

Continuous Monitoring of Glyphosate in Water

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Summary:

Reliable detection of glyphosate remains challenging, particularly in real water samples. Here, we present a modification-free electrode that directly oxidizes glyphosate as a promising route to a robust detection system. Additionally, we show how dynamic conditions under microfluidic flow enhance mass transport and improve the detection limit compared with static operation, while a molecularly imprinted polymer preconcentrator mitigates matrix effects from common interferents. Together, these elements enable a proof-of-concept continuous sensing scheme for monitoring glyphosate in water.

Keywords: glyphosate, environmental monitoring, electrochemical sensor, microfluidics, molecularly imprinted polymer

Introduction

Glyphosate has been widely used since its commercialization in 1974, with further expansion following the adoption of glyphosate-tolerant crops [1]. Growing attention to potential health and environmental impacts has led to region-specific regulatory thresholds. In the European Union, authorization currently extends to 2033 and the drinking-water limit is set at 0.6 nM, whereas in the United States the corresponding limit is 4.1 μ M [2]. Consistent with its extensive application, glyphosate and its main metabolite aminomethylphosphonic acid (AMPA) are frequently detected in soils, waters, and foods [3], underscoring the need for sensitive environmental monitoring.

Current reference methods for glyphosate quantification rely on laboratory-based chromatography, typically high-performance liquid chromatography (HPLC) coupled to fluorescence detection or mass spectrometry (including tandem MS) [2]. However, these approaches do not enable continuous, in-situ monitoring. In this regard, electrochemical sensing provides a potential route to field-deployable, real-time detection, and selectivity has been pursued using molecularly imprinted polymers (MIPs), aptamers, metal-organic frameworks, and enzyme layers. Despite encouraging results, translation to robust products remains limited by matrix effects in real samples and by manufacturing constraints that impact reproducibility, operational stability, and selectivity [4]. Here, we evaluate a functionalization-free electrochemical approach based on the direct oxidation of glyphosate at gold electrodes, aiming to improve robustness, reversibility, scalability, and long-term stability. We further

assess dynamic operation under microfluidic flow to enhance mass transport and lower the limit of detection, and we integrate a MIP-based preconcentration step to mitigate matrix effects and enable detection at lower glyphosate concentrations.

Results

Direct electrochemical oxidation of glyphosate was first characterized by cyclic voltammetry (CV), comparing the response of the bare gold electrode in supporting electrolyte (blank) with that obtained after addition of glyphosate. A distinct oxidation peak is observed at ≈ 0.65 V vs Ag/AgCl (Fig. 1). This potential region was therefore selected for chronoamperometric detection using a fixed potential (Fig. 1, inset).

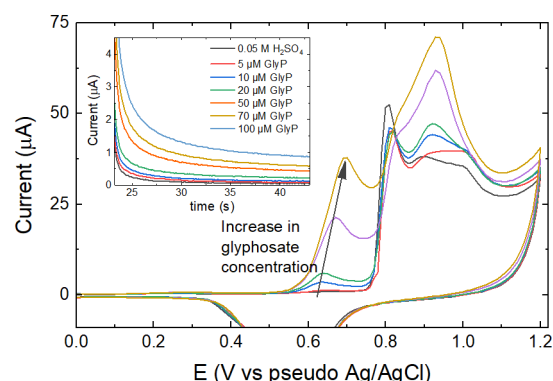


Fig. 1. Cyclic voltammetry of different glyphosate concentrations in 0.05 M H_2SO_4 (up to 1 mM) and inset showing chronoamperometry at 0.7 V vs Ag/AgCl.

Notably, the chronoamperometric current increases with increasing glyphosate concentration. The signal can be sampled at different times during the potential hold, yielding distinct

calibration sensitivities. Figure 2 shows calibration curves taken out at readout of 2 s in 0.05 M and 0.5 M H_2SO_4 . Interestingly, the performance is comparable in both acidic solutions, with a limit of detection (LOD, $\approx 5 \mu\text{M}$) and sensitivity ($\approx 135 \text{ nA M}^{-1} \text{cm}^{-2}$).

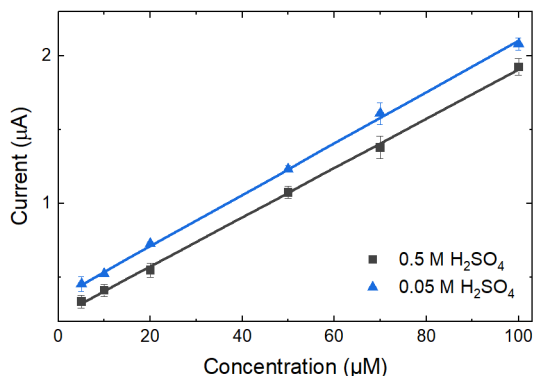


Fig 2. Calibration curves in 0.05 M and 0.5 M H_2SO_4 at 0.7 V and 0.75 V vs Ag/AgCl, respectively.

Although these results validate the sensing concept and agree with prior work [2], LOD remains substantially above the regulatory threshold for drinking water. To improve sensitivity, we implemented hydrodynamic measurements using a flow cell. Forced convection enhances mass transport to the electrode, increasing the oxidation current at a given glyphosate concentration. As shown in Fig. 3, this approach enables detection down to $0.05 \mu\text{M}$ leading to a 100-fold improvement relative to static operation.

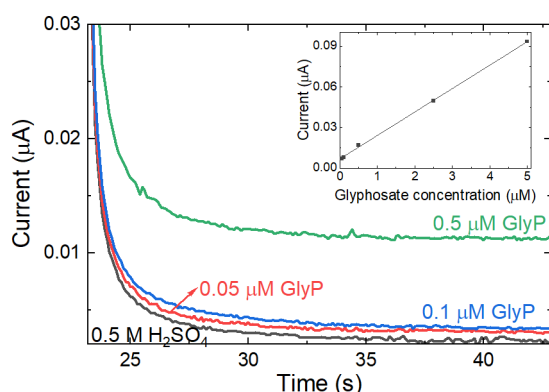


Fig 3. Chronoamperometric measurement in a microfluidic cell, at the flow of 1 mL/min, inset showing calibration curve in the range between 0.05 and $5 \mu\text{M}$.

We further evaluated common ionic interferents found in water. Chloride (Cl^-) markedly affected

glyphosate quantification due to its specific adsorption which lead to significant perturbation of glyphosate oxidation signal. To mitigate matrix effects and further lower the effective detection limit, we tested a commercially available MIP-based preconcentrator, as proposed by Uka et al. [2]. Using spiked water samples, we demonstrated a proof-of-concept for continuous glyphosate monitoring with the combined preconcentration and electrochemical detection scheme.

Conclusion

A functionalization-free gold electrode has been tested and evaluated for glyphosate detection, based on its direct oxidation. While static measurements yielded micromolar-level detection, operation under microfluidic flow enhanced mass transport and improved the LOD to $0.05 \mu\text{M}$ (100× versus static mode). Interference studies showed that chloride significantly perturbs the response due to its specific adsorption on gold and thus integrating an MIP-based preconcentrator mitigated matrix effects and enabled proof-of-concept measurements. Together, these results show the feasibility of a continuous, field-deployable glyphosate monitoring platform combining electrochemistry with upstream selective preconcentration.

References

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