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Abstract: Apples are one of the most widely consumed fruits in the world and are available year-round. In France, Pink Lady production has increased despite stable global production in recent years. To meet consumer expectations in terms of quality, apples must be at optimum ripeness. Traditional destructive methods are currently used to measure physicochemical parameters. To avoid such destructive measurements, it has been shown in the literature that near-infrared (NIR) spectroscopy can predict fructose and glucose content in apple juice, as well as firmness, titratable acidity and sugar content in Fuji. The present study demonstrates the relevance of the MicroNIR spectrometer to address agricultural sustainability concerns. This compact device is easy to use in the field and allows non-destructive monitoring of the physicochemical characteristics of Pink Lady. The device acquires NIR spectra from different areas of apples, followed by standard analyses to assess these characteristics. Results indicate no impact on measurements across different quarters of the apple, though there is a slight impact between the median zone and the poles. Firmness is predictable with a 77 N threshold (using partial least square regression), and juiciness prediction is reliable, though a larger database could improve the model. Predictions for sugar content and acidity still need improvement, which would confirm the MicroNIR device's potential for assessing Pink Lady apple ripeness in the field.

Keywords: NIRS; spectroscopy; apple zones; apple; pink lady; ripeness; sugar content; firmness; juiciness; acidity; sustainable technique

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1. Introduction

Apples belong to the *Malus domestica* species and the *Rosaceae* family and are among the world's most widely cultivated and consumed fruits [1]. Their generally sweet taste and year-round availability make them particularly popular. In 2022, global apple production was dominated by China, which produced almost 47.7 million tonnes, followed by Turkey (4.8 million tonnes), the USA (4.4 million tonnes) and Poland (4.3 million tonnes). France produced approximately 1.8 million tonnes annually, which ranks ninth among the apple-producing countries [2]. Apple production in France remains stable, with only a slight increase in harvested mass over the past six years [3,4]. Apple production in France is regionally specialised and includes a wide range of cultivated varieties, with Pink Lady accounting for an increasingly significant fraction of the market [5]. Currently, Pink Lady

accounts for 21% of apple production in France, making it one of the most widely grown varieties in the country [6].

To meet consumer expectations, apples must be harvested in November and sold when ripe. However, four stages of ripeness exist, particularly for consumption. At an advanced stage of ripeness, apples are no longer suitable for sale. The four stages of ripeness are listed below [7]:

- "Physiological" ripeness: when the apple is fully developed and may be harvested for long-term storage.
- "Commercial" ripeness: when the apple has reached the stage of "ripeness" and may be sold.
- "Consumption" ripeness: the physicochemical parameters of the apple have reached equilibrium.
- "Over-ripe": the apple may no longer be sold for bulk consumption.

Measuring the physicochemical parameters of apples permits one to assess apple ripeness. The physicochemical parameters are firmness, sugar content, juiciness and acidity. Economic loss may be caused by insufficient timely information on ripeness, which would allow greater control over the produce. For example, it may lead to apples remaining unharvested, improperly stored or sold at the wrong time. Therefore, it is essential to know the apples' level of ripeness.

Previous reports state that the sugar content of apples is affected by starch degradation during storage [8]. As the fruit ripens, starch degrades into simple sugars, increasing respiration. Glucose is the driving force behind respiration, which increases as the fruit ripens. During ripening, the apple juiciness reflects the change in cellular structure within the flesh of the fruit. Water accumulation in the fruit can dilute the constituents of the flesh during ripening. In addition, juiciness correlates with apple firmness and water content and the transformation of these elements during growth. Thus, juiciness reflects both the cell structure and water accumulation during ripening. Juiciness correlates with firmness and water content, both of which vary as the fruit ripens.

The acidity of apples is explained by the presence of different acids. Malic acid is the main acid in apples, although citric acid is also present. The decrease in apple acidity during ripening may be due to the fruit's respiration, which transforms organic acids into sugar. In addition, as apples age, they increase in volume, which may dilute any acids present. Fruit ripeness is assessed by physicochemical parameters such as firmness, sugar content, juiciness and acidity. Currently, destructive, time-consuming and non-sustainable techniques are commonly used to determine ripeness. Firmness is measured by using a penetrometer or texturometer, which determines the force required to penetrate the apple's flesh. By using a refractometer, sugar content is determined from juice extracted from apples. Juiciness is quantified by the ratio between the mass of a quarter apple and that of the juice obtained therefrom. Finally, acidity is measured by soda titration, which gives the pH of the apple juice [9]. According to Hêdible et al. (2017), the ripeness index of apples can be calculated as the ratio of sugar content (degrees Brix, or °Bx) to acid content (milliequivalent par 100 millilitres, or meq/100 mL; meq is the number of grams of a substance contained in 1 mL of a normal solution) [10]. The closer the ripeness index is to 1, the less ripe the fruit; conversely, the higher the index, the riper or overripe the fruit.

These techniques, although precise, destroy the apple samples, generating waste and economic loss, they are not sustainable techniques. In addition, the standard methods have long execution times, leaving less time for analysing the apple physicochemical parameters. However, novel, non-destructive methods have led to predictive models based on infrared analysis. Near-infrared spectroscopy (NIRS) has the advantage of being rapid and non-destructive, providing economic, accurate and precise data without destroying samples or producing waste. NIRS analysis offers significant advantages over standard techniques: it requires less time (the analysis of four parameters from a sample of 30 apples takes around 30 min with NIRS versus 1.5–2.0 h with traditional methods. Costs are also reduced because NIRS requires only an instrument and software, whereas standard techniques

require various instruments and reagents (i.e., consumables). In addition, the NIRS method reduces waste and environmental impact by avoiding chemicals such as soda and by being user-friendly. Finally, NIRS does not require skilled personnel.

Mureşan et al. [11] developed a mid-infrared spectroscopy (MIRS) model to predict sugar contents, specifically fructose and glucose, in different varieties of apple juice (Golden Delicious, Starkrimson and Jonathan). The results were relatively accurate for fructose (R^2 = 0.95 and standard error of model = 0.907 in validation) and for glucose (R^2 = 0.85 and standard error of model = 0.424 in validation) [11]. Further studies used NIRS to accurately predict the firmness, titratable acidity and soluble solids content of Fuji apples (accuracies in the range of 84.24%–89.52%) [12]. The technique has also been used to predict parameters such as colour, phenolic and flavonoid content and antioxidant activity, notably on Golden Delicious apples [13–15].

These MIRS and NIRS techniques offer significant advantages over standard methods, notably their speed and non-destructive nature, which allows the tested fruit to be reintroduced into the logistics flow after analysis. NIRS offers additional advantages over MIRS, specifically lower equipment costs and the possibility of using portable devices.

The aim of the present study is to demonstrate a portable NIRS device that can be used quickly and easily in the field to rapidly and non-destructively predict the physicochemical parameters that indicate the ripeness of Pink Lady apples. The target of the study is to detect "consumption" ripeness in Pink Lady apples, which involves determining the latter's specifications: high sugar content and a firmness exceeding that of other apple varieties such as Fuji [16]. To meet this objective, measurements will be carried out using MicroNIR without destructive sampling, and standard analysis methods with destructive sampling will be used to obtain reference values. This study provides new insights into determining the various physicochemical parameters (firmness, sugar content, juiciness, acidity) and subsequently estimates the ripeness of Pink Lady apples based on differences in NIR absorption of different areas of apple samples.

2. Materials and Methods

2.1. Pink Lady Apples

The samples are Pink Lady apples, harvested in November 2023 in Tarn-et-Garonne, France. The apples were stored in containers (12 paloxes of 180 kg and 12 cans of 55 kg) at 2 °C for 65 days to simulate long-distance transport under refrigeration after a storage period. The O_2 content varies between 20% and 25%, and the relative humidity was set between 85% and 100%. The fruit was then held at 25 °C for three days to promote ripening. Thirty samples with no physiological defects were taken from each of the 24 containers (paloxes and cans), making a total of 720 samples. Finally, the samples were left for one day in the analysis room at a constant temperature of 20 °C.

2.2. Methods of Analysis of Physicochemical Parameters

2.2.1. Firmness

To measure firmness (in Newtons), we used the Magness–Taylor penetration test. The apple skin was peeled back a few millimetres on one side of an apple, and then the apple was placed on a penetrometer plate (TA1S texture analyser, Stable Micro Systems, Scarsdale, NY, USA), with the peeled side facing up. The penetrometer's 1 cm^2 tip was positioned just above the surface of the fruit, without direct contact, and then lowered 7 mm into the fruit. One measurement was made for each apple.

2.2.2. Sugar Content

Sugar content was measured at the same time as firmness. Once the penetrometer tip penetrated the fruit, approximately 1 mL of juice was removed using a Pasteur pipette and a drop of the juice was placed on the measuring socket of the portable, manual refractometer (RHW-25ATC (Fuzhou Hedao Trade Co., Ltd., Fuzhou, China), dual scale 0%–40 °Bx or

0%–25% vol. alcohol), which measures in °Bx. The refractometer has an accuracy ranging from 0.2% to 0.5 °Bx. One measurement was made on each apple.

2.2.3. Juiciness

Juiciness was measured on batches of 10 apples. For each sample of 30 apples from a given container, three batches of 10 fruits were formed as follows:

- Apples 1 to 10 were taken from batch 1 of container 1;
- Apples 11 to 20 were taken from batch 2 of container 1;
- Apples 21 to 30 were taken from batch 3 of container 1.

Each of the 10 apples from a batch was cut into quarters, and two quarters from each apple were selected from opposite sides of the apple, avoiding the area used for measuring firmness. All the quarters selected from a batch were weighed, as well as the juice extracted using the centrifuge. Juiciness was defined as the percentage of the juice mass by the total mass of the selected quarters [9,17]:

$$juiciness\ (\%) = \frac{juice\ mass\ (g)}{mass\ of\ whole\ quarters\ (g)} \cdot 100. \quad (1)$$

This measurement was repeated 3 times for all 24 containers.

2.2.4. Total Acidity

The total acidity of the Pink Lady apples was determined using the juice obtained in the juiciness analysis. Three measurements were completed per container. To determine the total acidity, a 10 mL volume of the juice was placed in a beaker containing a bar magnet. The sample was stirred using the bar magnet and titrated with a sodium hydroxide solution (0.1 M NaOH) using an automatic titration burette with an HQ11d pH meter (Hach) [9].

The titrated volume was noted to produce a regression curve expressing the volume of titrated soda as a function of pH. A fit to the regression curve provided an equation for calculating the volume of soda required to reach a pH of 8.1. The pH target value is consistent with previous studies [9]. This equation was determined for each sample. Once the requisite volume of soda was determined, it was used in the following equation to calculate total acidity in meq/100 mL [9]:

$$Total\ acidity\ (meq/100\ \mathrm{mL}) = \frac{(100 \cdot V_{sh} \cdot c)}{V_0}, \quad (2)$$

V_{sh} is the volume in mL (millilitre) of sodium hydroxide solution titrated to obtain pH = 8.1, c is the concentration of the soda solution (0.1 M (molar or mol/L) (in this work) and V_0 is the volume in mL of the juice sampled (10 mL in this work).

2.3. Acquisition of Near-Infrared Spectra

Prior to physicochemical analysis, NIRS spectra were collected in a room at a constant temperature of 20 °C. An OnSite MicroNIR spectrometer (Viavi Solutions Inc., San Jose, CA, USA) was used in reflectance mode to acquire NIR spectra of apples (with skin) over the spectral range 908–1676 nm, producing 125 variables. Each scan was performed with the detector in contact with the apple skin; each apple was scanned ten times, and each spectrum was the average of 100 scans (Figure 1) Each scan was integrated for 10 ms and had a spectral resolution of 6.2 nm. The average reflectance spectra were then converted to absorbance spectra using the Viavi spectrometer software MicroNIR TM Pro v2.5.

Figure 1. MicroNir system scanning an apple in contact.

2.3.1. Collection of NIR Spectra from Different Apple Zones

Ensuring that the area from which the reflectance spectra were taken did not influence the result obtained was vital. An apple can be divided into several zones (or areas) of varying physicochemical properties. For example, exposure to the sun during growth can modify an apple's development (e.g., its pigmentation), including the development of the fruit from the flower [18,19]. The properties signalling ripeness also depend on the proximity to the peduncle. We must, therefore, analyse how the apple zone affects the NIR spectra if the spectra differ perceptibly between neighbouring zones.

To analyse the different ripeness levels deduced from NIR spectra acquired from different zones, the apple is conceptually divided into vertical and horizontal sections, and the NIR spectra collected from these zones are compared. Starting from the stem the apple is divided into three vertical zones starting from the stem (apical, medial and basal). Horizontal division into quarters produces four zones (Figure 2). The result is 12 zones.

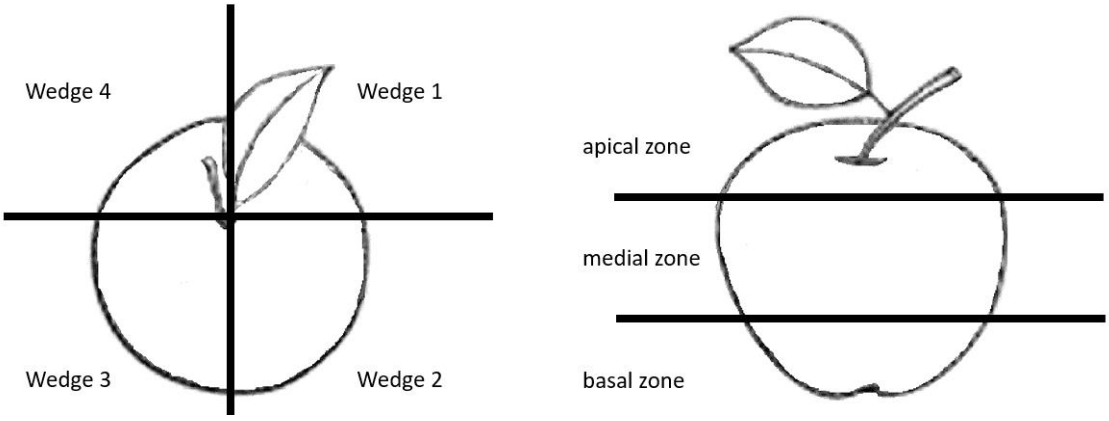

Figure 2. Schematic diagram of conceptual division of apple into zones (quarters and height).

The Pink Lady apple samples for NIR spectrum acquisition were in addition to those used for physicochemical and ripeness analyses and were stored under a controlled atmosphere identical to that described in Section 2.1. A total of 100 NIR reflectance scans were taken from each zone of each fruit for a total of 1200 scans per fruit (12 zones per fruit, 100 scans per zone).

2.3.2. NIR Spectra Collected over Entire Apple Surface ("Global Scan")

From each apple zone, 10 NIR reflectance scans were acquired and averaged to suppress outlying data. Each scan corresponded to 100 scans. Thus, each apple zone was scanned 1000 times (10 × 100). After removing outlying reflectance spectra, we were left with 711 global NIR reflectance scans from 711 apples.

2.4. Statistical Approaches and Data Mining

Databases were set up for each parameter studied: firmness, sugar content, juiciness, acidity, NIR spectra and information on the different zones of each apple (i.e., zones defined by height and quarter). Figure 3 shows the steps involved in creating the databases.

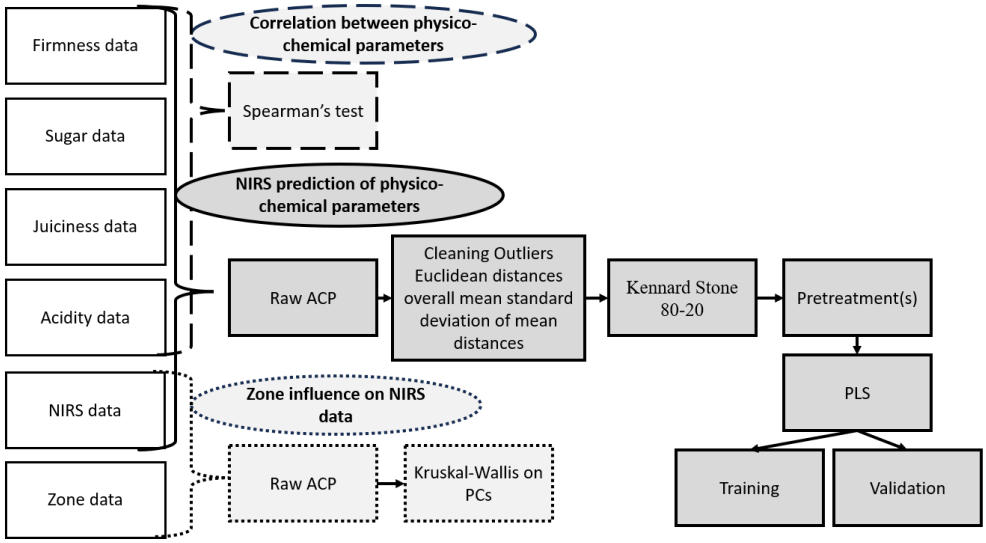

Figure 3. Diagram showing the various databases obtained and statistical analysis tools used.

The results obtained were combined to determine the maturity of the Pink Lady apples. The zonal spectra were used to determine whether the spectra depended on the acquisition zone of the apple. Predictive models for each of these parameters were developed based on this knowledge and by comparing the spectra of Pink Lady apples with data obtained by standard methods giving the physicochemical parameters. These models were then used to predict the ripeness of Pink Lady apples based on NIR spectra. Figure 4 shows the procedure for data acquisition and analysis.

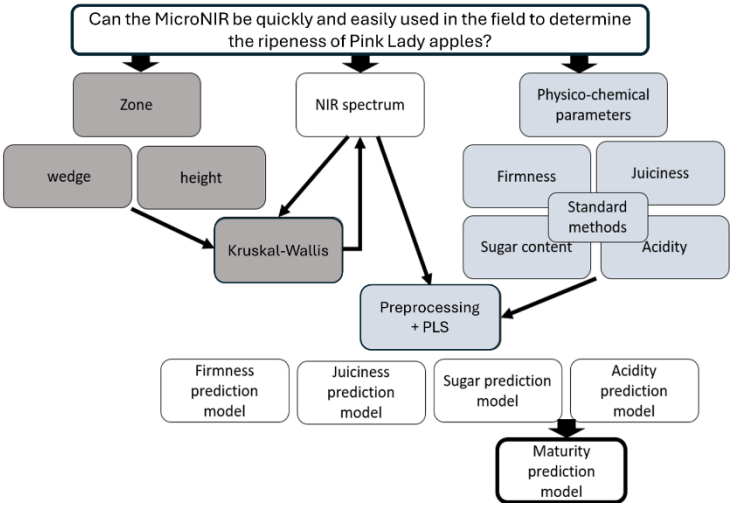

Figure 4. General flowchart for comparing standard destructive methods with the proposed NIRS method to determine Pink Lady ripeness.

2.4.1. Database Cleanup

We combined the databases for firmness, sugar content, juiciness, acidity and spectra to determine the physicochemical parameters based on NIR spectra sugar content. This combined database was first divided into four sub -databases: 1/firmness and spectra, 2/sugar content and spectra, 3/juiciness and spectra and 4/acidity and spectra. Each sub

-database was subjected to a principle components analysis (PCA) to obtain the dispersion of the data. Outliers were eliminated using an R script to calculate the Euclidean distances between sample replicates. The mean distance and standard deviation of the distances were calculated to identify outliers by comparing the mean distances to the overall mean plus two standard deviations. Samples identified as outliers were excluded from the database.

2.4.2. Analysis of Apple Physicochemical Parameters

We relied on databases containing firmness, sugar content, juiciness and acidity to detect correlations between the physicochemical parameters of Pink Lady apples. Spearman's correlation test was used to determine the links between pairs of physicochemical parameters [20].

2.4.3. Spectral Uniformity: Consistency of Spectra from Different Apple Zones

To analyse the spectral homogeneity with respect to fruit zones, we examined the NIR spectra and zone database. We first applied a PCA to reduce dimensionality of the spectral dataset from 125 variables to a few numbers of PCs determined using the Kaiser criterion (i.e., having eigenvalues above 1%). These PCs were submitted to Kruskal –Wallis and post hoc tests to compare the PC means as a function of apple zones.

2.4.4. Using NIR Spectra to Predict Apple Physicochemical Parameters (Firmness, Sugar Content, Juiciness, Acidity)

The cleaned databases were then separated into two sets using the Kennard and Stone method [21]: 80% of the data were used to train the model, and 20% of the data were used to validate the model. The following mathematical preprocessing methods and combinations thereof were then tested [20].

- Standard normal variate (SNV). The SNV method transforms each spectrum by centring it around zero with a unit variance. This normalisation reduces the effects of instrumental variations and concentration differences, facilitating comparative analyses of spectra.
- Multiplicative scatter correction (MSC). The MSC method corrects for light scattering and optical path variations. Spectra are transformed using coefficients obtained from a linear model, where each spectrum is regressed against a reference spectrum, often the average spectrum of the database.
- Raw spectra remain unchanged and are not corrected.
- First, second and third derivatives. These corrections improve the signal resolution and reduce interferences. The first derivative (D1) highlights changes in slope and, therefore, peaks and troughs in the spectrum. The second derivative (D2) highlights inflexion points and reduces background effects, thus improving resolution. The third derivative (D3) accentuates more subtle variations and enables a finer analysis of complex peaks.

The analysis may use any range within the NIR spectrum, which ranges from 908 to 1676 nm. The NIR spectrum is divided into four essentially equal spectral ranges, defined by the total number of spectral columns, in this case, 125. These spectral ranges are then combined to create new ranges; for example, the first spectral range may be used alone, the first spectral range and the second spectral range may be used together, or the entire spectrum may be used.

The various preprocessing combinations generate new databases, such as D1 + MSC or D2 + SNV, which are then used to perform partial least square regressions. The performance of each model is evaluated to compare with the remaining models. The best-performing model is selected using the following criteria [20,22]:

- Coefficient of determination (R^2). This criterion measures the fraction of the total variance of the dependent variable explained by the model.
- Root means square error (RMSE). This criterion quantifies the standard deviation of the residuals (prediction errors) and the model's overall accuracy.

- Ratio of performance to deviation (RPD). This criterion compares the accuracy of the model to the variability of the data, indicating the quality of the prediction in relation to the variation observed in the data. The RPD is calculated by dividing the standard deviation of the measured references by the RMSE.

3. Results and Discussion

3.1. Analysis of Physicochemical Parameters

The sugar content and firmness measurements of 711 apples were analysed. Table 1 summarises the sugar content and firmness of these apples.

Table 1. Description of unit databases for sugar content and firmness.

Statistic	Sugar Content	Firmness
No. of observations	711	711
Minimum	12.0 °Bx	35.38 N
Maximum	18.0 °Bx	122.03 N
First quartile	14.0 °Bx	60.96 N
Median	15.0 °Bx	81.01 N
Third quartile	15.0 °Bx	96.52 N
Mean	14.6 °Bx	79.32 N
Variance ($n-1$)	0.7 °Bx	370.34 N
Standard deviation ($n-1$)	0.8 °Bx	19.24 N

The sugar content of the samples ranged from 12.0 to 18.0 °Bx, with an average of 14.6 °Bx. The first quartile is 14.0 °Bx, while the median and third quartile are 15.0 °Bx. The results indicate that 25% of the apples had a sugar content of at least 15 °Bx. Thus, a quarter of the samples had the same sugar content, so the apples could be difficult to differentiate solely based on their sugar content. This result indicates that these apples had a similar ripeness.

The variance in sugar content is 0.7 °Bx, with a standard deviation of 0.8 °Bx, reflecting moderate variability in the data. The literature generally reports the sugar content of Pink Lady apples between 12.0 and 15.0 °Bx. The data obtained in this work are consistent with these values for 75% of the apples, whereas the data in the third quartile exceed this range [23,24]. This result indicates that the tested apples were highly mature.

The minimum firmness of the samples is 35.38 N, and the mean firmness is 79.32 N. The first quartile for firmness is 60.96 N, the median is 81.01 N, and the third quartile is 96.52 N, suggesting that most apples have a firmness exceeding 80 N. The maximum firmness was 122.03 N. The variance in firmness was 370.34, and the standard deviation was 19.24 N, indicating significant data variability. According to the literature, the firmness of Pink Lady apples is generally 87–107 N [25]. The data show that the firmness of less than 25% of the samples falls within this range, with measurements deviating by $\pm$20 N from this interval. Thus, the data obtained in this study differ from the literature data, possibly because of seasonality or storage method. The ripeness index may indicate that most apples were riper than the apples investigated in previous studies.

The juiciness and acidity of 72 apples were analysed. Table 2 summarises the results obtained for these two parameters.

The juiciness of the samples ranged from 57.7% to 75.3%, with a mean value of 66.7%. The first quartile for juiciness was 64.4%, the median was 66.3%, and the third quartile was 69.3%. This distribution suggests a relatively close set of values. The variance in juiciness was 0.1%, and the standard deviation was 3.4%, indicating low variability in the juiciness data.

According to the literature, apple juiciness generally ranges from 30.0% to 67.0% [17]. Over time, during ripening and storage in cold rooms under controlled atmospheres, juiciness tends to decrease [17]. Conversely, without storage in a controlled atmosphere, juiciness tends to increase due to the conversion by enzymes of insoluble sugars into soluble sugars. For the present study, the samples were first stored in a controlled atmosphere (maximum atmospheric oxygen content of 3%, temperature 2.5 °C) for 7 weeks and then

kept cold with a minimum atmospheric oxygen content of 21% to simulate cold transport of the fruit for 9 weeks. The hypothesis is that the apples initiated sugar conversion while in the controlled atmosphere, which reduces juiciness and then begins sugar transformation during storage at an oxygen level of 21%. Given that the second period is longer (i.e., oxygen at 21%), the various processes had more time to develop and increase the juiciness.

Table 2. Description of databases for juiciness and acidity.

Statistic	Juiciness	Acidity
No. of observations	72	72
Minimum	57.7%	3.11 meq/100 mL
Maximum	75.3%	9.02 meq/100 mL
First quartile	64.4%	4.79 meq/100 mL
Median	66.3%	5.13 meq/100 mL
Third quartile	69.3%	5.50 meq/100 mL
Mean	66.7%	5.22 meq/100 mL
Variance ($n-1$)	0.1%	0.75 meq/100 mL
Standard deviation ($n-1$)	3.4%	0.86 meq/100 mL

After the two storage periods described above, the apple acidity varied from 3.11 to 9.02 meq/100 mL, with an average of 5.22 meq/100 mL. The first quartile was 4.79 meq/100 mL, and the median and third quartile were 5.13 and 5.50 meq/100 mL, respectively. Thus, most of the samples had acidities close to the median acidity. The variance of acidity is 0.75, and the standard deviation is 0.86 meq/100 mL, indicating a moderate dispersion in the data.

In the literature, acidity in apples ranges from 3.00 to 7.00 g/L malic acid, which corresponds to an acidity of approximately 4.50 to 10.50 meq/100 mL [25–27]. The results show that 75% of samples fall within this standard range. However, 25% of samples in the first quartile fall below this range, which may be attributed to the more advanced ripeness of the apples in the present study.

By cross-referencing our data with published results, the apples analysed in this work were evaluated as mature for three-quarters of the apples and as very mature for the remaining quarter. This comparison places the maturity of apples in this study in the "commercial" category for ripeness. A minority of the apples in this study were "over-ripe".

3.2. Quantification of Firmness, Sugar Content, Juiciness, Acidity and Ripeness Using Near-Infrared Spectroscopy

3.2.1. Raw Near-Infrared Spectra

Figure 5 shows the spectra obtained with the MicroNIR instrument. They cover a wavelength range from 908 to 1676 nm and provide an initial indication of trends.

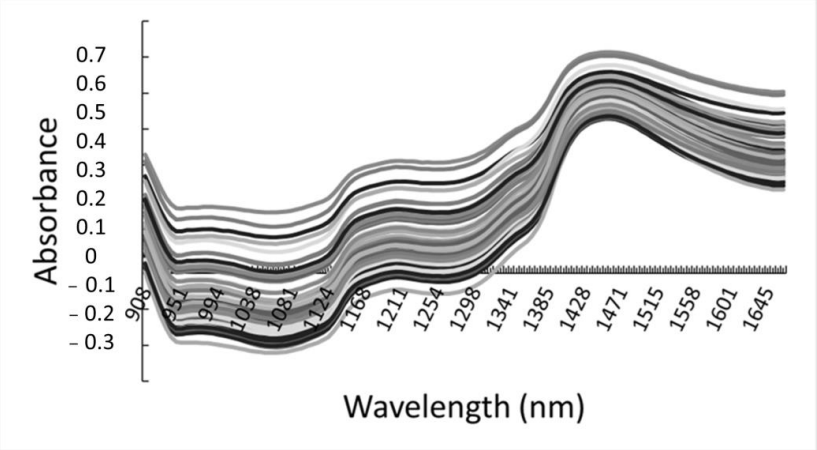

Figure 5. NIR absorbance spectra obtained using the MicroNIR instrument on 711 Pink Lady apples.

All the absorbance spectra follow the same pattern. Important absorbance peaks appear at 908–920, 1143–1236 and 1378–1502 nm.

3.2.2. Spectral Outlier Removal

The replicated spectra for each apple were examined individually to eliminate outliers within each group, resulting in a database with no outliers.

3.2.3. Impact of Collection Zone on NIR Spectra

To assess the homogeneity of NIR spectra over the various measurement locations on the apples, we analysed the differences between spectra acquired from different zones on the apples. Zones varying in both the vertical (height) and horizontal (quarter) dimensions were analysed. The raw spectra from different zones on the apples were subjected to a PCA to reduce the dimensionality of the spectral data and to summarise them, and the results are discussed below.

Vertical Variation in NIR Spectra (Apical, Medial and Basal Zones)

For the spectral data segmented in the vertical direction (apical, medial and basal zones), only PC1 (with an eigenvalue of 96%) and PC2 (with an eigenvalue of 3%) were retained (Kaiser criterion). A Kruskal –Wallis test was applied to these principal components to identify differences between the different zones. A Tukey post hoc comparison of means test was combined with this analysis to refine the results.

Significant differences appeared between the NIR spectra collected from the different vertical zones of the apples, either for PC1 (n = 312 spectra, $p < 0.0001$) or PC2 (n = 312 spectra, $p < 0.0001$), see Figure 6. The spectra collected from the medial area are significantly different from the spectra collected from the apical and basal areas. Therefore, spectral data must be collected from at least the median zone and another zone of a Pink Lady apple to be considered representative of the entire apple.

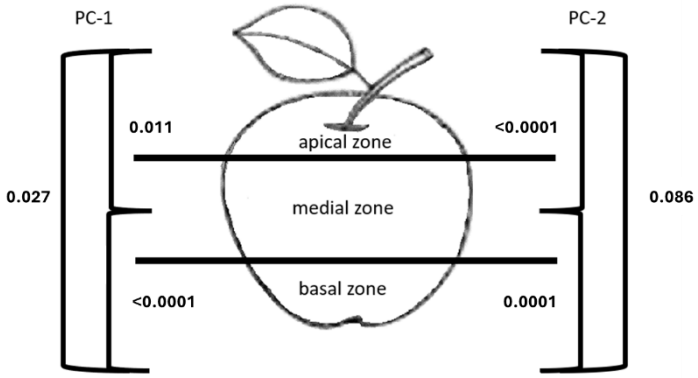

Figure 6. p-values resulting from Kruskal –Wallis and Dunn test for PC1 and PC2, the first two PCs obtained from NIR spectra from different vertical zones of Pink Lady apples (p-values).

Meridian Variation in NIR Spectra (Neighbourhood Effect)

We studied how the neighbourhoods affect the raw spectra using the same methodology for analysing the different vertical zones of the apples. The results of Kruskal–Wallis and Dunn tests confirm that, for both PC1 and PC2, no significant differences appear between meridian zones on the apples. The p values associated with these PCs all exceed 5% (PC1 is 0.881, and PC2 is 0.848, indicating that no significant differences in NIR spectra were detected between zones (Figure 7).

The results of the Kruskal–Wallis test indicate that the spectral data do not differ significantly between the different zones of the apple. This result, combined with the previous results regarding NIR spectra from different vertical zones on the apple, suggests that NIR spectra may be acquired from at least two horizontal zones and any vertical zone of the apple without compromising the representativeness of the data.

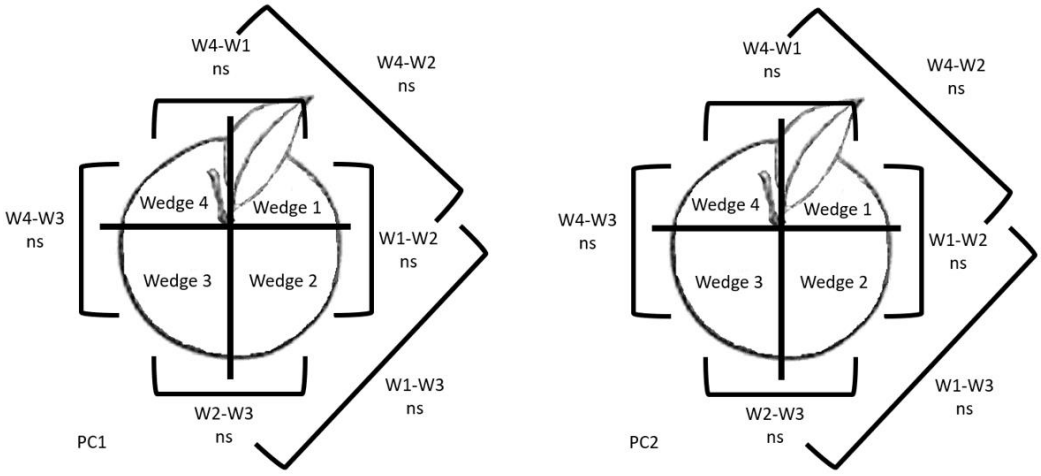

Figure 7. Results of Kruskal–Wallis and Dunn tests (at 5%) on PC1 and PC2 of Pink Lady apple quarters. ns = not significant.

Previous studies predicted apple sugars using NIR absorbance spectra, notably with Fuji apples [28], and found that the sugar predictions depended on the vertical zone from which the spectra were taken. The present work suggests that the NIR spectra from different zones of Pink Lady apples do not differ significantly except for the median zone.

The different results may be attributed to the use of relatively few wavelengths in the previous work, whereas the present work uses essentially a continuum of wavelengths evenly spaced over a broad spectrum. This continuum approach allows all available information to be considered, allowing nuances to be detected. In addition, a continuous absorbance spectrum from a given zone of a Pink Lady apple reveals other trends. On the downside, the continuum method can lead to data saturation, erasing small variations arising at specific wavelengths.

Another explanation of the different results may be related to the fact that the previous works analysed sugars only, whereas we consider overall fruit differentiation by analysing various parameters. Taking only one parameter into account may not capture all the information [28]. Since apples are composed of a complex matrix whose structure can be evaluated based on parameters in addition to sugar, they should be exploited to ensure consistent results.

3.3. Spectral Modelling of Physicochemical Parameters

3.3.1. Correlation Between Physicochemical Parameters of Pink Lady Apples

When analysing fruit ripeness, correlations are assessed between the various physicochemical parameters of the fruit, which can explain the interdependence of parameters and their joint evolution as a function of fruit maturity.

Table 3 shows the proximity matrix for the Pink Lady physicochemical parameters (i.e., juiciness, sugar content, firmness and acidity).

Table 3. Proximity matrix (Spearman's correlation coefficient r and *p*-value) of physicochemical parameters measured on Pink Lady apples.

***r* (*p*-Value)**	**Juiciness**	**Acidity**	**Sugar Content**	**Firmness**
Juiciness	1.00 (1.00)	0.199 (<0.0001)	−0.283 (<0.0001)	0.322 (<0.0001)
Acidity	0.199 (<0.0001)	1.00 (1.00)	−0.217 (<0.0001)	0.189 (<0.0001)
Sugar content	−0.283 (<0.0001)	−0.217 (<0.0001)	1.00 (1.00)	−0.252 (<0.0001)
Firmness	0.322 (<0.0001)	0.189 (<0.0001)	−0.252 (<0.0001)	1.00 (1.00)

The proximity matrix reveals different relationships between the physicochemical parameters. All parameters were statistically correlated (p-value < 0.0001).

These correlations suggest some dependency between these pairs of variables. Furthermore, juiciness and firmness are positively correlated, whereas sugar content is negatively correlated with juiciness and firmness.

3.3.2. Prediction of Pink Lady Sugar Content

The NIR spectra were averaged over 711 apples, and the data were divided into two subsets for model creation with validation, with 80% of the data used for training and 20% for validation. Models with various spectral data preprocessings were tested. The model with the best RPD for the training set (1.14) was built from unaveraged data, with MSC preprocessing and using the full spectrum (908–1676 nm). Using this model, with 16 factors, the predicted data were projected against the measured sugar content. The predicted data range from 12.5 to 17.5 °Bx, and the actual data range from 12.0 to 18.0 °Bx. This dispersion is reflected by an RMSE of 0.7 °Bx for all training data. This represents an important error with respect to the measurement scale (12.0–18.0 °Bx, see Figure 8).

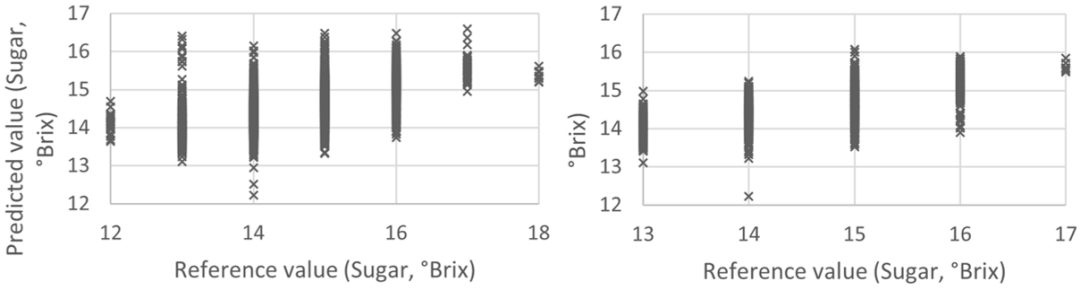

Figure 8. Predicted sugar content versus measured sugar content for the model applied to the training data (**left**) and the validation data (**right**).

For the results obtained from validation, the sugar content of Pink Lady apples appears highly dispersed. This strong dispersion is corroborated by an RMSE prediction error of 0.4 °Bx, which is a notable deviation given the measurement scale of 12.0–18.0 °Bx.

These results may be attributed to the use of manual tools to acquire sugar content data. A digital refractometer would make a more homogeneous and precise measurement, which could improve the accuracy of the reference data and, consequently, the model's performance [9]. Using a digital refractometer could thus reduce this margin of error and make the model more reliable for practical applications.

The error in the predicted sugar content may also be partly explained by the fact that the sugar content analysis involved only the flesh of the apple, whereas the NIR spectra were acquired non-destructively from the skin of the apple. Potential variations in sugar content between the skin and the flesh of Pink Lady apples could contribute to this disparity. According to the literature, the sugar content measured from apple skin averages around 14.0 ± 0.3 °Bx, whereas it is 15.5 ± 0.1 °Bx for the whole fruit. This difference between measurements and spectroscopic data could explain the prediction errors observed for the sugar content obtained via NIR spectra. Variations in sugar content between skin and flesh could therefore negatively influence the accuracy of the prediction model, underlining the importance of harmonising data acquisition methods to improve prediction accuracy [29].

The type of sugar present in apples also plays a crucial role in fruit ripeness. Apples contain several types of sugar, whose concentrations vary as the fruit ripens. According to the literature, as the fruit develops and ripens, the concentration of fructose and sucrose increases, whereas that of sorbitol decreases. The NIR spectra used in this study could correspond to the overall concentration of these sugars, without being sensitive to the concentrations of the individual sugars, which may influence the results. Thus, more precise measurements that detect the different types of sugars in apples would improve

the accuracy of the sugar content prediction model [30]. This approach would allow us to better understand and model variations in sugar content as a function of fruit maturity, thereby optimising model performance.

In conclusion, the model for predicting the sugar content of Pink Lady apples from NIR spectra is not sufficiently accurate to apply to new samples. The prediction error is too large for measuring the sugar content of Pink Lady apples in the field.

3.3.3. Predicting Pink Lady Firmness from NIR Spectra

Again, the apples were divided into two subsets for the model creation with validation, with 80% for training and 20% for validation.

We generated 108 partial least square models from 11 preprocessing combinations. The best model was selected based on the training set's RPD. The model with the best training RPD (1.22) was built from the unaveraged data without preprocessing and using only part of the spectrum, from 1069 to 1676 nm. Using this model, with 13 factors, the predicted data were projected against the actual firmness data. The data measured by the standard method have values between 35.00 and 120.00 N and the predicted values according to the model built on the NIRS data are between 40.00 and 110.00 N. The RMSE of calibration is 16.08 N for the training set, which is important in relation to the measurement scale, which ranges from 40.00 to 125.00 N. Figure 8 shows two relatively distinct data clouds separated near 77.00 N.

The firmness data are also scattered in the validation results. The firmness data for Pink Lady apples form two relatively distinct data clouds separated near 77 N (see Figure 9). The prediction error in validation is estimated to be 16.22 N, which is large in relation to the measurement scale, which ranges from 40.00 to 125.00 N.

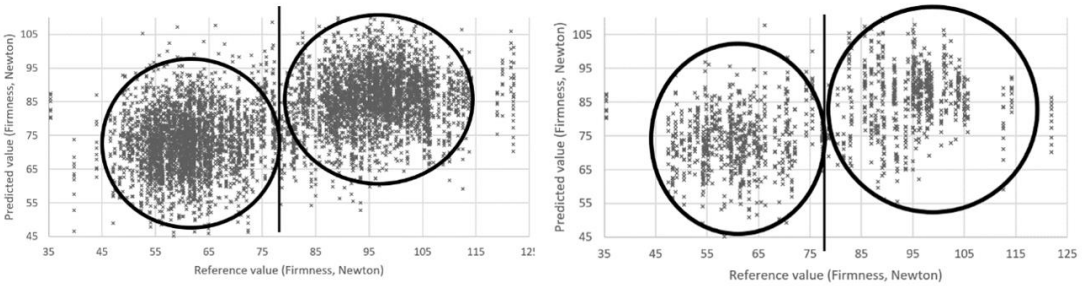

Figure 9. Predicted firmness versus measured firmness for the model applied to the training data (**left**) and the validation data (**right**).

In conclusion, the Pink Lady firmness prediction model based on NIR spectra can potentially be used to estimate the firmness of new Pink Lady samples. Although the prediction error exceeds 16 N, which is too high to use this technique in the field to predict firmness, the technique could be useful in a categorisation context. Apples could be classified into two distinct groups according to their firmness, with the separation between the groups being 77 N. Using 77 N as a threshold could thus differentiate between two groups of apples with different levels of firmness. Thus, the two categories of apples with different firmness parameters could reflect two stages of apple maturity.

This error in firmness may be due to the limitations of the methodology. The spectra are acquired from the skin of Pink Lady apples, whereas firmness is measured without the skin. The difference in cellular composition between apple flesh and apple skin could explain this discrepancy. Skin, with its densely arranged cells protected by the cuticle, differs considerably from flesh, which contains numerous intercellular spaces and vascular systems [31]. This structural difference could affect the accuracy of firmness predictions based on NIR spectra.

In addition to the differences in structure between apple flesh and epidermis, the epidermis contains a higher concentration of phenolic compounds than the flesh, such as

flavanols and anthocyanins [32]. These differences in composition could affect the NIR spectra and alter the firmness information, thus contributing to the discrepancy observed in predictions.

3.3.4. Predicting Pink Lady Juiciness from NIR Spectra

NIR spectra were averaged over batches, with a total of 72 batches, each containing 10 apples. The different models tested with various methods of data preprocessing were ranked according to the RPD of the training set. The model with the best RPD value for the training set (2.31) was based on averaged data with the SNV and derivative preprocessings. This model uses primarily the wavelength range 1069–1676 nm.

We used this optimal model with 11 factors to project the predicted data against the measured juiciness. Both the measured values and the predicted values range from 0.5% to 0.7%. This dispersion is also reflected by an RMSE of 0.02% for the training set results. For the validation of results, the juiciness prediction has an RMSE of 0.02%. This is a large deviation in relation to the measurement scale, which goes from 0.6% to 0.7% (Figure 10).

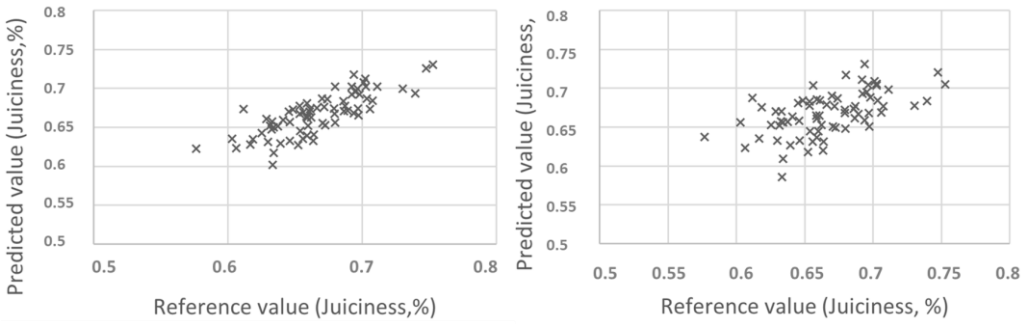

Figure 10. Predicted juiciness versus actual juiciness for the model applied to the training data (**left**) and validation data (**right**).

In conclusion, the juiciness prediction model for Pink Lady apples based on NIR spectra obtains reliable results on new samples. Although the model's error of ±0.02% must be considered, it suffices for using the model in the field to predict the juiciness of Pink Lady apples.

The observed error may be due to the precision of the sample acquisition method. Juice recovery with a juice extractor, although common, may cause the results to vary. To improve accuracy, alternative techniques should be considered, such as collecting juice using an absorbent filter after double compression of the fruit to obtain more homogeneous data and thereby minimise handling errors [33].

The error in the results may also be attributed to insufficient repetition in the data. In fact, the 72 batches analysed constituted a relatively limited data set. Adding further data may not only improve the robustness of the model but also better capture the annual variations in the specific conditions.

The results may also reflect enzyme-induced modifications in cell structure linked to fruit ripening. The literature reports that, during apple ripening, certain enzymatic activities, such as hydroperoxide lyase, pyruvate decarboxylase and alcohol dehydrogenase, promote the development of fruit flavours [34]. Other enzymes, such as superoxide dismutase, affect the epidermal structure by converting O_2^- ions into H_2O_2. This molecule, along with ethylene and respiration, increases during ripening, which may alter the cellular construction of the apple flesh and epidermis [35,36].

In addition, enzymatic activity, particularly that involved in pectin degradation, may also influence apple structure, firmness and juiciness. As the fruit ripens, enzymes transform the pectin that constitutes the cell walls. This transformation alters the cell structure, reducing cell solidity and increasing the liquid state of the compounds, which can directly affect the juiciness. Thus, variations in cell structure and reduced firmness are linked to juiciness because pectin transformation affects the apple texture and water content [37].

The juiciness predicted here may be affected by various enzymes at different stages in fruit development, leading to different mechanisms of cell wall degradation and, in turn, different results for juiciness.

3.3.5. Predicting Pink Lady Acidity from NIR Spectra

NIR spectra were averaged over batches, with each of 72 batches comprising 10 apples. Various models with different data preprocessing methods were evaluated, and the model with the best RPD for the training set was based on the averaged data and used the wavelength range 1031–1354 nm.

Figure 11 shows the projection of predicted acidity data versus the measured acidity data. The data are scattered, which is reflected by an R^2 of 0.01 and an RMSE of 0.87 meq/100 mL. These results indicate a poor accuracy of the acidity prediction model.

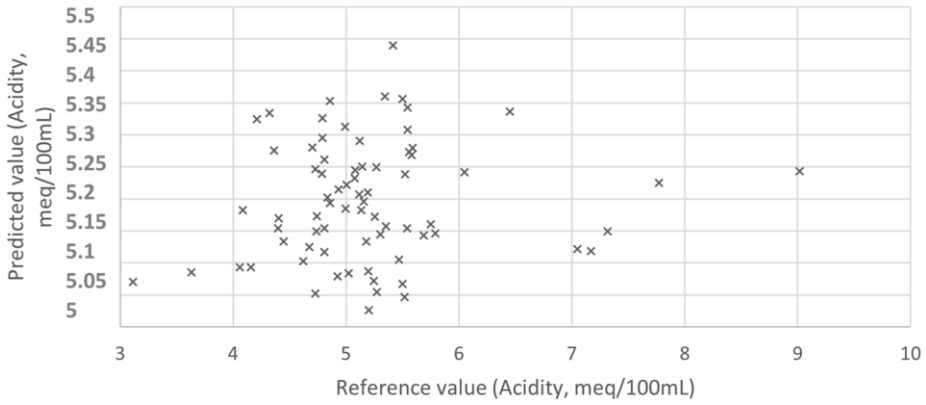

Figure 11. Predicted acidity obtained by applying the predictive model to the training database ver-sus actual acidity.

The model used to predict the acidity of Pink Lady apples by NIRS produces a significant error (RMSE = 0.87 meq/100 mL), which prohibits using the model in the field to analyse the ripeness of Pink Lady apples. However, the cross-validation was limited to only 72 spectra, so increasing the sample size could improve the model's accuracy. In conclusion, the NIR acidity prediction model may still be improved. The accuracy of measurements of total or malic acidity of Pink Lady apples could be refined in the future to improve the prediction accuracy.

The inaccuracy of the model for predicting acidity in Pink Lady apples may result from numerous factors, which we discuss below.

- Reading the titrated volume with the naked eye can introduce subjectivity because it depends on the visual interpretation of the experimenter. To minimise this subjectivity and avoid human handling errors, an automated electronic tool should be used to read the titrated volume. This type of instrument would standardise the measurements and improve the accuracy of results by eliminating variations due to human perception.
- The duration and volume of each addition of soda are important. Adding soda too rapidly may alter the evolution of the pH because a sudden chemical reaction may not proceed correctly. The result would be erroneous measurements. Thus, the soda must be added in a gradual, repeatable manner to ensure a homogeneous chemical reaction and accurate measurements.
- The interval between each addition of soda while stirring to stabilise the pH is also important because it allows all the target acids to be neutralised by the soda.
- The use of skin and flesh in analysis may also be a source of error. Given the different composition of flesh and epidermis, total acidity may vary. The instrument analyses the sample with the epidermis intact, so the depth of the analysis in the apple and the resulting ratio of flesh to skin could also introduce errors in the measurements.

- The initial pH of each batch of 10 apples is another possible source of error because it varies widely due to the composition of the apple juice. This factor increases the dispersion in the data.
- The age of the pH meter and its probe are another source of error because wear and tear alters the instrument's accuracy over time. This can lead to biased and erroneous measurements. A state-of-the-art tool should reduce these measurement errors.
- The standard method of analysing acidity involves a time interval between obtaining the juice and the end of the titration measurement. This time interval introduces a risk of oxidation of the juice because the sample remains exposed to the ambient air for several minutes before analysis.

The error in the results for acidity may also be explained by the lack of data: the 72 batches produced only 72 spectra. Increasing the sample size could provide a larger and potentially more reliable dataset. In addition, year-to-year variations also introduce errors, which could be accounted for by using the "round-robin method".

The acidity could also be linked to ethylene production and apple respiration, where organic acids become an energy source. This phenomenon may be linked to the establishment of an anaerobic system in the apple during storage in a controlled atmosphere with a very low oxygen concentration. The energy provided by the organic acids could lead to the production of various other acids in the fruit [38].

Finally, acidity measurements may be affected by the fruit size and water content. A larger and more hydrated apple would dilute the acidic components, thereby reducing the acidity of larger apples. Therefore, acidity may correlate with the water content and apple size as well as the apple ripeness.

3.3.6. Predicting Ripeness Index from NIR Spectra

Predicting the ripeness index of Pink Lady apples using NIR spectra would reduce the time required to obtain this data. This index could be estimated based on predictions of the fruit's sugar content and total acidity. To predict the ripeness index, we used NIR spectra averaged over batches of 10 apples, with a total of 72 batches.

Numerous models were tested with various methods of data preprocessing, and the models were ranked based on their RPD value for the training set. The model with the best RPD for the training set (1.83) is based on averaged data with first derivative preprocessing. The wavelengths range from 908 to 1645 nm. Figure 12 shows the projection of the predicted data against the actual ripeness index. The dispersion in the results is important, which is reflected by an R^2 of 0.1 and an RMSE of 0.4.

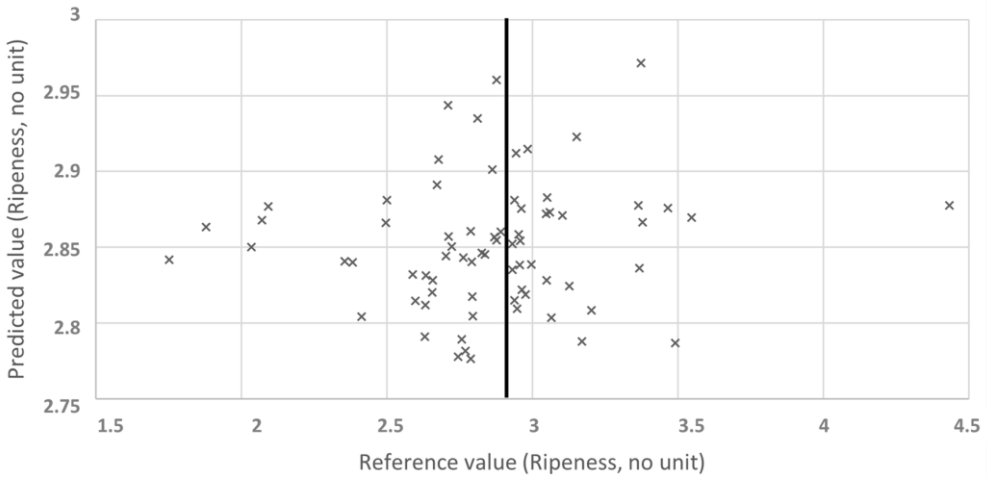

Figure 12. Predicted maturity obtained by applying the predictive model to the training database versus measured maturity data.

Only cross-validation tests were implemented because there were too few samples for external validation. Given that only 72 spectra were available to build the model, the addition of further data would be expected to improve the model's accuracy.

In conclusion, the model for predicting the apple ripeness index via NIR spectra may be used to classify samples with respect to a threshold, visually estimated in this work to be around 2.8. However, the model is not sufficiently accurate to obtain reliable results on new samples.

The model's accuracy may depend partly on the accuracy of sugar measurements, which could be improved by using electronic equipment. In addition, the complexity of sugars in Pink Lady apples could also influence the results.

The predicted results may also be affected by apple acidity, because standard methods of measuring acidity are inadequate, and variations in oxidation or enzymatic activity can influence the results of such measurements. In addition, the total acidity measured includes several different acids, which can degrade the accuracy of acidity predictions.

Finally, histology may also affect apple ripeness. The composition and structure of flesh and epidermal tissues can affect the various parameters measured.

4. Conclusions

The aim of this study was to test a portable NIRS device that can be used in the field to quickly and easily determine the ripeness of Pink Lady apples in a non-destructive manner based on the associated physicochemical parameters. For Pink Lady apples, an NIR sensor can acquire spectra from any quarter of the apple, but it is necessary to acquire spectra from at least the median zone along with either the top or bottom pole. This approach ensures that the measurements account for any slight variations, even though Pink Lady apples are generally homogeneous in maturity for such analyses.

Although juiciness is correctly predicted, sugar is not, mainly due to the data acquisition method and the nature of the sugars, which can influence the results. For firmness, the prediction is correct when using a classification system. This differentiation could be due to the presence of the epidermis during spectral acquisition, resulting in differences in composition and resistance. For acidity, the prediction is not sufficiently accurate for direct use in the field. The lack of data and the diversity of acids in Pink Lady apples may explain this inaccurate prediction. However, the study reveals that sugar, juiciness and firmness are correlated with each other, so predicting juiciness can already enable us to predict a level of ripeness. Thus, the handheld Micro-NIRS may be used in the field to non-destructively assess the ripeness of Pink Lady apples.

The ripeness index of Pink Lady apples can be predicted by applying a model built on NIRS data. However, the model performance is not entirely satisfactory due to difficulties in predicting acidity and sugar. Improving these predictions would produce a more reliable model.

This study thus demonstrates the use of a handheld device to non-destructively predict the ripeness of Pink Lady apples. It discusses the physicochemical parameters of Pink Lady apples during ripening and evaluates the ability of the handheld Micro-NIRS to predict these parameters. In addition, the study provides a better understanding of the differences in NIR absorption for the different zones of Pink Lady apples (height and quarter).

The spectra collected from different zones of the apples do not fully reflect the colour variations of Pink Lady apples, despite specifications requiring red colouration covering one-third to one-half of the surface. This difference could influence spectral measurements, which explains the importance of homogenising scans by including an equal number of areas of different colours (e.g., red, yellow) [39]. The literature reports that colour can indicate ripeness, as in the case of Fuji apples, where specific wavelengths (535–560 nm and 835–855 nm) are used to predict ripeness. However, although the wavelengths used in our analysis (908–1676 nm) do not directly capture colour variations, they provide relevant information on ripeness based on information on water content and sugars, which are essential for assessing apple quality. Thus, although our approach does not specifically

target colouration, it provides information about other crucial indicators of ripeness and overall fruit quality [15].

Future work may consider how the epidermis affects the accuracy of predictive models (because the epidermis affects data acquisition). It would also be interesting to explore how the model works at different stages of apple maturity and to reproduce these analyses over several harvests. The results could be compared with those of other apple varieties, such as Gala or Granny Smith, to reveal differences linked to variety-specific metabolisms.

An in-depth study of skin characteristics and how they affect measurements should improve our understanding of the models and explain their performance. The availability of a handheld NIRS instrument would simplify the selection of fruit for harvest, the sorting of batches for sale, and analyses based on ripeness or physicochemical parameters. This method, which is rapid and economical compared with traditional techniques, would also reduce environmental impact by reducing waste and the use of chemicals. Finally, such a device could be used by nonexperts and would allow them to estimate the physicochemical parameters and ripeness of Pink Lady apples.

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Conflicts of Interest: Amandine Arnal was employed by the company Absoger. The remaining author declares that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest. Jean Brustel was employed by the company LIDEA FRANCE. The remaining author declares that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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