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Construction of high-resolution dynamic spectral signatures of pesticides for food safety monitoring using infrared spectroscopy

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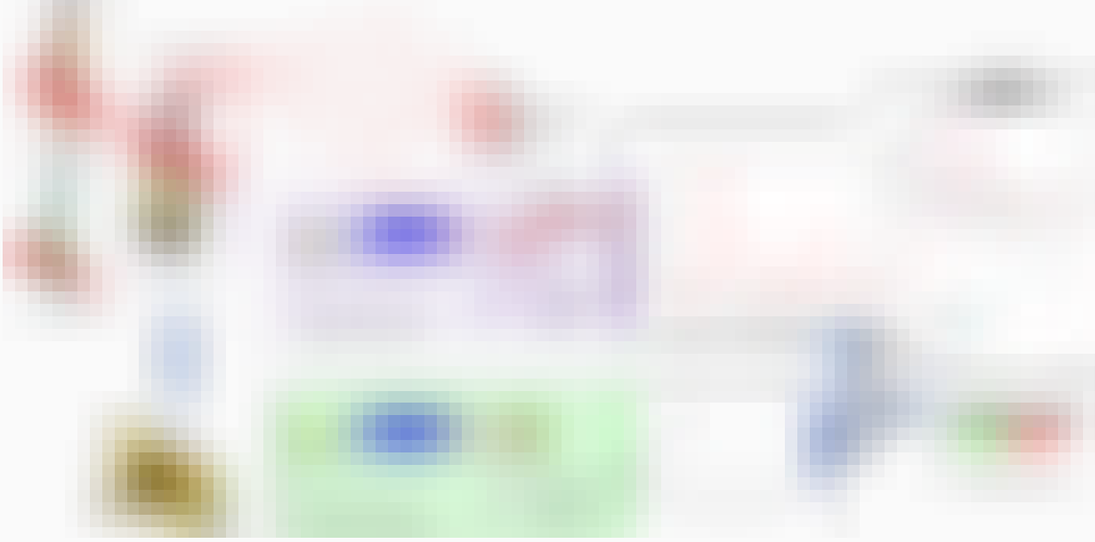
Construction of high-resolution dynamic spectral signatures of pesticides for food safety monitoring using infrared spectroscopy

Graphical abstract



Description

RESEARCH PROBLEM AND JUSTIFICATION

Last decades pesticides have been widely used for avoiding, devastating, and controlling any pest that interferes with the generation, preparing, storage, transport, or promoting of food, plants, or animals. Annually, two million tonnes of pesticides are distributed around Europe and USA being organophosphates and carbamates the most common used [1]. Thanks to pesticides, the balance among productivity and consumers food demand is keeping. However, to avoid high costs of chemicals purchase and irrigation, poor agricultural practices have led to the abuse or unreasonable application of pesticides [2], and in consequence, several adversely affects in non-target organisms, particularly in humans, which ingest pesticides residues in food [3]. In light of these hazards, international treats have been periodically developed and renovated to establish the maximum residues limits (MRLs) of pesticides in food, which depend on the pesticide type, the food, and the government of each country [4].

Given the worrisome increase of food containing pesticides that exceed the residue limits [5], and the hazardous effects on human health, the monitoring of pesticides levels in food is essential to guarantee good agricultural practices and safe health for consumers. This process has been widely developed in laboratory by conventional chromatography techniques, which successfully predict the concentration level of pesticides [6-8]. However, these methods are tedious, time-consuming, costly, contaminant and require complex sample preparation treatments, delaying the large-scale application in the food industry [9]. In contrast, IR spectroscopy technique along with data analysis methods displays as a potential tool for the accurate and fast detection of pesticides levels in food given its non-destructive nature and the several materials that have been easily characterized by this method. Several works have been developed in the qualitative and quantitative detection of pure pesticides [10-11] and pesticide residues in food [12-14], mainly in fruits and vegetables. This has been performed testing different parameters, among them the chemometric process thought the pretreatments and multivariate data analysis, reaching under some conditions better results in the detection. As a data processing technique, FEDS (Functionally Enhanced Derivative Spectroscopy) has been successful used to obtain spectral fingerprints of higher resolution and greater specificity, based on the differentiation and deconvolution of the spectral signals [15-16]. This makes FEDS a promising tool in the detection of pesticides in food.

Even when monitoring pesticides residues in food is crucial for human safety, it is also important to reduce them throughout the industrial process by dynamical procedures. Several food processing methods such as washing, peeling, juicing, freezing, cooking, among others, have been evaluated in vegetables, fruits, and dairy products [17-18]. As a result, a remarkable residue dissipation greater than 50% in pesticides was found, that clearly depends on the pesticide, the food, and the process or processes to which samples are subject.

Considering the above context, in this project we want to obtain the high-resolution, dynamic spectral signatures of pesticides for food safety monitoring using infrared spectroscopy along with FEDS method for analysis.

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Objectives

MAIN OBJECTIVES

To construct high-resolution, dynamic spectral signatures of pesticides for food safety monitoring using infrared spectroscopy.

SPECIFIC OBJETIVES

- To obtain and analyze characteristic spectra of pesticides frequently used in Colombia by infrared spectroscopy.
- To construct dynamic and high-resolution spectral signatures by deconvolution via Functionally Enhanced Derivative Spectroscopy (FEDS).
- To assess the analytical capability of FEDS-based spectral signatures to monitor pesticide contamination of foods.

FUNDAMENTALS

WHAT IS A PESTICIDE?

Agriculture sector mainly control food and plants production though cultivating the soil, growing crops, and raising livestock. Considering that crops are attack by more than 10000 types of insects and 30000 types of weeds, it is required the use of synthetic chemicals to control those pests and improve the agriculture industry [1]. According with Food and Agriculture Organization (FAO), all substance developed for avoiding, devastating, or controlling any pest that interferes with the generation, preparing, storage, transport, or promoting of food, plants or animals are named pesticides [2].
Depending on the target live form, pesticides are mainly categorized as insecticides –used to control insects–, herbicides –kill or inhibit the growth of unwanted plants–, and fungicides – used to control fungal problems like molds, mildew, and rust–. Moreover, they have been classified according with their chemical family in organophosphates, carbamates, pyrethroids, triazines and phenoxyacetic acid, that usually defines their mode of action, half-life in soil, human effects, and its level of toxicity [3].

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WHAT ARE THE POSITIVE AND NEGATIVE ASPECTS OF PESTICIDES?

The primary object of pesticide development is based on improving the food production and quality, which contributes positively to human progress. Thanks to pesticides, more than 2/3 of agriculture production is saved per year increasing the land recovered for agriculture and livestock. In addition, pesticide manufacturing promotes new jobs in agricultural and chemical sectors, control of malaria, typhus, and yellow fever, as well as the development of raw material for industry [1].

To guarantee safe products for consumption, food must be harvested a certain period after pesticide application, time that depends on the pesticide type and the crop. However, to speed up the food production, this period of time is not always respected, and even when it occurs, the amount of pesticide using during the cultivation is higher than the recommended dose [2]. In consequence, pesticide residues remain in the environment contaminating soil, water, and air to adversely affect non-target organisms, including humans.

Given that pesticides residues remain in fruits, vegetables, dairy products and meat before consumption, many acute intoxications by ingestion of pesticide have been produced worldwide. Among the most tragic with 400 dead and 3000 people affected was in Turkey between 1960 and 1963 caused by hexachlor-benzene in flour [3], follow by the intoxication of 1350 people with 80 dead in California due to the consumption of watermelon with Aldicarb in 1985 [4]. In Colombia, massive intoxications have been reported in Boyaca (1967), Meta (1970) and Pasto (1977) with 500 (63 dead), 190 (7 dead) and 300 (15 dead) people affected respectively, given the high levels of parathion in flour [5]. More recently in 2018, in Peru nine people dead and 103 were affected with beef that contains residues of parathion [6]. Annually, intentional (suicide) and unintentional (accidental or occupational) pesticide poisoning incidents are reported, estimated at about one million (20000 deaths) and two million, respectively [7]. In USA, occupational poisoning reached around 110000 cases in 2010 [8], follow by Brazil with 9357 cases including non-occupational [9]. Colombia on average reports 8400 cases of intoxication annually [10]. These worrying statistics are reported even when FAO and WHO (World Health Organization) since 1963 have established maximum residue limits (MRLs) for pesticide in food in an international treaty developed by neutral scientific evaluations to guarantee food quality [11].

As a result of this unintentional intoxications for ingestion of food with pesticide residues, it is imperative to evaluate these residues in food before consumption, which is an object of this project.

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WHAT ARE THE MOST USED PESTICIDES IN COLOMBIA?

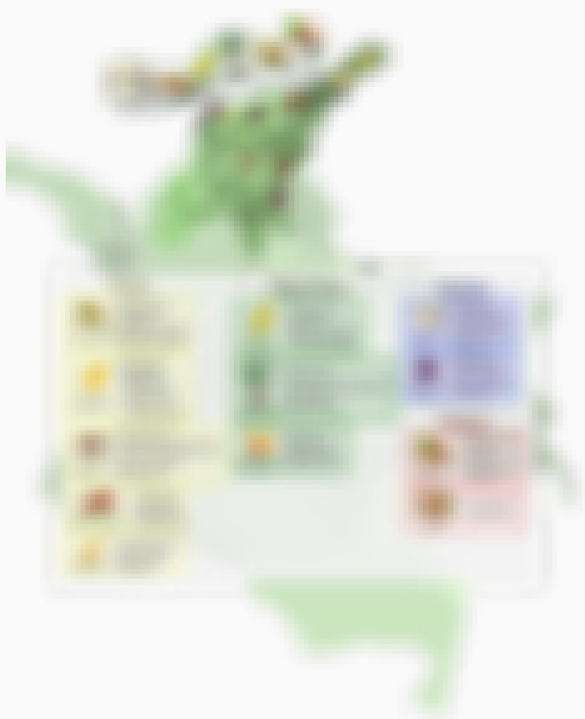
In 2018, Colombia ranking 18th on the top pesticide users worldwide with 37.7 thousand of pesticides according with FAO estimations [1]. In addition, this country produces and exports broad-spectrum pesticide products to several countries, providing annually almost five thousand of jobs and generate 68 million US dollars in exports [2]. According with the 10 top-selling report of 2016 presents by ICA (Instituto Colombiano Agropecuario), herbicides active ingredients represent around 50% of the total pesticide sales, being the most produced so far glyphosate with 14% followed by paraquat with 6%. For fungicides and insecticides, mancozeb and chlorpyrifos are the most sale with 6.9% and 7.5%, respectively [1].

Glyphosate has been widely used in Colombia for the control of weed emergent in rice, banana, coffee, sugar cane, plantain, and oil palm. Moreover, this herbicide has been also used by aerial spraying to eradicate illegal crops between 1984 and 2015 in disproportionate amounts promoting the rapid emergence of resistant weeds, and in turn, the requirement of higher concentrations and frequent applications. However, glyphosate has been classified as a moderately toxic pesticide which strongly affects soil and water, and in consequence, insects, amphibians, and even, humans with a carcinogenic effect [3].
Paraquat is a low-cost herbicide used for rapid effect in the control of grasses and dicotyledonous weeds. This has been used in Colombia mainly to control the pest in rice, corn, potatoes, banana, beans, plantain, carrot, coffee, tomatoes, sugar cane, among others. Nevertheless, this herbicide is also classified as highly toxic to humans causing serious damage in lung, kidneys, liver, and esophagus by inhalation [4]. Given these hazards, paraquat was banned in the Union Europe in 2007 [5], and it is highly restricted in USA [6]. In 2020, Colombia's Ministry of Agriculture prohibits importing and registering paraquat, measure that is still being implemented [7].
Similarly, mancozeb fungicide has been successful used to prevent and to control diseases in potatoes, bananas, watermelon, pumpkin, tomato, pepper, eggplant, gooseberry, lulo, etc., given its low-cost, broad-spectrum, and great effectiveness. However, this pesticide has been associated with chronic effects on human health [8].
Chlorpyrifos is a common insecticide used in homes to regulate cockroaches, fleas, and termites. Moreover, it has been used in agriculture to control pest in bananas, yucca, plantain, rice, cotton, coffee, oranges, papaya, lemon, tomatoes, pineapple, among others. This pesticide can be neurotoxic not only for insects, but also animals and humans; being children the most affected. Decrease in cognitive functions, autism, and attention deficit, are some of the neurodevelopmental effects consequence of the prenatal and postnatal exposure [9].

A list of more pesticides used in Colombia, along the food which they are applied, are presented in Figure 1. In this Figure, the main crops of Caribbean region in Colombia made up of Cordoba, Sucre, Bolivar, Magdalena, Cesar, Atlantico, and the Guajira departments are presented. This region has been particularly chosen given the place where the project will be mainly developed -Atlantico and Cordoba-. In common, these departments grow rice, corn, oil palm, plantains, yucca, and yam [10-11]. Additionally, Magdalena and Cesar farm coffee and beans, and in the Guajira successful grow up watermelon, bananas, and pumpkin. As was expected, glyphosate is the most frequent pesticide used in Colombian Caribbean region crops, followed by mancozeb, chlorpyrifos and carbendazim.

Given the popularity of these pesticides to control pest in Colombian agriculture, and the hazardous effects than produce in non-target living beings, in this project we will study the spectral signatures of some of them pesticides by IR spectroscopy.

Figure 1. Colombian caribbean region crops along the most used pesticides to control pests.



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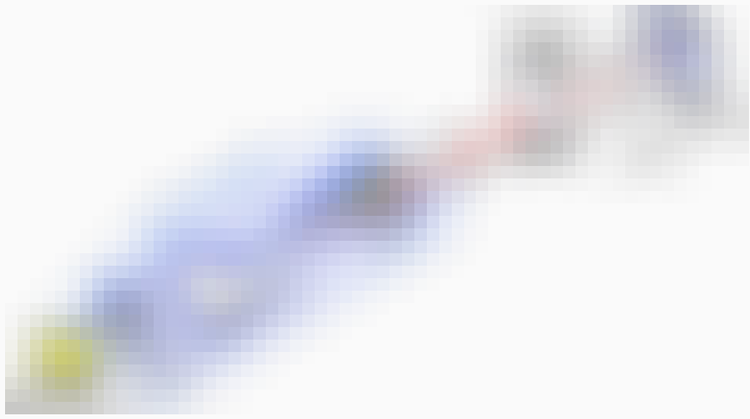
WHAT IS INFRARED SPECTROSCOPY?

In optical spectroscopy, a sample is irradiated with light, and the response to their interaction (absorption, reflection, scattering), which depends on the chemical and physical properties of the sample, is measured as a reflected or transmitted radiation by a detector. To gain maximum information, in this technique the intensity of the interaction is evaluated as a function of the radiation wavelength, which provides an optical spectrum, that is a signature of each compound. Given the large molecular composition of most substance and the limited resolution of the spectrometers, the spectrum exhibits hidden peaks, concavities, shoulders and overlapping of each individual optical response. In consequence, an adequate statistical method for decoupling, identification and selection is required. Using mathematical pretreatments and multivariate data analysis methods on the spectrum, information about sample composition and structure can be extracted [1-2].

Basically, these techniques require a light source, a wavelength selector (dispersion device) that separates the polyromantic light spectral regions into monochromatic frequencies, optics (lens) to direct the light from the source through the sample and onto the detector, a sample holder, and a detector that measures in the spectral range of interest [3]. The simplest optical spectroscopy setup is presented in Figure 2. Given its working principle and nature, spectroscopy techniques are non-destructive, rapid, sensitive, accurate and reproducible, which make them an attractive methodology in material characterization [4].

Figure 2. Scheme of the simplest optical spectroscopy setup in transmission configuration



Particularly, in IR spectroscopy at energies like photons have in the infrared region of the spectrum (around 1.7 – 1.24 meV equivalent to a wavelength range from 700 nm to 1 mm or 15000-10 cm-1) matter can exhibit vibrations of the atoms of a molecule, in particular, changes in the electric dipole moment of the molecule during the vibration. During the interaction, the energy associated with the frequency of the light can be strongly absorbed by some molecular bonds if the frequency corresponds to the natural molecular vibrational. As a consequence, the electronic charge of the bond is distributed from one side to the other changing the dipole moment [5]. Collecting the transmitted or reflected radiation emitted by the sample, the absorbed light at the corresponding frequency vibration can be obtained through an IR spectrum. To identify the compound evaluated, the intensity and location of the peaks in the spectrum are analyzed. Using reference tables, the spectrum is compared to identify the functional groups [6-7]. This analytical technique has currently been used in the study of a wide range of samples of different nature from pure substance to mixtures [8-9].

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DETECTION OF PESTICIDE BY IR SPECTROSCOPY

Last decades several works have been developed in the qualitative and quantitative analysis of pesticide residues in food using IR spectroscopy. In Table 1, we summarize the main characteristics of the works found in literature. The major reports studied fruits and vegetables, which are contaminated with pesticide in a controlled way on their surface at various concentration levels. Sample condition used for IR spectroscopy measurement have mainly been intact or DESIR. In the DESIR (dry-extract system for infrared analysis) method the amount of chemicals on the sample are concentrated on a solid substrate of low NIR absorptivity, embedding this substrate in the washing solution obtained by washing the sample with water or acetone. Then, the solvent is removed from the wet substrate by drying, and the NIR measurement is performed on the dried substrate. This method has been widely incorporated to improve the sensitivity of spectroscopic technique in relative low pesticide detection [1].

Table 1. Main information compiled of the works found in literature that qualitative and quantitative analyze pesticides residues in food using IR spectroscopy. The successful (non-successful) discrimination and/or prediction of the pesticide residues in food is represented by ✅(❌).

In all works, the optical spectrum measurement is carried out in near-infrared (NIR) range, considered for food the most sensitive and suitable region for pesticide detection. Some works include visible (Vis) and mid-infrared (MIR) ranges; however, the statistical data analysis is typically developed in the NIR region.
It is worth mentioning that in all evaluated works the pesticide concentrations are the response variables in the chemometric analysis, while the reflection/transmission detected at each wavelength is the predictor variable. Therefore, the pesticide concentration level is a common parameter of variation in the works analyzed, varying around 0 to 100 ppm in some cases [1, 4-5, 8-10], and around 0 to 4 ppm in others [3, 6, 11]. Additionally, parameters like sample condition, signal pretreatment, multivariate methods, and spectral range have been studied in order to find the optimal parameters for the accurate discrimination and prediction of pesticide residues in food. Several mathematical pretreatments methods have been tested, such as SNV (standard normal variate) [2-3, 5, 7-10], 1-2D (first and second derivates) [1-2, 4-6, 9-11], MSC (Multiplicative scatter correction) [3, 5, 8, 10-11], PSO (particle swarm optimization) [6], SPA (successive projections algorithm) [8], RF (random frog) [8], among others. Some of them works better than others depending on the IR signal, which in turn depends on the pesticide type, concentration levels and food. After this process, the treated signal is analyzed by multivariate methods such as PCA [3, 5, 10], PLSR [1, 4-6, 8-11] and PLS-DA [2-3, 10] to find accurate calibration and validation models for prediction and discrimination, respectively.
All works dedicated to discriminate pesticide presence/absence in food or above/below presence, show a good accuracy with PCCs greater than 80% (representing by); however, the prediction of the specific concentration levels of pesticide residues in food is more laborious, being usually successful at relative higher concentrations, but reaching poor accuracy and consistency (representing by ❌) at those concentrations established in the MRLs, that are the levels of interest.

According to the works consulted, for successful determination of pesticide residues in food by IR spectroscopy is important to evaluate experimental key parameters such as sample conditions, spectral range collected and the mode of measurement, as well as the appropriate statistical analysis data method to correctly interpret the spectrum information.

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WHAT IS FEDS?

Considering the complex spectrum that is obtained in this wide IR spectral range, a potential mathematical treatment is required to discern special characteristics. FEDS (Functionally-enhanced derivative spectroscopy) is a simple algorithm for mathematical transformation of FTIR spectrum based on the named Function P, that allows easily to enhance small changes in the FTIR spectrum by assignation of signals, the deconvolution of possible overlaps, and the identification and selection of main information that define a spectral footprint. Function P can be understood as a functional transformation that contracts the signals of FTIR spectrum in function of critical points without changing the relative position of them. FEDS have been shown as a potential approach to improve molecular differentiation, and quantitative and qualitative determination of pure substance and mixtures [1-3]. Using this method, the hydrogen bond interaction and dimerization of acetic acid in water were studied. Given the overlapping and displacement of the spectral signal caused by the water acetic acid dimerization, FEDS shows as a tool to easily identify the corresponding signals [1].

Improvements around this method have been developed. Recently, a complementary algorithm that remains with highly accuracy the position and the size of peaks, that define the spectral signature of the studied sample, have been proposed [4]. In this procedure the vicinity of the maximum points is cleared, reducing various segments of the line function to zero, which successful locates the main information of the signal and diminishes the amount of data achieving more accurate Pearson correlation coefficient (rF). In this work, one-phase binary mixture acetone/triethylamine (ACT/TEA) and agricultural soils were analyzed. In Figure 3b, the FTIR spectrum (original signal) and the spectrum after using FEDS methodology are compared. Clearly, FEDS signal provides a best location of interesting data for further analysis. In Figure 3a, the FTIR spectrum is presented as a function of the volumetric fractions, showing the dynamic of the signal, i.e., how the signal (size of the peaks, peaks location and overlapping) change as the mixture varies. Spectral similarity indices SSI (SSF -spectral similarity FEDS- and rF) were evaluated using the FTIR signal at different concentrations, and then compared with those obtained with FEDS improved spectra (FEDS0). It was found higher SSI for FEDS signal than FTIR given its thousands of irrelevant data that contribute to the statistic procedure. In addition, authors found that the selected spectral region for evaluation should allow an adequate spectral comparison, i.e., to exhibit notable differences in the spectrum when the samples have different chemical composition, being their spectral signatures easily traceable. Therefore, FEDS0 allows to select the adequate regions for spectral comparison between different samples, facilitating the finding of characteristic peaks.

Figure 3. (a). FTIR spectrum of the ACT/TEA mixture as the volumetric fraction varies. (b). Comparison between the FTIR spectrum (original signal) and the spectrum treated by FEDS method. Data taken from Ref [4].

As show in previous paragraphs, FEDS can be considered as a novel, simple and accurate method for data analysis easily applicable in any discipline, for that reason, in this project we want to implement this methodology in the construction of dynamic and high-resolution spectral signatures of pesticides.

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Results

EXPERIMENTAL METHODOLOGY

HOW DO WE PREPARE THE SAMPLES?

Pesticides at different concentrations

Figure 4. Pesticide sample obtained from the dilution of pesticide and NaCl.

In order to trace the pesticide signature, various samples at different concentrations are prepared using NaCl as a diluent given its very low IR absorbance. Pesticides in liquid presentation are applied onto NaCl powder according with the dilution factor that goes from 5 to 1000. Low dilutions are achieved using the serial dilutions method. The pesticides in original powder presentations are also mixed and shaken with NaCl (see Fig. 4). The pesticides used in this study are presented in Table 1 along its target form life, chemical family, and original concentration.

Table 2. Characteristics of the pesticides under study.

BANANA PEEL CONTAMINATED WITH PESTICIDE

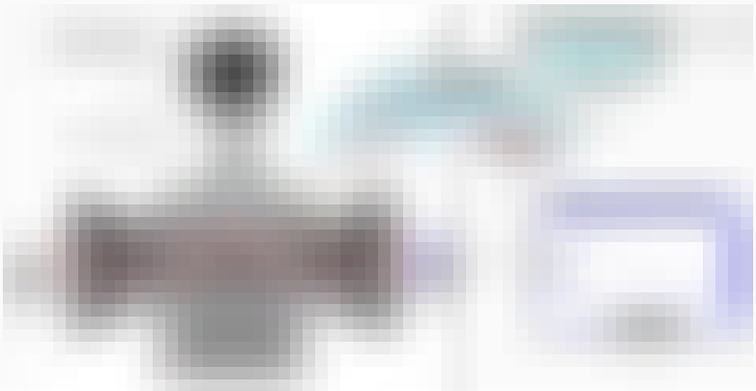
Bananas Valery are studied in their ripening stage. The banana peel is removed with a knife obtaining square samples of thin layer as shown in Figure 5. Samples are cleaned and dried. Then, they are impregnated with pesticide in liquid solution at six different concentrations from 5 to 0.25 g/l. Three samples are prepared for each concentration.
Samples are dried in an oven and stored in a dissector before the spectroscopy measurements.

Figure 5. Samples of banana peel contaminated with pesticide.

HOW DO WE OBTAIN THE IR SPECTRA?

Given the advantages of the optical spectroscopy, in particular, those provided by the FTIR (Fourier transform infrared spectroscopy) and ATR (total attenuate reflectance) systems in the easy, reliable, and accurate measurement of the reflectance or transmittance spectra [1], the IR spectrum of the samples is obtained by total attenuate reflectance Fourier transform infrared spectroscopy using an IR lamp in the spectral range from 4000 to 600 cm-1, a SeZn crystal as contact window and IRAffinity-1S spectrophotometer (Shimadzu Co). The scheme of the system is shown in Figure 6. Powder and solid samples are placed on the sample platform and by using the pressure tower and pression tip, are brought into close contact with the crystal. The absorbance spectra are collected with 5 repetitions and 16 scans.

Figure 6. Scheme of the working principle of ATR-FTIR system.



HOW DO WE OBTAIN THE IR SPECTRA? WHAT IS THE WORKING PRINCIPLE OF THE ATR-FTIR SYSTEM?

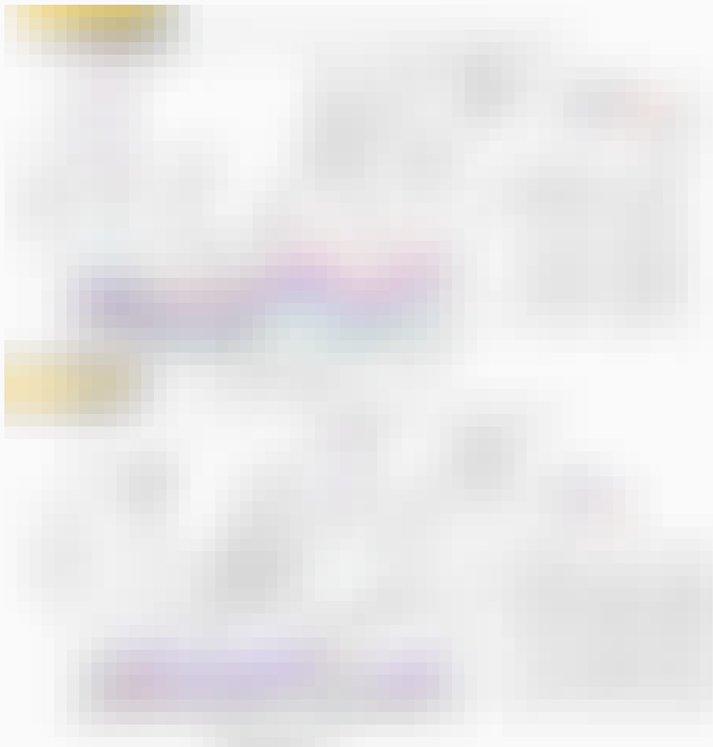
As its name suggest, ATR technique is based on the attenuated total reflectance optical principle. In this system a modulated IR beam, generated by the light source along an interferometer, impact on the crystal (medium of high refractive index) and travels inside it through multiple reflections (Fig. 6b). Depending on the light frequency, the angle of the light incidence changes in order to induce total internal reflection phenomenon. In this condition, some amount of the light energy escapes the crystal and extends a small distance beyond the surface in the form of waves to a medium of low refractive index (sample in close contact) (Fig. 6c). This energy is absorbed by the sample, which in turn depends on its structural, physical, and chemical properties. Then, this absorbance is translated into the IR spectrum of the sample (Fig. 6d) and treated by fast Fourier transform mathematical operations to determine the individual wavelength contribution [1].

RESULTS

IR SPECTRA OF THE PESTICIDES AND CHEMICAL ASSIGNMENT

In Figure 7, the FTIR spectra of Chlorpyrifos and Carbendazim are presented in the mid-IR range of 1800-600 cm-1 at different concentrations greater and lower than 1 g/kg. The reference signals corresponding to the maximum pesticide concentration and the diluent (NaCl) are also presented. In order to identify the principal bands, the signal assignment to the five principal peaks, bond, and vibration are identified in each case [2-5]. Signals present good repeatability, particularly at concentrations < 1g/kg, given the high intensity of the principal peaks. However, in practice, due to the different operations of washing, transport, and storage, the residuality of the pesticides may be diminished, being, consequently, the region of lower relative intensity the most likely to occur in practice. In this way, as expected, at a low signal-to-noise ratio, the differentiation of the signals entails great difficulty.

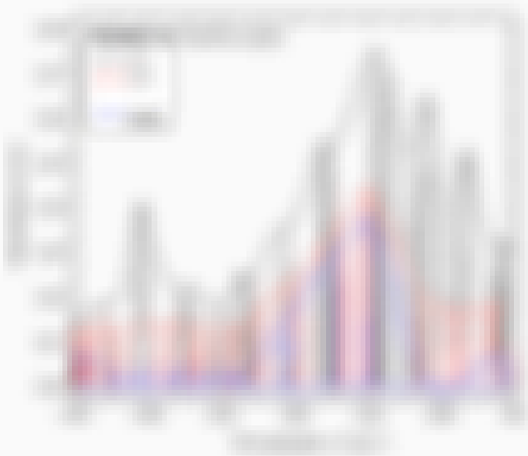
Figure 7. FTIR spectra of the pesticides chlorpyrifos and carbendazim at various concentrations. In the right side the spectral band of the principal peaks are specified. In cyan line the FTIR spectrum of NaCl.



HIGH-RESOLUTION SPECTRA: FEDS SPECTRUM

In Figure 8 in dashed line, the FTIR spectra of Chlorpyrifos for two concentrations along with the respective FEDS spectrum in solid line are presented. The NaCl is also present in order to visualize the spectral behavior, and the coincidence of the FEDS peaks in some regions of the spectrum. In this methodology the FEDS spectral coincidences are evaluated through the Pearson's coefficient r and the spectral similarity index SFF. Note that in some spectral zones, the coincidences between the diluent NaCl are major than in others, for which the pesticide signature should be searched regions which the target signal mainly do not correlated with the NaCl.

Figure 8. (Dashed-line) FTIR spectra of Chlorpyrifos at two concentration levels and the NaCl with their corresponding FEDS spectrum (solid-line).



PEARSON'S CORRELATION COEFFIICIENT AND SIMILAR SPECTRAL FEDS INDEX

As a general view, we present the spectral correlation between the different concentrations of pesticide with the MSS using the Pearson's correlation coefficient and spectral similarity index [6-7] in two wide spectral ranges as shown in Figure 9. As was expected, a higher correlation is observed at high concentrations with a linear tendency, with more standard error at low concentrations. In general, the good correlation of these graphs indicate that spectra contain zones in which the pesticide signature remains.

Figure 9. Pearson correlation coefficient and spectral similarity FEDS (SSF) as a function of pesticide concentration. Pesticide concentration axis is in logarithm scale.

Based on the individual correlation between the target signals and their references (MSS and NaCl), and on the group behavior of the studied concentrations according with the r and SFF parameters, the spectral zones in which the pesticide signature remain as the concentration decreases are successful found. It is found that these regions coincide with those in which the pesticide molecules exhibit the high polarity bond, which is expected given the IR spectroscopy nature.

The principal peaks present in the spectral range estimated are characterized evaluating the peak area for the concentration levels studied as shown in Figure 10 for Chlorpyrifos. A good linear model is proposed according to the parameters RPDs (residual prediction deviation) and RMSEs (root mean square errors) presented in the table inset [8]. This procedure was also developed with the relative absorbance intensity of the mid signal for the principal peaks. The limit of detection LOD and limit of quantification LOQ were also calculated.

Figure 10. Peak area as a function of the pesticide concentration in the spectral range of interest. In the table inset the model parameters RPD and RMSE at various spectral ranges.

DETECTION OF PESTICIDE RESIDUES IN BANANA PEEL

Once the pesticide signature of Chlorpyrifos is traced in NaCl, the idea is proving the methodology proposed in a more complex analytical matrix, such as banana peel. As a consequence, we contaminated banana peel at different concentration, as was explained in a previous section. In Figure 11a, the FTIR spectra of the contaminated and uncontaminated banana peel contaminated are presented, as well as the mid spectrum of the Chlorpyrifos. Note some characteristic peaks of Chlorpyrifos arise in the banana spectra, and their remarkable diminution as the pesticide contamination level decreases, such as at low concentrations there are not visible differences. In order to highlight the peaks associated with the pesticide signature and considering the repeatability of the signals between 1500-800 cm-1, a normalization process was developed and then the spectrum of the banana contaminated is normalized with the spectrum of the banana without contamination (see Fig. 11b).

Evaluating the correlation of the normalized signals with the banana spectrum and the pesticide spectrum as shown in Figure 11b, the spectral zone in which the pesticide signature presents is found. An eventually these zones coincide with the previous analysis developed for Chlorpyrifos.

Figure 11. FTIR spectrum of the banana peel in green ripening stage contaminated with different pesticide concentrations.

CONCLUSIONS

- The dynamic of the spectral signature of various pesticides has been measured by a Fourier-transform infrared spectroscopy (FTIR) system and analyzed with FEDS algorithm.
- The spectral fingerprints of high resolution and great specificity of each pesticide are obtained and characterized using FEDS spectrum and criteria parameters of correlation.
- The region in which the spectral signature remains as pesticide concentration decreases is highly correlated with the high polarity of the bonds.
- The relative peak intensity of the spectrum allows to characterize the tendency and to propose models for prediction.

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