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Research Article

In Situ Compositional Analysis of Tomato Plants and Cell Wall Using Fiber Optic Fourier-Transform Near-Infrared Spectroscopy

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This research was intended to define and interpret cell wall attributes and other chemical composition of eight different varieties of tomato plants by utilizing fiber optic Fourier-transform near-infrared spectroscopy (FT-NIR) to acquire in situ chemical signatures of leaf, flower, fruit, and stem of tomato plant and cell wall at different developmental stages. Chemical spectral signatures of the tomato's leaf, flower, fruit, and stem were only acquired during its session and in live mode such as green, yellow, and red in cell wall color. The spectral signature analysis of each tomato plant was performed to see substantial differences in chemical compositions using chemometric data modeling of FT-NIR spectra. In addition, principal component analysis (PCA) was performed to discriminate leaf, flower, fruit, and stem from the same variety. PCA was also performed to differentiate eight different varieties of tomato plants. The study showed how in situ FT-NIR could distinguish eight types of tomato leaf, flower, fruit, and stem chemical composition at different developmental stages related to cell wall and other attributes. This study has also demonstrated how in situ FT-NIR can discriminate between rusty vs. healthy leaf and intact fruit vs. off-the-plant fruit. The main objective of this study is to present the chemical signature differences in the live and developing tomato plants to improve crucial factors of tomatoes that would benefit plant breeding, tomato cell wall study, and ultimately human health.

1. Introduction

Fruit represents unique plant developmental systems and is essential to human and animal diets. Speaking of which, a popular item used on earth for everyday consumption is tomato. Tomato is the most consumable food product grown worldwide, and many by-products are manufactured worldwide. Tomato, an economically significant vegetable, is the principal model for fleshy fruit development, ripening, shelf life, and nutritional quality studies. However, many fundamental questions related to critical parameters of the development of each part of the plant, physiology, and quality traits, including environmental responses of leaf, flower, fruit, and stem of tomatoes, are sometimes very challenging because the majority of the time, we are not able to capture chemical signature from the live plants in a real-time manner. When any part of a plant is separated from the main structure of the plant, the chemical composition changes. Fourier transform Near Infrared Spectroscopy (FT-NIR) in conjunction with a fiber optic probe is a trustworthy and popular analytical technique to measure those compositional changes, which is beneficial for agricultural and food research. FT-NIR has been applied throughout several studies that helped scientists discover and better understand the plants' chemical properties in real time and in situ [1].

A tomato's function is crucial to humans as it supplies sugar, vitamins, minerals, lycopene, and other carotenoids. Most of the population globally consumes tomatoes; overall consumption in markets is 75% fresh and 25% processed. At the national level, tomatoes are ranked as the first crop among vegetables in production and cultivation, specifically around 200 million tons yearly [2]. However, current productions are increasing higher demands exponentially, so breeders are aiming and seeking to enhance the quality of

tomatoes internally and externally to supply the people's needs [3]. On the other hand, postharvest inflicts a substantial loss in production and quantity, especially in tomato productions. This problem is an obstacle for breeders, and the food quality is severely reduced. Enhancing and improving tomato plants would counter this problem, but it takes considerable time and examination.

Breeders have developed several tomato varieties for the last several years for better yield and quality. Identifying types of vegetable crops is essential during all stages of production and processing [4]. Most research involved characterizations of tomato fruit, not whole plants [5].

Characterizations of leaf, stem, fruit, and cell wall will help breeders identify leaf, stem, flower, and fruit phenotypes and spectrotypes and achieve higher yield and quality. Traditionally, the variety of tomatoes has been identified using morphological or phenotypic characteristics.

Morphological methods are commonly used for phenotypic studies; however, the lack of phenotypic variation in tomatoes makes it challenging to identify variety by conventional morphological methods.

Current tomato production demands rapid and discriminating techniques for better turnaround. In recent years, various analytical and prototype methods, such as molecular markers, have been available for quick identification. However, these techniques cannot perform in situ nondestructively or on-site measuring [6–9].

The previous studies by Tewari et al. performed fiber optic FT-NIR to identify origin and sugar content. Their studies successfully measured sugar content and identified different citrus varieties using chemometric spectra modeling [10]. A study was performed by SD Noble on discriminations of other leaves using NIR reflectance spectroscopy [11]. A successful study was also performed using NIR to discriminate transgenic corn kernels using NIR [12]. Other studies were performed on determining tomato quality attributes using near-infrared spectroscopy, where they successfully discriminated the tomato's quality attributes. All the NIR studies of plants were conducted offline but not in situ previously; therefore, this study could be highly beneficial for tomato plant breeding study [13].

In this study, our primary goal was to develop a fiber optic NIR technique to easily collect FT-NIR spectra of the different parts of the tomato plant at different development stages and interpret NIR chemical spectral signature analysis using chemometric data modeling such as principal component analysis (PCA).

In this article, we have interpreted attributes of eight different varieties of tomato plants such as Early Girl, Goodhearted, Husky Red, Hybrid Husky Red, Japanese trifle, Summerset Heart-Tolerant Hybrid, Supersweet 100, and Valentine Grape Tomato, and spectral analysis was performed on FT-NIR chemical signatures from leaf, flower, fruit, and stem of tomato plant at different developmental stages. The chemical spectral signatures of the tomato's leaf, flower, fruit, and stem were only acquired during its session from live plants, specifically the three main stages of tomato fruit: green, yellow, and red in cell wall color in in situ mode. It is well known that the outer surfaces of tomato cell wall cells comprise various polymers such as polysaccharides and proteins, phenylpropanoids, and lipid polymers. These polymers are synthesized, secreted, and assembled into elaborate matrices with architectures that vary according to the heterogeneity within individual cells' specific cell wall faces [5]. When FT-NIR spectra were directly collected from live leaf, flower, fruit, and stem without isolating the plant sample, we could capture the actual spectral signature of these components. The PCA on in situ data showed substantial differences in chemical compositions in different varieties, leaf, flower, fruit, and stem at different developmental stages and was able to discriminate the rusty vs. healthy leaf. The application of this study is to evaluate the real-time chemical composition of tomatoes to improve crucial factors of tomato fruit that would benefit plant breeding; the tomatoes' cell wall study mainly might be helpful to characterize drought responses of fruit and crop improvement and ultimately beneficial for human health.

2. Materials and Methods

2.1. Selection of Live Tomato Plants. All eight varieties of tomato plants, such as Early Girl, Goodhearted Tomatoes, Husky Red Tomato, Hybrid Husky Red, Japanese Trifle, Summerset Heat-Tolerant Hybrid, Supersweet 100, and Valentine Grape Tomato, were collected from Home Depot, Salem, NH, and Rogers Spring Hill Nursery, Methuen, MA, USA. All the tomato plants were collected in their early developmental stage.

2.2. Preparation of Tomato Cell Wall. Tomato skin from eight varieties of tomatoes was extracted from the primary fruit. The materials were thoroughly cleaned with distilled water to ensure no fruit residue was present in the cell wall sample. The FT-NIR spectra were immediately collected from the freshly removed skin from the fruits to ensure no change in the cell wall during the preparation. There are many publications on the extraction of the cell wall; however, in the study, we have used FT-NIR to get cell wall composition in a nondestructive way.

2.3. In Situ Fiber Optic FT-NIR Scanning Parameters. All the FT-NIR spectra of different tomato plants, fruits, leaves, flowers, and cell walls were collected using a Matrix-I FT-NIR fiber optic system from Bruker Optics, Billerica, MA, USA. All the FT-NIR spectra were collected from 4000 to 12500 cm^{-1}. The instrument was equipped with a germanium detector, operating at 8 cm^{-1} resolution and 0.32 cm/s mirror velocity. The helium-neon laser for continuous internal calibration of the Matrix-I spectrometer strengthens the stability and reliability of the measurement in single-beam mode. All the spectra were corrected against a background spectrum collected from a gold-coated internal background surface. All experiments were completed five times for chemometric data analysis. In addition, a fiber optic reflectance probe was used to collect all the NIR spectra. Throughout the measurement, experimental consistency was maintained.

2.4. In Situ Fiber Optic FT-NIR Scanning of Live Plants. The FT-NIR spectra of all eight varieties of tomatoes were collected by scanning five different areas of the tomato plant to compare its chemical compositions to other spectra obtained from different tomato plants. Additionally, the fruits from each tomato plant were scanned five times every 4-5 days to see a significant change in chemical compositions compared to the other fruits we acquired.

2.5. In Situ Scanning of Leaf, Stem, Flower, and Rusty Leaf. Figure 1 represents the in situ scanning procedure. Each leaf and each flower were placed on the metal spoon which was essential for the scanning since infrared waves could not detect metal. This helped the scan of the flower to be more specific and gave us more realistic data.

In this study, we have used a metal spoon to scan the thinner sample, such as a flower, as metal does not absorb the NIR beam. In addition, metal has a high reflection ability; therefore, we received a better signal. Figure 1 also represents leaf from live tomato plants that were rusty. Anthracnose is a common fungal disease that typically causes dark spots on the leaf. The main objective was to compare the healthy leaves to the rusted leaves and see the difference in spectral chemical signatures.

2.6. Scanning of Tomato Fruit. In situ FT-NIR spectra of tomatoes were directly collected from scanning the three stages of a tomato's ripening duration: green, yellow, and red. Figure 2 depicts the in situ scanning procedure of tomatoes in their early, middle, and ripened stages.

2.7. Chemometric Data Modeling. Chemometrics combines chemistry, math, and statistics that extract meaningful information from chemical systems by data-driven means. In this study, all FT-NIR spectra were preprocessed, and chemometric principal component analysis (PCA) was performed on leaf, stem, flower, and fruit using the Bruker Quant Chemometrics program (Bruker Optic, Billerica, MA).

PCA is a two-dimensional statistical method to reduce the dimensionality of a large FT-NIR dataset containing a more significant number of variables and generates new variables called PCs. In this study, we have presented PC1 vs. PC2 dimensions, which represent the most variability in the FT-NIR data [10].

In this study, FT-NIR spectra from 4000 to 12500 cm^{-1} were used after offset for the average absorbance. Baseline correction and area normalization features were used to eliminate all the spectral artifacts from the dataset. For the PCA study, various spectral preprocessing algorithms were used, such as first and second derivatives, vector and min-max normalization, straight line subtraction, and multiplicative scatter correction, to improve the discrimination ability of the PCA without overfitting the data. In this study, we have selected the second derivative preprocessed method to analyze all the FT-NIR data. The wavenumber range corresponds to each chemical signature from the leaf, stem, flower, and fruit, such as polysaccharides, proteins, phenylpropanoids, and lipid polymers. All the data were further studied using PCA to determine the relationships between variables. PCA was also used for pattern recognition using different components of the plant's varieties, fruits, stems, leaves, and cell walls. Based on the absorbance of these components, we have optimized the PCA to achieve the best multivariate statistics [10].

3. Results and Discussion

Fiber optic probe FT-NIR spectroscopic measurements from 4000 to 12500 cm^{-1} were carried out to evaluate chemical and physical spectral signature properties based on their first, second, and third molecular overtones and combination vibrations from mid-IR.

Fiber optic Fourier-transform near-infrared spectroscopy (FT-NIR) in a fiber optic reflectance mode is a rapid and nondestructive technique. FT-NIR recognized functional groups of the molecules correlated to the samples' constituents. Based on the molecular signature of the functional group, FT-NIR can be implemented for quantitative and qualitative studies [14].

Tomato's leaf, stems, flowers, and fruit all consist of cell walls, esters, amides, hydroxyls, carboxylates, and carbohydrates, and FT-NIR can sense all these components (Figure 3, FT-NIR spectra of leaf, stem, flower, and fruit). The FT-NIR reflectance spectrum of leaves, stems, flowers, and fruit contains spectral signatures of molecular bonds from the samples [14].

The NIR spectrum contains enriched information from the cell wall, leaf, stem, flowers, and fruit, precisely pattern distinct for leaves, stems, flowers, and fruit at different developmental stages.

Infrared spectroscopy in mid-IR generates more specific fingerprints of the organic molecule. At the same time, FT-NIR generates a particular spectral pattern based on overtone and combinational bands. FT-NIR induces invisible phenotypes or spectrotypes for leaf, stem, flower, and fruit molecules, particularly in plant cell wall structure and its architecture, which not only allows us to identify the sources of compositional variance but also allows us to identify the mutations in plant or cell wall as well.

FT-NIR with PCA can locate and classify spectral patterns characteristic of many plant components and plant deficiencies, such as cellulose deficiencies or alterations in the xyloglucan or pectin structure [15]. For example, Figure 1 represents the FT-NIR spectra of leaf, stem, flower, and green, yellow, and red tomatoes.

FT-NIR spectra of the leaf stem, flower, fruits, and cell wall contain a complex chemical composition and produce overtones and combinations of NIR bands from 4000-12500 cm^{-1}. However, most organic molecules absorb NIR beam between 4000 and 12500 cm^{-1}; therefore, we have considered the NIR range from 4000 to 10000 cm^{-1} for the analysis using the component's molecular overtone and combinational vibrations.

Figure 1: In situ scanning of live leaf, stem, flower, and rusty leaf.

Figure 2: In situ scanning of the green, yellow, and red tomatoes.

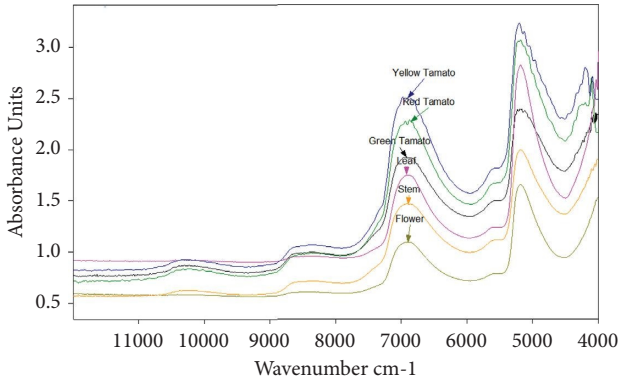

Figure 3: FT-NIR spectra of leaf, stem, flower, and green, yellow, and red tomatoes.

The reflectance or absorption bands of molecules in the NIR region from 4000 to 12500 cm^{-1} are complex and overlapping. The complexity of overlapped spectra makes analysis very challenging due to the invisible phenotypes or spectrotype absorbance of the molecule of the plant. Therefore, to extract meaningful information from the complex spectra required, chemometric analysis is for better interpretation and to identify the correlation of the components of interest in plant organs.

In this study, we have observed significant spectral differences in the NIR spectra from 4000 to 9000 cm^{-1} of leaf, stem, flower, fruit, and cell wall. NIR vibration ranges at 5150–5195 cm^{-1} of all the plant organs are primarily attributed to O–H asymmetric stretching and O–H deformation bands and C-H bonds corresponding to the absorption of water and phenolic compounds in the samples. The NIR bands at 5000–10000 cm^{-1} correspond to the vibrations of C–H bands, and those at 5000–12500 cm^{-1} are related to the third CH overtone of the OH stretch of H_2O. These bands also represent the sample's phenolics and antioxidant components [16, 17].

FT-NIR spectra show discrimination of different plant parts at different wavenumbers, which correlate with the different chemical compositions. To avoid any spectral artifacts in the spectra and to achieve correct discrimination or visualization, the pretreatment of FT-NIR spectra is the first step in interpreting spectral data to eliminate spectral artifacts such as noises and scattering. Each variety of tomato plant has a specific composition. Each organ of the tomatoes also contains concrete components as the plant cell wall is a very complex polymeric structure, and other attributes are chlorophyll, carotenoids, carbohydrate, cellulose, vitamins, sugar content, etc., making various parts of the plant very distinct from each other in their phenotypic or spectrotypic nature.

3.1. Discriminant Analysis of Leaf, Stem, Flower, and Fruit. Figure 4 represents the FT-NIR spectra of the leaf, stem, flower, and fruit. The spectra clearly show the difference between fruit and flowers; however, the leaf and stem spectra are very similar due to the similar chemical composition. In the FT-NIR spectra, significant compositional differences were observed between 7000–9000 $cm^{-1}$and 10000 to 10500 cm^{-1}. Figure 5 demonstrates the principal component analysis (PCA) of the leaf, stem, flower, and fruit of FT-NIR spectra, and the PCA plot correlates to raw FT-NIR spectra. The chemical composition of the leaf, stem, and fruit differ; however, the leaf and stem composition is very close. Differences in the developmental stage of the leaf, stem, flower, and fruit tissues also depend on the environmental conditions. However, the physical and chemical components such as dry matter, soluble solids, carbohydrates, pH, phenols, and nitrates content in the leaf, stem, fruit, and flower significantly affect all compositional constituents of the plant and its organs. The PCA plot clearly showed that all the main parts of the tomato plant have a different composition. PCA plot suggested that the leaf and stem designs are very close because of similarities in chemical composition such as cell wall composition, carbohydrate, and lignin. Figure 5 also represents the score chart of the outcome of PCA analysis using FT-NIR spectra without spectra pretreatment. PC1 or score one value contributed 80%, and PC2 contributed 8%. Score 1 is a component that explains the most significant variability in the NIR spectra, while score 2, score 3, and so on explain the remaining variability in the data. A few outliers were also detected in the PCA graph during the PCA analysis. Those can be useful; otherwise, they can be eliminated during the spectra pretreatment. The PCA graph of leaf, stem, flower, and fruit suggests that the significant difference is between flowers and fruits primarily due to the higher values for dry mass, carbohydrates, phenols, and titratable acidity and lower values for sugars, nitrates, and pH than the stem and leaf portion [17].

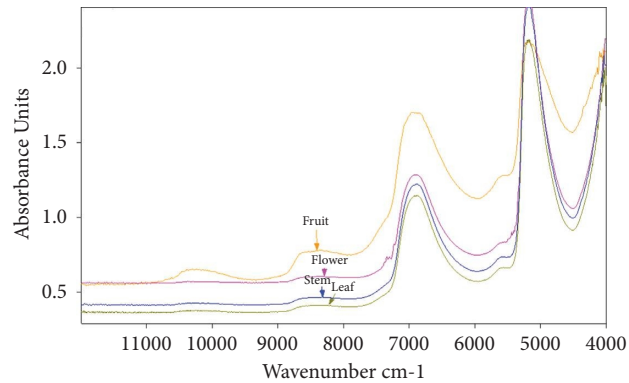

Figure 4: FT-NIR spectra of leaf, stem, flower, and fruit.

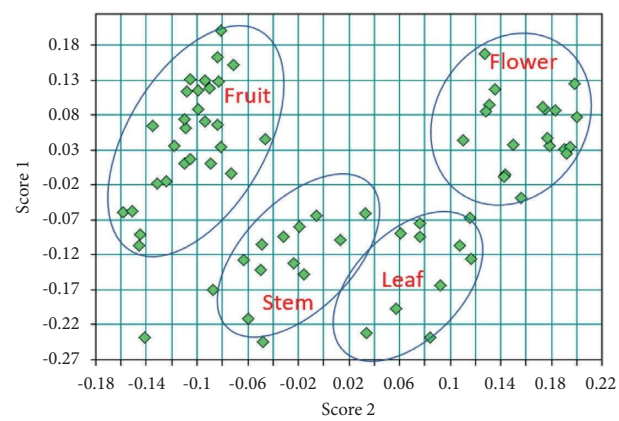

Figure 5: Principal component analysis (PCA) of FT-NIR spectra of leaf, stem, flower, and fruit.

The most considerable differences between the flower and fruit were observed in the nitrate and total soluble phenol content between 4000 and 4500 cm^{-1} [17].

3.2. Discriminant Analysis of Various Varieties of Tomato Leaf. Figure 6 represents the FT-NIR spectra of the leaf of Early Girl (EG), Goodhearted (GH), Husky Red (HR), Hybrid Husky Red (HHR), Japanese Trifle (JT), Summerset Heat-Tolerant Hybrid (SHTH), Supersweet 100 (SW), and Valentine Grape (VG). FT-NIR spectra of all the leaf varieties

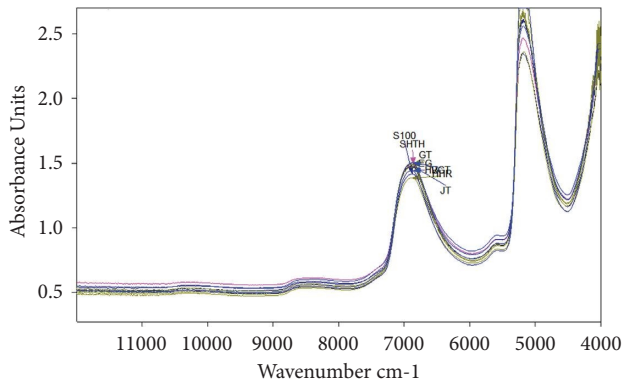

Figure 6: FT-NIR spectra of leaf of Early Girl (EG), Goodhearted (GH), Husky Red (HR), Hybrid Husky Red (HHR), Japanese Trifle (JT), Summerset Heat-Tolerant Hybrid (SHTH), Supersweet 100 (SW), and Valentine Grape (VG).

demonstrated very similar spectral features due to the similarities in chemical compositions. However, FT-NIR spectra also contain valuable and hidden information; therefore, chemometric analysis is necessary to identify spectrotype or genotypes. Since this study is mostly outside the leaf surface, FT-NIR spectra contain information mainly for the surface or cell wall of the leaf. Figure 7 represents the PCA plot of the leaf of all eight varieties of FT-NIR spectra. In this analysis, the full NIR range from 4000 to 12500 cm^{-1} was used to generate a discriminant analysis using PCA. For the FT-NIR spectral interpretations of the leaf, we have the most significant range from 4000 to 7400 cm^{-1}, indeed, due to the absorbance of cellulose, sugars, and lignins which is due to the stretching vibration (O–H, C–H, C–O, and C–C) and the overtone stretching band of O–H [5]. Since the chemical composition of all the varieties of tomato leaves contains carbon, nitrogen, carbohydrates, organic acids, polymers, and water, we have used the full NIR range (4000–12500 cm^{-1}) to generate the PCA plot. The PCA loading (not shown here) suggested that the significant difference is due to the high content of carbon and nitrogen and low concentration of nonstructural carbohydrates, mineral substances, and organic acids from 4000 to 10000 cm^{-1}.

Since the chemical absorbance of these components is in the same region, PCA cannot discriminate the different varieties of leaves after preprocessing the spectra. The main objective here is to differentiate the various varieties of leaves based on differences in their qualitative chemical composition, not a quantitative composition. The quantitative composition of the leaf is definitely different in each variety because each variety may contain higher or lower content of nonstructural polysaccharides, mineral substances, cellulose, lignin, nitrogen content, and soluble carbohydrates [18]. The heat-tolerated tomato hybrid leaf has some discrimination primarily based on their cellulose and other chemical composition differences; however, after preprocessing the spectra, the quantitative differences were eliminated. In the hybrid leaf, gene expression is common in many pathways which reflect the cell wall structure, which can be a significant chemical change in the gene level due to low sensitivity. Unfortunately, the FT-NIR cannot detect gene expression but can only see by-products of the gene in the detective range [5]. Therefore, it can be concluded here that FT-NIR can discriminate various varieties of leaves if there is a qualitative difference in chemical signatures; however, FT-NIR can determine quantitatively as all the chemical signatures are identical structurally, but their quantity is different as FT-NIR is well known for quantitative analysis.

3.3. Discriminant Analysis of Various Varieties of Tomato Stems. Like leaf discriminant analysis, Figure 8 represents FT-NIR spectra of all eight varieties of stems. The spectra are very similar to each other, and it is very difficult to identify the discriminant NIR bands without discriminant analysis. Figure 9 demonstrates the PCA plot of eight varieties of tomato stems using FT-NIR spectra. In this analysis, the full NIR range from 4000 to 12500 cm^{-1} was applied in the same manner as leaf analysis to generate a discriminant analysis using PCA. The tomato stem consists of cellulose, lignin, cell wall, dermal tissue, ground tissue, and vascular tissue. Tomato plant stems were scanned using an FT-NIR probe; however, the spectral signatures were mainly collected from the surface of the stem due to the thickness of the stem; therefore, the FT-NIR spectra contain only chemical signatures from the dermal tissues of the stem, which covers the outer surface of the stem for the protection from the water and gas exchange. While collecting the data from the stem, FT-NIR displayed high absorption intensity with apparent baseline discrepancies and reflectance peak shifts. Since in the NIR region, hydrogen-containing molecules have high absorption, tomato stem spectra are different in chemical signature NIR patterns and could be used for biological, physical, and chemical composition; however, as previously mentioned, this difference is due to only low and high values of the same components of the stem. In this particular study, FT-NIR cannot discriminate different varieties of stems based on their chemical signatures, mainly from the dermal tissues of the stem, due to the lack of depth of penetration of FT-NIR [5].

3.4. Discriminant Analysis of Various Varieties of Tomato Fruit. Figure 10 represents the FT-NIR spectra of all eight varieties of tomatoes containing specific overtone and combination bands. Different types of tomato plants have a unique chemical composition. Figure 11 represents PCA analysis of FT-NIR spectra of tomato fruits of Early Girl (EG), Goodhearted (GH), Husky Red (HR), Hybrid Husky Red (HHR), Japanese Trifle (JT), Summerset Heat-Tolerant Hybrid (SHTH), Supersweet 100 (SW), and Valentine Grape (VG). In this study, PCA discriminates different varieties of tomatoes due to their chemical composition. For example, SHIT and SW were clustered due to the sugar and water content differences. Different clusters have distinct spectrum patterns, mainly in the absorption bands related to water and sugars of overtone and combinational bands. Those are specific regions for water and sugar compound absorption

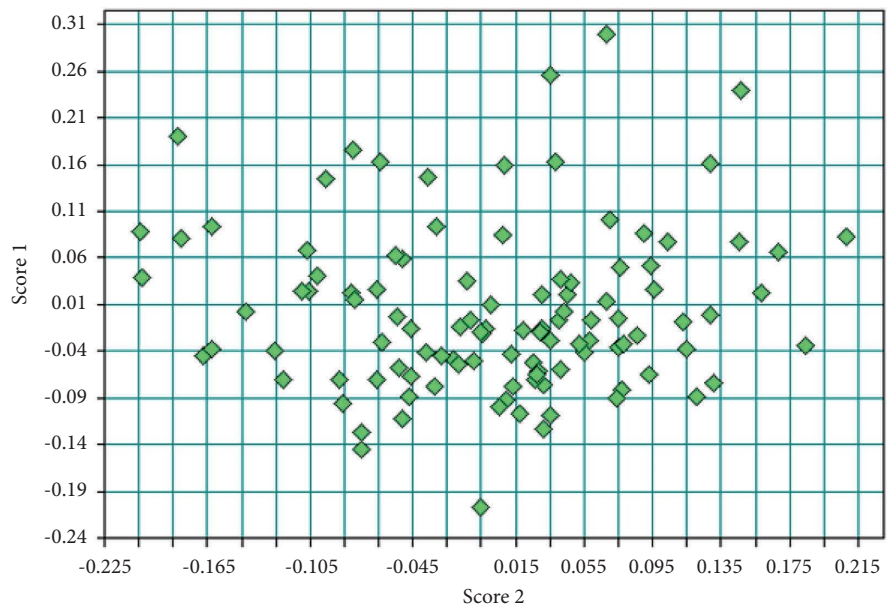

Figure 7: Principal component analysis (PCA) of FT-NIR spectra of leaves of Early Girl (EG), Goodhearted (GH), Husky Red (HR), Hybrid Husky Red (HHR), Japanese Trifle (JT), Summerset Heat-Tolerant Hybrid (SHTH), Supersweet 100 (SW), and Valentine Grape (VG).

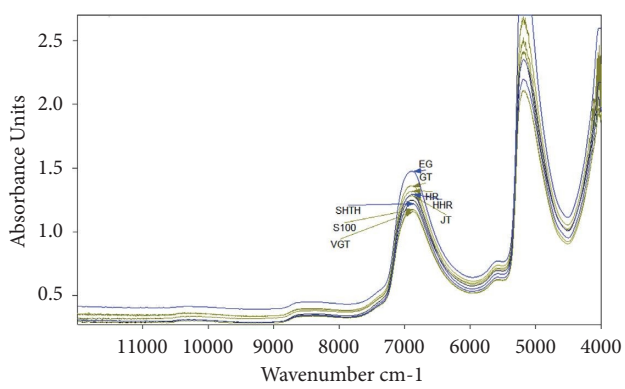

Figure 8: FT-NIR spectra of stems of Early Girl (EG), Goodhearted (GH), Husky Red (HR), Hybrid Husky Red (HHR), Japanese Trifle (JT), Summerset Heat-Tolerant Hybrid (SHTH), Supersweet 100 (SW), and Valentine Grape (VG).

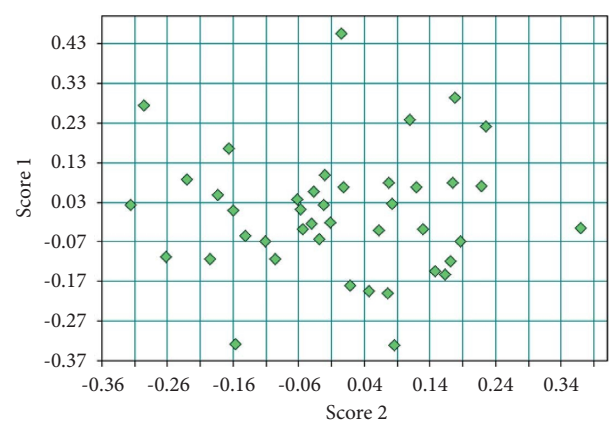

Figure 9: Principal component analysis (PCA) of FT-NIR spectra of stems of Early Girl (EG), Goodhearted (GH), Husky Red (HR), Hybrid Husky Red (HHR), Japanese Trifle (JT), Summerset Heat-Tolerant Hybrid (SHTH), Supersweet 100 (SW), and Valentine Grape (VG).

[19]. Various tomatoes show much variation in compositional changes, primarily due to the wide range of soluble solids, total acidity, and color. This variation can be observed at 5000-6000, 4000-5000, and 7000-9000 cm^{-1}. For the PCA, wavenumbers of 4000, 4500, 12000, and 12500 cm^{-1} were selected for soluble solids and titratable acidity, dry matter, and skin firmness [19]. The PCA score plot shows an excellent correlation for all eight varieties of tomato fruit. The center of the score plot offers the tomatoes similar physical structures such as color, peel, structure, and physical nature of pulp.

3.5. Discriminant Analysis of Developmental Stages of Tomato Fruit. All the FT-NIR spectra of the tomato samples were collected directly from the plant in-situ manner using a fiber optic reflectance probe. Figure 12 shows the FT-NIR developmental stages of tomatoes in different sizes and colors. FT-NIR spectra clearly show the difference in raw spectra at different wavenumbers, such as between 4000 and 11000 cm^{-1}. Therefore, all the FT-NIR spectra were analyzed using PCA using a range from 4000 to 11000 cm^{-1} for the discriminant analysis. Figure 13 represents the PCA score plot of FT-NIR spectra of fruit at different developmental stages from 2 weeks to 8 weeks of timeframe.

The genetic regulation of fruit development begins in the floral meristem, where the architecture and organization of this tissue are determined. Numerous physiological and biochemical changes happen during the developmental stages that determine flavor, color, texture, and aroma.

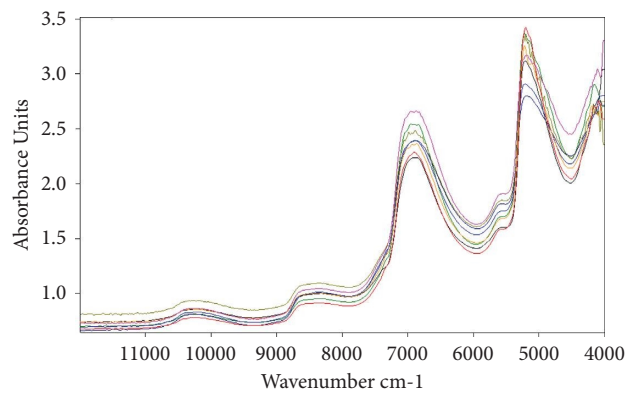

Figure 10: FT-NIR spectra of Early Girl (EG), Goodhearted (GH), Husky Red (HR), Hybrid Husky Red (HHR), Japanese Trifle (JT), Summerset Heat-Tolerant Hybrid (SHTH), Supersweet 100 (SW), and Valentine Grape (VG) tomatoes.

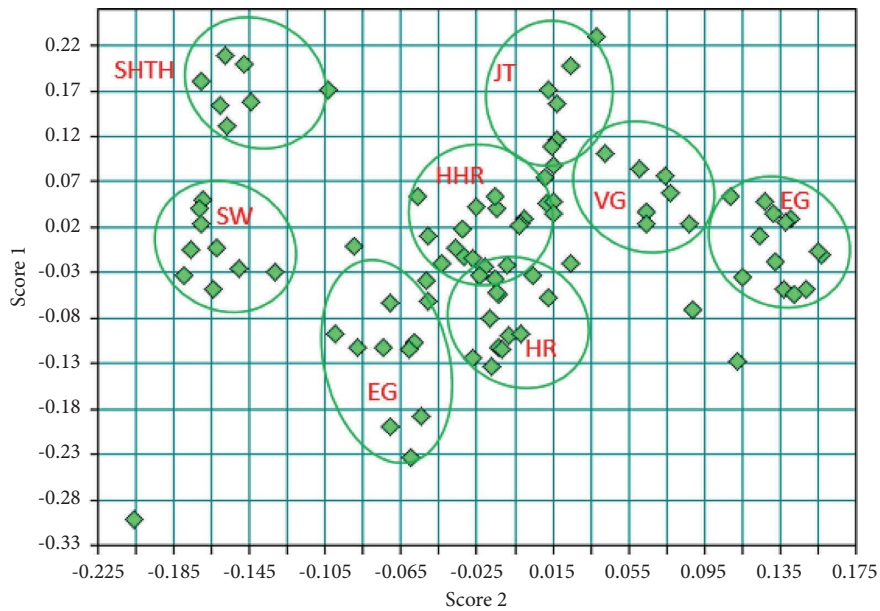

Figure 11: Principal component analysis (PCA) of FT-NIR spectra of fruits of Early Girl (EG), Goodhearted (GH), Husky Red (HR), Hybrid Husky Red (HHR), Japanese Trifle (JT), Summerset Heat-Tolerant Hybrid (SHTH), Supersweet 100 (SW), and Valentine Grape (VG).

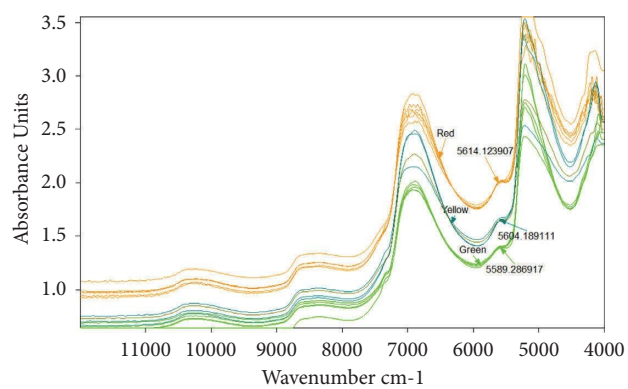

Figure 12: FT-NIR spectra development stages of tomato fruit.

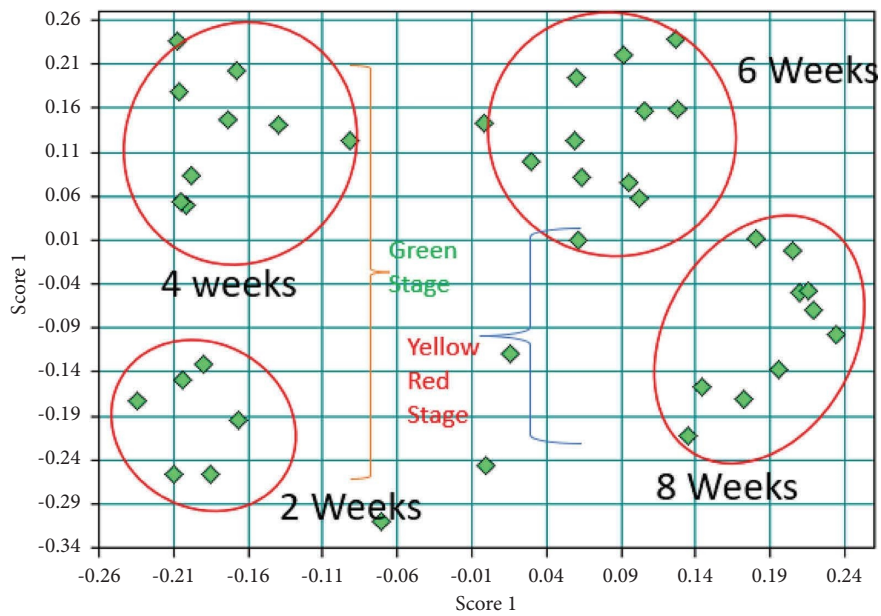

Figure 13: Principal component analysis (PCA) of FT-NIR spectra of fruits of Early Girl (EG), Goodhearted (GH), Husky Red (HR), Hybrid Husky Red (HHR), Japanese Trifle (JT), Summerset Heat-Tolerant Hybrid (SHTH), Supersweet 100 (SW), and Valentine Grape (VG) at different developmental stages.

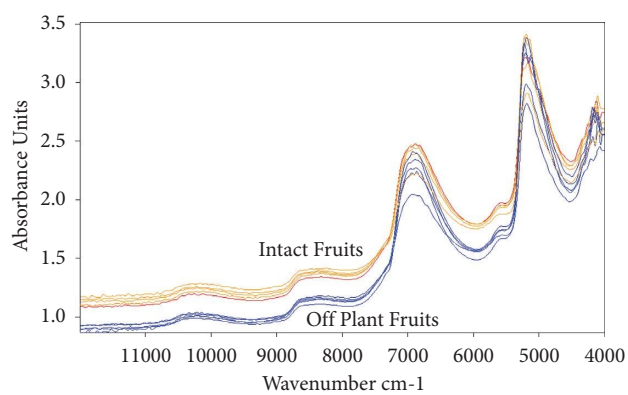

Figure 14: FT-NIR spectra of off-plant and in-plant tomato fruit.

FT-NIR can detect these physiological and biochemical changes in the samples.

Tomato fruit contains several chemical compounds such as vitamins, carotenoids, and phenolic compounds. FT-NIR can capture this information from the samples in the form of spectral signatures; however, environmental conditions also affect the development of the fruits. Therefore, this study section can also help with tomato fruit metabolism changes.

Fruit development is a complex process in plants that require the coordination of different hormones and the biosynthesis of auxins, cytokinins, and gibberellins. Therefore, Figure 13 suggests that the discrimination pattern might be correlated with the genetic, hormonal, and primary metabolism of fruit. Figure 13 clearly shows how a weekly development is consistent and how the clusters differ. This could be the links between primary and secondary metabolic pathways related to pigments, flavonoids, and fruit volatiles. The discrimination also suggests that tomato plants are sensitive to several abiotic stresses and other environmental conditions [20].

3.6. Discriminant Analysis of In-Plant and Off-Plant Tomatoes. Figure 14 represents the FT-NIR spectra of intact fruit vs. off-the-plant fruit. The FT-NIR spectra clearly show some deference in their raw ranges, particularly between 5000 and 6000 cm^{-1}. The difference is due to mostly sugar content, protein, cell wall composition, and other polysaccharides. NIR range from 8000 to 9000 cm^{-1} also shows compositional differences. This section aims to see the changes in the tomato fruit, intact in and off the plant. During fruit ripening, significant chemical changes occur, such as changes in chlorophyll and cell wall degradation and other compound formation. One of the main properties is

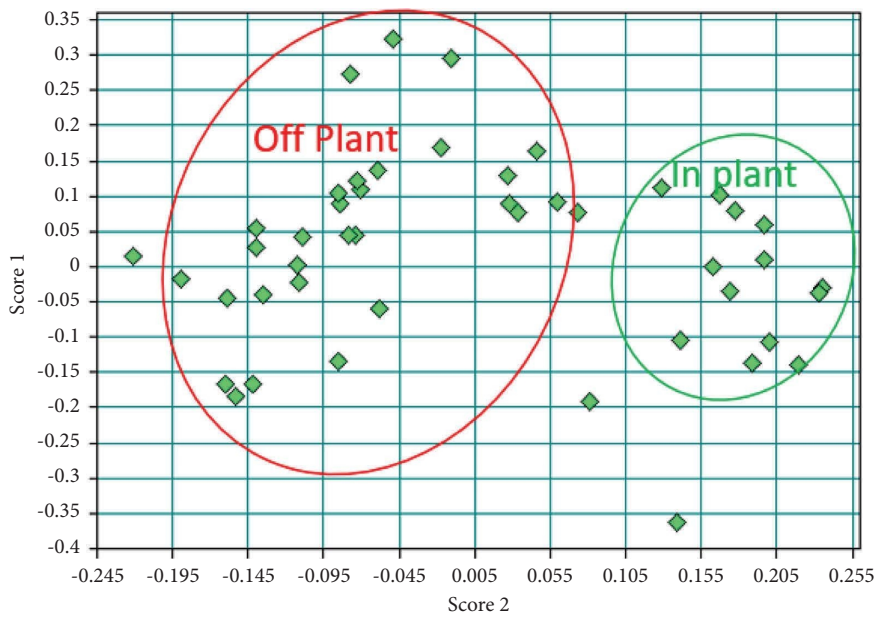

Figure 15: Principal component analysis (PCA) of FT-NIR spectra of off-plant and in-plant tomatoes.

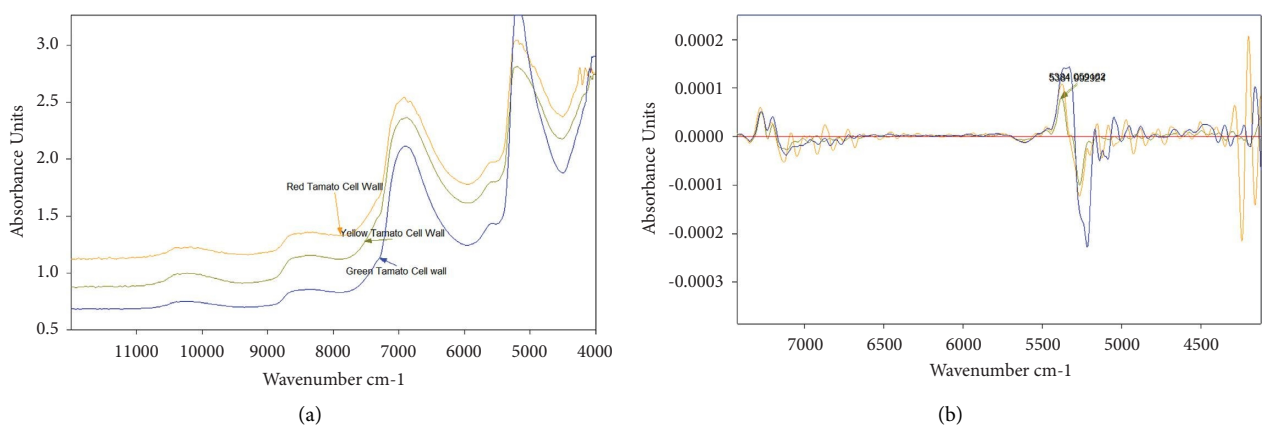

Figure 16: (a) FT-NIR raw spectra and (b) 2nd derivative spectra of tomato cell wall at green, orange, and red development stages.

aroma content specific to each kind of fruit [20]. When fresh produce is harvested, these chemicals are modified or changed in their chemical structure. FT-NIR can easily detect these changes and generate particular NIR bands; therefore, PCA discriminates the intact vs. nonintact fruit since their chemical signatures differ.

Figure 15 represents the PCA plot of on- and off-plant tomatoes using the FT-NIR spectra. The PCA plot can discriminate the tomatoes on the plant (intact) and off the plants, suggesting that the FT-NIR fiber optic technology can discriminate the freshness and the age of the fruits in a nondestructive manner. The spectra have unique spectral features from the live (on-the-plant) and off-the-plant tomatoes; therefore, PCA can discriminate the fruits mainly due to the variation in vitamin C, ascorbic acid, and dehydroascorbic acid, and genotypic and climatic conditions are also sensitive in PCA discriminational analysis [21]. Also, when the fruit is off the plant, microorganisms such as bacteria and mold start to deteriorate the fruit. The PCA plot clearly shows that when the chemical composition of fruit changes, their FT-NIR signatures also change, suggesting the fruit's freshness and age.

3.7. Discriminant Analysis of Tomato Cell Wall at Different Developmental Stages. Tomato skin and cell wall properties provide mechanical support to fruits and vegetables, which contain mainly pectin, hemicelluloses, and cellulose. Figure 16(a) represents FT-NIR raw spectra, and Figure 16(b) presents 2nd derivative spectra of the tomato cell wall at the green, orange, and red developmental stages. During sample preparation, the skin was removed entirely from the fruit and washed with distilled water to ensure no residue on the fruit. Figures 16(a) and 16(b) show the representative spectra for the green, orange, and red tomato cell wall skin from 4000–12500 cm^{-1}, which is directly

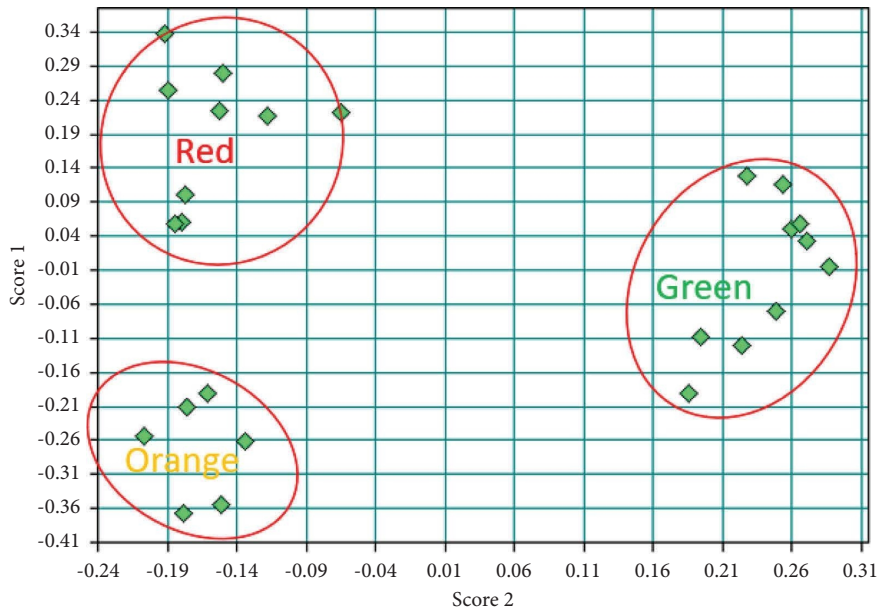

Figure 17: Principal component analysis (PCA) of FT-NIR spectra of tomato cell wall at green, orange, and red development stages.

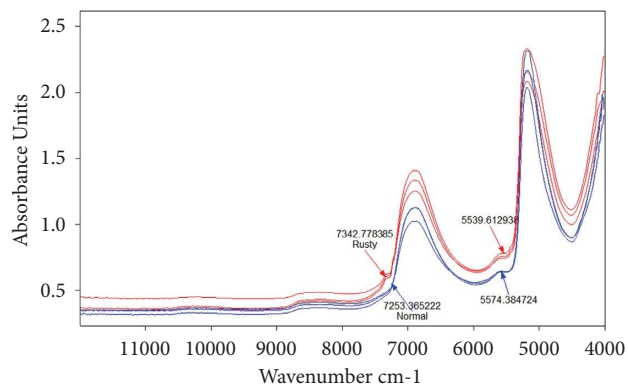

Figure 18: FT-NIR spectra of rusty vs. normal leaves.

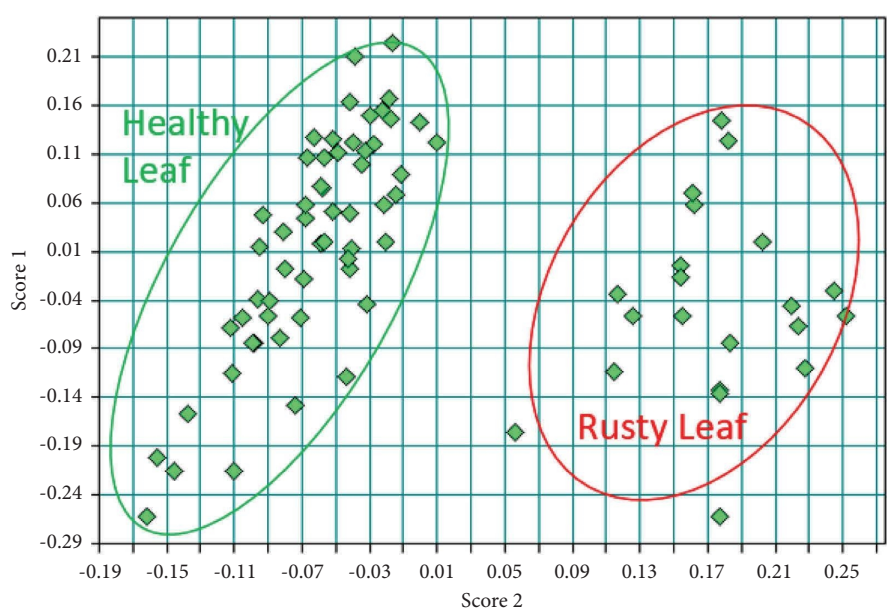

Figure 19: Principal component analysis (PCA) of FT-NIR spectra of healthy vs. rusty tomato leaves.

related to absorbance peaks O-H, C-H, and N-H bonds in the cell wall, which are also associated with inner compositions of cell walls such as sugar polysaccharides, cellulose, hemicellulose, and pectin, and structural proteins with some absorbance of skin pigmentation [22].

Figure 17 represents the PCA plot using FT-NIR spectra of the prepared tomato's cell wall at the green, orange, and red development stages. Since the first principal component (PC1) describes the combination of spectral variance in the plot, it may be directly correlated to all polysaccharides and another chemical component of the cell walls in the sample. The PCA plot also suggested that cellulose, hemicellulose, and lignin production is sequential in the life stages of a fruit cell wall development. However, FT-NIR can generate distinct peaks of these components. Therefore, the PCA can discriminate the cell wall at a different level of developmental stages of fruit using their FT-NIR spectra.

3.8. Discriminant Analysis of Rusty vs. Healthy Leaves. Figure 18 represents the FT-NIR spectra of rusty vs. typical leaves. The FT-NIR spectra clearly show some difference in their raw spectra, particularly between 5000 and 7500 cm^{-1}. Therefore, all the raw FT-NIR spectra from 5000 to 75000 cm^{-1} were analyzed using PCA.

The rust on tomatoes leaf is primarily due to *septoria* disease caused by a fungus called *Septoria lycopersici*. It is one of the most destructive diseases of tomato foliage and is particularly severe in areas where wet and humid weather persists for extended periods. The FT-NIR technology, combined with PCA, clearly showed the ability to distinguish two healthy vs. nonhealthy leaves based on their different chemical composition (Figure 19).

4. Conclusion

This research was intended to define and interpret attributes of eight different varieties of tomato plants such as Early Girl, Goodhearted, Husky Red, Hybrid Husky Red, Japanese Trifle, Summerset Heart-Tolerant Hybrid, Supersweet 100, and Valentine Grape Tomato for the discriminant analysis based on their cell wall structure, chemical composition changes during the development, off-plant vs. on-plant, and other compositional structure in a nondestructive manner. In this study, we have successfully demonstrated that in situ fiber optic Fourier-transform near-infrared spectroscopy (FT-NIR) can acquire in situ chemical signatures of leaf, flower, fruit, and stem and cell wall at different developmental stages. Furthermore, our study suggested that those chemical signatures are correlated to cell wall composition. The outer surfaces of the plant cell wall are comprised of various polymers, including cell wall polysaccharides and proteins, phenylpropanoids, and lipid polymers. The PCA was not able to discriminate between leaf and stem because the cell wall composition is relatively similar; however, PCA is able to discriminate other parts of the plants as well as different varieties due to the different chemical structures of the samples, such as differentiation in cell wall polymers as these polymers are synthesized, secreted, and assembled into elaborate matrices with architectures that vary down to the level of heterogeneity within the specific cell wall faces of individual cells at different developmental stages, which change substantially during cell growth and differentiation or in response to environmental conditions. The discrimination is also caused due to the heterogeneity of biological processes at the cell surface and in the interface between plants and their environments.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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