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Real-Sample Analysis of PMT Compounds Using Electrochemical Sensor Technology

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ABSTRACT

Persistent, mobile, and toxic (PMT) substances represent a serious threat to water systems due to their environmental persistence, high mobility, and adverse effects on both ecosystems and human health. Common examples of such compounds include bisphenols, benzisothiazolinone (BIT), and benzotriazole (BZT), which are frequently found in household and industrial products, therefore they can be easily found in environmental and also in the human body. Detection and monitoring of these chemicals are crucial for evaluating their environmental impact and informing mitigation measures. While conventional analytical techniques like chromatography provide reliable results, they are not suited for rapid field analysis. In contrast, electrochemical sensors offer a cost-effective, sensitive, and portable solution for on-site detection. This work presents the use of carbon-based screen-printed electrodes (SPEs) for the electrochemical detection of bisphenol S (BPS) in parking tickets and BIT in river water, while modified SPEs with composite material carbon-polymer layers for BZT detection. The results showed the effectiveness of the obtained electrochemical sensors for real-time detection of PMT compounds.

Keywords: screen-printed electrodes, benzisothiazolinone, bisphenol S, benzotriazole, voltammetry.

1. Introduction

Persistent, mobile, and toxic chemicals (PMT) pose significant risks to water resources, requiring additional protective measures. These chemicals are resistant to biodegradation, travel long distances in water, and can be toxic to both the environment and human health. (Hale et al. 2020) At the top of the priority list of PMT chemicals are bisphenols. Bisphenol S (BPS) is commonly found in everyday items like thermal paper, such as receipts from stores, parking tickets, and bus tickets. It has been identified as easily migrating from paper products onto human skin, subsequently entering the body and disrupting the endocrine system by imitating the estrogen hormone. (Biedermann et al. 2010; Takahashi et al. 2002) Another PMT of great concern is Benzisothiazolinone (BIT), which belongs to the isothiazolinones group, serves as an antimicrobial agent incorporated into various products, including laundry detergents, water-based paints, and food packaging paper, contributing significantly to the contamination of municipal wastewater.(Silva et al. 2020) BIT has been detected in municipal wastewater in France at concentrations of approximately 0.5 µg/L, raising concerns about its environmental impact. (Lundov et al. 2014; Paijens et al. 2021) The discharge or runoff of BIT-containing substances into water bodies poses a serious threat to aquatic ecosystems. (Kresmann et al. 2018; He et al. 2021; Yu et al. 2024) Benzotriazole (BZT) is a well-known corrosion inhibitor in deicing fluids for aircraft, automotive antifreeze formulations, brake fluids, metal-cutting fluids, and industrial cooling systems. (Weiss and Reemtsma 2005) Loos et al. (Loos et al. 2017) analyzed 71 water samples from the Danube River and its tributaries, and found that the most prevalent chemicals are benzotriazoles, with an average concentration around 0.3 µg/L. Similar to BPS, BZT is currently under assessment for classification as an endocrine-disrupting chemical, further underscoring the need for effective regulatory action.

Removing PMT chemicals from water remains a major challenge, as no single solution exists for eliminating all PMT contaminants. Assessing their persistence, mobility, and toxicity is difficult due to a lack of reliable data. Gaps in regulations, monitoring, risk assessment, and safe alternatives show the need for a “Safe and Sustainable by Design” (SSBD) approach. Stronger monitoring and more research are crucial to reducing the long-term impact of PMT chemicals. For that purpose, detection of PMT chemicals is of crucial importance.

Electrochemical techniques are powerful tools for detecting chemicals because they are simple, low-cost, portable, and highly sensitive. This study focuses on developing electrochemical sensors

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for detecting PMT chemicals for field monitoring. The data from these sensors will improve tracking models and help product designers, policymakers, and regulators understand the impact of PMT chemicals. This will support better strategies to reduce PMT chemicals in Europe and beyond.

2. Materials and methods

A screen-printed electrode (SPE) was obtained from Metrohm DropSens. Electrochemical analyses were conducted using cyclic voltammetry and square wave voltammetry with a PalmSens 4 potentiostat (Palm Instruments, The Netherlands). Detection of BPS in real samples was done on thermal paper – parking tickets. Parking tickets were collected from the local shopping center. They were cut into small pieces and sonicated in methanol. The solution was dried in a rotary evaporator and further diluted in a buffer solution. The obtained sample was used for further analysis using cyclic voltammetry (CV). CV measurements were done within a potential range of -0.4 to 1.2 V at a scan rate of 50 mV/s against the Ag reference electrode. For the detection of BIT and BZT in real samples, collected river water was spiked with BIT and BZT solutions. Square wave voltammetry (SWV) measurements were used for BIT and BZT detection. SWV for BIT detection was performed over a potential range of 0.2 to 1.0 V vs. Ag ref. el. with an amplitude of 30 mV, while for BZT a potential window was from – 0.9 V to – 1.7 V vs. Ag ref. el. and an amplitude of 50 mV. SPE based on carbon working electrodes was used for the detection of BPS and BIT, while for the detection of BZT working electrode was based on polyether ether ketone and functionalized carbon material.

3. Results and discussion

Figure 1a) illustrates the structure of the screen-printed electrode (SPE), where the working, reference, and counter electrodes are printed onto a ceramic substrate. The primary sensing component is the working electrode, composed of carbon nanoparticles with an average size of approximately 30 nm (Figure 1b)). For benzotriazole detection, the working electrode is modified with functionalized carbon materials and polyether ether ketone polymer to enhance sensitivity and selectivity.

The compact design of the SPE allows compatibility with various potentiostats, making it suitable for both laboratory and field applications. The sensor demonstrated reliable performance using both standard benchtop potentiostats (Figure 1c)) and portable electrochemical devices, such as IoT-enabled potentiostats or potentiostats connected to mobile phones for on-site analysis (Figure 1d)). This versatility makes SPE-based sensors highly practical for real-time monitoring of PMT chemicals in environmental samples, such as river water. The ability to perform rapid, low-cost, and efficient detection highlights the potential of SPE sensors as valuable tools for widespread environmental monitoring.

The carbon-based SPE was used to detect BPS in parking tickets collected from a local shopping center. Figure 2a) shows the cyclic voltammetry results, where an oxidation peak at 0.8 V vs Ag ref. el. confirms the presence of BPS in the samples. Based on the calibration curve from our previous research, the BPS concentration in parking tickets was estimated to be approximately 0.9 wt.%. (Vujančević et al. 2024) The sensor was further applied for BIT detection in river water using square wave voltammetry, a more sensitive electrochemical technique. An oxidation peak at approximately 0.6 V vs Ag ref. el. was observed, confirming the presence of BIT in the water sample. Finally, the modified SPE with functionalized carbon and polymer was used for BZT detection in river water. A redox peak was observed at –1.25 V vs Ag ref. el, indicating the successful detection of BZT.

The carbon-based SPE electrode showed a limit of detection for BPS of 0.2 mg/L. (Vujančević et al. 2024) According to the literature review, the majority of studies have focused on the detection of bisphenol A, while only a limited number have addressed the detection of bisphenol S. Most of these studies employed modified glassy carbon electrodes (GCE), which, although offering good sensitivity, are generally not suitable for on-site or field applications. Additionally, these sensors were primarily applied to the analysis of surface water and food samples. For instance, Hyder et al. modified GCEs with NiO nanoparticles functionalized with a para-hexanitrocalix[6]arene derivative, achieving a limit of detection (LOD) of 0.001 mg/L and possible application for the detection of BPS in river water. (Hyder et al. 2024) Another study utilized GCEs modified with functionalized multi-walled carbon nanotubes, reaching an LOD of 0.1 mg/L for the determination of bisphenols in food samples. (Çakıcı et al. 2023) In a separate study, GCEs were modified with a hybrid of iron nanoparticles and nanostructured graphene oxides, resulting in an LOD of 2.9 mg/L, and were employed for the detection of bisphenols in surface water.(Piña et al. 2023) As can be seen, studies have confirmed the presence of BPS in various water samples; however, to the best of our knowledge, its detection in parking ticket materials has not been previously reported.

Direct electrochemical detection of BIT has not yet been documented in the literature. Nevertheless, other isothiazolinone derivatives, such as methylisothiazolinone (MIT), have been detected electrochemically. For instance, Jakubczyk et al. reported a limit of detection of 0.24 mg/L for MIT using boron-doped diamond electrodes. (Jakubczyk et al. 2022) Furthermore, Abad-Gil et al. investigated the voltammetric detection of MIT using modified SPEs incorporating poly(diallyldimethylammonium) matrices and Au nanoparticles, obtaining a LOD of 2.6 mg/L.(Abad-Gil et al. 2021; 2020) In our studies, we obtained LOD for BIT 0.006 mg/L, which is significantly lower, highlighting the enhanced sensitivity achieved through optimization of both electrode composition and electrochemical technique.

Regarding benzotriazole, available studies on its electrochemical detection remain limited. Muschietti et al. reported an LOD of 0.4 mg/L using carbon nanofiber-based SPEs. (Muschietti et al. 2020) In comparison, our sensor, based on functionalized carbon SPE with polymer incorporation, achieved an improved LOD of 0.2 mg/L.

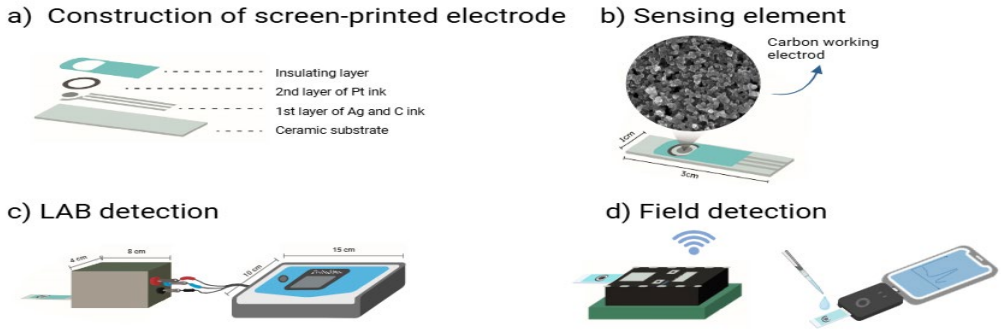

Fig. 1. Schema of the: a) construction of SPE, b) Schema of SPE with SEM image of carbon working electrode, c) standard benchtop potentiostats, and d) IoT potentiostat and potentiostat connected with cellphone.

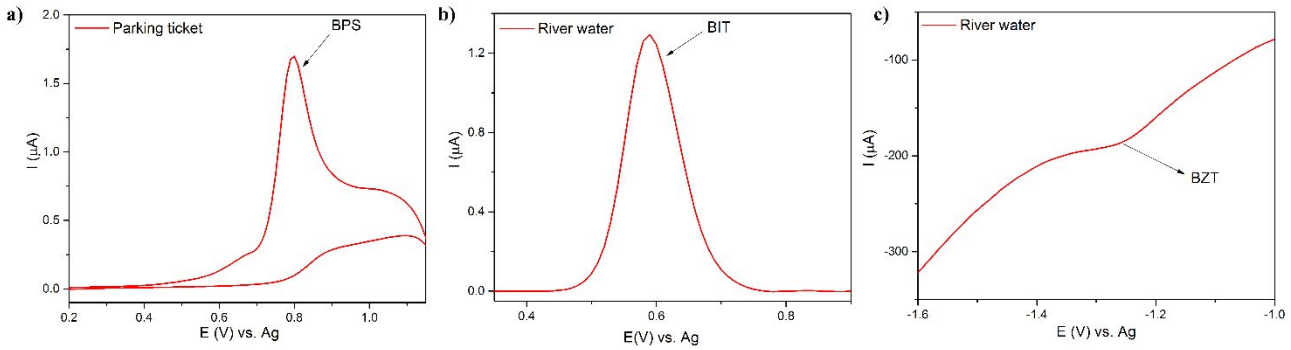

Fig. 2. Electrochemical detection of PMT chemicals in real samples: a) CV of BPS in parking tickets, b) SWV of BIT in river water and c) SWV of BZT in river water.

The improved detection limits achieved in our study underscore the potential of SPE-based sensors as a reliable, cost-effective, and sensitive platform for monitoring substances of persistent, mobile, and toxic concern in complex environmental matrices.

4. Conclusion

This study demonstrates the effectiveness of electrochemical sensors for detecting persistent, mobile, and toxic chemicals in environmental and consumer product samples. Screen-printed electrodes were successfully used for the detection of bisphenol S in parking ticket paper, as well as benzisothiazolinone and benzotriazole in river water. The results confirm the presence of BPS at approximately 0.9 wt.% in parking tickets, while BIT and BZT were detected in river water at characteristic oxidation and redox potentials of 0.6 V vs Ag ref. el. and −1.25 V vs Ag ref. el., respectively. The versatility of SPE sensors makes them suitable for both laboratory and field use, as they work with standard potentiostats and portable, IoT-enabled devices. Their low cost, ease of use, and high sensitivity make them a good alternative to expensive methods like chromatography. These findings highlight the importance of simple and effective detection tools for monitoring PMT chemicals and supporting environmental regulations. Future work will focus on improving sensor performance, increasing selectivity, and expanding detection to more contaminants. Developing better monitoring tools will help reduce the impact of PMT chemicals on both human health and the environment.

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References

Abad-Gil, Lucía, Mª. Jesús Gismera, Mª. Teresa Sevilla, and Jesús R. Procopio. 2021. 'Determination of Methylisothiazolinone in Waters. Comprehensive Study about Electrochemical Behaviour on Gold Electrode and Optimization of Square-Wave Voltammetric Methods'. *Journal of Electroanalytical Chemistry* 880 (January): 114831. https://doi.org/10.1016/j.jelechem.2020.114831.

Abad-Gil, Lucía, María Jesús Gismera, María Teresa Sevilla, and Jesús R. Procopio. 2020. 'Methylisothiazolinone Response on Disposable Electrochemical Platforms Modified with Carbon, Nickel or Gold-Based Nanomaterials'. *Microchimica Acta* 187 (4): 199. https://doi.org/10.1007/s00604-020-4157-3.

Biedermann, Sandra, Patrik Tschudin, and Koni Grob. 2010. 'Transfer of Bisphenol A from Thermal Printer Paper to the Skin'. *Analytical and Bioanalytical Chemistry* 398 (1): 571–76. https://doi.org/10.1007/s00216-010-3936-9.

Çakıcı, Maşide, Asiye Aslıhan Avan, Hayati Filik, and Ece Kök Yetimoğlu. 2023. 'Individual and Simultaneous Electrochemical Detection of Bisphenol A and Bisphenol S in Food Samples Using Triethylenetetramine Functionalized Multi-Walled Carbon Nanotubes'. *Food Analytical Methods* 16 (1): 225–37. https://doi.org/10.1007/s12161-022-02409-w.

Hale, Sarah E., Hans Peter H. Arp, Ivo Schliebner, and Michael Neumann. 2020. 'Persistent, Mobile and Toxic (PMT) and Very Persistent and Very Mobile (vPvM) Substances Pose an Equivalent Level of Concern to Persistent, Bioaccumulative and Toxic (PBT) and Very Persistent and Very Bioaccumulative (vPvB) Substances under REACH'. *Environmental Sciences Europe* 32 (1): 155. https://doi.org/10.1186/s12302-020-00440-4.

He, Wenze, Lilong Pan, Wenhao Han, and Xiaowei Wang. 2021. 'Isothiazolinones as Novel Candidate Insecticides for the Control of Hemipteran Insects'. *Antibiotics* 10 (4): 436. https://doi.org/10.3390/antibiotics10040436.

Hyder, Ali, Akbar Ali, Jamil Ahmed Buledi, et al. 2024. 'A NiO-Nanostructure-Based Electrochemical Sensor Functionalized with Supramolecular Structures for the Ultra-Sensitive Detection of the Endocrine Disruptor Bisphenol S in an Aquatic Environment'. *Physical Chemistry Chemical Physics* 26 (14): 10940–50. https://doi.org/10.1039/D4CP00138A.

Jakubczyk, Magdalena, Slawomir Michalkiewicz, Agata Skorupa, and Kinga Krajcarz. 2022. 'Electrochemical Characterization and Voltammetric Determination of Methylisothiazolinone on a Boron-Doped Diamond Electrode'. *Molecules* 27 (24): 9013. https://doi.org/10.3390/molecules27249013.

Kresmann, Simon, Arokia Hansel Rajan Arokia, Christoph Koch, and Bernd Sures. 2018. 'Ecotoxicological Potential of the Biocides Terbutryn, Octhilinone and Methylisothiazolinone: Underestimated Risk from Biocidal Pathways?' *Science of The Total Environment* 625 (June): 900–908. https://doi.org/10.1016/j.scitotenv.2017.12.280.

Loos, Robert, Simona Tavazzi, Giulio Mariani, Gert Suurkuusk, Bruno Paracchini, and Gunther Umlauf. 2017. 'Analysis of Emerging Organic Contaminants in Water, Fish and Suspended Particulate Matter (SPM) in the Joint Danube Survey Using Solid-Phase Extraction Followed by UHPLC-MS-MS and GC–MS Analysis'. *Science of The Total Environment* 607–608 (December): 1201–12. https://doi.org/10.1016/j.scitotenv.2017.07.039.

Lundov, Michael D., Barbara Kolarik, Rossana Bossi, Lars Gunnarsen, and Jeanne D. Johansen. 2014. 'Emission of Isothiazolinones from Water-Based Paints'. *Environmental Science & Technology* 48 (12): 6989–94. https://doi.org/10.1021/es500236m.

Muschietti, Alessandra, Núria Serrano, Cristina Ariño, M. Silvia Díaz-Cruz, and José Manuel Díaz-Cruz. 2020. 'Screen-Printed Electrodes for the Voltammetric Sensing of Benzotriazoles in Water'. *Sensors* 20 (7): 1839. https://doi.org/10.3390/s20071839.

Paijens, Claudia, Adèle Bressy, Bertrand Frère, et al. 2021. 'Urban Pathways of Biocides towards Surface Waters during Dry and Wet Weathers: Assessment at the Paris Conurbation Scale'. *Journal of Hazardous Materials* 402 (January): 123765. https://doi.org/10.1016/j.jhazmat.2020.123765.

Piña, Samuel, Pamela Sepúlveda, Alejandra García-García, Alejandra Moreno-Bárcenas, Carla Toledo-Neira, and Ricardo Salazar-González. 2023. 'Fast Simultaneous Electrochemical Detection of Bisphenol-A and Bisphenol-S in Urban Wastewater Using a Graphene Oxide-Iron Nanoparticles Hybrid Sensor'. *Electrochimica Acta* 468 (November): 143164. https://doi.org/10.1016/j.electacta.2023.143164.

Silva, Vânia, Cátia Silva, Pedro Soares, E. Manuela Garrido, Fernanda Borges, and Jorge Garrido. 2020. 'Isothiazolinone Biocides: Chemistry, Biological, and Toxicity Profiles'. *Molecules* 25 (4): 991. https://doi.org/10.3390/molecules25040991.

Takahashi, Yoshiyuki, Ayako Shirai, Takako Segawa, Tatsuya Takahashi, and Kazuhisa Sakakibara. 2002. 'Why Does a Color-Developing Phenomenon Occur on Thermal Paper Comprising of a Fluoran Dye and a Color Developer Molecule?' *Bulletin of the Chemical Society of Japan* 75 (10): 2225–31. https://doi.org/10.1246/bcsj.75.2225.

Vujančević, Jelena, Neža Sodnik, Anja Korent, et al. 2024. 'Rapid and Reliable Electrochemical Detection of Bisphenol S in Thermal Paper'. *Sensing and Bio-Sensing Research* 44 (June): 100662. https://doi.org/10.1016/j.sbsr.2024.100662.

Weiss, Stefan, and Thorsten Reemtsma. 2005. 'Determination of Benzotriazole Corrosion Inhibitors from Aqueous Environmental Samples by Liquid Chromatography-Electrospray Ionization-Tandem Mass Spectrometry'. *Analytical Chemistry* 77 (22): 7415–20. https://doi.org/10.1021/ac051203e.

Yu, Pengfei, Zhongyu Guo, Jieqiong Wang, Yuchen Guo, Tingting Wang, and Lilan Zhang. 2024. 'Insight into the Photodegradation of Methylisothiazolinone and Benzoisothiazolinone in Aquatic Environments'. *Water Research* 265 (November): 122301. https://doi.org/10.1016/j.watres.2024.122301.