

# Electrochemical Reduction of Trinitrotoluene on a Modified Platinum Electrode

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## 1. Introduction

The reduction of 2,4,6-trinitrotoluene (TNT) was investigated by cyclic voltammetry (CV) on a platinum electrode in aqueous sodium chloride solutions with acetonitrile (AcN).

The detection of TNT [1-3] has attracted considerable research attention in recent years due to urgent needs in public security and environmental protection.

The reduction of TNT occurs in three steps in accordance with the three nitro-groups in the aromatic molecule. CVs were recorded to determine the potentials corresponding to the peaks currents, which were found to be directly proportional to the TNT concentration [4-8].

The goal of this study was to detect and quantitatively determine TNT as simple as possible with respect to both the technique and the electrode used.

## 1. Experimental

The electrochemical reduction of TNT was investigated by CV using a sweep generator (PAR M175) driving a potentiostat (PAR M173). The electrochemical measurements were performed in a standard glass cell with a Pt wire of 0.32 cm<sup>2</sup> as the working electrode, a Pt wire as the counter electrode and a standard Ag/AgCl(3M KCl) electrode as the reference. In all the experiments the supporting electrolyte was 0.5 M NaCl. CV in 0.5 M H<sub>2</sub>SO<sub>4</sub> was applied to electrochemically polish the Pt electrode and to check the state of the electrode surface. In order to investigate the effect of the basic electrolyte (0.5 M NaCl with AcN) on the Pt electrode, CV experiments were performed and results were compared to the CVs obtained in pure 0.5 M NaCl. The concentration of AcN varied from 0.02-5 vol.%. A high degree of reproducibility was found in replicated experiments.

## 3. Results and discussion

CVs for a Pt electrode in oxygen free pure 0.5M NaCl and in ones with the addition of 0.02- 5vol.% of AcN are presented in the Fig.1. With addition of AcN the Hs and Hw peaks correspond to adsorption and desorption of hydrogen are being increasingly suppressed starting from the lowest concentration of 0.02 vol.% up to the total disappearance for the concentration of 0.5 vol.% and higher. It can be supposed that adsorption of AcN occurs and inhibits H adsorption on the Pt surface; when the supporting electrolyte contained AcN in concentration as low as 0.5 vol.%, extent of its chemisorption achieves saturation, and the electrode surface becomes effectively modified.

In order to establish the potential regions of oxygen reaction for the conditions corresponding to real systems when atmospheric oxygen is dissolved in the solution, CVs were recorded for the different negative and positive potential limits, Fig.2. For an anodic potential limit of 1.0 V, a maximum current for oxygen reduction wave, OR, was achieved at the potential of -0.20 V.

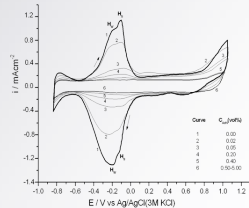


Fig.1. CVs for a Pt electrode recorded in oxygen free 0.5M NaCl solution without (Curve 1) and with addition of 0.02-5 vol.% of AcN(Curve 2-6). Potential scan rate was 200mVs<sup>-1</sup>.

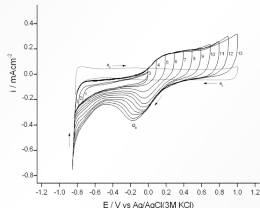


Fig. 2. CVs for a Pt electrode in a solution of 0.5M NaCl containing AcN obtained without purging of electrolyte, as a function of the negative and positive potential limits (Curves 1-13). CV of acetonitrile modified Pt electrode obtained in the oxygen free electrolyte is presented by Curve e<sub>7</sub>. Potential scan rate was 200 mV s<sup>-1</sup>.

As an example, the CVs on the Pt electrode from the basic electrolyte containing 220 μM TNT are presented in Fig.3.

The effects of the potential scan rate, v, and TNT concentrations on the peaks currents, I<sub>p</sub>, of the TNT reduction are shown in Fig.4 and Fig.5, respectively.

The first reduction peak is particularly useful for quantitative work; its height is proportional to the TNT concentration, as indicated from the resulting linear calibration plot in the concentration range 4.4 – 638.4 μM, as shown in Fig. 6.

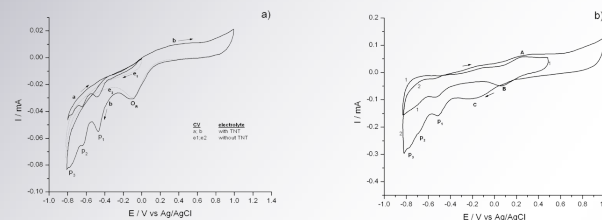


Fig.3. The CVs of TNT reduction on the Pt electrode in a solution of 0.5 M NaCl with AcN containing 220 μM TNT as a function of the anodic potential limits at a potential scan rate of: a) 20 mV s<sup>-1</sup>; b) 200 mV s<sup>-1</sup>.

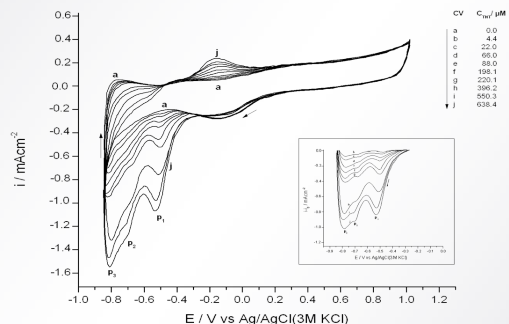


Fig. 5. CVs of TNT reduction on the Pt electrode obtained in a solution of 0.5 M NaCl with AcN containing different concentrations of TNT. Potential scan rate was 200 mVs<sup>-1</sup>. Inset shows TNT reduction currents obtained by subtracting the background current.

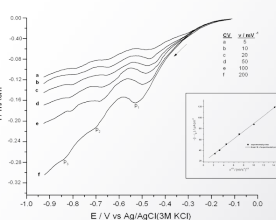
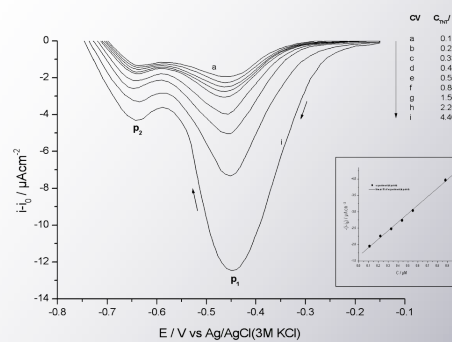


Fig. 4. CVs of TNT reduction obtained on the Pt electrode in a solution of 0.5 M NaCl with AcN containing 220 μM TNT as a function of the potential scan rate. Inset shows the dependence of the first peak current on the scan rate where the background current (I<sub>0</sub>) obtained in the absence of TNT was subtracted.

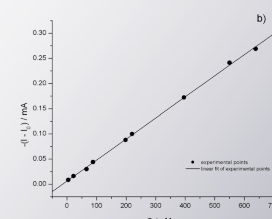


Fig. 6. The dependence of the first peak current from the inset of Fig.5 on the TNT concentration.

Furthermore, an attempt was made to determine the detection limit. As shown in Fig.7, when the concentration was 0.11 μM, the reduction peak at -0.45 V was still detected. The linear relationship of the first peak current on the TNT concentration was also obtained, as shown in the inset of Fig.7. On the basis of these observations we can estimate that detection limit is as low as 0.11 μM.

Fig.7. CVs of TNT reduction on the Pt electrode in a solution of 0.5 M NaCl containing AcN and 0.1 – 4.4 μM of TNT obtained at a potential scan rate of 20 mVs<sup>-1</sup>, with the subtracted background current (I<sub>0</sub> is the same as e<sub>1</sub> in Fig.3a). Inset shows the dependence of the first peak current on the TNT concentration.

## 4. Conclusions

The present investigation of electrochemical reduction of TNT on a platinum electrode by CV confirmed the previously observed stepwise reduction of the nitro groups in the TNT molecule.

The obtained CVs exhibited three well-pronounced reduction peaks in the potential range -0.43 to -0.8 V (vs. an Ag/AgCl reference electrode).

The potentials of the peaks were dependent on the potential scan rate as well as on the TNT concentration, indicating the irreversibility of the reduction process.

A calibration curve as a linear dependence of the first peak current on the TNT concentration was obtained in the range 4.4 – 638.4 μM and 0.11- 4.4μM for two scan rates: 200 mVs<sup>-1</sup> and 20 mVs<sup>-1</sup>, respectively.

The detection limit was 0.11 μM.

The Pt electrode in aqueous sodium chloride solutions with acetonitrile exhibited an electrochemically stable behaviour and provided for very high reproducibility over prolonged time and voltammetric cycling. Hence, it could be used for the detection and quantitative determination of trinitrotoluene.

The accuracy of the method presented in this work was tested in river water and it was confirmed that TNT could be successfully detected by acetonitrile modified Pt wire.

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