FABRICATION OF SILVER NANOWIRES ON PAPER BY INKJET PRINTING AND USING THEM FOR PESTICIDE DETECTION ON THE SKIN OF FRUITS

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INTRODUCTION :

Pesticides are chemical substances used to kill insects and animals that destroy crops. They are characterized by pronounced persistence against chemical/biological degradation, high environmental mobility, strong tendency for bioaccumulation in human and animal tissues, and significant impacts on human health and the environment, even at extremely low concentrations.

With the human population at over 7 billion, there is an unprecedented need for clean air, water, food, security and health care. Chemical and biological sensors play a tremendous role in the assurance of the quality of food we consume, the safety of the environment we live in and the well-being of our health.The current gold standards for trace detection utilize techniques such as High Performance Liquid Chromatography (HPLC) and Mass Spectrometry (MS) for chemicals, and bioassays such ELISA and Western blot for biological agents. While sensitive, these tests are often time consuming, expensive and require skilled technicians. Recent advances in sensing such as Micro Total Analysis Systems (µTAS) and Lab-on-chip (LOC) technology, have focused on addressing the time and labor aspects of the problem without addressing the issue of cost, in the hope that cost is reduced when the technology gains traction.

The need for highly sensitive detection is pervasive across a wide range of industries, including:

- Food contamination
    - Melamine in milk
    - Unsafe pesticide levels
- Anti-counterfeiting
    - Weakened/inactive counterfeit drugs
    - Counterfeit perfumes and liquors
- Drug or explosive residue detection (e.g. at ports of entry)

- Cocaine, heroin, THC

SERS has emerged as a practical trace detection technology enabled by a portable detector and a cleverly-engineered substrate.SERS is faster and easier to perform compared to the most commonly used techniques such as those which use mass spectrometry and gas chromatography which maintains measurement sensitivity and reliability while solving issues of cost and complexity.

Surface enhanced Raman spectroscopy (SERS) is a highly sensitive optical detection modality that has great potential for chemical and biomolecule detection. The specificity of Raman fingerprint spectra combined with the strong localized plasmonic enhancement of noble metal nanostructures has led to reports of label-free single molecule identification.

In a nutshell,the SERS effect is about amplifying Raman signals by several orders of magnitude. The amplification of the signals in SERS comes mainly through the electromagnetic interaction of light with metals, which produces large amplifications of the laser field through excitations generally known as plasmon resonances. To profit from these, the molecules must typically be adsorbed on the metal surface, or at least be very close to it (typically ≈10 nm maximum).

Benefits of SERS

While the current widespread trace detection technologies offer similar detection performance, SERS has a number of appealing features:

- Inexpensive, portable equipment
- Simultaneous detection of multiple sample constituents
- Minimal false positives
- Portable, detection at the point of sample collection
- Mitigates fluorescence issues found in real-world samples

There are several methods of fabricating SERS substrate such as depositing nanostructures using seeded growth,self assembly,adsorption from colloidal solution, brushing, inkjet printing, physical vapour deposition,screen printing,or by in situ formation using chemical reduction. Amongst these, the use of additive drop-on-demand printing technology offers a cost-effective route for manufacturing of SERS substrates

Inkjet printing is a material-conserving deposition technique used for liquid phase materials. These materials, or inks, consist of a solute dissolved or otherwise dispersed in a solvent. Inkjet-printing jets the single ink droplet from the nozzle to the desired position, therefore, no waste is created, resulting in an economical fabrication solution and the printing is uniform throughout the substrate.

Paper-based sensors are a new alternative technology for fabricating simple, low-cost, portable and disposable analytical devices for many application areas including clinical diagnosis, food quality control and environmental monitoring. Apart from being a cheaper material than other substrates, paper is eco-friendly and biodegradable.Devices made of paper inherently support sample handling capabilities such as analyte separation and concentration through fluidic flow, but here instead of fluid flowing along a channel as in conventional microfluidic devices, the flow is driven by capillary wicking of the underlying cellulose.

As mentioned earlier,there are many techniques to detect pesticides.In this present work we have developed a simple and inexpensive but exceptionally sensitive portable chemical and biological sensing platform through the innovative use of paper combined with Surface Enhanced Raman spectroscopy (SERS).A chromatographic methodology was developed to separate some dyes and the separated dyes can be detected by SERS.

This method can be mimicked to identify,quantify some types of organochlorine and organophosphorus pesticide residues in fruit samples.But the solvents must be used selectively for each pesticide to be separated.

MATERIALS USED :

1. CHEMICALS (For fabricating SERS substrate)

   - Silver Nitrate
   - Ascorbic Acid
   - Potassium Bromide
   - Potassium Iodide
   - Isopropyl Alcohol
   - Ethanol
   - Sodium Sulphite anhydrous
   - Metol(Monomethyl p-aminophenol hemisulphate)
   - Quinol
   - Borax
   - De-Ionised Water

2. DYES

   - Rhodamine 6G (R6G)
   - Methyl Orange
   - Methylene Blue
   - Malachite Green

3. SOLVENTS FOR CHROMATOGRAPHY

   - Water
   - Ethanol
   - Isopropyl alcohol
   - Toluene

- Chloroform

- Dichloromethane

- Acetronitrile AR

- Petroleum ether

4. APPARATUS

- Deskjet printer (HP 1010 series)

- Black Ink Cartridges (HP 802)

- Halogen Lamp (Crompton Greaves J240V 500 W R7S, 9500 Lumens)

- Laminar Hood (Esco)

- Sonicator (Bransonic® Ultrasonic Cleaner)

- Syringe Filter (Millex ® GV Filter unit)

- 4 probe multimeter (RCHEK-model RC2175)

5. SOFTWARES

- Microsoft Office PowerPoint 2016

- OriginPro

- Fityk

6. PREPARATION OF SOLUTIONS

All the chemicals used were used as received from SDFCL, Fisher Scientific and Merck Chemicals and are of higher purity. All the solutions were prepared using DI water. 0.25M $AgNO_3$ and 0.5M KX solutions were prepared to print on paper. KX is a mixture of KBr and KI in the ratio 95: 5.KI was added to enhance the photosensitivity. The molar ratio of $AgNO_3$ to KX is always 1:2, to ensure complete conversion of AgX on paper. 0.5M KCl solution was prepared to print over the silver nanowires to get AgCl layer on paper. The developer solution was

prepared by dissolving 20g Sodium Sulphite, 0.4g Borax, 1g Quinol and 0.4g Metol in 100mL deionized water.

EXPERIMENTAL METHODS :

1.Fabrication of SERS substrate :

A HP Deskjet 1010 series printer was used for printing the precursor salt solutions on a paper(A4 copier paper,80 gsm).Two separate HP 802 black ink cartridges were used for printing KX and $AgNO_3$ solutions.The cartridges were thoroughly cleaned removing the sponge holding the black ink and rinsing the reservoir in flowing tap water,finally with DI water.If required, sonication is done and the DI water was filled in reservoir and some test patterns were printed on paper until there was no evidence of black ink.

The loading of the cartridge was found out by weighing the cartridge before and immediately after printing with DI water. This was repeated for five printings and the average of difference in their weights was noted. Knowing the density of water, the volume to be used per print could be found out. The loading of 0.25M of $AgNO_3$ was found to be $0.05 mg/cm^2$. The DI water loading was found to be $1.17 \ mg/ \ cm^2$

In this work, plausible print-expose-develop mechanism was followed. Six $4.5x4.5 \ cm^2$ (each) square patterns were drawn on Microsoft Office PowerPoint 2013 and printed alternatively with 0.25M $AgNO_3$ and 0.5M KX for six times.

The reducing agent KX was printed on paper at first because it enhances the conductivity and adheres to the paper properly while $AgNO_3$ does not stick well to paper. The number of printings was increased to ensure uniform printing of the solutions on the paper and to increase the conductivity of silver on the printed area. As a result of alternate printings, AX layers were formed on the paper. This is identified by the greenish tint on the printed surface(may be majorly because

of AgBr). The paper should be dried properly after each print,otherwise printing on wet paper may block the print head and lead to cartridge failure.

After all the printings, the printed area was then exposed to light from the halogen lamp for approximately 15 minutes. Keeping the sample for prolonged time under the lamp showed no appreciable effect. The color of the sample changed to dark greenish, indicating the formation of Ag latent clusters.The sample was then sequentially immersed for 10 min in a standard photographic developer solution (D-76),which is a reservoir of electrons and hence reduces Ag+ ions to Ag. These ions on reduction change its lattice structure by breaking the clusters and forming Ag nanowires on paper. After development,printed area changed to dark greenish-brown color.Developing the solution immediately after exposure showed higher conductivity compared to the exposed prints which were developed after few days.This shows the direct dependence of Ag nanowire formation on temperature. It was put in the DI water for another 5-10 min and was shaken intermittently for removal of any unreacted ions. It was put in a laminar hood for complete drying.The resistance values in all the six squares were measured using the four-point meter and found to be 9 Ω/cm2, 8 Ω/cm2,7 Ω/cm2,9 Ω/cm2,18 Ω/cm2 and 20 Ω/cm2.Since the resistance is less, their conductivity will be more. The mean resistance was found to be as low as 10.6Ω.The standard deviation of resistance was found to be 5.32 .
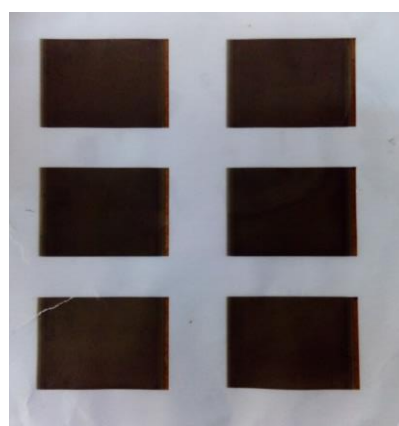

**Fig.1.Fabrication of inkjet printed Silver nanowire substrate**
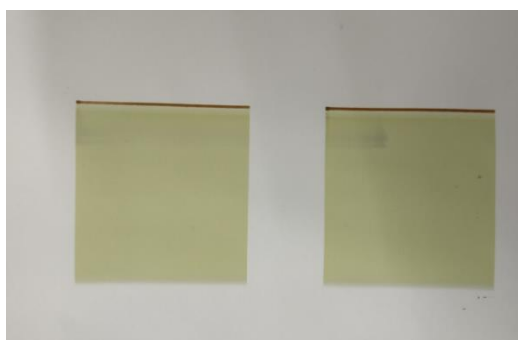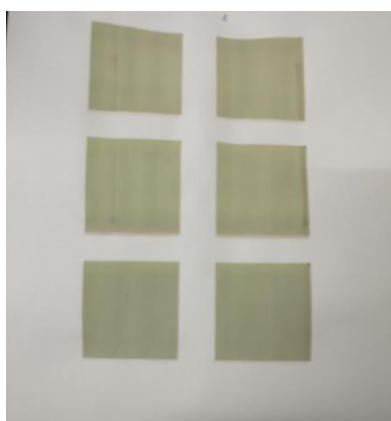
Fig.2a. After exposing under

halogen lamp

Fig.2b. After development

of nanowires

The printed silver base substrate was then used for chromatography for dye separation and later for SERS to detect the dyes.

2. **CHROMATOGRAPHIC SEPARATION** : Printed paper based silver nanowire substrate is used to separate the dyes by the phenomenon of 'paper chromatography'.Chromatography is used to separate mixtures of substances into their components.The mixture of dyes separated are Rhodamine 6G,Methyl Orange,Methylene blue and Malachite green. Different components travel at different rates. In paper chromatography, the stationary phase is a very uniform absorbent paper. The mobile phase is a suitable liquid solvent or mixture of solvents.
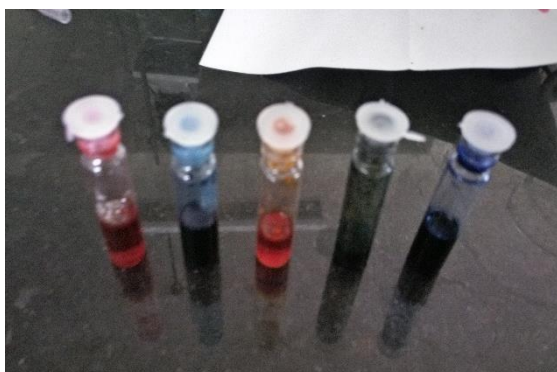
Fig.3a. Rhodamine 6G,Methylene blue,Methyl

orange,Malachite green and the mixture of dyes

Fig.3b. Chromatography setup

To perform chromatographic separation of a sample, a pipette is used to place a small drop of the sample onto the printed paper SERS substrate. After drying, the substrate is placed upright inside a sealed jar that has been pre-saturated with the mobile phase while making sure that there is no contact with the sides of the jar. The mobile phase solvents differ depending on the sample and target components being separated. The level of the mobile phase is adjusted so that the meniscus is 1 cm below that of the position of the applied droplet. As the solvent is wicked up the chromatographic strip, the components of the sample are separated on the strip.I have maintained a run time of 30 min. After performing the separation, the solvent front is marked using a pencil and the chromatogram is air-dried. To achieve separation of closely related species, 2D chromatographic separation is employed. This is done by rotating the strip by 90 degrees (after drying) and then performing another separation step using a second mobile phase.

Fig.4) Paper Chromatography of R6G & methyl orange using plain A4 copier paper, Kimwipe paper, Silver base paper

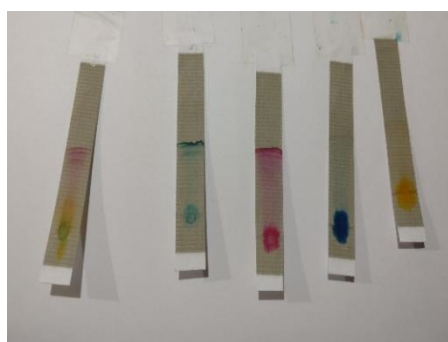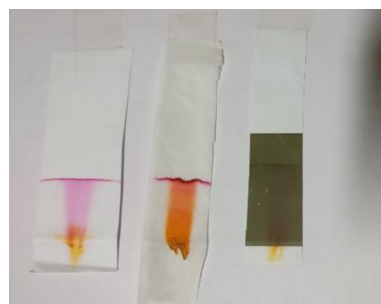4a. Ethanol as solvent
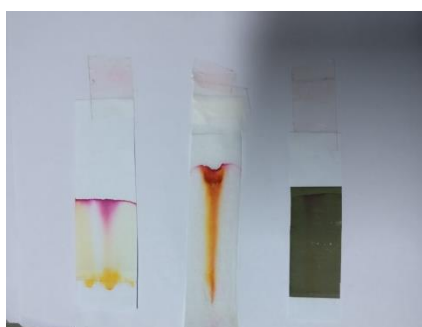
4b. Isopropyl alcohol as solvent

Fig.5a)Paper chromatography using AgX nanowire substrate with IPA(left) and ethanol(right).
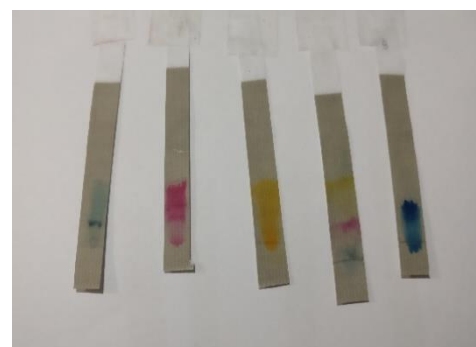
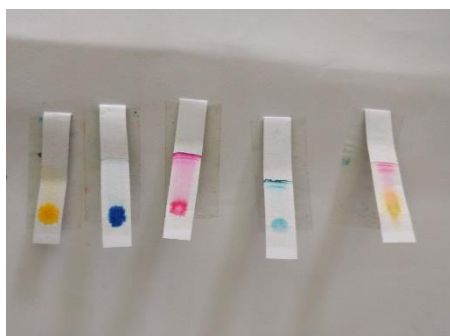Fig.5b) Rear side of chromatography papers – with IPA(left) and ethanol (right)

Fig.6) Dyes after separation are sticked on a glass slide for SERS where

i) Plain paper

ii) Ag base paper

iii) Pure R6G

iv) Pure methylene blue

v) Pure methyl orange

vi) R6G from mixture

vii) Methyl Orange from mixture

viii) Green colour from mixture

ix) Blue + some green from mixture

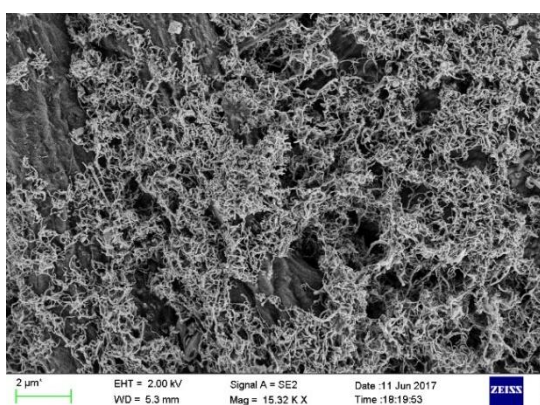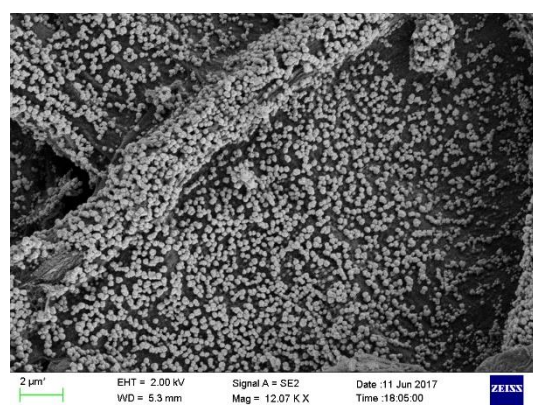## RESULTS AND DISCUSSIONS :

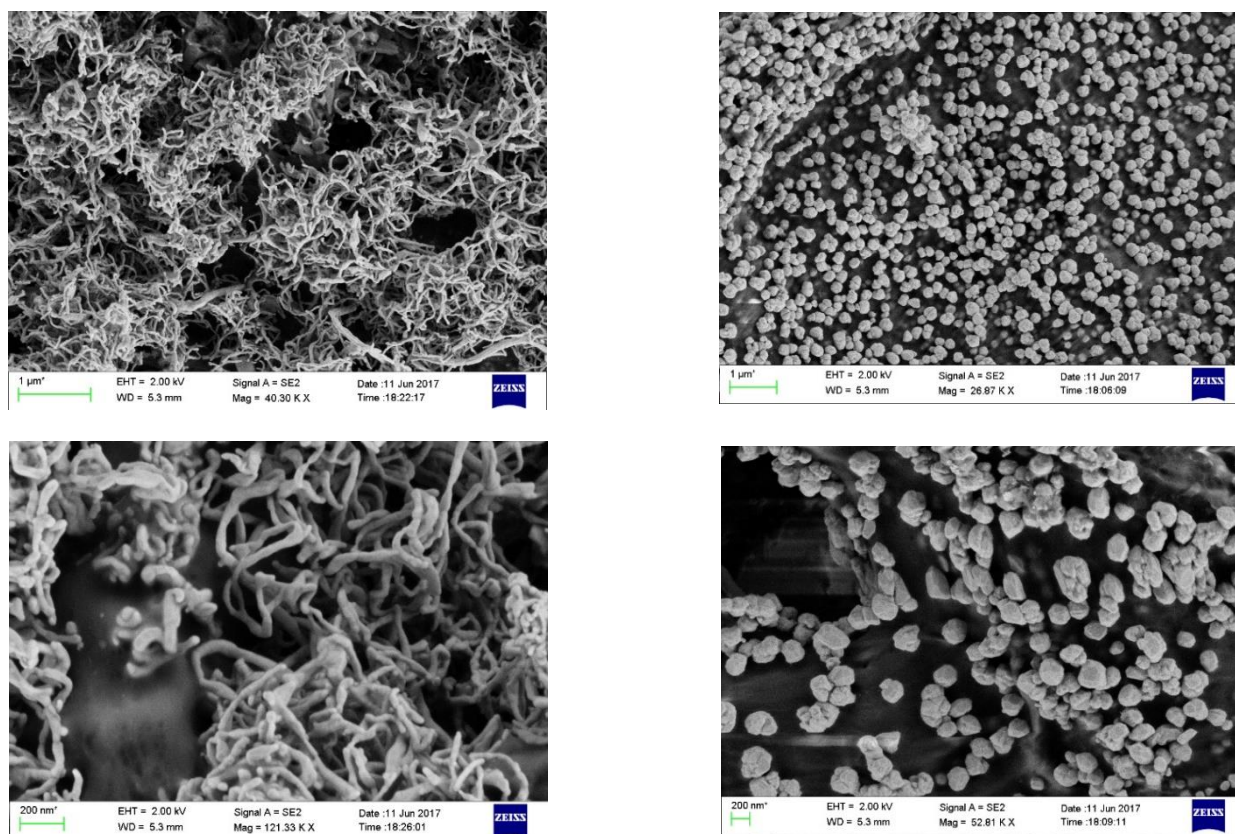## SEM IMAGES :

Fig.6a. Silver nanowires

Fig.6b. Silver nanoparticles

Fig.6a. Formation of Ag nanowires due to the usage of KX along with AgNO$_3$

6b. Formation of Ag nanoparticles due to the usage of KCl and AgNO$_3$

CHROMATOGRAPHY ANALYSIS :

The heights travelled by various dyes in a given time during paper chromatography using various solvents as mentioned below.

For AgNO$_3$ & KX print (in cm)   Duration : 30 min

Solvents	R6G	Methyl Orange	Methylene Blue	Malachite Green	Mixture			
					R6G	Orange	Blue	Green
Acetonitrile	1.2	2.2	0.7	2.7	0.5	1.8	0.4	2.5
Petroleum ether	0.5	0.4	0.2	0.2	0.3	0.3	0.3	0.3
Chloroform	2.9	0.3	2.8	2.5	2.2	2	0.2	0.3
Dichloromethane	2.8	0.5	3.7	3	3.3	0.2	0.2	3.2
Toluene	0.4	0.3	0.2	--	0.2	0.2	0.2	--
Ethanol	1.2	1.4	1	1.4	0.9	1.9	0.4	--
Isopropyl alcohol	2.1	1.8	2.2	1.8	2.1	0.9	0.3	0.3

For AgNO$_3$ & KCl print (in cm)   Duration : 30 min

Solvents	R6G	Methyl Orange	Methylene Blue	Malachite Green	Mixture			
					R6G	Orange	Blue	Green
Acetonitrile	1	2.3	0.7	2.5	0.4	1.8	0.25	2.3
Petroleum ether	0.6	1	0.4	1.2	0.2	0.5	0.2	1.2
Chloroform	2.5	0.2	3.1	2.4	2.5	2.5	0.9	--
Dichloromethane	3.7	0.1	3.7	2.6	3.7	0.4	3.3	--

OBSERVATIONS :

- The time taken for Ag base paper to reach certain height was found to be less than that of A4 paper

- This is just the effect of increase in capillary action of paper due to Silver nanowire formation.

- For some solvents like acetonitrile,dichloromethane it is found that using KX print assured separation at greater heights than that for KCl indicating high capillary effect due to nanowires.

- Solvents like acetonitrile,dichloromethane and chloroform are found to be more volatile relatively,so proper enclosure has to be maintained during experiment to prevent their wastage by evaporation.
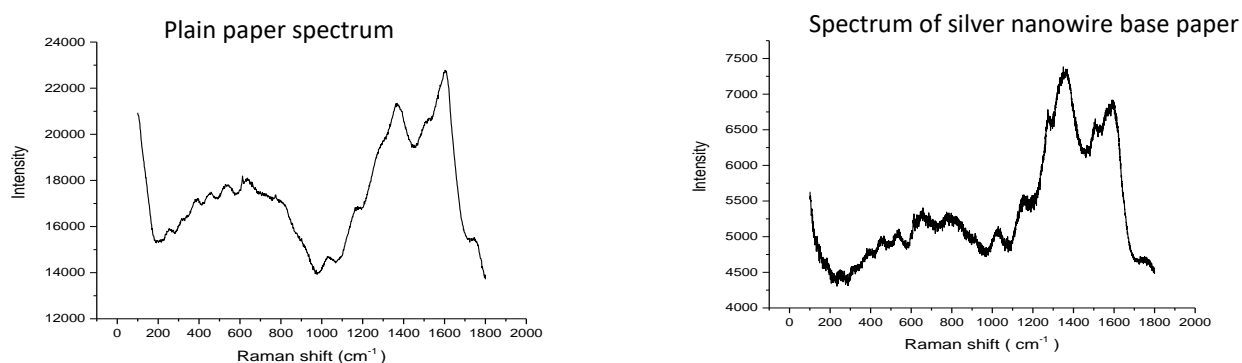
SERS MEASUREMENTS:

The separated dyes using Chloroform on chromatograms at various positions are cut and sticked on a glass slide.SERS measurements are performed using a 785 nm laser diode (Ocean Optics), a QE65000 (Ocean Optics) portable spectrometer, and a fiber optic probe (In Photonics). A laser power of 17 mW was used to interrogate the samples on paper and a 1-second CCD exposure was used for collecting the SERS spectra. The position of the target analytes on the chromatogram and their SERS spectra were recorded. To determine the signal intensity, the height of the most prominent peak from the Raman bands was calculated. This was repeated for three separate trials to determine their repeatability.

ANALYSIS OF SERS SPECTRUM : The averaged spectra of the data from three trials were plotted using ORIGIN PRO software. Background contributions from the substrates were accounted for by manually subtracting the SERS signals obtained from blank samples and compared. As the obtained spectra is not intense enough to co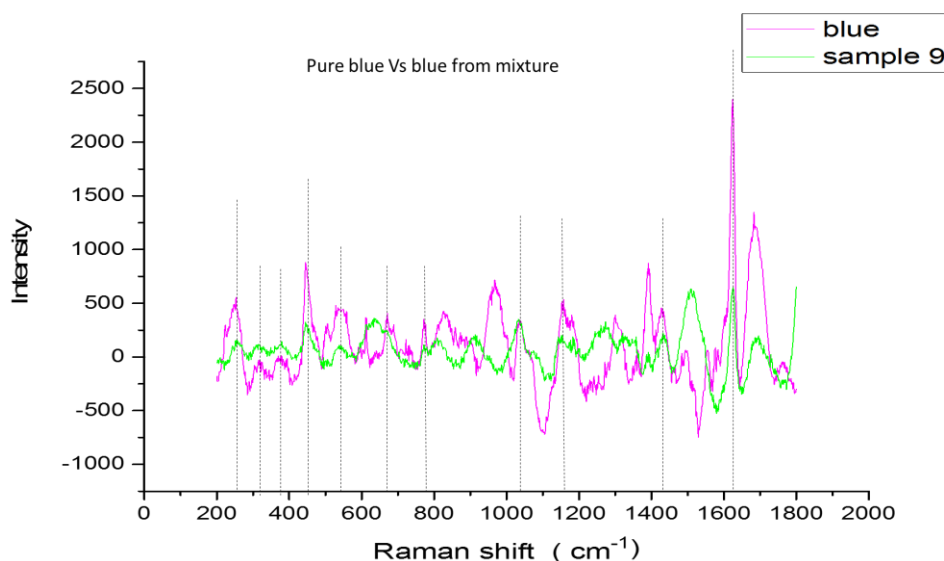mpare with the standard spectrum, I have used an open source FITYK software. Fityk is a program for nonlinear fitting of analytical functions (especially peak-shaped) to data (usually experimental data).

Fityk was helpful in removing the background signal and noise from the obtained raman spectra.As the plot I have obtained is broader and signal due to fluorescence has dominated over the signal due to raman spectrum,this software made me to remove the difficulties involved. Firstly,the text files of averaged Raman spectra were loaded in Fityk and then reference was selected for background signal removal.It was being saved as a DAT file which can be extracted directly in Origin pro software to get final plot.Then in the origin software,spectra of dyes from various samples are compared using the pure dye spectrum as a reference one.With the standard spectra of pure dyes,our obtained signals can be compared for the peaks at specific wavelengths and hence they can be detected.

Fig.7. Raman spectra of all the dyes separated from the mixture and comparing them with the reference spectra of pure dyes

Pure R6G Vs R6G from mixture

Pure orange Vs orange from mixture

Pure blue Vs blue from mixture samples
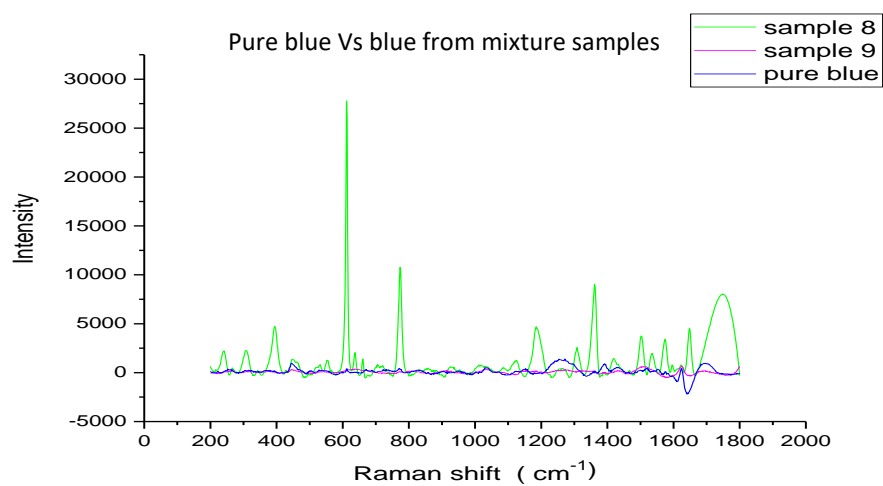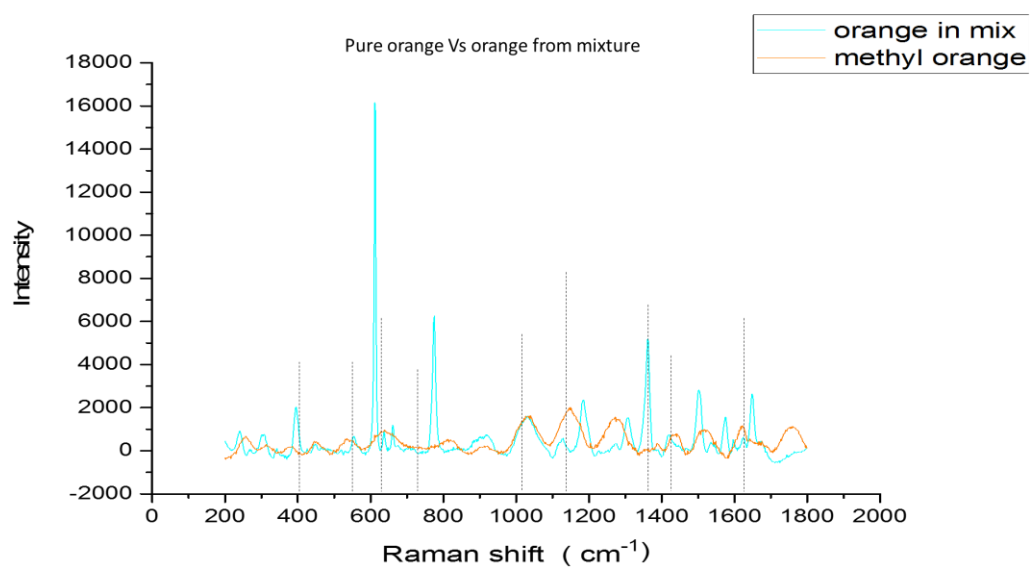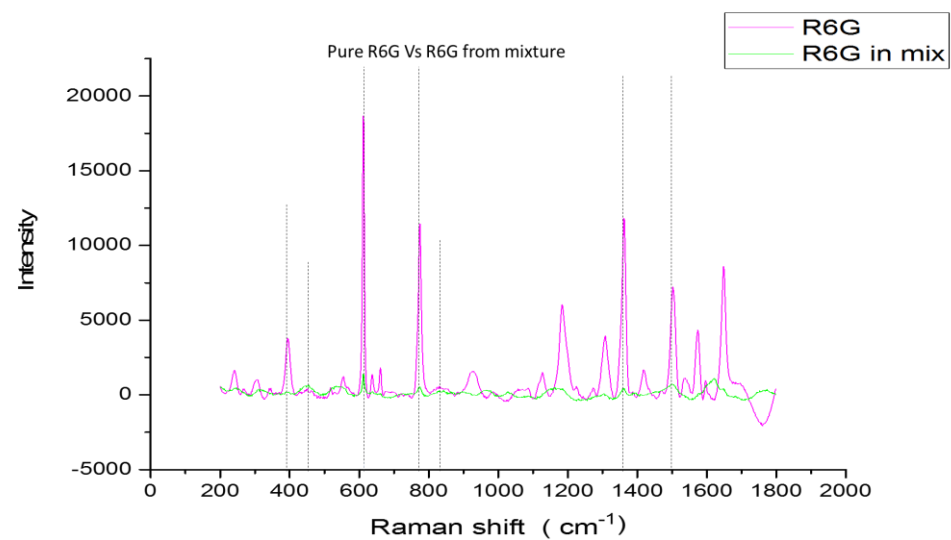
At the wavelengths of common peaks, dashed lines were drawn and shown in the above figures.With the comparison of peaks, the dyes were identified.Infact,a better comparison could be possible with proper plotting of Raman data eliminating noise.

PESTICIDE EXTRACTION :

This work can be mimicked for the pesticide detection as well.The below list is of the pesticides found on most common fruits and solvents used for their extraction.After extraction,pesticides can be tested for their identity by chromatography and hence detected by SERS.

Commonly found pesticides on fruits

FRUITS	PESTICIDES
Apple	Azinphos – methyl
	Thiophanate-methyl
	Carbaryl
	Dimethoate

	Fenitrothion
	Carbendazim
	Famoxadone
Figs	Dithiocarbamates
	Parathion-methyl
Watermelon	Acetamiprid
	Acephate
	Methamidophos
	Thiabendazole
Papaya	Chlorothalonil
	Dimethoate
	Dithiocarbamates
	Thiacloprid
Peach	Iprodione
Pear	Carbendazim
Plum	Dicofol
Table grapes	Captan
	Methomyl

Specific solvents for extraction of specific pesticides

PESTICIDES	SOLVENTS USED
Chlorinated pesticides	Acetonitrile
Organophosphorous pesticides	Acetone
Synthetic Pyrethroid	Acetone

N-Methyl Carbamate	Acetonitrile+dichloromethane
Acetamiprid	Methanol
Imidacloprid	Methanol/water (3 : 1 v/v)
Propiconazole	Methanol+dichloromethane
Thiram/Ferbam/Ziram	Chloroform
Maneb/Mancozeb/Zineb	EDTA
Nabam	Water
Dithiocarbamate residues	Isooctane
Chlorinated pesticides	Acetonitrile
Organophosphorous pesticides	Acetone
Synthetic Pyrethroid	Acetone
N-Methyl Carbamate	Acetonitrile+dichloromethane
Acetamiprid	Methanol
Imidacloprid	Methanol/water (3 : 1 v/v)
Propiconazole	Methanol+dichloromethane
Thiram/Ferbam/Ziram	Chloroform
Maneb/Mancozeb/Zineb	EDTA
Nabam	Water
Dithiocarbamate residues	Isooctane

FUTURE STUDIES :

The difficulty I have encountered is the low signal intensity of Raman spectra which in turn troubled in the detection part.This might be due to the penetration of dyes into the paper which can be overcomed by application of wax on the paper.But this can also affect the capillary action of paper.So proper steps are to

be taken to optimize the penetration of dye and hence the capillary action.This could help us to get proper intense Raman peaks for comparison.

For pesticide detection,surface swabs are used.In the surface swab experiments, 5 µL of sample was spotted arbitrarily over the surface of a microscope glass slide. After the sample had dried, the SERS-active paper was soaked with specific solvent(for eg.acetonitrile in the case of malathion) and wiped gently but firmly over the glass slide, while ensuring that the entire swab was in contact with the surface during the swab.After the swab had dried, it was placed into a vial containing 2 mL of solvent(here, acetonitrile),the solvent is quickly wicked up into the swab toward the detection tip. After 20 minutes of run time, the swab was allowed to dry and the detection zone was scanned to determine the strongest SERS signal. This was repeated for five separate trials, giving a total of five SERS measurements for each analyte concentration.

Method development for pesticide residues is expected to continue evolving as it has been in the past; researchers will apply and adapt technology, as it becomes available, to meet the needs resulting from pesticide usage and environmental contamination. Existing methods will continue to be used and expanded wherever practical. Special attention will be given to use of new determinative techniques.

However, new methods for residues not amenable to existing methods must be developed, and these will be multiresidue methods wherever possible.

CONCLUSION :

Inkjet Printer + Paper + Science = Cheap & Easy Pesticide Detection

The results show that the proposed method for the determination of dyes is simple, economical.With little changes, this can be made precise to mimic and analyze traces of pesticide residues on the skin of fruits.In this way,pesticides can be separated from fruits and detected at the point-of-use. Hence,the inkjet printed paper sensor could

be a pivotal tool for assessment of low concentrations of pesticides, affecting both humans and animals.

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