## A Review on Detection of Pesticides From Fruit And Vegetable Samples

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Abstract- Sensors like molecularly imprinted electrochemical sensor and SPR immunosensor were studied to detect the presence of pesticides like imazalil and myclobutanil on fruit and vegetable samples. These sensors are made using the process of electro polymerisation for MIP's and surface plasmon resonance for SPR based sensors. To increase the surface of the imprinted sensor substances like gold nanoparticles and graphene were used, and in case of SPR sensors SPR imaging system was used to increase the efficiancy. These sensors being very selective can detect the concentrations as minute as 10-7 M, and these sensors are inspired from receptors of our body which makes them very selective and reduces the risk of false detection. But as MIP's need to be prepared to in very clean environment to avoid the impurities in moulding which eventually leads to false detection due to irregular moulds. And detection output of both of these sensors is studied on the basis of change in voltage and optical intensity.

*Keywords*- Pesticide, Adverse Health Effects, Analytical methods, Molecularly Imprinted Sensor, SPR Immunosensor.

#### I. INTRODUCTION

Pesticides can be analysed by gas chromatography (GC) with electron capture detection, flame ionization detection, or nitrogen phosphorus detection and/or liquid chromatography (LC) with ultraviolet, diode array, fluorescence, or electrochemical detection.

A sensor is a device that detects change in environment and responds to some output on the other systems. People use sensors to measure temperature, detect smoke, regulate pressure and many other uses. Molecularly imprinted sensor is a Biosensor and uses change in EMF/Voltage to detect the presence of pesticides. SPR Immunosensor uses change in optical intensity to detect the presence of pesticides. These sensors can be used in very small place and are cost friendly in terms of production. As these sensors are working on very micro levels, the manufacturing should be done in ultra clean environment to avoid moulding of any contaminant resulting in false detection <sup>[1]</sup>. The aim of this study is to review the methods available to detect the presence of pesticide residue using sensors like MIP and SPR.

#### **II. MATERIAL AND METHODS**

#### 2.1 Balls-in-tube matrix solid phase dispersion (BiT-MSPD)

In this study, a new procedure called balls-in-tube matrix solid-phase dispersion (BiT-MSPD) is proposed based on simplifying the standard MSPD process since all sample preparation is performed directly in a closed domain tube with the help of metal balls (Fig. 1). Tandem mass spectroscopy was used with high performance liquid chromatography to detect 133 pesticide residues from fruits like apple,peach,pear and plum and a new method was also developed successfully using BiT-MSPD<sup>[2]</sup>.

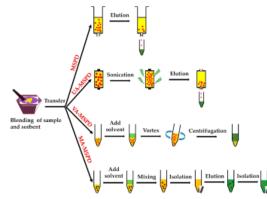


Fig. 1 Balls-in-tube matrix solid-phase dispersion

# 2.2 Development and validation of the 128 pesticide cutting method for bananas by modified QuEChERS and UHPLC analysis - MS / MS

А	detailed	method of	using	128
pesticide values	on	bananas is	describe	d.

Includes the use of a modified QuEChERS process followed by UHPLC - MS / MS (Ultra High-performance Liquid Chromatography combined with Tandem Mass Spectrometry analysis) (Fig. 2). This approach has been verified in accordance with the guidelines of the European Union SANCO / 12495/2011 and the Brazilian Manual of Analytical Quality Assurance <sup>[3]</sup>.

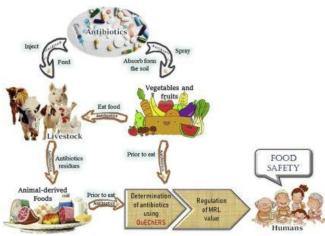


Fig. 2 Example of application of QuEChERS

## 2.3 Detection of Tebuconazole from fruit and vegetable sample using imprinted sensors

A molecularly imprinted electrochemical sensor is designed for the particular identification of tebuconazole in vegetable and fruit samples. To enlarge the specific area of gold nanoparticles graphene was introduced inside a glass electrode.. Prussian blue colour was bonded with gold nanoparticles to the converted electrode and acted as a weak probe, followed by electronically controlled polymerization of a cell-based polymer film as a causative agent. Systematic verification and depiction of the character is performed to ensure effective adjustment and processes of the blue polymers and electrodes embedded in the electrode (Fig 3). Key criterias, consisting of concentration of monomer, scanning cycles and pH, varied systematically to determine their effect on sensory function <sup>[4]</sup>.

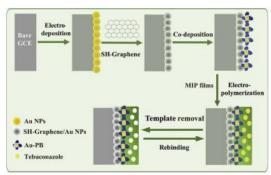


Fig. 3 Flowchart depicting method of MIP Sensors

2.4 Six pesticides, azoxystrobin, boscalid, chlorfenapyr, imazalil, isoxathion, and nitenpyram, were detected simultaneously using surface plasmon resonance (SPR) immunosensor (Fig. 4)

4-bromo-2-(4-chlorophenyl)-1-(ethoxymethyl)-5 (trifluoromethyl)pyrrole-3-carbonitrile(chlorfenapyr), 5.5 - 50 ng / mL of imazalil, 3.5 - 50 ng / mL of isoxathion, and 8.5 - 110 ng / mL of nitenpyram.

They claimed satisfactory recovery results in tomato samples: 104 - 116% azoxystrobin, 94 - 101% boscalid, 90 112% chlorfenapyr, 96 - 106% imazalil, 107 - 119% isoxathion, and 104 - 109% of bananas. The coefficient of correlation of liquid chromatography (HPLC or LC-MS / MS) using vegetable samples was also well matched: 0.91 -0.99 as R2 without being partial, without nitenpyram where the sensitivity of immonusensor of SPR was very less. SPR immunosensor will be very efficient in identifying pesticide residues in vegetable samples<sup>[5]</sup>.

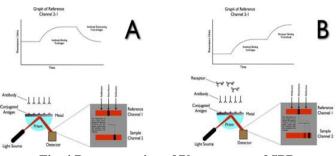


Fig. 4 Representation of Phenomenon of SPR

#### Methodology

There are two methods of detection of Pesticides we are going to study in this Review Paper. They are discussed below:

A. Detection by Molecularly Imprinted Polymer Sensors (MIPs):

- In this method a binding agent is used on gold electrode and some reagents are used to increase surface area and conductivity. Generally used reagents are gold nanoparticles and graphene.
- In some case reagents like [Fe (CN)<sub>6</sub>]<sup>4-/</sup> [Fe (CN)<sub>6</sub>]<sup>3-</sup> are used to increase conductivity <sup>[6]</sup>.
- Then this mixture is polymerized using electropolymerization. And then target pesticide molecules are rinsed using inert substances like nitrogen gas and ultrapure water. Leaving behind the moulds with the shape of target molecules.
- These sensors are very selective because of unique mould shapes of each molecule and are sensitive because of large surface area (Fig. 5)
- Output is measured on the basis of change in EMF or change in current <sup>[7].</sup>

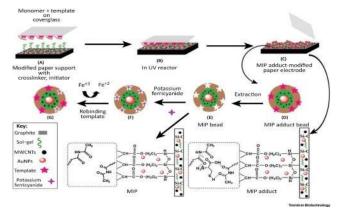


Fig. 5 Representation of Working of MIP Sensors

### B. Detection by Surface Plasmon Resonance Immunosensor (SPR):

- ELISA is created to detect pesticide residues in plants<sup>[8]</sup>. but can't identify multiple pesticides.
- To get rid of drawback, S.P.R Immunosensor with micro channel type sensor chip has been developed to detect fungicide, insecticide etc. in last few years.
- The SPR imaging system is utilize in the SPR constituents. The chip sensor used was Glass Prism on which the face was fastened with a Gold Thin Layer.
- For SPR Immunosensor, five grams each of vegetables and lemon samples were strenuously shaken with 25ml of methyl alcohol by reciprocal shaker for 30min to extract pesticide into liquid phase.
- For SPR Immunosensor, the pesticide extract which was centrifuged at 3000 rpm for 10 min at room temperature. This was made mild while diluting with distilled water to prepare a 10% Methyl alcohol equivalent solution and adjusted to the Working spectrum of SPR Immunosensor.
- SPR is a promising tool in sensor technology for Biomedical application (Fig 6).<sup>[9]</sup>

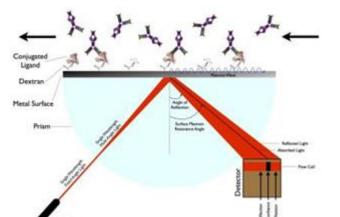


Fig. 6 Representation of phenomenon of SPR

#### **III. RESULT AND DISCUSSION**

Nowadays these sensors are widely used all over the world for chemicals like tebuconazole, trimethoprim etc. These sensors can be used for testing of pesticides on fruits and vegetables by easy-to-use methods providing us with healthy and safe lifestyle. Methods used in preparation of these sensors are cost friendly making it usable for everyone. Due to their high sensitivity these sensors can be used to detect even a small amount of pesticide residue present on a sample.

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#### REFERENCES

- Nollet L. M. L., Rathore H. S. Handbook of Pesticides: Methods of Pesticide Residues Analysis, ISBN 9780367577278, June 30, 2020 by CRC Press.
- [2] Xijuan Tu and WenbinChen, A Review on the Recent Progress in Matrix Solid Phase Dispersion, *Molecules*, 2018, 23(11), 2767.
- [3] ChenyuZhang,YaochengDeg, JiangfuZheg, YangZhn, Lih uaYag,ChanjuanLiao,LongSu,YaoyuZho,DaoxinGong,Li ngChen,AoLuo,*TrAC Trends Analytical Chemistry*, Volume 118, *September 2019*, *Pages 517-537*
- [4] Qi P., Wang J., Wang Z., Wang X., Wang X., Xu X., Xu H. ,ShanshanDi,Zhang H., Wang Q., Wang X., Construction of a probe-immobilized molecularly imprinted electrochemical sensor with dual signal amplification of thiol graphene and gold nanoparticles for selective detection of tebuconazole in vegetable and fruit

samples *Electrochimica Acta*, June 2018, volume 2741, pp 406-414.

- [5] Miyake S., Hirakawa Y., Yamasaki T., Watanabe E., Harada A., Iwasa S., and Narita H., Simultaneous Detection of Six Different Types of Pesticides by an Immunosensor Based on Surface Plasmon Resonance, *Analytical Sciences*, March 2020 Vol 36.
- [6] Ahmad O. S., Bedwell T. S., Esen C., Garcia-Cruz, A., Sergey A. Piletsky, A., Molecularly Imprinted Polymers in Electrochemical and Optical Sensors, March 2019, Volume 37, Issue 3, Pages 294-309.
- [7] Li S., Ge Y., Piletsky S. A., Lunec J., Molecularly Imprinted Sensors: Overview and Applications, Chapter 5, Page 94, Article 2.1, first edition publishing year 2012.
- [8] Zhen-LinXu, Hao Deng, Xing-Fei Deng, Jin-YiYang, Yue-Ming Jiang, Dao-Ping Zeng, Fang Huang, Yu-Dong Shen, Hong-Tao Lei, HongWang, Yuan-Ming Sun, Monitoring of organophosphorus pesticides in vegetables using monoclonal antibody-based direct competitive ELISA followed by HPLC–MS/MS, *Food Chemistry*, April 2012, Volume 131, Issue 4,, Pages 1569-1576.
- [9] Surface plasmon resonance (spr) sensor surface support; https://patents.google.com/patent/WO2003046526A1/en.