Rapid Compositional Assessment of Tomato Fruit by Using Portable Mid-Infrared Spectroscopy.

THESIS

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By

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Abstract

Tomatoes are consumed and cultivated all around the world. Specifically in 2012, the United States of America alone produced over 13 million tons of tomatoes. In order for the tomato to sustain its vital placement in the market, quality control poses high significance at all levels of the industry to gain the desired characteristics. Some quality traits of interest for fresh-market tomatoes can include color, ascorbic acid (vitamin C), citric acid, glucose, fructose, pH, soluble solids and titratable acidity. These attributes need to be tested through reference methods. However, the drawbacks of some reference methods include time-consuming sample preparation, use and disposal of hazardous solvents, low sample through-put, and a high skill-set for the testing personnel. Infrared spectroscopy is an ideal alternative in assessing multiple quality traits in fresh tomatoes. Mid-Infrared (FTIR) spectroscopy has become an alternative for traditional reference methods, because there is little sample preparation saving both time and money, operating the equipment is fast and simple to use, sample through-put is increased, less hazardous solvents are needed for analysis, and minimal background training is needed to operate the infrared equipment. Portable mid-infrared units are becoming popular for food manufacturers since the unit can easily be transported from laboratory, to in-plant, to in-field analysis. In fact, infrared spectroscopy has already achieved itself as a quality control tool for processed tomato products using a hot-break tomato juice sample for analysis of the quality traits. The aim of this research is to develop a rapid method for
assessing quality traits of fresh-market tomatoes by collecting infrared spectra on the fruit surface at any maturity stage. Fresh-market tomatoes can be harvested at any stage of maturity (mature green, pink or red-ripe) unlike processed tomatoes that are only harvested at the red-ripe stage of maturity. Thus, it is necessary to develop fast and reliable methods that can give reliable predictions of target quality traits within the fresh-market tomato fruit before it reaches the consumer. Our objective was to develop robust prediction models based on spectra collected on the tomato fruit surface for determination of ascorbic acid, citric acid, soluble solids, pH, titratable acidity, glucose, and fructose in order to better implement portable mid-infrared units into a field setting. Additionally, spectra of single tomato juices were used to generate models to compare prediction performances against the surface readings.

A total of 120 tomato samples were received from a fresh-market tomato producer throughout the 2014 summer season (June-August). The levels of acids (ascorbic and citric) and sugars (glucose and fructose), soluble solids, pH, and titratable acidity were determined using standard reference methods. For mid-infrared analysis, an attenuated total reflectance accessory equipped with a single-bounce diamond crystal was used to obtain the fruit surface spectra, while a transmittance accessory (DialPath) was used to obtain the fresh juice spectra. Partial least squares regression (PLSR) was used to generate the cross-validated, calibration models between the parameter concentrations and the sample spectra. Models based on infrared data from the tomato fruit surface did not perform as well as the fresh tomato juice models due to all of the acids and sugars not being directly introduced to the infrared beam, thus more uncertainty is incorporated into
the fruit surface models. Chemometric models based on surface infrared readings predicted quality attributes with mean correlation values (R) 0.60-0.83 and prediction errors (SECV) of 0.19 for Brix, 0.1 g/100g for estimation of sugars (fructose, glucose), 0.2 units for pH and 0.1% for TA (% citric acid), and 0.05 g/100g for citric and 2.6 mg/100g for ascorbic acids while models based on juice spectra showed improved performances with correlation coefficient (R\textsubscript{CV}) ranging from 0.84-0.96 and lower standard error of cross validation (SECV) with values of 0.11 for Brix, 0.06 g/100g for estimation of sugars (fructose, glucose), 0.12 units for pH and 0.05% for TA (% citric acid), and 0.02 g/100g for citric and 1.0 mg/100g for ascorbic acids. Because the portable mid-infrared units are easy to handle and carry, the FTIR systems can provide fresh-market tomato growers and producers a rapid method to evaluate tomatoes within a laboratory setting, within a plant facility, or even in the tomato growing field.
Dedication

This thesis is dedicated to my loving family.
Acknowledgments

First, I would like to thank my advisor, Dr. Rodriguez, for his guidance and support through my career as both an undergraduate and graduate student. It has truly been a very rewarding experience that I will forever remember.

Secondly, I would like to thank all of my lab mates (Mei-Ling, Peren, Marcal, Huseyin, Wen, Crystal, and Congcong) for their encouragement and support. You all are amazing people and I will cherish the times we spent together.

And finally, I would like to thank the California League of Food Processors for funding this research based on tomatoes.
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Fields of Study

Major Field: Food Science and Technology
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1.1 The Tomato Industry

To a consumer the tomato, *Lycopersicon esculentum*, may be a vegetable that one can grow in a garden, but it is in fact a very large cash crop to the world market. In 2012, the United States of America alone produced over 13 million tons of tomatoes. This may seem like a very large number, but the U.S.A was actually fourth in quantity produced in the 2012 crop production. According to the Food and Agricultural Organization (FAO) of the United Nations (2014), China was first with 50.1 million tons, then China, mainland with 50 million tons, India was third with 17.5 million tons, and finally the United States was fourth with over 13 million tons. Financially, the tomato crop in the United States for both fresh and processed tomatoes brings in around $2 billion annually in receipts. Tomato varieties are bred in different ways in order to serve certain requirements that are needed for either the fresh or processed markets (Economic Research Service 2012).

**1.1.1 Fresh Versus Processing Tomatoes**

Fresh-market tomatoes are either grown in greenhouses or are grown in the field (Costa and Heuvelink 2005). Tomatoes grown for processing are produced under contract between growers and processing firms, they are machine picked, and processing tomatoes are monitored in order to be the most efficient during processing into a final product.
(Economic Research Service 2012). In both cases, tomatoes start as transplants and are staked to keep the fruit away from soil. Pruning is also a common practice for fresh-market tomatoes; this is done to increase the fruit size (Costa and Heuvelink 2005). The fresh-market tomatoes are typically produced and sold largely in the open market, and they tend to be priced higher than processed tomatoes due to larger production costs and greater market uncertainty (Economic Research Service 2012). Processing tomatoes are priced cheaper because they are harvested by machinery at the red-ripe stage and are immediately transported to a processing plant. While fresh-market tomatoes are hand harvested at the mature green, partially ripe or fully ripe stage (Saltveit 2005). Tomatoes for fresh consumption are typically round-shaped fruits with a thick peel; they are juicy and sweet and show a red color in the mature stage. Processing tomatoes tend to be blocky or oval-sapped fruits; the fruits are extremely firm and have good internal color and thick walls that give a high-consistency product. These processing tomatoes are typically used in both peeling and dicing applications (Garcia-Valverde et al. 2013). Quality characteristics of fresh-market tomatoes are similar to processing tomatoes, but the qualities that are apparent to the consumer such as color, firmness, flavor, and aroma dominate the other characteristics (Saltveit 2005).

1.1.2 Varieties in the Fresh Market

There many varieties and cultivars of fresh-market tomatoes ranging in color, shape, size, smell, and flavor. There are five major groups of fresh-market tomatoes. They are as listed: classic round tomatoes, cherry and cocktail tomatoes, plum and baby plum tomatoes, beefsteak tomatoes, and vine or truss tomatoes. Classic round tomatoes are the
most popular cultivar and varieties of all tomatoes. An average fruit can weigh 70 – 100 g and the diameter 4.7 – 6.7 cm. These tomatoes are typically used in salads, or for grilling, baking or frying, or can be one of the ingredients in a sauce or soup. Cherry and cocktail tomatoes are smallest of tomatoes in these five groups mentioned. Their average fruits can weigh 10 – 20 g and diameter 1.6 – 2.5 cm. Cocktail tomatoes are larger than cherry tomatoes (Costa and Heuvelink 2005). However, both are well known for their sweetness and their high nutrient content (Jones 2008, Costa and Heuvelink 2005). To the consumer cherry tomatoes can be eaten whole in a raw or cooked form, while cocktail tomatoes can be used in salads or grilling. Plum and baby plum tomatoes are typically oval in shape. The flesh on the tomatoes is firm and not as juicy in the center. These tomatoes are typically used for barbeques, and processed for pizzas and pasta dishes. The beefsteak tomato is larger than a traditional round tomato with its weight varying between 180 and 250 g. The consumer will use these tomatoes for stuffing and baking whole, and the consumer will typically slice the tomatoes for salads and sandwiches. The last group, vine or truss tomatoes, can be any of the tomatoes mentioned above, but are sold in the markets still attached to the fruiting stem. The reason they are sold on the stem is because the stem gives that distinct tomato aroma, not the tomato fruits themselves (Costa and Heuvelink 2005). Monitoring the quality of the whole tomato is mandatory for the industry in the different stages of the tomato production including the breeding of the tomatoes, and management practices of harvesting (Scibisz et al. 2011). Because the purpose of this thesis research is focused on improving the quality analysis
methods of tomatoes, it is important to review the tomato’s qualities and how they are monitored.

1.2 Quality Control within the Whole Tomato Industry

1.2.1 Seven Stages of Maturity as a Means to Quality Control

The quality of a whole tomato is assessed through many means. However, the first quality aspect is maturity. As a tomato fruit ripens a series of ordered physiological and biochemical changes can occur to the tomato (Prasanna et al. 2007). Color has been used as a major method in determining the maturity of a tomato; however, the skin color of a tomato fruit varies from cultivar to cultivar even at the same maturity stage (Molyneux et al. 2004). According to Saltveit (2005), tomatoes are harvested at different color stages of ripeness for different purposes. There are seven different ripening stages that are based on tomato surface color: immature, mature-green, breaker, turning, pink, light-red, and red-ripe. The immature stage is when the fruit is not sufficiently developed to ripen to an acceptable level of quality. Mature-green is when the tomato fruit will ripen into an acceptable level of horticulture quality, and the surface of the fruit is either white or green with no red color visible. The breaker stage of maturity is when there is a definite break in color from green to tannish-yellow, pink or even red on the blossom-end of the tomato. Turning stage is when there is more than 10% but less than 30% of the tannish-yellow, pink or red color change. The pink stage of maturity is when there is more than 30% but less than 60% of the surface of the fruit shows pink or red. The light-red stage is when there is more than 60% but less than 90% red color on the surface of the tomato. And
finally, the red-ripe stage of maturity is when there is more than 90% red color on the surface of the tomato (Sargent and Moretti 2002). As mentioned earlier, not just physiological changes but many biochemical changes occur to a tomato as it ripens (Prasanna et al. 2007); the typical nutrition facts for a single red-ripe tomato can be seen in Figure 1. As seen from the figure, one medium sized tomato is low in calories, fat, and sodium: 35 and 0.5 g and 0.5 mg respectively. The tomato contains a high amount of both vitamin A and vitamin C due to both contents being over 20% (Jones 2008).

<table>
<thead>
<tr>
<th>Amount Per Serving</th>
<th>Calories 35</th>
<th>Calories from Fat</th>
<th>% Daily Value*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Fat</td>
<td>0.5g</td>
<td></td>
<td>1%</td>
</tr>
<tr>
<td>Cholesterol</td>
<td>0mg</td>
<td></td>
<td>0%</td>
</tr>
<tr>
<td>Sodium</td>
<td>5mg</td>
<td></td>
<td>0%</td>
</tr>
<tr>
<td>Total Carbohydrate</td>
<td>7g</td>
<td></td>
<td>2%</td>
</tr>
<tr>
<td>Dietary Fiber</td>
<td>1g</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sugars</td>
<td>6g</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Protein</td>
<td>1g</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vitamin A</td>
<td>20%</td>
<td>Vitamin C</td>
<td>40%</td>
</tr>
<tr>
<td>Calcium</td>
<td>2%</td>
<td>Iron</td>
<td>2%</td>
</tr>
</tbody>
</table>

*Percent Daily Values are based on a 2,000 calorie diet. Your daily values may be higher or lower depending on your calorie needs.

Source: PMA’s Labeling Facts

Figure 1: Nutrition facts for a tomato (Source: Jones 2008).

1.2.2 Quality Differences between Varieties

The tomato comes in many different varieties, from small cherry types to much larger beefsteak types. Because of the different cultivars, the composition of tomatoes differs which can be seen in Table 1. As seen from Table 1, the beefsteak tomato and cherry tomato are very similar in most components such as water, calories and fat content.
However, the cherry tomato does have a higher content of vitamin C and vitamin A, while the beefsteak has a higher amount of fiber and potassium (Jones 2008). The composition content of the fresh tomato may serve different purposes to the consumer such as flavor or texture.

Table 1: Approximate nutrient composition of tomato varieties (Source: Jones 2008).

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Beefsteak (%)</th>
<th>Cherry (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>93.5</td>
<td>93.2</td>
</tr>
<tr>
<td>Calories</td>
<td>22</td>
<td>22</td>
</tr>
<tr>
<td>Carbohydrate</td>
<td>4.75</td>
<td>4.90</td>
</tr>
<tr>
<td>Protein</td>
<td>1.05</td>
<td>1.00</td>
</tr>
<tr>
<td>Fat</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Fiber</td>
<td>0.55</td>
<td>0.4</td>
</tr>
<tr>
<td>Ash</td>
<td>0.5</td>
<td>0.7</td>
</tr>
<tr>
<td>Calcium</td>
<td>12</td>
<td>29</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>26</td>
<td>62</td>
</tr>
<tr>
<td>Potassium</td>
<td>244</td>
<td>N/A</td>
</tr>
<tr>
<td>Sodium</td>
<td>3</td>
<td>N/A</td>
</tr>
<tr>
<td>Magnesium</td>
<td>14</td>
<td>N/A</td>
</tr>
<tr>
<td>Iron</td>
<td>0.5</td>
<td>1.7</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Beefsteak (mg)</th>
<th>Cherry (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vitamin A</td>
<td>900</td>
<td>2000</td>
</tr>
<tr>
<td>Vitamin C</td>
<td>25</td>
<td>50</td>
</tr>
<tr>
<td>Vitamin B1</td>
<td>0.06</td>
<td>0.05</td>
</tr>
<tr>
<td>Vitamin B2</td>
<td>0.04</td>
<td>0.04</td>
</tr>
<tr>
<td>Niacin</td>
<td>0.7</td>
<td>N/A</td>
</tr>
</tbody>
</table>

There are also many factors, including genetic ones such as cultivar or variety, environmental factors such as light, temperature, air composition, mineral and growth medium, and cultural practices including ripening stage at harvest, training system, and
irrigation system that all affect the chemical composition of tomatoes. These factors explain the wide variety of concentration values found in literature for lycopene, ascorbic acid, citric acid, soluble solids, concentration of glucose and fructose, titratable acidity, pH and overall color (Garcia-Valverde et al. 2013).

1.2.3.1 Carotenoids within Tomatoes

Even though the beefsteak and cherry tomatoes are slightly different in composition, they are both a vibrant red in color when the tomato fruit is mature. This is due to the red pigmented carotenoid found within most tomatoes called lycopene. The lycopene content increases as the tomato matures on the vine (Jones 2008), thus the color of a tomato is a good quality control parameter in deciding the maturity of the tomato and when to harvest. Once the tomato is fully ripened, the lycopene constitutes about 75-83% of the total carotenoids found within the tomato, while the β-carotene, a yellow pigmented carotenoid, only contributes 3-7% within the tomato (Dorais et al. 2001). Typical carotenoids found within tomatoes are listed: lycopene, α-carotene, β-carotene, γ-carotene, ξ-carotene, phytoene, phytofluene, neurosporene, and lutein (Shi and Le Maguer 2000). Food carotenoids are usually C_{40} tetraterpenoids derived from the acyclic C_{40}H_{56} conjugated polyene lycopene (Inbaraj and Chen 2008). Figure 2 shows lycopene’s chemical structure.
1.2.3.1.1 Lycopene’s Antioxidant Activity

Lycopene is one of the most potent antioxidants among carotenoids due to it having a physical quenching rate constant with singlet oxygen almost twice that of β-carotene in both *in vitro* and *in vivo* studies (Kaur and Kapoor 2008). The most bioavailable source of lycopene is typically cooked tomatoes or processed tomato products due to the lycopene being released upon cooking. This means that processed tomato products have a higher bioavailability than their fresh counterparts (Jones 2008, Gartner et al. 1997, Shi and Le Maguer 2000). Tomato consumption has been shown to reduce risks of cardiovascular disease and certain types of cancer, such as prostate, lung and stomach cancers (Giovannucci 1999, Canene-Adams et al. 2005). When reviewing the lycopene concentrations that are reported in literature, there is a large range in values as the tomato matures from green to red. In a study performed by Garcia-Valverde et al. (2013), tomatoes picked at random from different stages of maturity (green, breaker, pink and red) were analyzed for lycopene. The averages of total lycopene for the four different maturity stages are as follows 0.063, 1.220, 2.676 and 11.666 mg/100g of fresh weight, respectively. In another study performed by Nguyen et al. (2001), the lycopene content within fresh-market tomatoes at different maturity stages did increase as the tomato
matured, agreeing with the results found by Garcia-Valverde et al (2013). According to Nguyen et al. (2001), the lycopene content for green, breaker and ripe fresh tomatoes was 0.52, 3.84, and 5.09 mg/100 g of wet weight, respectively.

1.2.3.2 Ascorbic Acid

Another quality component that is important as a nutrient source for consumers and is a quality control factor for growers of fresh tomatoes is the amount of ascorbic acid, or vitamin C, within a tomato. Ascorbic acid (Figure 3) is significant to human health due to epidemiological studies showing that the risk of stomach, esophagus, pharynx, lung, pancreas and cervix cancers all decrease in people with high levels of intake of vitamin C due to its antioxidant activity (Negri et al. 2000). According to Jones (2008), the daily consumption of a medium-sized tomato weighing 8 oz (226.9 g) will supply 47% vitamin C of the recommended daily adult requirement as set by the United States Food and Drug Administration (Nutrition Labeling and Education Act of 1990). The overall antioxidant activity of a tomato depends primarily on both genetic and environmental factors (Hart and Scott 1995). According to Garcia-Valverde et al. (2013), ascorbic acid might increase with ripening due to enhanced respiration of the fruit. However, this percentage amount does change with storage and processing of the tomato due to the low stability of vitamin C associated with its easy oxidation (Olives et al. 2008). One common technique in order to measure the quantity of ascorbic acid within a tomato is via high performance liquid chromatography (HPLC) (Beullens et al. 2006, Chinnici et al. 2005). These methodologies of HPLC have been studied greatly in order to reduce costs, cut sample preparations, and lessen the run time (Sierra-Cadavid and Rodriguez-Saona 2014).
1.2.3.3 Soluble Solids (°Brix) and Titratable Acidity

A quality parameter that is both important to taste and texture of a tomato is soluble solids. Soluble solids is typically measured with a refractometer that is calibrated in °Brix. Juice is usually extracted from homogenized tomato tissue and then a few drops are placed onto the optical prism of the refractometer to get a reading. Readings are mainly influenced by the amount of sugars in the tomato juice samples, but the other water soluble components, such as organic acids and soluble pectins, in the sample may also contribute significantly to the final °Brix reading. The °Brix can range from 4.5% to 7.0% (Jones 2008). Sugars accumulate, meaning that the soluble solids content rises, through the tomatoes importation from photosynthesizing leaves and after harvest from the hydrolysis of stored starch (Saltveit 2005). Reducing sugars contribute to over half of the soluble solids content, while one-eighth is acids (Jones 2008). Soluble solids and titratable acidity are two very important aspects when considering the fresh tomato’s flavor quality. Titratable acids are composed primarily of the organic acids citric acid and malic acid (Saltveit 2005). Titratable acidity is usually measured through the titration of
0.1N NaOH until the sample solution reaches the pH of 8.2 and then calculations are made based on the type of acid present within the food (AOAC 2000). The range of titratable acidity is typically 0.28 – 0.43 % citric acid. The individual amounts of titratable acidity and soluble solids, and their combined ratio are both important to the overall flavor of a fresh tomato. Table 2 clearly portrays how flavor is affected by the ratios of soluble solids to titratable acidity. Tomatoes that are high in both acids and sugars have excellent flavor, while tart or flavorless tomatoes have very low soluble solids and titratable acidity (Saltveit 2005).

**Table 2**: Titratable acidity and soluble solid levels affecting flavor (Source: Saltveit 2005).

<table>
<thead>
<tr>
<th>Titratable Acidity</th>
<th>Sugars (soluble solids)</th>
</tr>
</thead>
<tbody>
<tr>
<td>High</td>
<td>Good</td>
</tr>
<tr>
<td>Low</td>
<td>Bland</td>
</tr>
</tbody>
</table>

**1.2.3.4 Sugars**

The two major sugars found within tomato fruit are about equal amounts of glucose (Figure 4) and fructose (Figure 5) (Saltveit 2005). In order to quantify the amount of each sugar present HPLC is used (Beullens et al. 2006, Chinnici et al. 2005). Each sugar contributes about 22% dry weight. There is a very small amount of sucrose which contributes only about 1% dry weight (Saltveit 2005).
1.2.3.5 Citric Acid

Citric acid (Figure 6) is the main acid found in tomatoes and tomato juice, and this organic acid is typically quantified by using HPLC (Jones 2008, Beullens et al. 2006, Chinnici et al. 2005). Citric acid contributes about 9% dry weight, while malic acid, which is the second most abundant acid within tomatoes, contributes about 4% dry weight (Saltveit 2005). As the tomato fruit matures and ripens the citric acid also increases (Jones 2008). While the total organic acids only make up 0.4% of the fresh
tomato, it is emphasized that the acids are very important attributes to the final taste of a tomato and are therefore monitored very closely by the tomato industry (Saltveit 2005, Malundo et al. 1991, Salles et al. 2003, Flores et al. 2009). Variation in the fruit’s acid content has a much greater impact on flavor than the limited variation in sugar content that exists in different tomato cultivars (Saltveit 2005).

![Chemical structure of citric acid C_6H_8O_7.]

**Figure 6**: Chemical structure of citric acid C_6H_8O_7.

### 1.2.3.6 pH

Another quality parameter that is important to growers of fresh tomatoes is pH. The typical pH for a whole tomato fruit is 4.5 or less, making the tomato an acidic food (Jones 2008, Saltveit 2005). The reported pH range for tomato fruit is between 4.0 and 4.5 (Jones 2008). Storage and handling procedures of the tomato fruit are done to hold the tomato’s acidic pH in order to prevent the growth of microorganisms such as *Clostridium botulinum*. Storage at higher temperatures (above 35°C) tends to increase pH due to the metabolism of organic acids. Also, fungal infections, such as *Fusarium solani*, tend to increase pH of infected and adjacent tissue within the tomato (Saltveit 2005). The pH is normally measured when the tomato juice sample has reached room temperature. Once
the measurement had been taken with a pH meter, the probe is cleaned with distilled water and wiped clean in between readings (Wilkerson and Rodriguez-Saona 2012).

1.2.4 Controlling Quality Parameters

Color is one of the most important characteristic that determines the overall quality of the tomato. Many changes happen to a tomato as it progresses from the mature-green stage to red-ripe state. However, the biggest one is the loss of green chlorophyll and the accumulation of red lycopene. The tomato fruit color can be determined either subjectively or objectively. Subjective evaluations of fruit maturity are done by reference to standard charts showing color images of fruit at different stages of ripeness. Objective measurements are done by measuring the extracted concentration of individual pigments through spectroscopy. However, the objective procedures are more suited to laboratory investigations than to determining fruit ripeness in a commercial setting (Saltveit 2005). Various analytical methods have been developed for laboratory use, such as chromatography, and provide vast raw data about the sample being analyzed. However, the problem with the chromatography methods is that they are time-consuming, require sample preparations, expensive equipment to run the analysis that can easily break down, and require a large volume of both aqueous and non-aqueous solvents (Luong et al. 1997). Therefore, because of these disadvantages, it is necessary to develop fast and reliable methods that analyze the concentrations of target components within a product.
1.3 Infrared Spectroscopy

Infrared spectroscopy can be used as a dependable tool in a commercial setting as a fast and reliable way to determine the concentrations of quality attributes within whole tomatoes. Spectroscopy is defined as the study of the interaction of an electromagnetic wave and matter. Electromagnetic waves differ in energy, frequency, hertz, and wavelengths. From the longest to the shortest wavelength they are listed as such: radio, microwaves, infrared, visible, ultraviolet, X-ray and γ-ray (Dufour 2009). The focus of this paper is on infrared (IR) waves. They are also broken down into different wavelengths: Far-IR (400 to 50 cm⁻¹), Mid-IR (4,000 to 400 cm⁻¹), and Near-IR (14,000 to 4,000 cm⁻¹) (Smith 1999). The electromagnetic spectrum is depicted in Figure 7.

**Figure 7**: The electromagnetic spectrum (Source: Keeler and Wothers 2014).
When IR radiation is exposed to a food sample the material will absorb the energy and cause vibrations, bending, or twisting of the chemical bonds within the sample. In order for a molecule to show infrared absorptions, it must possess a certain feature such as a functional group (Stuart 2004, Smith 1996). These functional groups always tend to absorb radiation in the same spectral area regardless of the type of molecule the functional group is in (Smith 1996, Santos 2010).

1.3.1 Mid-Infrared Region of the Electromagnetic Spectrum

The mid-infrared spectrum that ranges from 4,000 to 400 cm\(^{-1}\) can be broken down into four main sections and the nature of a group frequency may generally be determined by the region in which it is located. The regions are as follows: the X-H stretching region (4,000 to 2,500 cm\(^{-1}\)), the triple bond region (2,500 to 2,000 cm\(^{-1}\)), the double bond region (2,000 to 1,500 cm\(^{-1}\)) and the fingerprint region (1,500 to 600 cm\(^{-1}\)). The vibrations in the X-H region are generally caused by O-H, C-H, and N-H stretching.

Since food contains all of these components, it can be further broken down into the following bands: O-H stretches in the range of 3,700 to 3,600 cm\(^{-1}\), N-H is 3,400 to 3,300 cm\(^{-1}\), and C-H stretching in the range of 3,000 to 2,850 cm\(^{-1}\). The triple bond region can differentiate between C≡C (2,300 to 2,050 cm\(^{-1}\)), which tends to have a weak absorption band range, and C≡N (2,300 to 2,200), which tends to have a stronger absorption. The principle bands in the double bonded region can be broken down into specific regions. The carbonyl group (C=O) is one of the easiest absorptions to detect in an infrared spectrum, because it is usually the most intense band in the 1830 to 1650 cm\(^{-1}\) region. The C=C stretching is typically much weaker and occurs around 1650 cm\(^{-1}\), but it can be
absent due to symmetry or dipole moment reasons. \( \text{C=N} \) also stretches in the same region and is typically stronger than \( \text{C=C} \). Hundreds of other molecules that are present in a food sample may not bend or stretch as those assigned above. This is why they are assigned to the fingerprint region of 1,500 to 600 cm\(^{-1} \) (Stuart 2004). The mid-infrared region of the spectrum is a good tool to use for quantitative and qualitative analysis because of the intensity of absorption bands due to the vibrations of certain functional groups (Guillen and Cabo 1997). This makes mid-IR (MIR) a good tool for qualitative analysis, including identification of unknowns and confirming identities of compounds, and quantitative analysis by finding the concentrations of certain functional groups and their related components in a food (Smith 1999, Li-Chan and others 2010).

1.3.2 Fourier-Transform Infrared Spectroscopy

Fourier-Transform Infrared (FTIR) spectrometer units have been manufactured and sold commercially in the United States since the 1960s. This is because these instruments can acquire high resolution data in a short period of time (Smith 1996), there is little sample preparation needed before a reading is taken, and the use of hazardous solvents is minimized. Because of these three attributes, time and money are saved and the amount of sample throughput is increased (Rodriguez-Saona and Allendorf 2011). The layout of a FTIR unit is seen in Figure 8.

At the heart of this unit is the interferometer. The purpose of the interferometer is to take a beam of infrared light, split it into two beams, and make one of the light beams travel a different distance than the other by using both a beam splitter and a moving versus stationary mirror. The intensity of light that reaches the sample and eventually the
detector is plotted against the constructed or deconstructed optical path difference. This is referred to as the interferogram. This interferogram is then Fourier transformed in order to turn the data into intensity versus frequency spectrum (Smith 1996). 

**Figure 8**: The general layout and mechanism of a FTIR unit (Adapted from Baeton and Dardenne 2002).

1.3.2.1 **FTIR Transmission Technique**

The most popular way to obtain infrared data on a specific sample is to pass the infrared light spectrum through the sample and collect the intensity readings with a detector on the other side of the sample. This is depicted in **Figure 9**. This type of sampling technique can work on solid, liquid, gas, and polymer samples. This is because there is high signal
from this technique with little noise, and the tools are relatively inexpensive. However, the major problem with the transmission technique is sample thickness. If a sample exceeds 20 microns, then the sample will absorb too much infrared radiation, making it impossible to gain a good spectrum (Smith 1996).

**Figure 9**: Simple figure depicting the transmission sampling technique of FTIR (Adapted from: Tirpak and Young 2008).

1.3.2.2 Attenuated Total Reflectance (ATR) Technique

Attenuated Total Reflectance (ATR) technique or reflectance technique is different from transmission techniques, because the infrared laser beam of light is reflected off the sample instead of passing through the sample. The ATR is depicted in **Figure 10**. The platform that the sample is placed upon, so that infrared light is reflected against the sample must be an infrared transparent material of high refractive index. Typical crystals that are used include: zinc selenide, KRS-5 (thallium iodide/thallium bromide), diamond, and germanium. Because of the mirror that comes with the equipment, it brings the infrared light to focus on the face of the crystal. The beam of light first comes into contact with the crystal, the beam penetrates the sample, reflects off the crystal, hits
the sample one more time in what is called the evanescent wave and the light finally escapes to the detector. So, when a sample is brought into contact with a crystal, it can interact with the evanescent wave, absorb infrared radiation, and have its infrared spectrum detected. The evanescent wave is attenuated by the sample’s absorbance, giving the technique’s name, attenuated total reflectance (Smith 1996).

**Figure 10:** Diagram of an attenuated total reflectance accessory (Source: Smith 1996).

One advantage of ATR is that this technique is a simple sampling technique. The sample, which had no sample preparation, is brought into contact with the crystal and then the spectrum is obtained. This points out another advantage of ATR; it is a nondestructive sampling technique. Like any other FTIR unit, ATR can also be used to quantify multiple chemical components in a food sample within a single reading (Smith 20
1996). Because ATR can be used on both solid and liquid samples and is very easy to get a spectral reading, this makes ATR a very good quality control tool for the food industry.

1.4 Portable Infrared Systems

A current technology trend is portable FTIR units that can be used for quality control purposes. They are convenient, easy to use, and simple to move from one area to the next for rapid-in plant analysis of multiple components (Sierra-Cadavid and Rodriguez-Saona 2014). These portable units have been found to be just as robust and offer good performance as compared to their large and non-portable benchtop counterpart (Wilkerson and Rodriguez-Saona 2012).

Agilent Technologies® offers one of the smallest portable benchtop FTIR units called the Agilent Cary 630 FTIR Spectrophotometer (Figure 1). This unit with all its different accessories is versatile, innovative, and can provide superior qualitative and quantitative information for routine analysis on solid, liquid and gas samples (Agilent Technologies 2011a). Different accessories vary in type of cells of modules in order to gain good data on the different food matrixes that exist in nature (Wilkerson and Rodriguez-Saona 2012). The different accessories include: transmission, DialPath, TumblIR, diamond ATR, germanium ATR, ZnSe multi-bounce ATR, specular reflectance, and diffuse reflectance (Agilent Technologies 2011a). The FTIR unit and some of its different accessories are in Figure 12.

The diamond ATR and DialPath accessories are unique advantages to the Cary 630. This is because the diamond ATR provides high quality spectra with no sample preparation
(Agilent Technologies 2011a). The diamond crystal can also withstand a great amount of pressure from a solid food sample for good contact, unlike ZnSe, due to the diamond’s strength (Wilkerson and Rodriguez-Saona 2012). The DialPath also provides high quality spectra from its ZnSe windows that are set into three different path lengths: 30, 50 or 100 microns (Agilent Technology 2011a). This unit is perfect for liquid samples and can be used for qualitative and quantitative analysis (Wilkerson and Rodriguez-Saona 2012). Because this unit weighs about 8 pounds and is only 6 inches high (Agilent Technologies 2011a), this technology is perfect for the tomato industry since it can give fast and accurate results for quality control.

**Figure 11:** Portable Agilent Cary 630 FTIR spectrophotometer (Source: Agilent Technologies 2011a).
1.5 Multivariate Analysis

Improvements from computer technology associated with spectroscopy have led to expansions in quantitative and qualitative analysis (Stuart 2004). Multivariate analysis uses statistical and mathematical methods to design or select optimum procedures and experiments, and to provide the maximum chemical information by analyzing chemical data. Chemical compounds, reactions, samples, and technological processes are multivariate in nature. Therefore, multivariate data analysis considers many variables together and often attains newer and higher quality in data evaluation (Varmuza and Fitzmoser 2009). The application of statistical methods to the analysis of an experimental data is chemometrics (Stuart 2004). One of the more common methods of factor analysis that can also be used for quantitative analysis is Partial Least Squares Regression (PLSR) (Smith 1996, Wold et al 2001). PLSR is relating two data matrices,
the X (spectral data) and the Y (composition of food matrix), by a linear multivariate model (Wold et al. 2001). In other words, the primary purpose of using a regression technique, such as PLSR, is to construct models allowing multiple values of the dependent variable, Y, which is usually a concentration, to be predicted from the experimental absorbance data represented by the independent variable, X (Romia and Bernardez 2009). Marini (2012) states PLSR looks for components which compromise between explaining the variation in the X variables and predicting the responses in the Y. This modeling technique of PLSR has been found to be very useful due to its ability to analyze thousands of data points that can be noisy and incomplete for both X and Y variables. PLSR has also increased its desirable property in that it increases the models robustness as the number of relevant variables and observations increases (Wold et al. 2001). A few characteristics of PLSR are that it is a flexible calibration method, the full mid-infrared spectrum can be used within the creation of the PLSR model, and the method is compatible with inverse and indirect calibration (Romia and Bernardez 2009).

1.6 IR Application in Food Science

Both near and mid infrared techniques may be used to obtain both qualitative and quantitative information about food samples. Foods are complex matrices that are mainly composed of water, proteins, fats and carbohydrates (Stuart 2004). The major fundamental vibrating bands are listed in Table 3. A few examples of infrared spectroscopy in the food industry are discussed. Infrared spectroscopy can be used to determine the amount of moisture, fat and protein within meat products (Gangidi and
Also, it can be used to analyze whether fish have been frozen-thawed and it can be used to determine the amount of moisture and sodium chloride in cured, smoked salmon (Uddin and Okazaki 2009). In the food industry, IR techniques are typically used to measure moisture, protein, starch, and fiber content in whole maize and in maize products (Jespersen and Munck 2009). The dairy industry has utilized this technology to monitor the process, quality, geographical origin, and adulteration of dairy products such as milk, milk powder, cheese and butter (Fagan et al. 2009). Various research studies have been done on fruits and vegetables, including the nondestructive determination of soluble solids content of raw apples, aging of citrus oils from the oxidation of $\gamma$-terpinene and formation of $p$-cymeme, and monitoring the chemical properties within the cell walls of fruits and vegetables, focusing mainly on the degree of esterification (Schultz and Baranska 2009). The applications of infrared to fruit juice analysis involve the determinations of sugars and acids contents, and the brix to titratable acidity ratio (Huang et al. 2009). Infrared is used in beer and wine to determine the amount of ethanol (Cozzolino and Dambergs 2009). And finally, infrared spectroscopy can be used in the egg industry in order to determine egg quality during storage, egg shell quality, the concentrations of moisture, fat, and protein in spray-dried whole egg, and it can determine the amount of protein, total lipid, and total solids contents within liquid egg products (Karoui et al. 2009). A food that needs to be examined more by using infrared spectroscopy is the tomato.
Table 3: Mid-infrared fundamental vibration bands within food (Stuart 2004).

<table>
<thead>
<tr>
<th>Wavenumber (cm⁻¹)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3600–3200</td>
<td>Water O–H stretching</td>
</tr>
<tr>
<td>1650</td>
<td>H–O–H stretching</td>
</tr>
<tr>
<td>1700–1600</td>
<td>Proteins Amide I</td>
</tr>
<tr>
<td>1565–1520</td>
<td>Amide II</td>
</tr>
<tr>
<td>3000–2800</td>
<td>Fats C–H stretching</td>
</tr>
<tr>
<td>1745–1725</td>
<td>C=O stretching</td>
</tr>
<tr>
<td>967</td>
<td>C=C–H bending</td>
</tr>
<tr>
<td>3000–2800</td>
<td>Carbohydrates C–H stretching</td>
</tr>
<tr>
<td>1400–800</td>
<td>Coupled stretching and bending</td>
</tr>
</tbody>
</table>

1.6.1. Current IR Technology in Relation to Tomatoes

Two advantages of using MIR spectroscopy for the tomato industry is that the analysis is fast and the food samples may be in any state when analyzed; such as, liquids, solutions, pastes, powders, films, fibers, gases and surfaces (Stuart 2004). Infrared spectroscopy has already shown good tomato juice prediction models for soluble solids, titratable acidity, pH, reducing sugars, organic acids (Beullens et al. 2006, Scibisz et al 2014, Wilkerson and Rodriguez-Saona 2012, Sierra-Cadavid and Rodriguez-Saona 2014) and carotenoids content (De Nardo et al. 2009, Rubio-Diaz et al. 2011). However, some of these models were made with processed tomato juice alone and were created from large,
non-portable, bench top systems that are not convenient for those in a commercial setting. However, most studies were performed with processed tomato juice, which can slow the rapidness of the method and increase the cost of the analysis since a juicer, processing equipment, and containers are needed. The processed juice also does not fit the profile of a fresh tomato for both its fruit and when it is freshly juiced due to the processed tomato juice components being heat treated. For instance, lycopene contents and ascorbic acid contents are very different from fresh versus processed tomato products (Kaur et al. 2007). Also, most previous studies have only focused on one maturity stage, such as red-ripened, since processed tomatoes are only harvested at the red-ripe stage of maturity. Fresh-market tomatoes can be harvested at any stage of maturity (mature green, pink or red-ripe). The various maturity stages for fresh-market tomatoes must be analyzed via infrared spectroscopy on both their fruit surface and as a fresh tomato juice that has not been exposed to processing due to there being this gap in scientific knowledge. Also, more improvements are needed for prediction models based on tomato fruit surface and juice spectral data that are gathered on portable infrared systems. The objective of this research was to create robust prediction models based on the tomato fruit surface and fresh juice spectra versus the reference values of ascorbic acid, citric acid, soluble solids, pH, titratable acidity, glucose, and fructose in order to better implement portable mid-infrared units into a commercial setting.

1.7 References


Li-Chan EC, Griffiths PR, Chalmers JM. 2010. Applications of vibrational spectroscopy in food science; Volume 1: Instrumentation and fundamental applications. United Kingdom: John Wiley & Sons, Ltd. p 4-80.


Chapter 2: Quality Control over Multiple Traits by Using Portable Mid-Infrared Units on the Tomato Fruit Surface and Tomato Juice

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2.1 Abstract

Two sets of prediction models based on tomato fruit surface spectra and fresh juice spectra were created from a portable FTIR unit for target quality traits within fresh-market tomatoes. A total of 120 tomato samples were received. Levels of acids (ascorbic & citric) and sugars (glucose & fructose), soluble solids, pH, and titratable acidity were determined using standard reference methods. For mid-infrared analysis, the ATR accessory for the portable FTIR unit was used to obtain fruit surface spectra, and the DialPath accessory was used to obtain juice spectra. Partial least squares regression (PLSR) was used to generate cross-validated, calibration models between the parameter concentrations and the sample spectra. Prediction models based on juice spectra showed good performance in estimating all quality parameters due to high correlation coefficient ($R_{CV} > 0.80$) and low standard error of cross validation (SECV). The models based on the fruit surface did not perform as well as the juice models due to all of the acids and sugars not being directly introduced to the infrared beam, thus more uncertainty is incorporated into the fruit surface models. However, both models support the use of portable FTIR units for rapid assessment of multiple quality traits within fresh-market tomatoes.
2.2 Introduction

Tomatoes are consumed and cultivated all around the world. Specifically in 2012, the United States of America alone produced over 13 million tons of tomatoes (FAO 2014). The tomato is also a very large cash crop for the United States; the fresh-market value of the America’s tomato crop was $860 million (USDA 2012). The fresh-market tomatoes are typically produced and sold largely in the open market, and they tend to be priced higher than processed tomatoes due to larger production costs and greater market uncertainty (Economic Research Service 2012). In order for the tomato to sustain its vital placement in the market, quality control must pose a high significance at all levels of the industry to gain the desired characteristics (Sayajon and Rodriguez-Saona 2011). Monitoring the quality of the whole tomato is mandatory for the industry in all of the different stages of the tomato production including the breeding programs, agricultural practices, and postharvest management decisions (Scibisz et al. 2011). Some quality traits of interest for fresh-market tomatoes can include color, ascorbic acid (vitamin C), citric acid, glucose, fructose, pH, soluble solids and titratable acidity (Wilkerson and Rodriguez-Saona 2012, Scibisz et al. 2011, Sierra-Cadavid and Rodriguez-Saona 2014, Sayajon and Rodriguez-Saona 2011).

A key parameter that is directly linked with microbiological safety and food spoilage, which is very important to the tomato industry, is pH. The typical pH for a whole tomato fruit is 4.5 or less, making the tomato an acidic food (Jones 2008, Saltveit 2005). Storage and handling procedures are done to not increase the pH level of the tomato in order to prevent growth of microorganisms such as Clostridium botulinum. Storage above room
temperature tends to increase pH due to the metabolism of organic acids (Saltveit 2005). The pH of a tomato is determined by its organic acid content which is influenced by the amount of ascorbic and citric acid present (Wilkerson and Rodriguez-Saona 2012). Soluble solids and titratable acidity both greatly impact the flavor and texture of a fresh tomato. The amount of each and the ratio of titratable acidity to soluble solids are both important (Saltveit 2005) and contribute to the sweetness and tartness of a tomato.

Traditional methods for sugar and acid qualitative and quantitative analysis include the use of enzymatic kits and chromatography (Horowitz 2000). Chromatographic methods are typically accurate and allow for the identification and quantification of multiple components from a single sample. However, the drawbacks include time-consuming sample preparation, use and disposal of hazardous solvents, low sample through-put, and a high skill-set for the testing personnel (Wilkerson and Rodriguez-Saona 2012).

Infrared spectroscopy is an ideal alternative in accessing multiple quality traits in fresh tomatoes. Infrared analysis has become an alternative for traditional reference methods because there is little sample preparation saving both time and costs, operating the equipment is fast and simple to use, sample through-put is increased, less hazardous solvents are needed for analysis, and minimal background training is needed to operate the infrared equipment (Rodriguez-Saona and Allendorf 2011). The mid-infrared region of the electromagnetic spectrum (4000 – 400 cm\(^{-1}\)) is a good tool to use for quantitative and qualitative analysis because of the intensity of absorption bands due to the vibrations of certain functional groups (Guillen and Cabo 1997). Fourier-transform infrared (FTIR) spectroscopy, when combined with multivariate analysis is a powerful tool for fresh
tomato breeders and harvesters because the data is transformed into intensity versus frequency spectrum (Smith 1996). Therefore, this allows for a direct correlation between functional groups and specific chemical parameters of interest (Ellis and Goodacre 2006). Portable mid-infrared units are becoming more popular today due to the ease of analysis for a food manufacturer since the unit can easily be transported from laboratory, to in-plant, to in-field analysis. Portable mid-infrared systems are simple to use and require very little sample preparation. In fact, infrared spectroscopy has already achieved itself as a quality control tool in tomato analysis and tomato processing (Sayajon and Rodriguez 2011, Scibisz et al. 2011, Rubio-Diaz et al. 2010, Wilkerson and Rodriguez-Saona 2012, Sierra-Cadavid and Rodriguez-Saona 2014). However, most studies were performed with processed tomato juice, which can slow the rapidness of the method and increase the cost of the analysis since a juicer, processing equipment, and containers are needed. The processed juice also does not fit the profile of a fresh tomato for both its fruit and when it is freshly juiced due to the processed tomato juice components being heat treated. For instance, lycopene contents and ascorbic acid contents are very different from fresh versus processed tomato products (Kaur et al. 2007). Also, most previous studies have only focused on one maturity stage, such as red-ripened, since processed tomatoes are only harvested at the red-ripe stage of maturity. Fresh-market tomatoes can be harvested at any stage of maturity (mature green, pink or red-ripe). The various maturity stages for fresh-market tomatoes must be analyzed via infrared spectroscopy on both their fruit surface and as a fresh tomato juice. Thus, it is necessary to develop quick
and reliable methods that can give those in the commercial tomato industry the concentration of target quality traits within the fresh-market tomato fruit.

Our objective was to develop robust prediction models based on spectra collected on the tomato fruit surface for determination of ascorbic acid, citric acid, soluble solids, pH, titratable acidity, glucose, and fructose in order to better implement portable mid-infrared units into a field setting. Additionally, spectra of single tomato juices were used to generate models to compare prediction performances against the surface readings.

2.3 Materials and Methods

2.3.1 Plant Material

A total of 120 fresh tomatoes were received. Within that set, nine commercial varieties were obtained from four different fresh-market tomato growing locations in the United States during the 2014 growing season. The growing locations included: Florida, California, Virginia, and South Carolina. The tomatoes were harvested five different times, ranging from early June through early August. The three main types of tomatoes were Grape, Roma, and Round Beefsteak. The three different types of tomatoes were also at three different maturity stages: green (immature), pink (between immature and mature), and red (mature). The tomatoes were received by the Department of Food Science and Technology at The Ohio State University.

2.3.2 Sample Preparation

All whole tomato fruits were rinsed with water and towel dried once they were received. Any tomatoes that were split open from the shipping conditions were discarded. The
tomato fruits were then sorted according to three different maturity stages: green, pink, and red. Then one to three tomatoes were picked at random from each of the ripening stages of each commercial variety within the five shipments. This totaled to 120 samples analyzed in this study. Spectral data was immediately collected on the tomatoes’ surfaces. After the spectral data was collected, the tomatoes were immediately blended to juice by using a juicer (Omega® Juicers with twin gears, Omega, Harrisburg, PA), and were stained through a 0.55 mm and 0.80 mm screen. The juice was stored in 50 mL Fisherbrand® plastic centrifuge tubes (Waltman, MA) at -40°F for later analysis. The reference analyses included: soluble solids, pH, titratable acidity, and HPLC analysis for quantities of ascorbic acid, citric acid, glucose and fructose. Further FTIR analysis was performed on the tomato juice. During all analytical stages, samples were protected from excessive light, oxygen, and heat exposure.

2.3.3 Reference Analysis: Soluble Solids, pH, and Titratable Acidity

2.3.3.1 Soluble Solids (°Brix) Determination

For the soluble solids content, the blended tomato juice was first vortexed in order to get a homogenous solution. The tomato juice (50 µL) was then placed onto the optical prism of the refractometer to get a reading. The refractometer used in this study was the Leica Mark II Plus Abbe Refractometer Model 10494 (Leica, Buffalo, NY). After measurements were recorded in duplicate for each tomato juice sample, 70% ethanol solution was used to clean the optical prism in between each reading and it was dried with a Kimwipe tissue (Kimberly-Clark Corp. LLC, Roswell, GA). Distilled water was
also used to blank the refractometer after the optical prism was cleaned with the ethanol solution. The refractive index was expressed as % soluble solids in °Brix.

2.3.3.2 Automatic Determination of pH and Titratable Acidity

Tomato juice samples were evaluated for titratable acidity using titration with 0.1M NaOH (AOAC 2000). The juice was first allowed to reach room temperature before 2 mL of tomato juice sample was mixed with 38 mL of HPLC grade water. The combined solution was then introduced to the automatic titration system, Easy pH Titrator (Mettler Toledo, Columbus, OH). About two minutes later, the automatic titrator system produced both the pH of the tomato juice, and the titratable acidity, which was later converted into g citric acid/100 g juice. Readings were done in duplicate.

2.3.4 HPLC Reference Analysis for Concentrations of Ascorbic and Citric Acids

Ascorbic acid, or vitamin C, and citric acid were determined by using a method similar to Vazquez Oderiz and others (1994), but a few alterations were made. A 1.5 g sample of blended tomato juice that was at room temperature was first weighed into a centrifuge tube. The sample was then centrifuged for 15 min at 10,000 rpm at 25°C and the top layer of tomato serum was collected into a plastic 1.0 mL syringe. About 1.0 mL to 1.5 mL of serum solution was transferred to a HPLC vial by using the syringe, and the serum solution was filtered through 0.45 µm pore Fisherbrand nonsterile syringe filter. Filtered tomato serum solutions (5 µL) were injected into an Agilent system (Agilent Technologies Inc., Santa Clara, CA). This system was equipped with a degasser (G1322A), a quatpump (G1311A), an ALS (G1313A), a colcum (G1316A) and a DAD (G1315B) for acid analysis. A Prevail Organic Acids column (5µ particle size, 20 x
4.6mm) (Waters Corp., Milford, MA) that was C18 based was used to induce separation at 25°C between the different acids within the injected serum solution. For this method, the system was under isocratic conditions of 0.8 mL/min from time 0 to 10 minutes, 1.2 mL/min from 10 to 15 minutes, and finally back to 0.8 mL/min to 16 minutes with a 1 minute post run time. The mobile phase was acidified HPLC grade water (pH 2.2) with sulfuric acid (Fisher Scientific, Fair Lawn, NJ). Chromatograms were analyzed using Agilent OpenLAB CDS ChemStation LC & CE Drivers A.01.05[021] (Agilent Technologies Inc., Santa Clara, CA). Ultraviolet detection was at 245 nm for the determination of ascorbic acid, while detection was at 220 nm for citric acid. Commercial standards of L-ascorbic acid (Sigma Aldrich, St Louis, MO) and citric acid (Fisher Scientific, Fair Lawn, NJ) were used as external standards to validate the detection and quantification of both target acids within the tomato juice by looking at both retention times and spectrum absorbances.

2.3.5 HPLC Reference Analysis for Concentrations of Glucose and Fructose

Glucose and fructose concentrations were identified and quantified using a reverse-phase HPLC. This method is similar to Sierra-Cadavid and Rodriguez-Saona (2014). Room temperature tomato juice (1.5 g) was weighed into centrifuge tubes. They were then immediately centrifuged at 10,000 rpm for 15 min at 25°C. The supernatant was collected into a 1 mL syringe and was filtered through a 0.45 µm pore Fisherbrand nonsterile syringe filter. The filtered supernatant was then injected (10 µL) into a Shimadzu UFLC (Shimadzu, Columbia, MD). This system was equipped with dual LC-6AD pumps, SIL-20AHT auto-sampler, a CTO-20A column oven and RID-10A
refractive index detector (Shimadzu, Columbia, MD). A stainless steel Aminex® HPX-87C carbohydrate column with a 7.8 MM ID x 300 mm dimensions and a micro-guard Carbo-C cartridge with 4.6 MM X 30 mm dimensions (Bio-Rad laboratories, Hercules, CA) was used to carry out an isocratic separation at 80°C. The HPLC grade water was used as the mobile phase with a 1.0 mL/min flow rate for a 30 min run time. Chromatograms were analyzed using LC Solutions software version 3.0 (Shimadzu, Columbia, MD). The identification and quantification of glucose and fructose within the tomato sample was determined by using a standard calibration curve. This was done by preparing pure glucose and fructose standards (Fisher Scientific, Fair Lawn, NJ).

2.3.6 Infrared Spectroscopy Analysis: Tomato Surface and Tomato Juice.

Once the whole tomato fruits were collected, prepared, and sorted, the surface spectra were collected immediately by a portable Fourier Transform Mid-infrared (FTIR) spectrometer Cary 630 (Agilent Technologies Inc., Santa Clara, CA) using the single-bounce diamond attenuated total reflectance (ATR) accessory with a deuterated triglycine sulfate (DGTS) detector. The Cary 630 unit was programmed to have the spectral resolution of 4 cm⁻¹, and interferograms of 32 scans were co-added from every reading in order to improve the signal-to-noise ratio. Spectral data were collected from 4,000 to 700 cm⁻¹. This was done by holding the blossom end of the tomato directly to the diamond crystal for spectral acquisition. The collections of spectral data took less than two minutes per tomato surface reading. Duplicate, independent measurements were taken on each tomato surface. A background of 64 scans was collected every five minutes to account for environmental variations. In-between spectrum collections, the diamond was
cleaned with pure acetone and dried with a Kimwipe tissue (Kimberly-Clark Corp. LLC, Roswell, GA).

The tomato juice that was later collected for each individual tomato was also used to gain spectral data once the juice reached room temperature. This time the juice (50 µL) was directly applied to the DialPath transmittance accessory (Agilent Technologies Inc., Santa Clara). The accessory contains a zinc selenide (ZnSe) beam splitter and a deuterated triglycine sulfate (DTGS) detector, and the infrared radiation was selected at the 2 position of 50 micron path length. The Cary 630 unit was programmed to have the spectral resolution of 4 cm\(^{-1}\), and a total of 64 scans were co-added from every reading in order to improve the signal-to-noise ratio. The wavenumbers were collected within the same range as the surface spectra. The infrared spectrum took less than two minutes per reading. The background of 64 scans was taken every ten minutes. Duplicate, independent measurements were taken for each tomato juice sample. This time, however, the crystal was cleaned with a 70% ethanol solution and dried using a 100% cotton cloth. Resolution Pro Software (Varian, Palo Alto, CA) was used to display the spectra for both the tomato fruit surface and tomato juice.

2.3.7 Chemometrics: Partial Least Square Regression (PLSR)

PLSR, which is a pattern recognition technique, was used to analyze the complex spectral data and to generate the predictive models for the different tomato quality parameters. Spectral data was imported into the chemometrics program (Pirouette® version 4.0, Infometrix, Inc., Woodville, WA, USA). The spectral data was compared to the concentrations of each quality parameter, but first the spectral data had to be transformed.
The data was normalized and second derivative transformed (Savitzki-Golay second order polynomial filter with a 45 point window). Separate PLSR models were created from the spectral data gathered from the ATR and the DialPath accessories. Cross-validation using the leave-one-out approach was used to internally validate the calibration models for each quality compound of interest. Outlier Diagnostic (Standard Residual of Sample versus Leverage) was used in order to identify outliers; this was so that the data would fit the model’s regression line and not introduce noise or artifacts. Any points that held unusual patterns and had a high leverage were removed during the development of a model. The number of factors, standard error of cross validation (SECV), and correlation coefficient ($R_{CV}$) were calculated in order to determine the performance of the regression model.

2.5 Results and Discussion

2.5.1 Reference Values for the Compounds of Interest

HPLC analysis was able to separate the different acids (Figure 13) and sugars (Figure 14) within the tomato samples. This analysis detects the different types of sugars and acids within the tomatoes that were juiced down and their different concentration levels. Figure 13 represents the acid chromatogram the same red Beefsteak tomato from the same commercial variety and harvest date, but with different lambda maxes. The ascorbic acid lambda max was at 245 nm (blue line) while citric acid was at 220 nm (dark green line). The retention time of ascorbic acid was 3.690 min and the retention time for citric acid was 6.622 min.
Figure 13: Chromatogram of organic acids at 245 nm (blue) and at 220 nm (green).

Sugars were also analyzed using HPLC. Figure 14 represents the chromatogram of two different tomatoes. As seen, the red line represents a Round Beefsteak tomato, while the black line represents a Roma tomato. The first major peak at 6.603 min is glucose, while the second main peak at 8.400 is fructose. As seen from this example of two different types of tomatoes, there is a large range of values present within the samples analyzed in this study.
After performing HPLC and the other reference methods, the concentrations of the target quality components were calculated. The large number of commercial varieties, growing locations, maturity stages, and harvesting dates resulted in wide ranges of the compositional levels (Table 4). For all tomatoes in this study, the reported ranges are as such: 4.20 – 6.80 °Brix (soluble solids), 3.80 – 5.04 (pH), 0.10 – 0.79 g citric acid (titratable acidity), 0.15 – 0.59 g/100g (citric acid), 0.07 – 22.66 mg/100g (ascorbic acid), 0.52 – 1.56 g/100g (glucose), and 0.21 – 1.72 g/100g (fructose).
### Table 4: Reference method ranges of quality parameters for the various tomatoes.

<table>
<thead>
<tr>
<th>Type</th>
<th>Commercial Variety</th>
<th>Location</th>
<th>Variety</th>
<th>Harvest Date</th>
<th>Soluble Solids (°Brix)</th>
<th>pH</th>
<th>Titratable Acidity (g citric/100g)</th>
<th>Citric Acid (g/100g)</th>
<th>Ascorbic Acid (mg/100g)</th>
<th>Glucose (g/100g)</th>
<th>Fructose (g/100g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grape</td>
<td>BHN 784</td>
<td>SC</td>
<td></td>
<td>6/16/2014</td>
<td>5.60-6.80</td>
<td>4.18-4.44</td>
<td>0.14-0.73</td>
<td>0.21-0.46</td>
<td>0.08-0.20</td>
<td>0.89-1.56</td>
<td>1.13-1.68</td>
</tr>
<tr>
<td></td>
<td>RPR 1777</td>
<td>FL</td>
<td></td>
<td>6/3/2014</td>
<td>4.20-5.30</td>
<td>3.80-4.42</td>
<td>0.38-0.74</td>
<td>0.27-0.59</td>
<td>0.12-1.34</td>
<td>0.60-1.22</td>
<td>0.83-1.07</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SC</td>
<td></td>
<td>6/9/2014</td>
<td>4.30-6.50</td>
<td>4.03-4.58</td>
<td>0.40-0.69</td>
<td>0.20-0.44</td>
<td>0.07-7.84</td>
<td>0.88-1.03</td>
<td>1.28-1.72</td>
</tr>
<tr>
<td>Roma</td>
<td>Galilea</td>
<td>CA</td>
<td></td>
<td>7/28/2014</td>
<td>4.50-5.30</td>
<td>4.45-4.74</td>
<td>0.18-0.35</td>
<td>0.15-0.29</td>
<td>0.43-14.23</td>
<td>0.92-1.35</td>
<td>0.84-1.31</td>
</tr>
<tr>
<td></td>
<td>RPR 1601</td>
<td>FL</td>
<td></td>
<td>6/3/2014</td>
<td>4.40-5.15</td>
<td>4.10-4.75</td>
<td>0.17-0.64</td>
<td>0.21-0.31</td>
<td>7.01-13.98</td>
<td>0.52-0.91</td>
<td>0.52-1.06</td>
</tr>
<tr>
<td></td>
<td></td>
<td>VA</td>
<td></td>
<td>6/9/2014</td>
<td>4.55-5.40</td>
<td>4.47-5.04</td>
<td>0.14-0.40</td>
<td>0.20-0.38</td>
<td>0.07-10.33</td>
<td>0.89-1.03</td>
<td>0.77-0.99</td>
</tr>
<tr>
<td></td>
<td>RPR 1642</td>
<td>FL</td>
<td></td>
<td>6/9/2014</td>
<td>4.55-5.30</td>
<td>4.55-4.82</td>
<td>0.17-0.40</td>
<td>0.23-0.39</td>
<td>5.32-14.51</td>
<td>0.71-1.05</td>
<td>0.83-1.19</td>
</tr>
<tr>
<td>Round Beefsteak</td>
<td>Q27</td>
<td>CA</td>
<td></td>
<td>7/28/2014</td>
<td>4.45-5.60</td>
<td>4.24-4.50</td>
<td>0.27-0.40</td>
<td>0.15-0.31</td>
<td>10.09-15.29</td>
<td>0.83-1.33</td>
<td>0.88-1.47</td>
</tr>
<tr>
<td></td>
<td>Q47</td>
<td>CA</td>
<td></td>
<td>7/28/2014</td>
<td>4.70-5.60</td>
<td>4.45-4.83</td>
<td>0.19-0.36</td>
<td>0.16-0.29</td>
<td>7.85-15.19</td>
<td>1.01-1.34</td>
<td>0.97-1.25</td>
</tr>
<tr>
<td></td>
<td>RPR 1438</td>
<td>FL</td>
<td></td>
<td>6/3/2014</td>
<td>4.50-5.20</td>
<td>4.10-4.57</td>
<td>0.12-0.68</td>
<td>0.19-0.41</td>
<td>4.33-22.66</td>
<td>0.74-0.99</td>
<td>0.86-1.05</td>
</tr>
<tr>
<td></td>
<td></td>
<td>VA</td>
<td></td>
<td>6/9/2014</td>
<td>4.60-5.05</td>
<td>4.31-4.73</td>
<td>0.18-0.37</td>
<td>0.20-0.31</td>
<td>10.8-8.72</td>
<td>0.83-1.08</td>
<td>0.81-1.17</td>
</tr>
<tr>
<td></td>
<td>RPR 1453</td>
<td>FL</td>
<td></td>
<td>6/9/2014</td>
<td>4.80-5.50</td>
<td>4.36-4.79</td>
<td>0.24-0.47</td>
<td>0.23-0.46</td>
<td>0.74-9.93</td>
<td>0.63-1.12</td>
<td>0.71-1.19</td>
</tr>
<tr>
<td></td>
<td></td>
<td>VA</td>
<td></td>
<td>6/16/2014</td>
<td>4.25-5.20</td>
<td>4.05-4.48</td>
<td>0.29-0.79</td>
<td>0.24-0.36</td>
<td>1.75-10.97</td>
<td>0.55-1.16</td>
<td>0.21-1.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>8/4/2014</td>
<td>4.60-5.20</td>
<td>4.46-4.61</td>
<td>0.15-0.55</td>
<td>0.27-0.42</td>
<td>8.61-19.12</td>
<td>0.68-1.00</td>
<td>0.91-1.04</td>
</tr>
</tbody>
</table>

The °Brix is very close to that of Sierra-Cadavid and Rodriguez-Saona’s (2014) processing tomato juices with a °Brix range of 4.23 – 7.12. The pH range of the tomatoes fall within in range than what is reported by Saltveit (2005) of 4.12 – 4.20. The citric acid range is within the 0.25-2.02 g/100 g of juice reported by Sayajon and Rodriguez-Saona (2011). The ascorbic acid level is also similar to the values reported by Saltveit (2005) and Garcia-Valverde et al. (2013) of 12.5-22.5 mg/100g of juice and the 0.30-29.76 mg/100g of juice, respectively. And finally the glucose and fructose
concentrations are very similar to the average values of 1.6 g/100g of glucose and the 1.5 g/100g of fructose reported by Scibisz et al. (2014). Overall, the values within this study are very comparable to those already reported in literature. This is necessary for this type of study because there needs to be as little error incorporated because any incorporated error will be apparent once the prediction models are created. There are slight deviations possibly due to many different factors, including genetic ones such as cultivar or variety, environmental factors such as light, temperature, air composition, mineral and growth medium, and cultural practices (Garcia-Valverde et al. 2013). The wide range of values should be seen as a positive for this type of analysis. This is because the robustness of a model increases as the variety of the food sample increases. These wide ranges will only improve the strength of the prediction models for those in the tomato industry.

2.5.2 Calibration Models for Quality Components in Tomato

Spectra obtained from the single-bounce diamond ATR accessory was used to evaluate the tomato peel’s chemical state. The infrared spectrum of the tomato surface is presented in Figure 15. In this mid-infrared spectrum (4000 – 700 cm\(^{-1}\)), there are the fundamental vibrations that are associated with the chemical state of the tomato’s surface. An identifying band region is the waxes (3000 – 2800 cm\(^{-1}\)); the alkene (CH\(_2\), CH\(_3\), and C=C) backbone’s fundamental vibrations are found in this region. There are also the ring vibrations of the carbohydrate or sugar backbone (1200 – 900 cm\(^{-1}\)), where the vibrating groups are C-O-H, O-C-H, and C-C-H. And finally there is the ester carbonyl (C=O) specifically at 1732 cm\(^{-1}\).
**Figure 15:** Example of an Infrared Spectrum of the Tomato Fruit Surface from Grape Tomato, Harvested on June 16 in the Green stage using the Diamond Attenuated Total Reflectance (single bounce) Accessory for the Cary 630 unit with the Major Vibrations Identified.

Spectra were also obtained on the tomato once it was made into a fresh juice, by using the DialPath accessory on the portable mid-infrared unit as presented in **Figure 16.** In this figure, there are strong water absorption bands around 1500 – 1700 cm\(^{-1}\) and from 2900 – 3600 cm\(^{-1}\) (Sierra-Cadavid and Rodriguez-Saona 2014, Wilkerson and Rodriguez-Saona 2012, Scibisz et al. 2013). These regions are void of any useful information (Grdadolnik 2002). This results from the strong dipole moment that occurs in a H\(_2\)O molecule when radiated with infrared light. The important bands are within the finger print region which is 1500 – 900 cm\(^{-1}\). This region provides a vast amount of information that can be used in creating the prediction models. Within this region there are important band vibrations within the 900 – 1200 cm\(^{-1}\) range that can be attributed to C-O and C-C stretching modes. Also, the 1200 – 1500 cm\(^{-1}\) band vibrations are attributed to the O-C-H, C-C-H, and C-O-

![Infrared Spectrum of Fresh Tomato Juice](image)

**Figure 16:** Example of an Infrared Spectrum of Fresh Tomato Juice from a July Harvested Roma Tomato in the Red-ripe stage using the DialPath Accessory for the Cary 630 unit with the Major Vibrations Identified.

Different spectral regions were selected to perform the statistics that generated the prediction models. The selection of specific wavenumber ranges improved the prediction model instead of using the entire mid-infrared spectrum. This was done by removing variables that were uninformative or noisy from the models (Hemmateenejad et al. 2007). However, further spectral transformations were needed. They included normalization, and second derivative transformation. Normalization is used to avoid samples in the data set with large numbers that can highly influence the model construction, and the second derivative is used to enhance the resolution of overlapping infrared bands and eliminates baseline drift between samples (Sierra-Cadavid and Rodriguez-Saona 2014).
**Figure 17** represents the ascorbic acid, titratable acidity, °Brix, and glucose PLSR models. The PLSR models maximize the covariances between the reference values and the spectral data. These models plot the reference values versus the predicted infrared levels of the target quality traits obtained from the tomato fruit surface spectra (Figure 17A) and tomato juice spectra (Figure 17B). These models are good visualizations of the relationship between the measured quality traits and the prediction of the infrared system.

It needs to be noted that the models developed using the peel surface spectra do not include the Grape type tomatoes. Due to their small size, the Grape tomatoes did not produce a sufficient amount of fresh juice for the analyses. Therefore, about three of the samples were pooled together in order to get the concentration values for the Grape tomatoes. However, it was found that the analysis this way was not sufficient, because each single tomato concentration must be directly related to the spectrum. The Round Beefsteak and Roma tomatoes did not have this problem, because they produced enough juice to perform all of the analyses. On the contrary, the models developed using the juice spectra do include all tomato types.

As seen in **Figure 17**, there are more dispersive points along the regression line when the model was predicting based on the spectra of the tomato fruit surface. On the other hand, the points were more tightly packed along the regression line when the model was predicting based on the fresh tomato juice spectra. This was expected since there is a more direct correlation of the sugars and acids once they are exposed in the juice to the infrared beam. The tomato fruit surface reading model will have more uncertainly since
there is no direct correlation due to all of the sugars and acids not being fully exposed to the infrared beam.

A.  Fruit Surface

B.  Fresh Juice

**Figure 17:** PSLR correlation plots for selected quality parameters in tomatoes by using reference values and the tomato fruit surface spectra (Figure 17A) from the ATR accessory or tomato juice (Figure 17B) from the DialPath accessory on the Cary 630 FTIR unit.
The performance statistics for the models can be found in Table 5. Models created using the tomato fruit surface spectra typically generated higher amount of factors, higher standard errors of cross validation (SECV), and lower correlation coefficients ($R_{CV}$). On the other hand, the models generated with the tomato juice spectra more accurately predicted the quality components of interest by incorporating less factors, having lower SECVs and a higher $R_{CV}$. The range of factors (Table 5) for the tomato fruit surface was 4 – 7, and the range for tomato juice was 2 – 7. In general, calibration models generated from the juice spectra used fewer latent variables, or factors, than those from the tomato fruit surface spectra for the same quality trait. Typically, the lower the amount of factors, the less noise that is incorporated into that prediction model. Adding in more factors can incorporate more relevant and informative data into the model; however, the number of optimal factors cannot be too high as to draw too much noise into the model (Wang and Rodriguez-Saona 2012). Because the models based on the juice spectra generally have a lower amount of factors, they incorporate less noise into the model. The SECV (Table 5) for the quality parameters of the tomato fruit surface were 0.19 °Brix (soluble solids), 0.18 pH, 0.09 g citric acid (titratable acidity), 2.61 mg/100g juice (ascorbic acid), 0.05 g/100g juice (citric acid), 0.10 g/100 g juice (glucose), and 0.10 g/100 g juice (fructose). The SECV for the quality parameters of the tomato juice were 0.11 °Brix (soluble solids), 0.12 pH, 0.05 g citric acid (titratable acidity), 1.03 mg/100g juice (ascorbic acid), 0.04 g/100g juice (citric acid), 0.06 g/100 g juice (glucose), and 0.06 g/100 g juice (fructose).
Table 5: Prediction of the PLSR performance based on the quality parameters from the tomato fruit and tomato juice.

<table>
<thead>
<tr>
<th>Quality Trait</th>
<th>PLSR Parameter</th>
<th>Spectral model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Juice</td>
</tr>
<tr>
<td>Soluble Solids</td>
<td># of Factors</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>SECV (°Brix)</td>
<td>0.11</td>
</tr>
<tr>
<td></td>
<td>Rcv</td>
<td>0.93</td>
</tr>
<tr>
<td>pH</td>
<td># of Factors</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>SECV</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td>Rcv</td>
<td>0.84</td>
</tr>
<tr>
<td>Titratable Acidity</td>
<td># of Factors</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>SECV (g Citric Acid)</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>Rcv</td>
<td>0.93</td>
</tr>
<tr>
<td>Ascorbic Acid</td>
<td># of Factors</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>SECV (mg/100 g juice)</td>
<td>1.03</td>
</tr>
<tr>
<td></td>
<td>Rcv</td>
<td>0.92</td>
</tr>
<tr>
<td>Citric Acid</td>
<td># of Factors</td>
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</tr>
<tr>
<td></td>
<td>SECV (g/100 g juice)</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>Rcv</td>
<td>0.96</td>
</tr>
<tr>
<td>Glucose</td>
<td># of Factors</td>
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</tr>
<tr>
<td></td>
<td>SECV (g/100 g juice)</td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td>Rcv</td>
<td>0.93</td>
</tr>
<tr>
<td>Fructose</td>
<td># of Factors</td>
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</tr>
<tr>
<td></td>
<td>SECV (g/100 g juice)</td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td>Rcv</td>
<td>0.95</td>
</tr>
</tbody>
</table>

Because the SECV values were lower for the juice, this indicates the DialPath accessory on the Cary 630 unit has a better prediction ability for tomato juice samples than the
tomato fruit surface infrared readings from the single-bounce ATR accessory. The coefficient of determination ($R_{CV}$) (Table 5) range for the tomato fruit surface was 0.60 – 0.83, while the range for fresh tomato juice was 0.84 – 0.96. Because the juice predictions models have a higher $R_{CV}$ range, and all models have a $R_{CV} > 0.8$ that indicate better accuracy on desirable variable prediction (Zhang et al. 2014). Thus, the fresh tomato juice calibration models can be used for accurate predictions and quality control applications, while there are some opportunities for further development for the tomato fruit surface predictions. This was expected because when a tomato is juiced down, the sugars and acids are directly exposed to the infrared beam. It is emphasized that there is more of a direct correlation when creating the prediction models based on the fruit juice. On the other hand, there is more of an indirect correlation for the tomato surface, thus more uncertainty is brought into the models based on the fruit surface infrared data. Calibration models based on tomato fruit surface infrared spectra are not readily found in the literature. However, the models developed in this study can be compared when focusing on the juice models. The models based on the juice infrared readings within this report are similar in performance to those previously reported for both benchtop and portable FTIR systems (Wilkerson and Rodriguez-Saona 2012, Sierra-Cadavid and Rodriguez-Saona 2014, Scibisz et al. 2011, Sayajon and Rodriguez-Saona 2011). A few improvements can be noted when comparing these results to the previous reports. The titratable acidity models have improved when compared to the calibration models reported by Sayajon and Rodriguez-Saona (2011), and Wilkerson and Rodriguez-Saona (2012). This is likely associated with a better performance and precision of an automatic
titrator system as compared to a sensory determined color change. Also, glucose, fructose and citric acid models are improved when compared to Wilkerson and Rodriguez-Saona (2012). These improvements result from the use of a more sensitive HPLC method rather than the enzymatic kits used by Wilkerson and Rodriguez-Saona (2012). Even though there is a lack of reported information in literature based on the surface spectral readings of tomatoes, these prediction models can still be useful tools to save both money and especially time to predict the quality parameters of interest because it will take more time and costs to prepare juice from different types of tomatoes.

One opportunity for further development would be to add more tomato samples into the current prediction models. This will help reduce random noise and it will improve the predictive analysis of the PLSR models. Another improvement that can be made to the models based on the tomato fruit surface reading is to test the performance of a triple-bounce ATR. For this experiment a single bounce ATR was used, which allows for one interaction of the infrared beam with the food sample. Use of a triple bounce ATR would allow for three interactions of the infrared beam with the food sample, consequently the overall response would be much higher. Nevertheless, it is important to note that the prediction models created in this study for both tomato fruit surface and fresh tomato juice can be used in predicting certain quality traits within fresh-market tomatoes. This study supports the use of portable mid-infrared spectrometer units owing to little sample preparation, and readings take less than a minute. The unit is sensitive, and is able to give the spectral finger print of the target quality traits within the whole tomato.
2.6 Conclusions

Reliable infrared spectroscopy methods and prediction models were developed for determining multiple quality parameters within tomatoes based on both the tomato fruit surface spectra and the fresh tomato juice spectra for multiple tomato cultivars and various maturity stages. By incorporating over 100 tomato samples into this study and blending together infrared data with wet chemistry methods via chemometrics, this study proves that portable infrared units can give fresh tomato producers a fast and reliable method to test for quality components of interest. Further development is needed, especially for the models based on the fruit surface infrared data. One improvement is to incorporate more samples into these prediction models. This will improve the predictive analysis and help remove random noise. Also, the use of a triple bounce ATR will definitely improve the response of the infrared data and therefore will help improve the models based on the fruit surface infrared data. However, the results that are reported in this study support the use of portable mid-infrared spectrometers for rapid assessment of many quality parameters within fresh-market tomatoes. Because the portable units are easy to handle and carry, the FTIR systems can provide fresh-market tomato growers and producers a rapid method to evaluate tomatoes within a laboratory setting, within a plant facility, or even in the tomato growing field.

2.7 References


Combined References


Li-Chan EC, Griffiths PR, Chalmers JM. 2010. Applications of vibrational spectroscopy in food science; Volume 1: Instrumentation and fundamental applications. United Kingdom: John Wiley & Sons, Ltd. p 4-80.


