

# Voltammetric Sensing of Benzotriazole at Single-Walled Carbon Nanotube Modified Screen-Printed Electrodes

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## Summary:

Benzotriazole and its derivatives are ubiquitous in industries due to their diverse applications, yet their persistence in the environment poses ecological concerns. This study proposes a carbon nanotube-Nafion-modified screen-printed electrode for electrochemical detection of benzotriazole, addressing the need for cost-effective and rapid monitoring methods. Electrochemical analysis revealed a single reduction peak, leading to an LOD of 2  $\mu\text{M}$  with square wave voltammetry. This approach offers a comparable alternative to commercial electrodes, underscoring its potential for environmental monitoring.

**Keywords:** Benzotriazole, persistent organic pollutant, voltammetric sensor, screen-printed electrode, single-walled carbon nanotubes.

## Introduction

Benzotriazole (BTA) and its derivatives are extensively utilised in various industries for their properties as corrosion inhibitors, UV radiation filters and plastic stabilisers. BTA is therefore found in food packaging, dishwashing detergents, textiles, lubricants, antifreeze, aircraft de-icing fluids and other commercial and industrial products. [1,2]

Due to its solubility in water and resistance to biodegradation, BTA can persist in the environment. The inclusion of BTA as an additive in dishwashing detergents and tablets leads to its direct discharge into wastewater treatment plants, where it is only partially removed during the treatment process. As a result, BTA is prevalent in natural waters at nanomolar concentrations. While these concentrations may not pose an immediate threat to human health, the persistent nature and potential bioavailability of BTA can lead to long-term environmental consequences, which have yet to be sufficiently investigated. [1,2]

Currently, the primary methods for analyzing BTA in environmental samples involve solid-phase extraction followed by gas chromatography-mass spectrometry or liquid chromatography-mass spectrometry. However, there is a need for cost-effective, fast, reliable, in-situ detection of BTA for real-time monitoring of environmental samples. Given that BTA and

some of its derivatives can be electrochemically reduced at low potentials, electrochemical detection on screen-printed electrodes (SPE) emerges as a promising approach. SPEs offer a more cost-effective, portable alternative to traditional electrochemical setups, which use conventional electrodes such as glassy carbon and mercury drop electrodes. In this work, a sensor based on carbon nanotube-Nafion-modified SPE (SPE-C/SWCNT) is proposed.

## Materials and Methods

1 mg/mL dispersions of carboxyl-functionalised single-walled carbon nanotubes (SWCNT) were prepared in a 1:1 (v/v) mixture of DMF and water containing 1 wt.% Nafion. The dispersions were sonicated until fully dispersed. The sensor was fabricated by drop-casting 4  $\mu\text{L}$  of the CNT suspension on the working electrode of the SPE (DRP-150, Dropsens, Metrohm) and allowing it to dry at room temperature overnight.

BTA solutions were prepared in Britton-Robinson buffer (pH 2.4) and analysed using cyclic voltammetry (CV) and square wave voltammetry (SWV). The electrochemical measurements were carried out by the PalmSens4 potentiostat.

## Results and discussion

The coverage of the working electrode by the drop-casted material was assessed using scanning electron microscopy (SEM). As seen in Fig.

1, the SWCNTs are anchored to the working electrode by a Nafion membrane, resulting in satisfactory surface coverage.

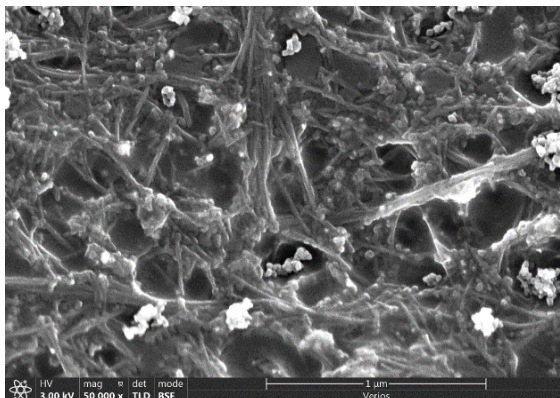


Fig. 1. SEM image of the working electrode surface modified with SWCNT and Nafion.

The electrochemical behaviour of BTA on the SPE-C/SWCNT was evaluated via CV. BTA exhibited a single reduction peak around  $-1,4$  V with no observable oxidation peak during the reverse scan.

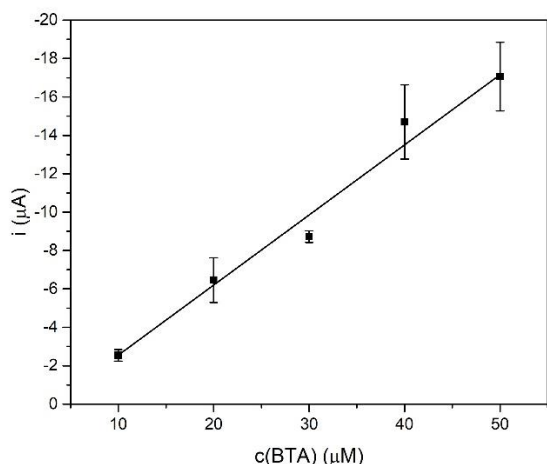


Fig. 2. Plot of the reduction peak current recorded on SPE-C/SWCNT for different concentrations of BTA in Britton-Robinson buffer at pH 2.4.

The SPE-C/SWCNT exhibited significant adsorption capacity for BTA. As a result, SWV analysis was performed after a 60 s preconcentration period at  $-1$  V. With this approach, an LOD of  $2 \mu\text{M}$  was achieved. This LOD is comparable to that obtained for BTA detection using commercially available SPE with a SWCNT working electrode [2], indicating that homemade modified SPEs offer a versatile alternative to commercial counterparts. Furthermore, by adjusting the composition, it may be possible to achieve an even lower LOD, comparable to those achieved using modified glassy carbon electrodes [3], making the proposed sensor suitable for real sample monitoring.

## References

- [1] A.N. Ababneh, M.A. Abu-Dalo, C. Horn, M.T. Hernandez, Polarographic determination of benzotriazoles and their sorption behavior on granular activated carbon, *International Journal of Environmental Science and Technology* 16 (2019) 833–842. <https://doi.org/10.1007/s13762-018-1706-y>.
- [2] A. Muschietti, N. Serrano, C. Ariño, M.S. Díaz-Cruz, J.M. Díaz-Cruz, Screen-printed electrodes for the voltammetric sensing of benzotriazoles in water, *Sensors (Switzerland)* 20 (2020). <https://doi.org/10.3390/s20071839>.
- [3] Y. Zheng, F. Yang, J. Zhang, W. Pu, C. Yang, Voltammetric behaviors of an emerging pollutant benzotriazole on multiwall carbon nanotubes (MWNTs)—Nafion modified electrode in various pH mediums, *Ionics (Kiel)* 22 (2016) 2059–2066. <https://doi.org/10.1007/s11581-016-1738-6>.

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