

Glyphosate Detection with Mass-sensitive sensors using Molecularly Imprinted Polymers: Polymerization Strategies and Application

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Summary:

Molecularly imprinted polymer (MIP) coatings were fabricated on quartz crystal microbalance (QCM) sensors for the detection of glyphosate (Gly). The 16-mercaptohexadecanoic acid (16-MHDA) coupled with 2-hydroxyethyl methacrylate (2-HEMA) functionalized gold surface of the QCM was confirmed by Attenuated Total Reflectance - Fourier Transform Infrared Spectroscopy (ATR-FTIR). The MIP demonstrated enhanced binding to glyphosate compared to the non-imprinted polymer (NIP). The optimized MIP exhibited a high imprinting factor, achieved using a 60:40 citrate:ethanol solvent system and a 1:8:24 glyphosate:itaconic acid (ITA):N,N'-methylenebisacrylamide (BIS) molar ratio. These findings highlight the potential of the MIP-coated QCM sensor for glyphosate detection.

Keywords: Molecular Imprinted Polymer, Glyphosate, Quartz Crystal Microbalance, Maximum Residue Limit (MRL)

Introduction

Glyphosate is a widely used organophosphorus herbicide for weed control. It has been classified as a "probable human carcinogen" by the International Agency for Research on Cancer (IARC) [1]. Detecting glyphosate is particularly challenging due to its high polarity and lack of chromophores.

Residues of glyphosate in food, water, and the environment pose a significant threat to human health. Glyphosate inhibits acetylcholinesterase, an enzyme essential for proper central nervous system function. Therefore, monitoring glyphosate residues is critical to ensure they do not exceed the established MRL of 0.1 mg/kg [2]

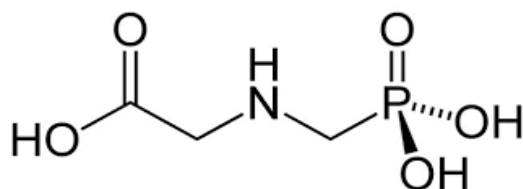


Fig. 1. Glyphosate Structure

MIPs are synthetic materials with highly selective recognition sites complementary in shape, size, and functional groups to a target molecule. In this study, MIPs were developed as selective coatings for QCM sensors to enable sensitive and selective detection of glyphosate.

Description of the New Method or System

The QCM gold surface was first functionalized with 16-MHDA to form a self-assembled monolayer. This was followed by coupling 2-HEMA to it via EDC/NHS chemistry to introduce polymerizable groups for covalent attachment. The MIP was synthesized using ITA as the functional monomer, BIS as the crosslinker, 2,2'-Azobis(2-methylpropionamide) dihydrochloride (AAPH) as the initiator, and Gly as the template. The pre-polymerization mixture was heated to 60 °C until the gel point was reached, then spin-coated onto the functionalized QCM surface. The NIP was prepared under identical conditions without adding the template molecule.

Sensor Measurements

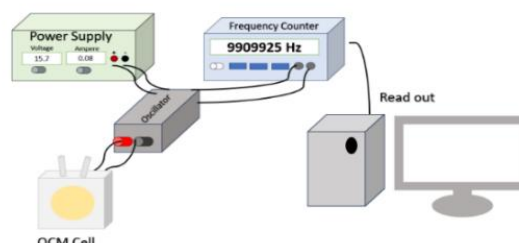


Fig. 2. QCM Measurement Setup

Figure 2 shows the QCM measurement setup. The dual-electrode QCMs were custom-made by screen-printing gold paste onto quartz blanks. The measurement setup consisted of an

oscillator connected to a QCM cell, a frequency counter, and a laboratory power supply. Resonance frequency changes were recorded and analyzed using a computer interface.

Results

Functionalization of QCM Surface

The functionalization of the QCM Surface is confirmed by ATR-FTIR. The 16- MHDA has a C-H band at 2920 cm^{-1} from its Alkyl chain. A peak at 1723 cm^{-1} , Ester C=O indicates successful coupling of MHDA and 2-HEMA.

QCM Sensor Response

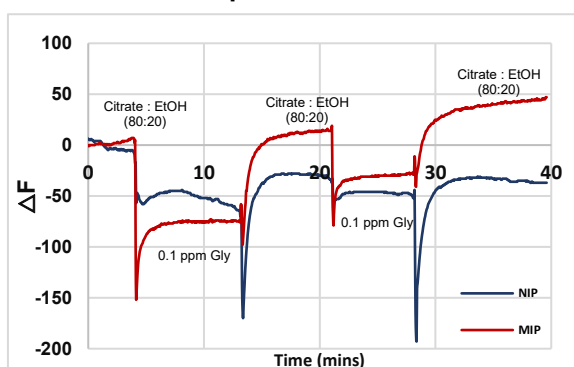


Fig. 3 QCM Measurement Graph of Coated Sensor (1:8:20 Gly:ITA: BIS)

The MIP-coated QCM (Fig.3) exhibits a 32 hz frequency shift than larger the NIP, indicating stronger, binding interactions with glyphosate. This confirms successful imprinting.

Optimization of Polymerization Parameters

The molar ratio of template: monomer: cross-linker governs MIP recognition capacity and selectivity [3].

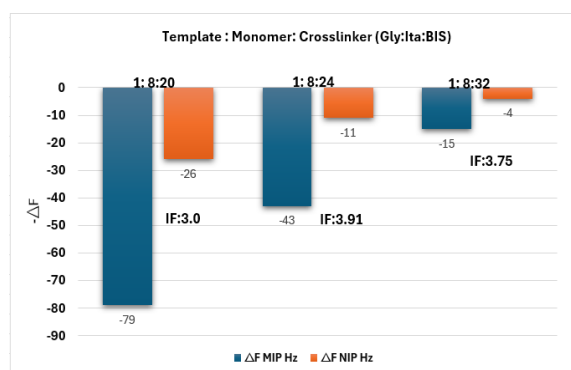


Fig. 4. Template: Monomer: Crosslinker Ratio (60:40 Citrate: Ethanol, 0.1 ppm Gly)

Fig 4 shows that 1:8:24 (Gly:Ita:BIS) produces the highest imprinting factor. Crosslinking density is sufficient to restrict the non-specific diffusion through the NIP network.

The 1:8:24 Gly:Ita:BIS formulation, combined with the previously optimized solvent system (60:40 Citrate:EtOH), defines the current

optimized parameters for the glyphosate-MIP QCM Sensor. Further work will be performed, including optimization of the pH, calibration curve, and selectivity. It will establish analytical performance for the evaluation of the QCM Sensor

References

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