

# Electrochemical determination of dissolved nitrogen-containing explosives



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## ABSTRACT

Screen printed carbon electrodes (SPCE), produced close to industrial manufacturing processes as well as commercially available electrodes using nano-tubes and gold nano-particles (DRP-110CNT-GNP) were investigated with respect to the determination of nitroaromatic compounds like 2,4,6-trinitrotoluene (TNT) and 2,4-dinitrotoluene (DNT) in aqueous solution. Dynamic electrochemical measuring methods such as differential pulse voltammetry (DPV) and square wave voltammetry (SWV) are suited to measure traces of such compounds. The two peaks obtained can be separated clearly and assigned to the reduction of nitro groups. On bare carbon electrodes TNT and DNT could be determined in the concentration range between 1.2 ppb and 1500 ppb TNT ( $R^2 = 0.994$ ) with high reproducibility. The coating of commercial electrodes with carbon nano-tubes and gold nano-particles provided similar results for comparison purposes. The reproducibility of the results obtained on SPCE was demonstrated over a period of up to 1.5 years. The results were verified by gas chromatography with mass spectrometry (GC-MS).

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## 1. Introduction

Nitroaromatics like TNT and DNT are persistent organic pollutants in natural water and soil caused mainly by military disposal. These substances are very difficult to degrade by natural processes, and the intermediates themselves are problematic for the ecology. They are classified as particularly dangerous for the environment and human health. The detection and the monitoring of contaminated soil and water is regulated by law (e.g. in Germany by BBodSchG [1]) to ensure public safety and environmental protection.

Established standard methods for the determination of TNT and other explosives have been reported, e.g. liquid chromatography–mass spectrometry (LC-MS) [2], chromatography by using a porous graphitic carbon (PGC) [3], surface enhanced Raman scattering (SERS) [4,5] and electrophoresis [6,7]. But these methods are not suitable for field application and *in situ* analysis. The determination in special labs is expensive and inflexible. Furthermore, the sampling can cause errors.

Electrochemical methods have been used successfully for the determination of explosives and are well established in analysis.

Especially, the dynamic methods have become more and more attractive due to their high sensitivity and simplicity in data acquisition. Small and inexpensive portable potentiostats are available today for field application. In particular, the amperometric and voltammetric studies to determine the nitroaromatics are qualified because the electrochemical reduction of the nitro groups by the inclusion of 2, 4 or 6 electrons takes place preferentially [8]. Up to now most of the carbon electrodes reported in literature were prepared as single-items for scientific investigation. Very little information about their reproducibility could be found in literature [9,10]. Furthermore, there are several papers which focused on modification of carbon layers e.g. by nano-tubes and metallic nano-particles like gold to improve the electrocatalytic behaviour [11]. More recently electrodes using such nano-particles and nano-tubes are offered commercially for analytical purposes [12–14]. Electrochemical carbon electrodes manufactured by methods suitable for mass production such as screen printing could be an impressive alternative due to its simple and cheap production. In several articles the characterization, performance and application of unmodified printed carbon electrodes (bare SPCEs) for electrochemical measurement of TNT have been reported [15–18].

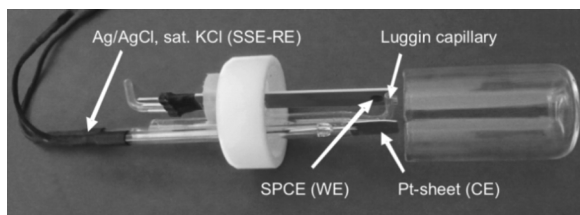
It is the aim of this work to investigate screen printed carbon electrodes (SPCE) for TNT detection in aqueous solutions and to compare the results with those obtained with commercial carbon film electrodes containing carbon nano-tubes and gold

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**Fig. 1.** Commercial electrode (DRP-110CNT-GNPE) above, screen printed carbon electrode (SPCE) below.



**Fig. 2.** The three-electrode measuring cell (max. volume: 5 mL).

nano-particles. In order to replicate on field conditions, the influence of parameters like dissolved oxygen and pH value on the TNT measuring signal have been also studied.

## 2. Experimental

### 2.1. Electrodes

The electrode was prepared as follows: On an alumina substrate the platinum ring electrode was printed with glass-free platinum paste (ESL, UK). For the SPCE, the substrate was coated with a diameter of 3 mm, using a commercial carbon ink (DuPont). The graphite layer of the electrode could be deposited according to the desired surfaces with high reproducibility. The Pt contact path was insulated with a polymer paste an epoxy resin from ESL, UK. The screen printing was carried out by means of the semi-automatic screen printer (EKRA mat S30, Germany). The setup of the electrodes is seen in Fig. 1. Commercial carbon electrodes (DRP-110CNT-GNP from DropSens, Spain) which contain carbon nano-tubes and gold nano-particles are used in this work for comparison.

All voltammetric measurements were carried out in a three-electrode cell arrangement seen in Fig. 2. The carbon electrode (without and with modification), platinum plate electrode (1 cm x 1 cm), and a miniaturized Ag/AgCl, Cl<sup>-</sup>(sat.) electrode (SSE) were used as working, counter and reference electrodes, respectively. The cell could be purged via a gas inlet by gases with different oxygen concentrations prepared by a gas mixing apparatus (Wösthoff Bochum, Germany).

### 2.2. Apparatus

Scanning electron microscopic (SEM) images of electrode surface areas were obtained with a “DSM 982 GEMINI” instrument from ZEISS (Germany).

For GC-MS analysis, columns and parameters were modified based on [19]. Solid-phase micro-extraction (SPME) was used to selectively pre-concentrate different explosives from analytes in aqueous solution for GC-MS analysis (TRACE-DSQ II, Thermo Scientific). SPME fiber (65 μm Polydimethylsiloxane/Divinylbenzene-PDMS/DVB) and fiber holder assembly were used as such from Supelco, Sigma-Aldrich Chemie GmbH.

The fused-silica capillary fibers of the SPME were immersed in a 5 mL solution of 0.1 M KNO<sub>3</sub> + 0.1 M KCl containing explosives. The time for adsorption of the analyte was assigned to 30 minutes at room temperature. Inside the heated GC injector, the analyte was desorbed for 5 minutes (splitless) or 10 minutes (split) and subsequently detected by MS (SPME-GC-MS). Separation was carried out on a 30 m x 0.25 mm ID x 0.25 μm BpX-5 capillary column. The column oven was initially held at 100 °C for 2 min, followed by a programmed heating to 200 °C at a rate of 10 K·min<sup>-1</sup>, then to 250 °C at 20 K·min<sup>-1</sup> (hold for 5 min). The carrier gas, helium was used at a flow-rate of 1.2 mL·min<sup>-1</sup> (set at 100 °C). The head-pressure was set to 100 kPa.

### 2.3. Chemicals

All chemicals in this work were of analytical-reagent grade and were used as received without further purification unless specified otherwise. Ultra pure water (< 0.05 μS·cm<sup>-1</sup>) was used for preparing all solutions.

Acetonitrile (HPLC grade), TNT and DNT standards (1000 μg·mL<sup>-1</sup> in acetonitrile) were supplied by Supelco (Sigma-Aldrich Chemie GmbH). Stock solutions of 10 and 100 mg·L<sup>-1</sup> of TNT and DNT were prepared from these standards in acetonitrile. 0.1 M acetate buffer-solution (Acb, pH=4.6), 0.1 M phosphate buffer-solution (Phb, pH=6.9) and 0.1 M KNO<sub>3</sub> + 0.1 M KCl (pH=5.6) served as supporting electrolytes during the experiments. Chemical precursors needed for the preparation of the supporting electrolytes were purchased from Sigma, Fluka or Roth, respectively. 2-Nitrotoluene (2-NT), 3-nitrotoluene (3-NT) and 4-nitrotoluene (4-NT) were obtained from Aldrich.

Natural water was collected in Meinsberg (Zschopau river) and Chemnitz (Chemnitz river) both from the state of Saxony in Germany. The river water was used without any pH adjustment (natural pH 7.3). It was run through a Schleicher&Schuell membrane filter (S&S) no. 575 (180 mm diameter) just before use.

### 2.4. Procedure

Each electrode was conditioned in the pure supporting electrolyte by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). All organic binder and impurities could be successfully removed from the electrode surface by electrochemical pre-treatment. The potential range of -1 V to +1 V was chosen for cyclo-voltammetric measurements such that no oxygen and hydrogen evolution took place at the electrodes, with scan rates from 0.01 to 0.05 V·s<sup>-1</sup>. For the analytical determination this potential range was diminished. The parameters for the DPV were selected as follows: scan rates of 15 mV·s<sup>-1</sup> to 20 mV·s<sup>-1</sup>, amplitude of 50 mV and step height of 5 mV; for square wave voltammetry (SWV) scans at 10 Hz and 15 Hz, respectively, 4 mV step height and 25 mV amplitude. A potential range of 0 to -0.9 V was chosen for both voltammetric methods.

All experiments were carried out at room temperature (23 ± 1 °C) under argon or gas mixtures with different oxygen concentrations.

## 3. Results and discussion

### 3.1. Characterization of the electrode surfaces

Compared to metallic or glassy carbon electrodes, SPCEs have a larger active surface area with a highly porous structure as seen in the SEM image (Fig. 3). The SEM image of the commercial DRP-110CNT-GNP-electrode shows that the surface of the carbon nano-tubes is covered with evenly distributed Au-nano-particles (Fig. 4).

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