was kept at 30°C. A mobile phase consisting of 50% water, 38% methanol and 12% acetonitrile (vol %) was used at a flow rate of 1.5 ml/min. For the external calibration, at least three replications were performed for each standard concentration. The mean value was then used for calibration curve.

Before performing the experiments, the cell with electrodes were cleaned in acetone and washed in distilled water. Cyclic voltammetry in 0.5 M H_2SO_4 was applied to electrochemically polish the Pt electrode and to check the state of the electrode surface until a voltammogram with hydrogen adsorption and desorption peaks characteristic for a Pt electrode in H_2SO_4 was obtained. The potential was cycled from -0.2 to 1.0 V using a 200 mVs^{-1} scan rate.

An acetonitrile modified platinum electrode was prepared by cycling the potential from -0.85 to 1.0 V with 200 mVs^{-1} scan rate in the supporting electrolyte (0.5 M NaCl) with 5 vol% of acetonitrile [7].

Additionally, the river water, which was only filtered, was used for testing the method in natural media. pH of the river water was 7.6 ± 0.2 , which was close to $\text{pH } 7.0 \pm 0.2$ of a supporting electrolyte.

The galvanostatic pulse method was used. Current pulses have been obtained from a potentiostat / galvanostat (PAR M173) with a programmer (PAR 175). Time responses of the potential have been recorded on a memory scope (Nicolet Instrument Corp.) and subsequently transferred onto an X-Y-t recorder (Houston Instrument 2000R).

Examination of the reduction process was carried by applying constant current pulses from 0.04 to 1.4 mA for a period of 2ms to 20s depending on the concentration of TNT in the electrolyte (with 1 μ s – 5ms interval between the recorded points).

The electrode was held at the open circuit potential for 30 minutes before each experiment in electrolytes without and with TNT.

In some cases, the electrolyte was purged free of oxygen by bubbling with highly purified nitrogen for 30 minutes prior to the galvanostatic measurements. All experiments were performed at room temperature (25 °C).

All measurements are repeated at least three times and a high degree of reproducibility was found in replicated experiments.

3. RESULTS AND DISCUSSION

3.1. TNT reduction process

When TNT was present in the solution, two transitions of the potential were recorded leading to higher steady-state polarization level. For the higher concentration range, reaching steady-states took few seconds , while at lower concentration range (up to 4.4 μ M) that was accomplished after few ms. It should be emphasized that no transition was observed on the potential-time response on the constant current pulse obtained in the basic electrolyte without TNT and the steady-state was reached in a few ms.

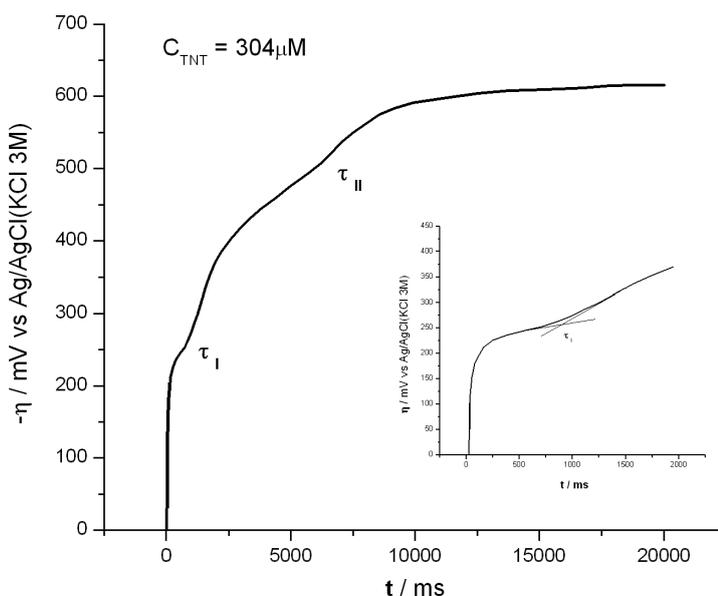


Figure 1. The E-t response on the constant current pulse (0.1mA) obtained in the basic electrolyte (0.5 M NaCl with acetonitrile) containing 304 μ M of TNT. Inset of the Fig.1 shows the way of the transition time determination.

The cathodic galvanostatic transients for TNT reduction in basic electrolyte (0.5 M NaCl with acetonitrile) with TNT obtained by applying the constant current pulse of 0.1mA, are presented on the Fig.1 for the TNT concentrations of 304 μ M as an example. The obtained E-t curve, as the response on the constant current pulse, showed two distinct transitions (with transition times τ_I and τ_{II}) before the steady-state was achieved, which refer to multistep process of TNT reduction. Reaching steady-state took 15sec. The first transition time (τ_I), corresponding to the reduction of the first nitro group, is particularly useful for quantitative work; its square root ($\tau_I^{0.5}$) is proportional to the TNT concentration [23]. Because of that, the first transition is presented on the following figures. The determination of the transition time, τ_I , is shown as an inset of the Fig.1.

3.2. TNT determination in the samples solutions

3.2.1. The calibration plot construction

Galvanostatic study of TNT reduction on the acetonitrile modified Pt electrode in the neutral electrolyte was performed with the aim to obtain a calibration plot for its quantitative determination.

The E-t responses on the constant current pulse (0.1mA) obtained in the basic electrolyte (0.5 M NaCl with acetonitrile) containing different concentrations of TNT are presented on the Fig.2.

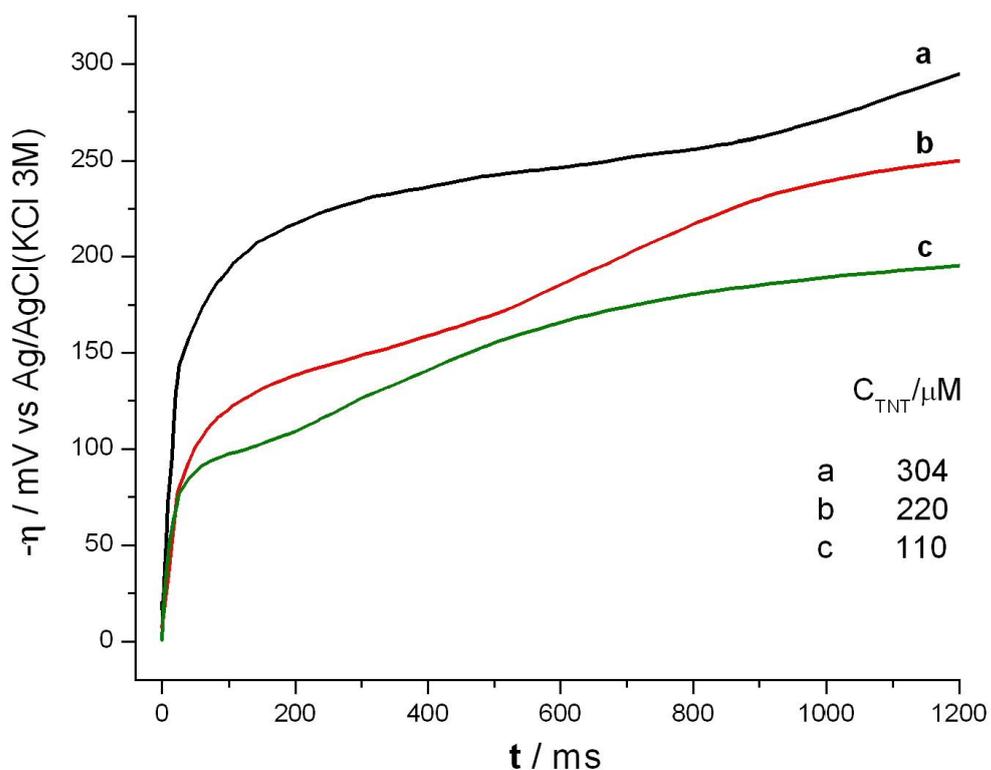


Figure 2. The E-t responses on the constant current pulse (0.1mA) obtained in the basic electrolyte (0.5 M NaCl with acetonitrile) containing different concentrations of TNT.

The first transition time for a given concentration was determined from the corresponding E-t curve, and the obtained values are given in the Table 1. The linear dependence of the square root of the first transition time ($\tau_1^{0.5}$) on the TNT concentration was obtained in the range 4.4 – 303.8 μM , as shown in the Fig.3.

Table 1. The first transition times (τ_1) determined from E-t curves obtained for the different TNT concentrations

N_0	$C_{\text{TNT}}/\text{mgL}^{-1}$	$C_{\text{TNT}}/\mu\text{M}$	τ_1/ms
1	0.02	0.09	0.56
2	0.05	0.22	0.64
3	0.20	0.88	0.81
4	0.60	2.64	1.44
5	1.00	4.40	2.25
6	2.50	11	5.76
7	5.00	22	16.00
8	10.00	44	33.64
9	25.00	110	144
10	50.00	220	484
11	69.00	304	900

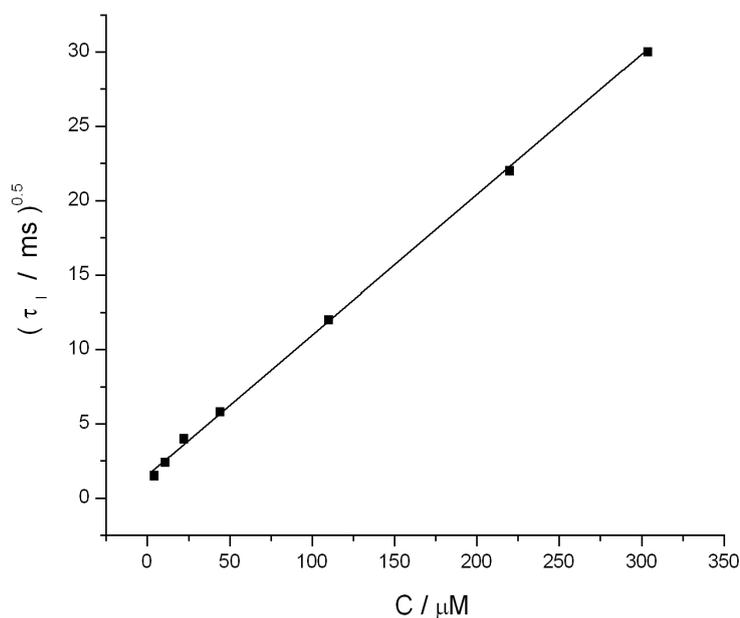


Figure 3. The dependence of the square root of the first transition time ($\tau_1^{0.5}$) on the TNT concentration in the range of 4.4 – 304 μM ; the coefficient of determination, R^2 , is 0.9995.

3.2.2. The detection limit determination

The detection limit was determined by reducing the concentration of TNT in the solution below 4.4 μM . The time scale was 3.5ms (with 1 μs interval between recorded points).

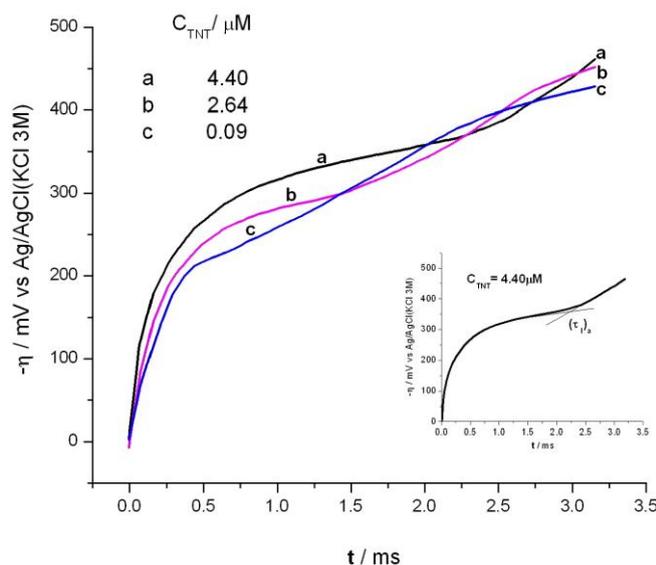


Figure 4. The E-t responses on the constant current pulse (0.1mA) obtained in the basic electrolyte (0.5M NaCl with acetonitrile) containing 0.09 – 4.40 μM of TNT. Inset shows the way of the transition time determination.

Table 2. Review of recent literature data on the electrochemical determination of TNT obtained under different experimental conditions

Ref. No.	Technique	Electrode Material	Supported Electrolyte	Linear Range	Detection Limit(μM)
7	CV	AcN modified Pt	a)0.5M NaCl + can b) river water+AcN	0.11 – 4.40 μM 4.4 – 638.4 μM	0.11
9	CV SWV	Glassy-Carbon	0.1M tetrabutyl ammonium bromide+AcN	38-139 ppm	4.4
15	CV	Core-shell Sn(C)	0.5M NaCl+AcN	1-20 ppm	
14	SWV	Carbon-fiber	Sea water +AcN		1.76
32	Electrophoresis	Electroless deposited gold	0.1M HClO ₄		0.11
11	SWV	Boron doped diamond	a) KCl 0.5M+AcN 5 vol% b) sea water + AcN 1 vol%	a) 0.12-2.38mgL ⁻¹ 11-219 μgL ⁻¹ b) 25-396 μgL	~0.04 0.11
18	Electrochem. Impedance	Pt mod. anthracene	10mM KCl		
12	SWV	Screen-printed Carbon	a) 0.05M phosphate buffer (pH 6.5) b) river water	a) 1-10 ppm	0.88
33	Amperometric detection	Microchip Carbon electrode	a) 15mMborax+15mMsodium dodecylsulfate b) river water+15mMborax+15mM sodium dodecylsulfate	0-5 ppm	0.05-0.23
2	SWV	Carbon-fiber	a) 0.01 phosphate buffer (pH 7.4) b)river water	b) 0.2-2.0 mgL ⁻¹	0.88
13	SWV	Carbon-fiber	a) sea water b) river water+AcN	a) 0.25-2.90 mgL ⁻¹ b) 0.5-5.0 mgL ⁻¹	0.11

When the concentration was 0.09 μM , the first transition on the potential-time curve was still pronounced, as can be seen from the Fig.4. The linear dependence of the square root of the first transition time ($\tau_1^{0.5}$) on the TNT concentration was also obtained, as shown in the Fig.5, indicating the possibility of detection and quantitative determination of TNT at very low concentrations. On the basis of these observations we can estimate that detection limit is as low as 0.09 μM .

This is in agreement with the value of 0.10 μM , calculated by the calibration plot method [27]. The detection limit of 0.09 μM , which was obtained by galvanostatic pulse technique is for about 18% lower value than one of 0.11 μM which had been obtained by cyclic voltammerty investigation in our previous study [7] and is rather low and comparable with the best values cited in the literature (Table 2).

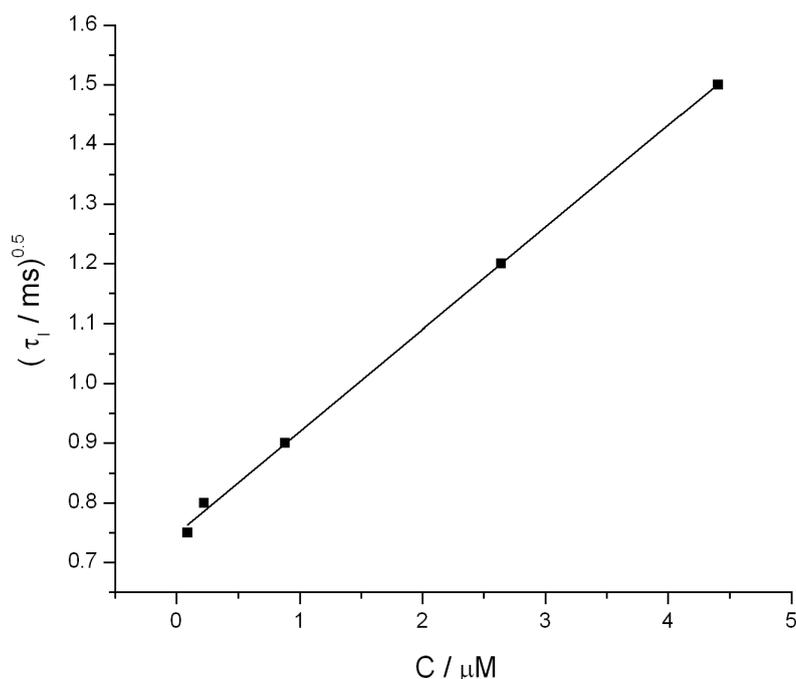


Figure 5. The dependence of the square root of the first transition time ($\tau_1^{0.5}$) on the TNT concentration in the range of 0.09 – 4.40 μM ; the coefficient of determination, R^2 , is 0.9994.

3.3. TNT detection in river water

As it is determined in previous work [7], the Pt electrode becomes stable with the addition of 0.5vol% of acetonitrile in river water. Therefore, the solution containing 0.5 vol% of acetonitrile in river water was used as the basic electrolyte for TNT reduction investigation. As the river water samples did not contain any TNT, they were spiked with different concentrations of TNT (given in the Table 3) and analyzed.

Result of the testing of TNT reduction on the acetonitrile modified Pt electrode in river water containing TNT is presented on the Fig.6 for TNT concentration of 220 μM as an example. The first

transition time for the given concentration of TNT was determined from the E-t curve (Fig.6). The concentration of TNT in the river water sample was checked by using the calibration plot for the whole concentration range (Fig.3 and Fig.5 together) and the obtained value of the transition time from the Fig.6. The same procedure was applied for the other lower concentrations and results were given on the Fig.7 and the Table 3. As can be seen (Fig.7), good agreement was achieved. Since the first transition on the potential-time curve was still pronounced even for small concentration of 0.22 μM , it can be confirmed that TNT can be successfully detected in river water.

Table 3. Recoveries of TNT in river water

Sample	The amount of TNT added (μM)	The amount of TNT detected (μM)	Recovery (%)
1	0.22	0.21	95.4
2	2.64	2.52	95.4
3	22.0	21.0	95.4
4	110	105.7	96.1
5	220	219.8	99.9

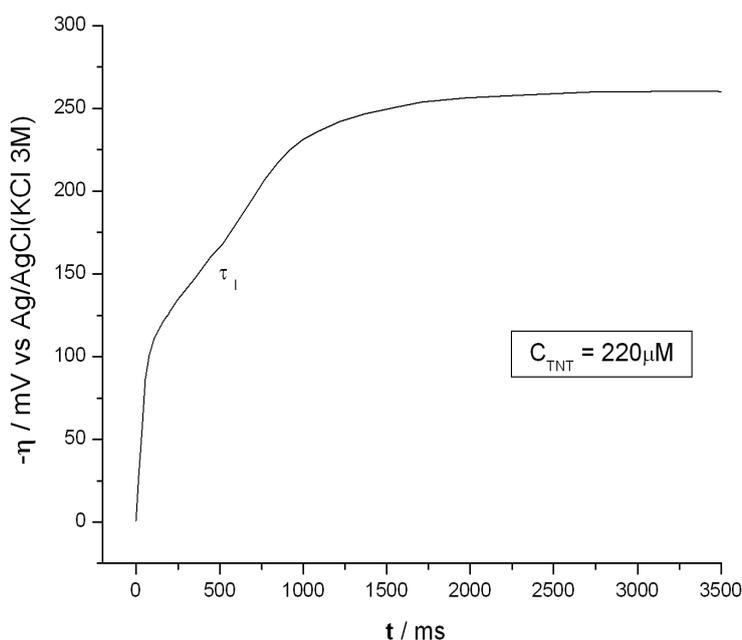


Figure 6. The E-t response on the constant current pulse (0.1mA) obtained in river water with 0.5vol% of acetonitrile containing 220 μM of TNT.

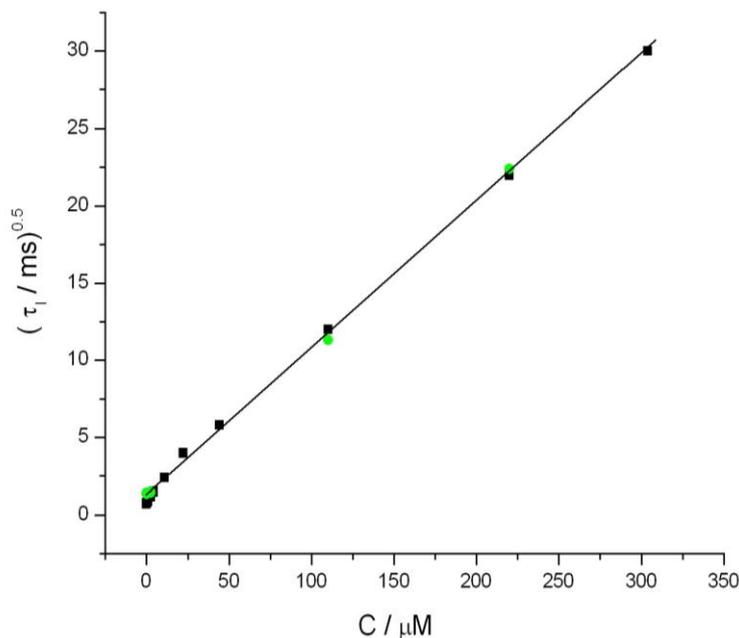


Figure 7. The calibration plot as dependence of the square root of the first transition time ($\tau_1^{0.5}$) on the TNT concentration in the range of $0.09 - 308\mu\text{M}$, with experimental points obtained in the river water (\bullet); the coefficient of determination for the experimental points obtained in the river water, R^2 , is 0.9992.

As shown in the Table 3, the average recoveries ranged between 95.4% and 99.9%. The results demonstrated that this method could be applied for the TNT determination in the river water.

3.4. Determination of the number of the electrons which take part in the reduction process - Electron transfer number (n)

Electron transfer number (n) is the basic parameter of an electrode reaction which provides an additional understanding towards the electrochemical process. In the case of TNT reduction process electron transfer number is usually four or six depending on the conditions employed for the reduction process [1,10,15].

By voltametric examination it was shown that the reduction of TNT in neutral solution on acetonitrile modified platinum electrode was irreversible and diffusion controlled process [7]. Under galvanostatic condition for an irreversible and diffusion controlled process the *Sand equation* [23] can be applied for determination of the number of the electrons which take part in the reduction process. The calculated values obtained for different concentrations of TNT and applied constant current of 0.1mA are given in the Table 4.

The *Sand equation*:

$$\frac{i\tau^{0.5}}{C_0} = \frac{nFAD^{0.5}\pi^{0.5}}{2} \quad (1)$$

The number of the electrons which take part in the reduction process (n):

$$n = \frac{2i\tau^{0.5}}{C_0 FAD^{0.5}\pi^{0.5}} \quad (2)$$

Where are:

i – current (A)

τ – the transition time (s)

C_0 – concentration (mol cm⁻³)

n – the number of the electrons

A – electrode surface (cm²)

F – the Faraday constant; charge on one mol of electrons (C)

D – the diffusion coefficient (cm² s⁻¹)

Table 4. The number of the electrons which take part in the reduction process of the first nitro-group in TNT molecule

Sample	TNT concentration (μM)	The first transition time(τ ₁) (ms)	The electron transfer number (n)
1	44	28.1	4.45
2	110	144	4.03
3	220	484	3.69
4	304	900	3.65

The calculated average value of the *electron transfer number* (n) is 3.96. It can be concluded that four electrons are involved in the reduction process of the first nitro group in TNT molecule indicating that the reduction product in a neutral electrolyte was hydroxylamine.

3.5. Determination of the coefficient of diffusion

The average measured value of the *transition time constant* ($i\tau^{0.5}/C_0$) obtained at various currents (from 0.04 to 1.4 mA) and TNT concentration of the 110 μM was used to determine the *coefficient of diffusion*. As can be seen in the Table 5, the obtained *transition time constant*, $i\tau^{0.5}/C_0$ is independent of i , which is case of well-behaved system. The calculated value of the *coefficient of diffusion* using the *Sand equation* and $i\tau^{0.5}/C_0$ from the Table 5 is $0.994 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ which is very close to the value of $10^{-5} \text{ cm}^2 \text{ s}^{-1}$ which was used for calculation of *electron transfer number*.

Table 5. Determination of the transition time constant from E-t curves obtained for the different applied current pulses and TNT concentration of 110 μM

$i / \text{A} \times 10^{-4}$	τ / s	$i \tau^{0.5} / \text{As}^{0.5} \times 10^{-4}$	$i \tau^{0.5} / C_0 \text{As}^{0.5} \text{mol}^{-1} \text{cm}^3$
0.40	0.900	0.380	345.55
1.00	0.144	0.379	344.54
1.20	0.100	0.379	344.54
1.40	0.074	0.380	345.55

4. CONCLUSIONS

The present investigation of the possibility of galvanostatic determination of trinitrotoluene (TNT) by the acetonitrile modified platinum electrode in neutral solutions further clarified the process of TNT reduction and confirmed the previously observed stepwise reduction of the nitro groups in the TNT molecule.

The obtained potential-time responses on the applied constant cathodic current pulses showed two potential transitions before achieving the steady-states which refer to the multi-step reduction process.

From the first transition on the E-t curves it was found that four electrons are involved in the reduction process of the first nitro group, indicating that the reduction product in a neutral electrolyte was hydroxylamine.

A calibration curves as a linear dependence of the square root of the first transition time on the TNT concentration were obtained in the ranges 4.4 – 304 μM and 0.09 – 4.40 μM . The detection limit was 0.09 μM .

The results of the testing the method in the river water demonstrated that this method could be successfully applied for the TNT detection and quantitative determination in the river water.

ACKNOWLEDGEMENTS

The authors are grateful to Ministry of Education and Science of the Republic of Serbia for support (projects: 45005 and 45001).

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