Prototype instrument development for non-destructive detection of pesticide residue in apple surface using Raman technology

Sagar Dhakal [a], Yongyu Li [a], Yankun Peng [a,*], Kuanglin Chao [b], Jianwei Qin [b], Langhua Guo [a]

[a] China Agricultural University, National R&D Centre for Agro-Processing Equipments, Beijing 100083, China
[b] Environment Microbial and Food Safety Laboratory, Agricultural Research Service, United States Department of Agriculture, 10300 Baltimore Avenue, Bldg 303 BARC-East, Beltsville, MD 20705, USA

ARTICLE INFO

ABSTRACT

Apple is one of the highly consumed fruit and also a major source of pesticide carrier to human health. This study explores the application of Raman spectroscopy for detection of commercially available organophosphorus (chlorpyrifos) pesticide in apple surface. Optical instrument prototype equipped with Raman spectroscopy system with 785 nm laser excitation source was developed for non-destructive, rapid and accurate detection of pesticide residue in apple surface, overcoming the loopholes of traditional detection methods. Software was self developed to control the functionality of Raman CCD, acquire and process the Raman spectral data and display result in real time. The samples detected by the developed system were tested in High Performance Liquid Chromatography. The result shows that the developed system can detect chlorpyrifos residue to minimum limit of 6.69 mg/kg in apple surface within less than 4 s. This innovative and promising system can be a breakthrough technology for pesticide detection in fruits and vegetables.

1. Introduction

Pesticides are any chemical substance that are used in farm land before harvest to repel pests from crops to get better yield free of diseases or after harvest to obtain longer self life of crops. Application of pesticides is increasing rapidly all over the world (Sergio and Miguel, 2007). Various pesticides are applied worldwide for crop protection to increase their quality, increase the yield as well as extend the storage time (Ticha et al., 2008). Although proper use of pesticides result in beneficial yield and better economic benefit, but excessive use of pesticide has caused serious attention for supervisory control. Improper use of pesticides in fruits and vegetables cause pesticide poisoning which when consumed might result in several health risks (Li et al., 2012). Although the use of pesticide has economic benefit, there are repeated cases of excessive pesticide application for more economic gain by farmers (Chen et al., 2010). Apple is rated as one of the most extensively pesticide contaminated fruit item by Environmental Working Group (Anonymous, 2012).

Several technologies for the detection of trace amount of pesticides have been reported in literatures. Several analytical methods such as High Performance Liquid Chromatography (HPLC) (Tsochatzis et al., 2010; Tuzimski, 2011), Chromatograph Mass Spectrometer (Hu et al., 2011; Lavagnini et al., 2011), Gas Chromatography (Ortelli et al., 2005) are reported in literatures for the detection of trace amount of pesticide. Although accurate, but these technologies are limited to laboratory analysis because of their complex sample preparation method, long detection time requirement, destructive in nature and requirement of skilled or semi skilled man power for operation. Moreover, complex operation and expensive operational cost has limited these technologies for detection of few samples rather than for all individual agriculture products. As such these analytical technologies are not able to meet the requirement of agricultural product processing industries for real time, rapid and non-destructive detection of pesticide residue in foods and vegetables. Differing with analytical technology, optical technologies are gaining its importance in recent decade for real time and rapid detection of agricultural products (Dhakal et al., 2011; Peng and Lu, 2008; Qin et al., 2010; Zhang et al., 2006; Liu et al., 2012). In recent few years Raman technology has gained its importance for detection of trace amount of food additives such as melamine (Qin et al., 2010), pesticide content in fruits (Liu et al., 2012; Li et al., 2012; Liu et al., 2013), lycopene changes in tomatoes (Qin et al., 2011). Raman technology is also gaining momentum for detection of different types of pesticide residue in fruits and juices. Tang et al. (2011) reported detection of three different kinds of pesticide to trace amount by the application of Surface Enhanced Raman Spectroscopy (SERS) using silver colloid. Similarly, Liu et al. (2012) reported detection of pesticide residue in fruits peel

---

by application of silver coated gold nanoparticles for Raman enhancement. Liu et al. (2013) detected organophosphorous and carbaryl pesticide in apple and tomato surface by the application of Raman spectroscopy coupled with gold nanostructures. The works reported in these researches are innovative and promising, but, all these methodologies are sample destructive, require surface enhancement making the detection process complex, time consuming and expensive and hence could not fulfill the need for non-destructive, rapid and real-time detection of pesticide residue in fruit surface. The study presented is a novel method to fill the loopholes in detection technology and develop a reliable system prototype and methodology for industrial application. The primary objectives of the research were to:

1. Develop system prototype equipped with Raman technology and software system to detect pesticide residue in apple surface.
2. Develop a methodology to classify apple into contaminated and uncontaminated based on minimum detectable threshold.

2. Prototype development

2.1. Development of hardware system

The hardware part of the system consists of Raman spectral system, sample holding device, control device, computer and dark box. The overall system was mounted on optical bread broad. Fig. 1 illustrates operational control diagram of the lab set-up developed in this study.

Raman spectral system consisted of 16 bit high performance spectroscopic charged couple device (CCD) camera (Andor Newton DU920PBR-DD, Andor Technology, Inc., South Windsor, Conn.) with area array of 1024×256 pixels. A USB cable was used to connect the camera with computer for data transfer and camera control. A Raman spectrometer (Raman Explorer 785, Headwall Photonics, Fitchburg, Mass) especially designed for 785 nm laser excitation was mounted to the camera. Spectrum stabilized laser module of 785 nm wavelength (10785MM0350MS, Innovative Photonic Solutions, Monmouth Junction, N.J.) was used for sample excitation. A bifurcated optical fiber mounted to optical probe was connected to the output of laser module at one end to act as light source and other end was connected with Raman spectrometer to collect Raman signal emitted by sample. The optical probe was equipped with internal long pass filter to permit light passage above 785 nm only. Input slit of 50 µm was used to interface the optical probe with spectrograph. Selection of input slit was based on comparison of spectral data of sample under different laser power and exposure time which is discussed in the following chapter of this paper. To minimize dark current, the CCD was thermoelectrically cooled at $-50\,°C$ to $-70\,°C$ depending upon the laboratory ambient temperature.

Raman spectral signal are weak and affected by fluorescence background. At the mean time, the distance between the optical probe and sample surface greatly affects the Raman spectral data. It is essential to maintain certain working distance between the optical probe and sample to be scanned. Range of best working distance required by the optical probe is generally provided by manufacturer. Based on result of preliminary experiments, a distance of 7 mm between optical probe and apple sample surface was chosen to be the best working distance for this study. However, individual apple varies in shape and size and influences Raman signal significantly if proper working distance is not maintained. To overcome the shortcoming, a simple mechanical sample holding device was designed and fabricated as illustrated in Fig. 2. The device was designed to hold apple sample of different size and shape. At the same time, the device (designed as prototype) could also hold samples and rotate it at fixed degree (in the equatorial region) so as to collect Raman data from different points of apple equatorial region. Spring was mounted horizontally in the shaft of clamp 2 to hold samples of different size. Also two springs were mounted vertically to adjust working distance of 7 mm between point of detection and optical probe. Four phase stepper motor with $1.8°$ stepping angle was mounted to horizontal shaft of clamp 1 to rotate sample. Programmable System on Chip (PSoC) programmed in C language was used to control the motor. RS 232 was used to interface the PSoC and computer for signal transfer. Motor driver connected the stepper motor and PSoC. Three input signals were used to control the direction, speed and halt time of the motor, thus controlling the motion of sample. The overall control unit including PSoC, motor driver, and electric connections were mounted in self fabricated control box. The control unit was developed for portability to test the system in industrial floor.

After fabrication of the sample holding device, experiments were performed to observe the device functionality. It was observed that the device could hold apple sample with minimum size diameter (stem-calyx position) of 56.7 mm and maximum size diameter (stem-calyx position) of 74.08 mm. However, device could not clamp a sample of 59.27 mm in diameter (stem-calyx position) due to its irregular shape. Similarly, irregular shape of sample also affected the device to maintain precise working distance between the sample surface and optical probe at the point of detection. During the experiment it was realized that shape of sample was more challenging factor to overcome compared to size of the sample.

2.1.1. Selection of input slit

Input slit mounted in the spectrometer is an interface between spectrometer and optical probe. The Raman signal from the optical probe is passed through input slit. The concave mirror then guides the input light from the input slit to the reflection grating (Qin et al., 2010). As input slit is connected between optical probe and spectrometer, choice of proper input slit is very important to pass
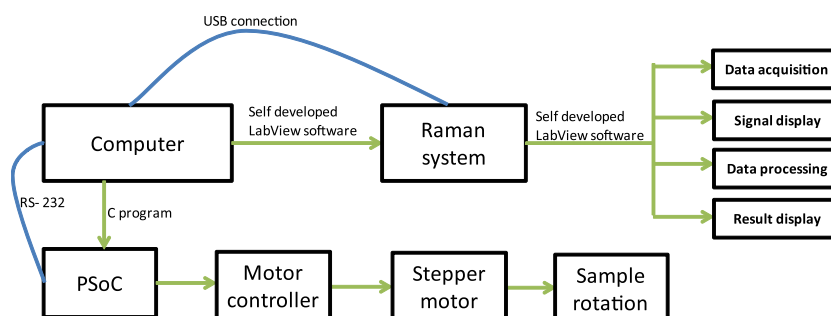

Fig. 1. Operation control diagram of the developed system.