

Ethylene Glycol Detection in Pediatric Syrups: Rapid Screening MIP Based Electrochemical Sensor

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Summary:

A molecularly imprinted polymer (MIP) electrochemical sensor is developed on screen-printed gold electrodes, advancing toward a portable lab-on-a-chip device for screening ethylene glycol (EG) in pediatric syrups. Through optimized 15-cycle electropolymerization and template extraction, validated via Electrochemical Impedance Spectroscopy (EIS), the sensor was able to detect 10 μM EG concentration, below the World Health Organization (WHO) safety threshold. This work presents a highly viable approach for rapid, on-site EG screening.

Keywords: electrochemical sensor, molecularly imprinted polymer, ethylene glycol, rapid screening, field-deployable

Introduction

Glycerin-based pediatric syrups are highly susceptible to toxic contamination by ethylene glycol (EG) [1, 2]. Existing detection methods (e.g., Gas Chromatography-Mass Spectrometry, Spatially Offset Raman Spectroscopy [3]) are cost-prohibitive, lack field applicability, or miss sensitivity targets. Molecularly imprinted polymer (MIP) based sensors offer a robust, cost-effective alternative. They form synthetic matrices with specific template-shaped cavities, exhibiting high affinity and exceptional selectivity [4].

This ongoing research aims to develop a portable lab-on-a-chip MIP sensor. In this study, we optimized the MIP layer on screen-printed gold electrodes (SPE) to establish a highly sensitive recognition matrix, meeting the WHO's 0.1% (~16.1 mM) safety threshold.

Experimental Method

The MIP sensor was fabricated in four steps. Commercial gold working electrodes were cleaned in 0.5 M H_2SO_4 via 20 cyclic voltammetry (CV) cycles using Pt wire as counter and Ag/AgCl as reference electrodes. A self-assembled monolayer (SAM) was formed by dropcasting 100 mM 4-aminothiophenol in ethanol and incubating for 30 min, followed by an ethanol wash.

Recognition cavities were created by co-electropolymerizing 5 mM *o*-phenylenediamine (OPD) and 20 mM EG in acetate buffer via CV. Polymer thickness was optimized by testing 10,

15, and 20 electropolymerization cycles. For template extraction, electrodes were initially immersed in 0.1 M acetic acid-methanol (1:1 v/v) for 20 min. To maximize template removal efficiency from the optimized polymer film, the extraction solution was then upgraded to 0.2 M acetic acid-methanol (1:1 v/v).

Sensor performance was characterized via EIS in the frequency range of 100 kHz - 0.1 Hz and Differential Pulse Voltammetry (DPV) in 10 mM $\text{Fe}(\text{CN})_6^{3-/4-}$ with 0.1 M NaCl.

The measurement relies on steric hindrance. Bound targets physically obstruct the redox probe's surface access, decreasing DPV peak current (I_p) and increasing EIS charge transfer resistance (R_{ct}).

Results and Discussion

CV scans during OPD/EG electropolymerization (Fig. 1) exhibited an oxidation peak at ~0.42 V, consistent with OPD oxidation [5]. The progressive current decrease across successive cycles confirmed non-conductive film growth.

To optimize polymer thickness, the current suppression percentage ($\Delta I/I_0$) was evaluated. This yielded suppression values of 9.0%, 16.7%, and 11.3% for polymer films deposited with 10, 15, and 20 cycles, respectively. The 15-cycle polymerization provided the optimal polymer structure, offering more recognition sites than the 10-cycle process without making the polymer film excessively insulating, as observed at 20 cycles.

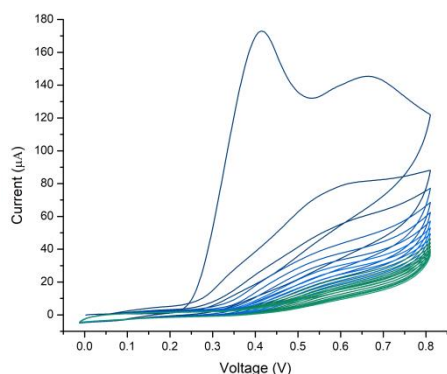


Fig. 1. 15-cycle CV scans during electropolymerization. Current decreases from initial (blue) to final cycles (green), indicating an insulating film growth.

Increasing the extraction solvent to 0.2 M acetic acid demonstrated highly efficient template removal, yielding a 38.9% current suppression ($\Delta I/I_0$) upon rebinding 10 μM EG in acetate buffer (Fig. 2). While the signal recovery trend aligns with typical electropolymerized MIPs on bare gold [6], our modified removal solution drastically improved current suppression.

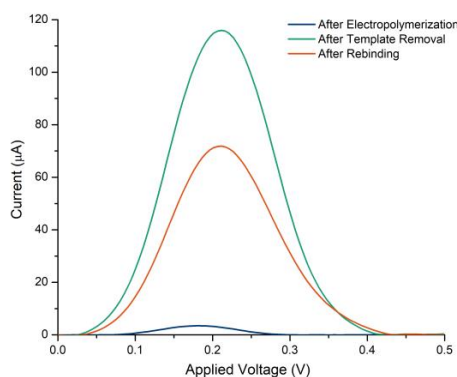


Fig. 2. DPV responses showing a 38.9% current suppression. A voltage window of 0-0.5 V was used.

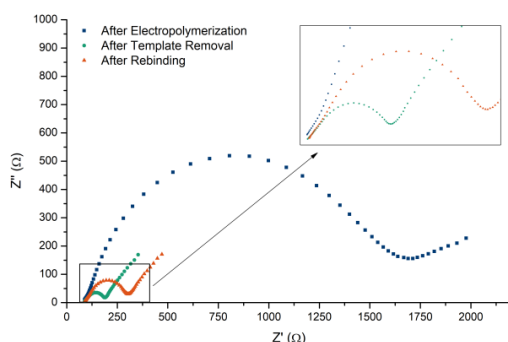


Fig. 3. Nyquist plots of step-wise modification. The semicircle (R_{ct}) expands with the MIP layer, shrinks after extraction, and re-expands upon EG binding.

These findings were quantitatively validated via EIS. Nyquist plots (Fig. 3) were fitted to a modified Randles circuit $R_s(CPE[R_{ct}W])$, using a Constant Phase Element (CPE) for surface roughness.

Fitted parameters (Tab. 1) revealed a stable solution resistance ($R_s \approx 90 \Omega$). Post-electropolymerization, R_{ct} increased to 1540 Ω due to the insulating polymer layer. Template removal drastically reduced R_{ct} to 93.0 Ω , confirming successful cavity creation. Upon rebinding 10 μM EG, the sterically hindered cavities raised R_{ct} to 204 Ω .

Tab. 1: Fitted EIS parameters using the modified Randles circuit.

Modification Step	R_s (Ω)	R_{ct} (Ω)
After Electropolymerization	90.6	1540
After Template Removal	89.3	93.0
After Rebinding	92.1	204

Conclusion

A highly sensitive MIP electrochemical sensor for EG detection was successfully established on SPEs. A robust 15-cycle MIP layer and an optimized 0.2 M extraction protocol, verified via DPV and EIS, provide a strong analytical foundation. Future work will integrate custom thin-film electrodes with a microfluidic channel for simultaneous on-chip MIP polymerization and continuous sample measurements.

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