Light Reflection Spectrum Comparison of Pesticides Free Foods, Organic Foods and Conventional Farming Foods for VIS NIR Filter Creation

Oumy Diop

Antibes, France,
Email : diop.oumydiop@gmail.com

Umberto Cerasani

CERAGOS Electronics and Nature
Sophia Antipolis, France
Email: cerasani@ceragos.org

Abstract— **A method for determination of food contaminants, including pesticides, is described in this document. Using Visible Near InfraRed spectroscopy results obtained from food samples with different levels of pollution, the creation of pesticides free food filters were realized. Methodology and data extraction are meticulously addressed. Finally, implementation of these filters in an embedded device, communicating with smartphone application is discussed allowing users to monitor food contaminants.**

Keywords—pesticides; organic farming; Vis NIR spectroscopy; filter creation; data collection and analysis

I. INTRODUCTION

Pesticides are widely used in agriculture to protect crops and seeds and may have contributed to improvement in society health and economy. At the same time, widespread use of pesticides has led to serious harm on the environment and human health [1]. With the increasing demand for a high quality agricultural products, new quality and safety control devices are being investigated. Because pesticides damaging effects are invisible and cannot be directly warned by visible observation or simple testing, pesticides estimation in soil or in foods prior to their consumption, requires complex techniques and remains very challenging [2].

A number of analytical methods, including mass spectroscopy gas and liquid chromatography gas chromatography–mass spectrometry (GC-MS), have been reported to detect various pesticides contamination in foods and these methods are very sensitive and reliable [2]. However, these classical analytical approaches are usually confined to a laboratory environment and require costly, long sample preparation time, solvent wasting, and hazardous samples contact [2] [4]. Additional disadvantages of these methods include the restricted database mapping of pesticides analysis and the possibility of false negatives in the results [5].

Biosensors provides a promising alternative for the detection of pesticides. Biosensors convert the signal produced by the immobilized biological element that detect the analyte into an electrically detectable signal and can be classified from their signal transduction techniques into electrochemical, optical, piezoelectric and mechanical biosensors [6]. Many biosensors designed for pesticides detection are based on the inhibition reaction or catalytic activity of several enzymes

after pesticides contact [7]. Electrochemical transducers are usually simple to design, small and affordable making them candidate of choices for portable pesticides detection [6]. For instance, Enzyme-Linked ImmunoSorbent Assays (ELISA) have grown rapidly as tools for pesticide measurement, although still challenged [7]. Since a number of pesticides have a similar mode of action affecting the activity of the same enzyme, most of ELISA based biosensors suffer poor individual pesticide specificity although improper to detect total pesticide content. On the other hand, immunosensors are biosensors that senses specific pesticides using antibodies (Ab) or antigens (Ag) taking advantage of the newest development of Ab technologies, targeted against pesticide molecules. Immunosensors are therefore able to provide concentration-dependent results in a certain range [7][8] . For instance in [9], Triazines were assayed using florescent antibodies (conjugated with with fluoresceine isothiocyanate binding to the fibre surface). After contact with the pesticide Triazines the fluorescence signal decreased since less antibodies were binding to the fibre. The detection limit using this immunosensor was very satisfying (around 0.1 ng/ml) [9]. However, there is a time gap between current status in the field and the most recent created immunosensors [7]. In addition, immunosensors usually requires specific testing procedures and have low reusability capacity without loss of sensitivity for most of them [10][11][12].

Due to the great amount of pesticides currently being used, there is an augmented concern in the investigation and creation of rapid and non-destructive methods for pesticides detection [13]. In the last few years, advanced in optical instruments allowed the residuals of insecticides detection from agricultural samples [5]. Detection of hydrophobic organic pollutants via UV, Raman, and IR spectroscopic methods directly at solid sorbent phases are usually reported to be less sensitive than conventional chromatographic analysis, but permit on-site pollution measurements [4].

Near Infrared spectroscopy (NIR) is a well described method to assess the composition and quality of products in the food industry, since it has the capability to analyze organic substances rapidly and cost-effectively, although suffering of low spectral resolution for samples in aqueous solutions due to strong water infrared absorption. As an example, a model for the quality control of herbicide Diuron in intact olives with 85.9% of accuracy using reflectance NIR spectroscopy is

presented in [14]. Peppers are a frequent object of food safety alerts in various member states of the European Union since they frequently contain unauthorised pesticide residues. Near Infrared Reflectance Spectroscopy (NIRS) for the measurement of pesticide residues in peppers using commercially available spectrophotometers and demonstrating satisfying results is proposed in [15]. Spectral information in the ranges 1644–1772 and 2014–2607 nm without baseline correction and Partial Least Square (PLS) model interpretation were used to detect Buprofezin, Diuron and Daminozide without any sample pre-treatment and sample destruction in [16].

Diuron determination in pesticide formulations was also analyzed after its extraction with acetonitrile and subsequent transmittance NIR measurements (2021 and 2047 nm). Diuron limit of detection reached 0.013 mg.g^{-1} with this methodology which was 10 times higher than that the results obtained by Liquid Chromatography (LC), making NIR vibrational method appropriate for the quality control of pesticide commercial formulations [17]. Fourier transform near infrared (FT-NIR) spectroscopy is also of value for the determination of pesticides in agrochemicals. Following previous extraction of the active principles and transmission measurements were performed on Chlorsulfuron, Metamitron, Iprodione, Pirimicarb, Procymidone and Tricyclazole, leading to detection values limits ranging from 0.004 to 0.17 mg.g^{-1}, 10 times faster than chromatography analysis [18]. Chlopyrifos residue detection in white radish, based on NIR spectroscopy and PLS regression is proposed in [20]. PLS was mainly permitted the determination of the optimum wave number range.

Field portable NIR spectrometer (from 360 to 1690 nm) was able to determine nutrient composition of beef feedlot manure in [19]. On the basis of analysis of dried mannure samples, the field-portable NIR spectrometer allowed fast determination of Carbon, Nitrates, and several other parameters. [19]. Field portable pesticides detectors, based on NIR spectrometry could be therefore considered for pesticides detection using a similar procedure.

Infrared (IR) spectroscopy provides a rapid, low cost and highly reproducible diagnostic screening tool. IR spectroscopy is currently employed for soil surveillance systems, crops health and water quality assessment. [22]. For instance, soil absorption over the Visible/Near-InfraRed (Vis/NIR) wavelength regions (350–2500 nm) is mostly associated with (1) the vibrational energy transitions of the dominant molecular bonds of Fe-oxides (which have absorptions over the visible (350–780 nm) and short-wave NIR (780–1100 nm) spectral regions), (2) clay minerals (which have absorption over the long-wave NIR (1100–2500 nm) regions), (3) water (which has strong absorption features over Vis/NIR regions, most visibly near 1400 and 1900 nm), and (4) organic matter (which has distinct absorption features over the Vis/NIR, due to the various complex chemical bonds) [21]. Under certain conditions, such as very high concentration in soil, some transition elements (including Ni, Cu, Co) may also exhibit

absorption features in the Vis/NIR spectral regions [21], permitting direct soil characterization and estimation of pesticides utilization in fields. A Vis/NIR mobile soil sensor was developed in [24] composed by optical unit to detect soil extractable phosphorous (305 and 1711 nm in reflectance mode).

Vis/NIR spectroscopy also permits pesticides and other food contaminants detection. It may be particularly suited for free space measurement and field studies. Internal and external pesticides damage detection of various fruits in Korea and Japan were detected using non damaging methods, such as Vis/NIR Spectroscopy [23].

Many aromatic pesticides are either naturally fluorescent or photodegrade into fluorescent byproducts and are hence suited for fluorescent spectroscopy detection [25]. For example, Polycyclic Aromatic Hydrocarbons (PAHs), pesticides are naturally fluorescent in aqueous solutions and allows for trace elements detection without previous pesticides concentration procedures [25]. Portable fluorometers are now available on market in a single portative device and with fiber-optic probes that permit remote observations [25].

Progress in Raman spectroscopes and in embedded computation equipment have enabled Raman spectroscopy to be used as an analytical tool for both solid samples and aqueous solutions, offering information permitting to determine the internal content in samples [2]. Because Raman spectrum of compound can furnish narrow and highly resolved bands it contains more complete vibrational information than IR spectrum. It may not require stabilizing materials and needs no chemical or mechanical pretreatment and allows nondestructive extraction of physical information [2][5].

Raman spectroscopic techniques mostly gathers dispersive Raman spectroscopy, Fourier transform Raman spectroscopy and Surface Enhanced Raman Spectroscopy (SERS) [2]. Because conventional Raman spectroscopy is limited to a small scattering cross section and requires large amount of specimen and strong incident light, the employment of SERS greatly enhances the sensitivity of the conventional Raman spectroscopy and offers more elevated measurement speed and sensitivity [5].

In food industry, spectroscopy has been satisfactorily used to monitor food quality and safety. For instance Raman spectroscopy was applied to discriminate between transgenic and normal crops in various breeding such as tobacco. Different Raman spectrum were obtained between the transgenic tobacco and the wild type, since for transgenic tobacco, the expression of cinnamyl alcohol dehydrogenase was greatly depleted after cinnamaldehyde lignin incorporation [2]. In addition, Raman spectroscopy was successfully used to distinguish the Brassica napus 'Drakkar' from the new genetically modified line [2].

Furthermore, the use of Raman spectroscopy permitted carotenoids content quantification in fruits and vegetables [2]. Other antioxidant quantification such as lycopene could be

obtained by NIR-FT-Raman spectroscopy method [2]. FT-Raman spectroscopy method in conjunction with Hierarchical Cluster Analysis (HCA) may accurately assess the energetic value and total carbohydrates, protein, and fat of powdered milk infant formulas [2].

Raman spectroscopic techniques are not only applied in quality control but also in safety control of various beverages, most specifically for microorganisms contamination and adulterants adjunction. The identification of oil adulteration is of great importance from both market and health perspectives in the olive oil industry. Unsaturation of oil Free Fatty Acids (FFA) and total degree of unsaturation could be estimated using spectroscopy measures [2]. Since Raman spectroscopy has been successfully applied to organic compounds detection in food and beverage, its employment for pesticides detection is particularly adequate. Most particularly identification and detection of large family of sulfur-containing pesticide residues at various fruit peels was performed utilizing the shell thickness-dependent Raman enhancement of silver-coated gold nanoparticles [26].

Transmittance spectroscopy is particularly suited for free space measurements without sample preparation and may be applied to pesticides detection. For example, using a transmittance spectroscopy (in the 550 and 980 nm region), insect infested cherries within a tart cherry fruit were detected with accuracy varying from 82% to 87% [27].

Data clustering analysis following spectroscopy data is often required to distinguish food contaminants. Spectroscopy such as SERS coupled with clustering analysis has been shown to enable the trace-level detection of various pesticides [28]. For instance, cluster analysis, following Wavelength Dispersive X Rays Fluorescence Spectroscopy may permit classification of black tea and green tea from tea mineral elements [29]. Clustering algorithms often requires variable fitting or selection methods. Most commonly employed methods are: Stepwise Regression Analysis, Uninformative Variable Elimination, Interval Partial Least Squares (IPLS) regression, Clonal Selection Feature Selection algorithm [13]. As an example improving PLS regression models, used in spectrum data post-processing, may hence result in more specific database inquiries and sample chemical identification.

In this paper, we studied the spectral characteristic of pesticides contamination using Vis-NIR reflectance spectroscopy. Since there are several thousand of different active pesticide molecules reported [30][31], current pesticides detection is limited to few types of pesticides chemical and does not ascertain pesticides free products. We worked from another perspective by comparing the spectral information obtained from pesticides free and pesticides contaminated foods, irrespective of the pesticide types. We searched for particular traces in the spectroscopy spectrum that could be characteristic of pesticides contamination. Mostly two cases could be found: (1) the pesticides grown foods spectra contains additional traces which could be related with pesticides own spectral characteristics or modified

endogenous food proteins [32][34], (2) oppositely the absence of spectral components in particular wavelength in pesticides contaminated foods compared to organic or totally natural foods (grown without pesticides addition) may also be used as a spectral indicator of food purity since certain food proteins may not be expressed when pesticides are utilized [35][38].

Further database characterization of these specific spectral components may permit chemical characterization and possibly lead to the creation of a new biomarker for pesticides detection.

Finally, algorithm implementation inside a portative device with an embedded spectrometer, as depicted in Figure 1, permits user centered device for pesticide estimation. For easier user data reading, a wireless communication device (such as WIFI module) is integrated in the embedded system for user's smartphone communication. A specific smartphone application is created for embedded spectrometer results monitoring. To diminish the costs of the overall device, sunlight is used as spectroscopic light source, limiting device utilization in bright areas.

Our document will be organized into 3 main sections: first, the methodology of our experiment will be introduced with the devices used, then, the Vis-NIR spectroscopy results are reported and analyzed, finally a conclusion is drawn with possible future work direction propositions.
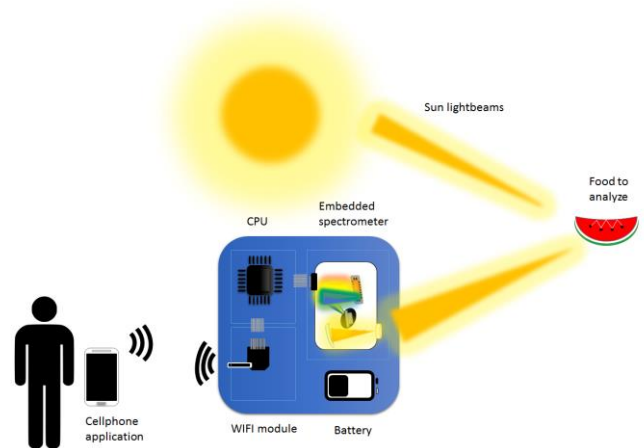

Figure 1. User centric based device for food pesticides monitoring

II. METHODS

Measurements detailed information and equipment used are presented in this Section.

A. Food samples variety

TABLE I. VEGETABLE TYPES AND VARIETIES USED FOR THE EXERIMENT

Food Variety (botanical name)	Food suppliers			
	Market gardener (pesticides free)	Organic shop	Supermarket 1	Supermarket 2
Poataoes	*Solanum tuberosum ´Charlotte´ (yellow), Solanum tuberosum ´Desiree´ (red),*	*Solanum tuberosum ´Charlotte´ (yellow)*	*'Cherie'*	*'Cherie'*
Zucchini	*Cucurbita moschata, Cucurbita pepo 'De Nice à fruit ronds´*	*Cucurbita pepo ´Verte non coureuse´*	*Cucurbita pepo ´Verte non coureuse´*	*Cucurbita pepo ´Verte non coureuse´*
Tomatoes	*Lycopersic on escubentum*	*Lycopersicon escubentum, Solanum lycopersicum*	*Lycopersic on escubentum Lycopersic on esculentum*	*Lycopersicon escubentum Lycopersicon esculentum*

We tested 3 different food categories: tomatoes, zucchini and potatoes. The precise variety of vegetable tested is reported in Table I. Food were bought directly from (1) a market gardener that did not used any pesticides or chemical contaminant, (2) an organic store and from 2 famous French supermarket brands, where we assumed that plants were grown using pesticides ((3) and (4)). Although several pesticides are contained in the vegetable peel, we decided to perform the measure on the decorticated vegetable to avoid peel color bias. Each vegetable was tested in 3 different areas.
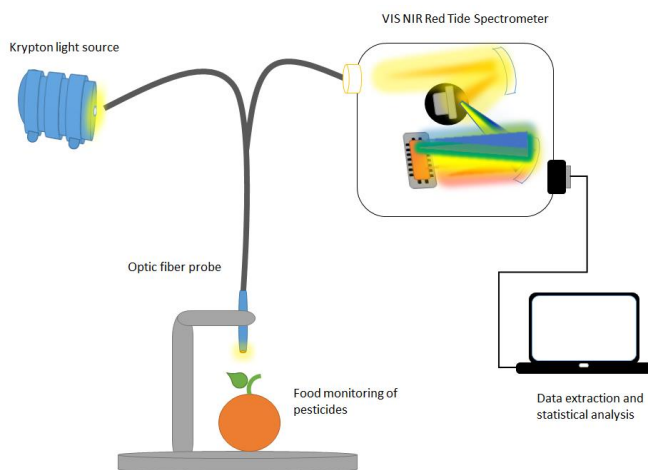
B. Test system description:

Figure 2. Test bench diagram used for Vis-NIR spectroscopy measurements in various vegetables

Reflectance spectroscopy measures were performed using the test bench described in Figure 2. We used the Ocean Optics kit including the ECOVIS Krypton Lightsource, the USB-650 Red Tide Spectrometer (preconfigured in the 350-1000 nm wavelength range), a 200 um Bifurcated Fiber (Vis-NIR) and the OceanView software. The results were then extracted and manipulated with Matlab software. The distance between the bifurcated fiber and the sample to measure was fixed to 5mm, and the reflectance robe was positioned at an angle of 90° to the flat surface of the sample to analyze.

C. Data analysis:

The data were analyzed using Matlab software. First, correction of the light intensity was performed by dividing each sample with its respective Area Under Curve value. Then, we computed the mean value associated with one food type and origin. Mean values of the pesticides free foods spectral data were used to create filters in order to highlight the particular wavelength associated with food pesticides addition.

III. RESULTS

Tomatoes spectroscopy measures from different supplier's origin are presented in Figure 3, after division by their respective Area Under Curve, to remove the measures light intensity drift. Pesticides free tomatoes spectral data mean value is reported in thick blue line for initial comparison. Each subfigure represents the spectral measurements realized on tomatoes from a market gardener that did not used any pesticides or chemical contaminant (top left subfigure), an organic store (top right subfigure) and from 2 famous French supermarket brands, where we assumed that plants were grown using pesticides (bottom left and bottom right subfigures). For each different tomatoes supplier, measures were performed on several vegetable samples to decrease the samples intervariability bias and were reported in different color thin lines in each subfigure. As an example, the top right subfigure of Figure 4 green thin line outlines the relative light intensity of the first pesticide free tomato analyzed and the magenta thin lines outlines the relative light intensity of the third pesticide free tomatoes analyzed.

Figure 4 and Figure 5 depict the spectral measures associated with zucchini and potatoes from different food supplier's origin respectively. For easier data interpretation, light intensity drift is removed by similar integral division. The mean relative light intensity values of the pesticides free zucchini and potatoes are both reported in blue thick lines in each figure. Similarly to the previous figure results, subfigures describe the spectral measurements associated with the 4 different vegetables origin (from pesticide free market gardener, organic store, supermarket 1 and supermarket 2). In each subfigure, the colored thin lines, outline the relative light intensity associated with a specific vegetable sample but from the same supplier origin.
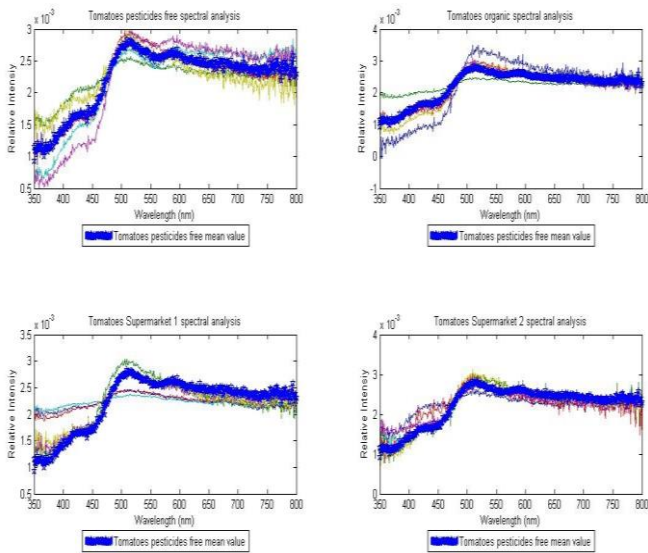
Figure 3. Tomatoes spectral analysis comparison. The samples data are displayed by the colored thin lines and the mean value (only associated with the pesticides free spectrum) is depicted with the thick blue line.
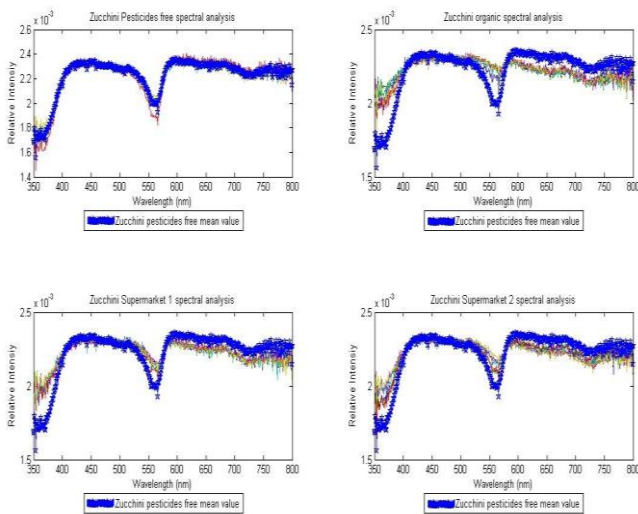

Figure 4. Zucchini spectral data comparison. The sample data are displayed by the colored thin lines and the mean value (only associated with the pesticides free spectrum) is depicted with the thick blue line.
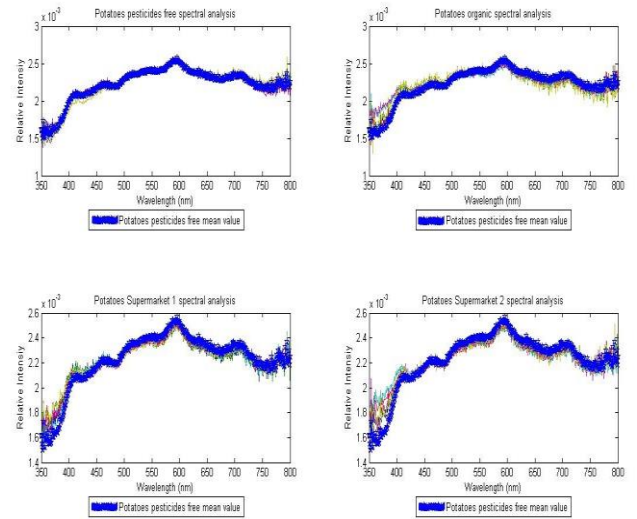

Figure 5. Potatoes spectral data comparison. The sample data are displayed by the colored thin lines and the mean value (only associated with the pesticides free spectrum) is depicted with the thick blue line.

Spectral filtration of mean spectral data from organic shop (blue line), supermarket 1 (green line) and supermarker 2 (red line) with tomatoes, zucchini and potatoes pesticides free mean value are respectively presented in Figure 6, Figure 7 and in Figure 8.

Figure 6 shows that spectral relative intensity in the 350 nm – 400 nm region is particularly characteristic of the tomatoes added chemicals. Other spectral rays (435 nm, 587 nm, 672 nm, 781nm, 791 nm, etc.) deserve extended analysis and database characterization.

Although characterization of food additives or pesticides contaminants for zucchini seems straightforward with two large peaks at 374 nm and 570 nm compared to pesticides free zucchini (Figure 7), the analysis may be more complex. In fact, as presented in Table I, the zucchini variety of the organic shop, supermarket 1 and supermarket 2 (*Cucurbita pepo 'Verte non coureuse'*) is not exactly the same as the one proposed by the pesticide free market gardener (*Cucurbita moschata* and *Cucurbita pepo 'De Nice à fruit ronds')*. Modification in chromophore molecules between these two varieties of zucchini may explain the large results variation. For more conclusive analysis, data obtained from organic zucchini should be used for spectral filter construction, although we further noted that in these wavelength areas, data obtained from organic stores also differ from the ones associated from the two supermarkets. Of particular interest seems to be the spectral rays of 715 nm, 774 nm, 450 - 456 nm area and need deeper investigation.

Spectral filtration of mean spectral data from organic shop (blue line), supermarket 1 (green line) and supermarket 2 (red line) with potatoes pesticides free mean value is described in Figure 8. Except in the 350 nm - 450 nm region, spectral data obtained from the two supermarkets (green and red curves) seems to be closer to the pesticide free spectrum. Several

explanations may exist. Like for zucchini, not the same potato varieties were compared, explaining the discrepancies between results. A second explanation is the presence of specific food additional substances, possibly pollutants, in organic food compared to supermarket ones (organic foods are not entirely devoid of pesticides [39]).
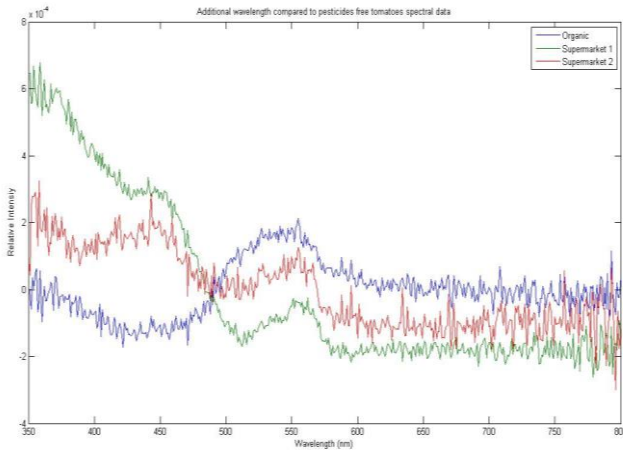

Figure 6. Additional relative light intensity compared to pesticides free tomatoes spectral data
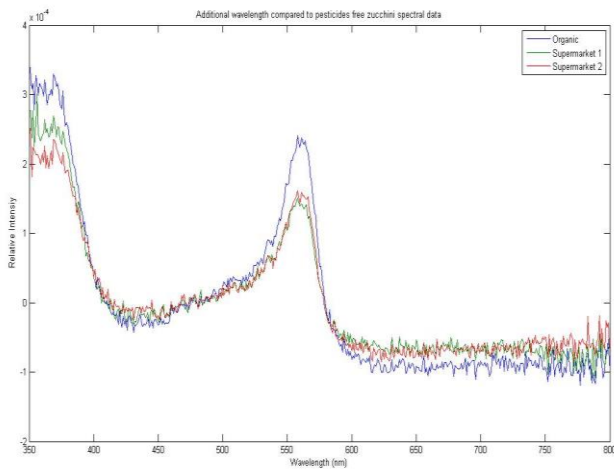

Figure 7. Additional relative light intensity compared to pesticides free zucchini spectral data
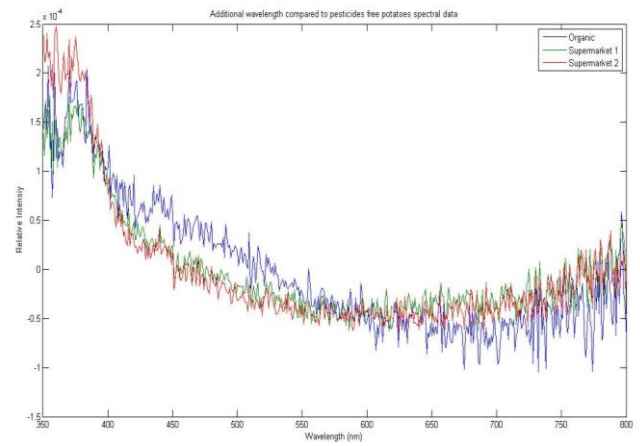

Figure 8. Additional relative light intensity compared to pesticides free potatoes spectral data

IV. CONCLUSION AND FUTURE WORK

Although insufficiently characterized and currently incomplete, spectroscopic analysis of food in the Vis-NIR wavelength range, seems to permit food quality estimation. We propose an innovative method based on Vis-NIR spectroscopy for detecting food contaminants using spectral filters constructed from pesticides free food samples data. Our methodology choices was mainly dictated by the countless number of food contaminants, which are currently limiting the detection to only a restricted number of well-known contaminants spectrum traces for filters creation. In contrast we used the Vis-NIR spectral trace of pesticides free foods for filter creation.

From early conclusion, our methods seems promising and easy to implement. However very meticulous data should be obtained first for each pesticides free food variety studied. Modification of the internal food coloration including food maturity levels, seeds number, etc. can lead to different light intensity spectral analysis, generating important unpredictability in the reference spectral data.

Once extracted the particular wavelength associated with food pollutants, such as pesticides, database search may further permit pollutants chemical characterization.

Moreover, because of the access difficulties to many varieties of pesticides free grown foods, organic foods may be used in first approximation although not always devoid of contaminants.

Finally, the implementation of such algorithm in an embedded platform with a microspectrometer module may allow device user estimation of foods chemical contaminants.

REFERENCES

[1] D. Pimentel, "Environmental and economic costs of the application of pesticides primarily in the United States," *Environment, development and sustainability,* vol. 7, pp. 229-252, 2005.

[2] D. Yang and Y. Ying, "Applications of Raman spectroscopy in agricultural products and food analysis: A review," *Applied Spectroscopy Reviews,* vol. 46, pp. 539-560, 2011.

[3] D. Lee, S. Lee, *et al.*, "Quantitative analysis of methyl parathion pesticides in a polydimethylsiloxane microfluidic channel using confocal surface-enhanced Raman spectroscopy," *Applied spectroscopy,* vol. 60, pp. 373-377, 2006.

[4] M. Karlowatz, M. Kraft, and B. Mizaikoff, "Simultaneous quantitative determination of benzene, toluene, and xylenes in water using mid-infrared evanescent field spectroscopy," *Analytical chemistry,* vol. 76, pp. 2643-2648, 2004.

[5] K. Wong-Ek*, et al.*, "Portable surface-enhanced Raman spectroscopy for insecticide detection using silver nanorod film fabricated by magnetron sputtering," in *SPIE BiOS*, 2011, pp. 791108-791108-11.

[6] A. Sassolas, B. Prieto-Simón, and J.-L.Marty, "Biosensors for Pesticide Detection: New Trends," *American Journal of Analytical Chemistry,* pp. 210-232, 2012.

[7] X. Jiang, *et al.*, "Immunosensors for detection of pesticide residues," *Biosensors and Bioelectronics,* vol. 23, pp. 1577-1587, 2008.

[8] C. R. Suri, M. Raje, and G. C. Varshney, "Immunosensors for pesticide analysis: antibody production and sensor development," *Critical reviews in biotechnology,* vol. 22, pp. 15-32, 2002.

[9] F. Bier, W. Stöcklein, M. Böcher, U. Bilitewski, and R. Schmid, "Use of a fibre optic immunosensor for the detection of pesticides," *Sensors and Actuators B: Chemical,* vol. 7, pp. 509-512, 1992.

[10] M.-I. Baraton, *Sensors for Environment, Health and Security: Advanced Materials and Technologies*: Springer Science & Business Media, 2008.

[11] M. Ferrari, M. Ozkan, and M. Heller, *BioMEMS and Biomedical Nanotechnology: Volume II: Micro/Nano Technologies for Genomics and Proteomics* vol. 2: Springer Science & Business Media, 2007.

[12] O. Tigli, *Novel SAW devices in CMOS for biosensor applications: design, modeling, fabrication and characterization*: ProQuest, 2007.

[13] L. Xue, J. Cai, J. Li, and M. Liu, "Application of particle swarm optimization (PSO) algorithm to determine dichlorvos residue on the surface of navel orange with Vis-NIR spectroscopy," *Procedia Engineering,* vol. 29, pp. 4124-4128, 2012.

[14] L. Salguero-Chaparro, A. J. Gaitán-Jurado, V. Ortiz-Somovilla, and F. Peña-Rodríguez, "Feasibility of using NIR spectroscopy to detect herbicide residues in intact olives," *Food control,* vol. 30, pp. 504-509, 2013.

[15] M. T. Sánchez, K. Flores-Rojas, J. E. Guerrero, A. Garrido-Varo, and D. Pérez-Marín, "Measurement of pesticide residues in peppers by near-infrared reflectance spectroscopy," *Pest management science,* vol. 66, pp. 580-586, 2010.

[16] S. Armenta, S. Garrigues, and M. de la Guardia, "Partial least squares-near infrared determination of pesticides in commercial formulations," *Vibrational Spectroscopy,* vol. 44, pp. 273-278, 2007.

[17] J. Moros, S. Armenta, S. Garrigues, and M. de la Guardia, "Near infrared determination of Diuron in pesticide formulations," *Analytica chimica acta,* vol. 543, pp. 124-129, 2005.

[18] J. Moros, S. Armenta, S. Garrigues, and M. de la Guardia, "Univariate near infrared methods for determination of pesticides in agrochemicals," *Analytica chimica acta,* vol. 579, pp. 17-24, 2006.

[19] D. Malley, C. McClure, P. Martin, K. Buckley, and W. McCaughey, "Compositional analysis of cattle manure during composting using a field-portable near-infrared spectrometer," *Communications in Soil Science and Plant Analysis,* vol. 36, pp. 455-475, 2005.

[20] Y. Zhou, B. Xiang, Z. Wang, and C. Chen, "Determination of chlorpyrifos residue by near-infrared spectroscopy in white radish based on interval partial least square (iPLS) model," *Analytical Letters,* vol. 42, pp. 1518-1526, 2009.

[21] T. Shi, Y. Chen, Y. Liu, and G. Wu, "Visible and near-infrared reflectance spectroscopy—An alternative for monitoring soil contamination by heavy metals," *Journal of hazardous materials,* vol. 265, pp. 166-176, 2014.

[22] K. D. Shepherd and M. G. Walsh, "Infrared spectroscopy—enabling an evidence-based diagnostic surveillance approach to agricultural and environmental management in developing countries," *Journal of Near Infrared Spectroscopy,* vol. 15, pp. 1-19, 2007.

[23] S.-H. Noh and K.-H. Choi, "Nondestructive quality evaluation technology for fruits and vegetables," in *International Seminar on Enhancing Export Competitiveness of Asian Fruits, Bangkok, Thailand*, pp. 1-15, 2006.

[24] M. Maleki, A. Mouazen, H. Ramon, and J. De Baerdemaeker, "Optimisation of soil VIS–NIR sensor-based variable rate application system of soil phosphorus," *Soil and Tillage Research,* vol. 94, pp. 239-250, 2007.

[25] R. D. JiJi, G. A. Cooper, and K. S. Booksh, "Excitation-emission matrix fluorescence based determination of carbamate pesticides and polycyclic aromatic hydrocarbons," *Analytica Chimica Acta,* vol. 397, pp. 61-72, 1999.

[26] B. Liu, *et al.*, "Shell thickness-dependent Raman enhancement for rapid identification and detection of pesticide residues at fruit peels," *Analytical chemistry,* vol. 84, pp. 255-261, 2011.

[27] J. Xing and D. Guyer, "Detecting internal insect infestation in tart cherry using transmittance spectroscopy," *Postharvest biology and technology,* vol. 49, pp. 411-416, 2008.

[28] B. Saute, R. Premasiri, L. Ziegler, and R. Narayanan, "Gold nanorods as surface enhanced Raman spectroscopy substrates for sensitive and selective detection of ultra-low levels of dithiocarbamate pesticides," *Analyst,* vol. 137, pp. 5082-5087, 2012.

[29] G. Chunhui, Z. Guoqiang, G. Liangquan, L. Jun, and W. Ziqiang, "Determination of trace elements in tea by wavelength dispersive X-ray fluorescence spectroscopy," *Nuclear Techniques,* vol. 36, 2013.

[30] L. R. Goldman, "Managing pesticide chronic health risks: US policies," *Journal of agromedicine,* vol. 12, pp. 67-75, 2007.

[31] C. f. D. C. a. Prevention. (2013). *CDC - Pesticide Illness & Injury Surveillance - NIOSH Workplace Safety and Health Topic*.

[32] S. Parvez and S. Raisuddin, "Protein carbonyls: novel biomarkers of exposure to oxidative stress-inducing pesticides in freshwater fish Channa punctata (Bloch)," *Environmental Toxicology and Pharmacology,* vol. 20, pp. 112-117, 2005.

[33] J. Dorts, *et al.*, "Oxidative stress, protein carbonylation and heat shock proteins in the black tiger shrimp, Penaeus monodon, following exposure to endosulfan and deltamethrin," *Environmental toxicology and pharmacology,* vol. 28, pp. 302-310, 2009.

[34] J. J. Fortunato, *et al.*, "Malathion-induced oxidative stress in rat brain regions," *Neurochemical research,* vol. 31, pp. 671-678, 2006.

[35] S. B. Ceyhun, *et al.*, "Deltamethrin attenuates antioxidant defense system and induces the expression of heat shock protein 70 in rainbow trout," *Comparative Biochemistry and Physiology Part C: Toxicology & Pharmacology,* vol. 152, pp. 215-223, 2010.

[36] R. M. Johnson, J. D. Evans, G. E. Robinson, and M. R. Berenbaum, "Changes in transcript abundance relating to colony collapse disorder in honey bees (Apis mellifera)," *Proceedings of the National Academy of Sciences,* vol. 106, pp. 14790-14795, 2009.

[37] H. T. Hogberg, A. Kinsner-Ovaskainen, T. Hartung, S. Coecke, and A. K. Bal-Price, "Gene expression as a sensitive endpoint to evaluate cell differentiation and maturation of the developing central nervous system in primary cultures of rat cerebellar granule cells (CGCs) exposed to pesticides," *Toxicology and applied pharmacology,* vol. 235, pp. 268-286, 2009.

[38]   M. Collotta, P. Bertazzi, and V. Bollati, "Epigenetics and pesticides," *Toxicology,* vol. 307, pp. 35-41, 2013.

[39]   B. P. Baker, C. M. Benbrook, E. G. III, and K. L. Benbrook, "Pesticide residues in conventional, integrated pest management (IPM)-grown and organic foods: insights from three US data sets," *Food Additives & Contaminants,* vol. 19, pp. 427-446, 2002.