TESTING OF A NIR SYSTEM FOR THE OPTIMIZATION OF STORED APPLES MANAGEMENT

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ABSTRACT Non destructive and rapid tools in fruit production are required to monitor fruit quality during postharvest period for a better preservation during storage. An automatic desk Vis/NIR system (QS_200, Unitec spa®) was tested to predict fruit quality during postharvest phases in the wavelength range 600-1200 nm. The aim of the work was to select homogeneous lots of apples in a non destructive way to manage cold store at best. A total of 1152 apples (Golden Delicious and Stark Red Delicious) were analyzed with Vis/NIR device in order to classify apples in two different ripeness classes (ripe and not ripe). PLS regression models were built on the samples of the two apple varieties. Models based on spectral data of Vis/NIR device show, for both varieties, good prediction skills for soluble solids content and firmness. Seven monthly samplings were done during the whole period of apples conservation in cold store with controlled atmosphere in a storage centre in Valtellina (Lombardia, Italy). TSS and firmness predictions carried out with Vis/NIR device were compared with analytical data obtained by standard destructive analysis. The 72% of the analyzed samples of Golden Delicious and the 69% of Stark Red Delicious show a difference from reference value lower than 1° Brix. Encouraging results were obtained for firmness evaluation too. This study based on class selection in a non destructive way with QS_200 system pointed out that is possible to select homogeneous lots of fruits in order to optimize cold store management and plan their opening sequence on fruits features.

Keywords: Apple, Vis/NIR spectroscopy, non destructive analysis

INTRODUCTION

Apples produced in the European Union represent about 20% of total world apple production (about 60 million tons). Italy is the biggest producer among EU member countries. Italian apple production is about 2 million tons and it covers a specialized land surface of about 77,000 hectares. Apple production, though widespread throughout Italy, is concentrated in Trentino Alto Adige, Emilia Romagna, Veneto, Campania and Piemonte. These regions produce 90% of the apples grown in the country. The
technologies developed for product conservation (low temperature and controlled humidity), allow a long storage of apple maintaining their physical, chemical and sensorial characteristics. This is also made possible by the particular consistency of the apple skin and of the waxy layer (pruina) on its surface that creates a barrier preventing the evaporation of water from the fruit. Until just a few years ago, the control of the quality of the fruit and vegetables pulp required the use of invasive methods which inevitably resulted in the destruction of the sample. These techniques also required lengthy preparation of samples, the occasional use of solvents, long analysis times, the use of specialized trained personnel and significant costs. Such a long and laborious methodology meant that only a few samples from every batch could be tested. Today, innovative technologies based on NIR and Vis/NIR spectroscopy has opened up new ways for testing which are not encumbered by any of the above mentioned inconveniences (Baranski, Baranska & Schultz, 2005), (Xing, Bravo, Moshou, Ramon & De Baerdemaeker, 2006), (Peirs, Lammertyn, Ooms & Nicolai, 2001). The use of Vis/NIR spectroscopy for the testing of product quality is simple, quick, non-destructive and applicable to a great number of samples. It is based on the measurement of the optical properties of the fruit and on the correlation between the spectral response given by the instrument and the content of a chemical component or a physical property of the fruit. The apple is the type of fruit which has been most involved in the experimentation of non-destructive testing methods to determine a variety of sensorial parameters. The results achieved have encouraged the inclusion of other sophisticated problems related to fruit firmness (Harker, Maindonald, Murray, Gunson, Hallett & Walker, 2002), (Mehinagic, Royer, Bertrand, Symoneaux, Laurens et. Al, 2003) and in particular farinosity (Farkas, Whalen, Strasser, Shennk & Ramon, 2003), problems inside the pulp (Wulf, Herppich, Geyer & Zude, 2003), chlorophyll content (Zude-Sasse, Truppel & Herold, 2002) and nutraceutic compounds (Merzlyak, Solovchenko & Gitelson, 2003).

The purpose of this work was the use of a desk sorting system, able to quickly evaluate in a non-destructive way by Vis/NIR technology the total soluble solids (TSS) content and the degree of firmness of apples, in order to separate the harvest apples in two different ripeness classes (ripe and not ripe). In this way it will be possible to optimise apple storing.

MATERIALS AND METHODS

Vis/NIR system. An automatic desk Vis/NIR system (QS_200, Unitec spa®, fig. 1) was tested to predict fruit quality during postharvest phases in the wavelength range 600-1200 nm. The sensor head takes measurements of reflections and the registered spectra are used to compute a PLS regression models which give a quick quantitative estimate of the quality indexes for batches of unknown apples of the two studied varieties.

Principal elements of QS_200 Vis/NIR system:

- halogenous light source
- fiber optic probe
- spectrometer Vis/NIR (600-1200 nm)
- PC and specific software which manages the data acquisition process in a automated way

Figure 1 – Image of QS_200 desk system and particular of spectral acquisition process

**Apple sampling.** Apples sampling was carried out in the town of Ponte in Valtellina (Sondrio, Italy). It involved the two most representative apples varieties of Valtellina production: ‘Golden Delicious’ and ‘Stark Red Delicious’.

Sampling process consists of three phases. During the first one 200 apples were analyzed, 100 of each variety, both with traditional techniques (firmness and total soluble solid content) and innovative technologies (QS_200). With this data it was possible to create a model used to classify both varieties in two classes, “not ripe” and “ripe”. During the second phase only QS_200 Vis/NIR system was used for the classification of 576 apples for each cultivar, according to two level of ripeness, for a total of 1152 samples analyzed. All the samples classified were stored in modified atmosphere cold storage (1% O2 and 2.5-3% CO2). During the third phase, 72 Golden Delicious apples (36 classified by the QS_200 as ripe and 36 as not ripe) and 72 Stark Red Delicious apples (36 ripe and 36 not ripe) were taken monthly to follow the evolution of quality parameters during the shelf-life. Each month samples were analyzed both with the Vis/NIR device and with destructive testing to verify the accuracy of the system.

**Destructive analysis.** The total soluble solids (TSS) were determined by a digital portable refractometer (Atago DBX-55).

Consistency measurements were performed by the Instron Universal Machine (mod. 4301 Instron Ltd High Wycomd, UK) equipped with a 1kN load cell and cylindrical probe (4 mm diameter). The measurements were made using a cross-head speeds of 2 mm*s⁻¹. The firmness (J) was calculated as the energy needed to penetrate the pulp.

**Data processing.** Chemometric analysis was performed using The Unscrambler software package (Version 9.8, CAMO ASA, Trondheim, Norway). The Vis/NIR spectra were correlated with ripening parameters (TSS and firmness) using the Partial Least Square (PLS) regression algorithm. In PLS regression latent variables (LV) are combined one by one to realize an orthogonal matrix. Each LV is oriented along directions of maximal covariance between the spectral matrix X and the response vector Y. In this way it is ensured that the latent variables are ordered according to their relevance for predicting the
Y-variable. Interpretation of the relationship between X-data and Y-data (the regression model) is then simplified as this relationship is concentrated on the smallest possible number of latent variables. The PLS method performs particularly well when the various X-variables express common information, i.e., when there is a large amount of correlation, or even co-linearity, which is the case for spectral data of intact biological material (B.M. Nicolai et al., 2007).

To evaluate the model accuracy the statistics used were the correlation coefficient in calibration (r_{cal}), the root mean standard error of calibration (RMSEC), the coefficient of correlation in cross-validation (r_{eval}) and the root mean standard error of cross-validation (RMSECV).

Correlation coefficient (r_{cal} or r_{eval})

\[
 r_{cal} \quad \text{or} \quad r_{eval} = \sqrt{1 - \frac{\sum_{i=1}^{n} (y_i - \hat{y}_i)^2}{\sum_{i=1}^{n} (y_i - \bar{y})^2}} \quad (1)
\]

with y_i the reference values and \( \hat{y}_i \) the predicted values by the PLS-model; \( \bar{y} \) is the averaged reference value.

Standard error of calibration/prediction (RMSEC or RMSECV)

\[
 \text{RMSEC or RMSECV} = \sqrt{\frac{\sum_{i=1}^{n} (y_i - \hat{y}_i)^2}{n}} \quad (2)
\]

with n the number of validated objects, \( \hat{y}_i \) and \( y_i \) the predicted and measured value of the \( i^{th} \) observation in the calibration or cross-validation set, respectively. This value gives the average uncertainty that can be expected for predictions of future samples. The optimum calibrations were selected in order to minimize the RMSECV.

RESULTS AND DISCUSSION

A total of 200 apples, 100 of each variety, were analyzed both with traditional techniques (TSS and firmness) and with innovative technologies (QS_200) for the creation of PLS regression model. These models were subsequently used to classify apples in two different ripeness classes (ripe and not ripe).

Vis/NIR spectra and PLS regression model built on ‘Stark Red Delicious’ samples for TSS are shown in Fig. 2. The most important statistic parameters to evaluate the model accuracy, both for TSS and firmness, are reported in table 1. Quite good results were obtained particularly for TSS for both variety with r values around 0.8 coupled with low standard error.
Figure 2 - Vis/NIR spectra and Calibration and Cross-validation line of PLS-model built on ‘Stark Red Delicious’ samples for TSS (°Brix)

Table 1. Results of PLS models for Golden Delicious and Red Delicious samples

<table>
<thead>
<tr>
<th>Golden Delicious</th>
<th>LV</th>
<th>CALIBRATION</th>
<th>VALIDATION</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>r</td>
<td>RMSEC</td>
</tr>
<tr>
<td>TSS (° Brix)</td>
<td>5</td>
<td>0.76</td>
<td>0.56</td>
</tr>
<tr>
<td>Firmness (Joule)</td>
<td>5</td>
<td>0.72</td>
<td>3.48</td>
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</table>

<table>
<thead>
<tr>
<th>Stark Red Delicious</th>
<th>LV</th>
<th>CALIBRATION</th>
<th>VALIDATION</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>r</td>
<td>RMSEC</td>
</tr>
<tr>
<td>TSS (° Brix)</td>
<td>5</td>
<td>0.82</td>
<td>0.68</td>
</tr>
<tr>
<td>Firmness (Joule)</td>
<td>1</td>
<td>0.75</td>
<td>4.32</td>
</tr>
</tbody>
</table>

After classification, apples of both variety were stored in a storage centre with controlled atmosphere. Seven monthly samplings were done during the whole period of apples conservation to study their shelf-life.
During sampling, moreover, TSS and firmness predictions carried out with QS_200 Vis/NIR device were compared with analytical data obtained by destructive analysis. During the whole sampling a total of 576 spectra were acquired for each variety.

![Graph showing TSS evolution during controlled atmosphere storage for 'Golden Delicious' apples](image)

**Figure 3 - Evolution of TSS during controlled atmosphere storage for the 2 ripeness classes for ‘Golden Delicious’ apples**

Trend analysis during storage shows the effectiveness of the classification with Vis/NIR device. Separation between the two selected classes was good during the storage time for both parameters analyzed. For example Fig. 3 shows the evolution of TSS during controlled atmosphere storage for the 2 ripeness classes for ‘Golden Delicious’ apples.

The differences between the data estimated by the system and the reference data were calculated for each sample. An acceptability threshold corresponding to an error in the estimates of 10% has been defined. For this aim 1 °Brix was chosen like threshold value for TSS and 3 Joule for firmness. In Fig. 3 and 4 results for TSS and firmness for ‘Golden Delicious’ are shown.

![Histogram showing frequency of error for predicted data compared to reference results on ‘Golden Delicious’ samples for TSS](image)

**Figure 3 - Frequency of error for predicted data compared to reference results on ‘Golden Delicious’ samples for TSS. Different colors show acceptability threshold corresponding to an estimation error of about 10%**
Figure 4 - Frequency of error for predicted data compared to reference results on ‘Golden Delicious’ samples for Firmness (penetration energy of apple pulp). Different colors show acceptability threshold corresponding to an estimation error of about 10%.

The graphs show good results for the ‘Golden Delicious’ with 72% of the predictions showing a difference from reference value less than 1 °Brix for TSS. Slightly worse results were obtained for firmness, with only 63% of samples with a prediction error below 10%.

Fig. 5 and 6 show results for TSS and firmness for ‘Stark Red Delicious’ apples.

Fig. 5 - Frequency of error for predicted data compared to reference results on ‘Stark Red Delicious’ samples for TSS. Different colors show acceptability threshold corresponding to an estimation error of about 10%.

For the ‘Stark Red Delicious’ variety, the best results were achieved for the prediction of TSS which showed a difference of less than 1 °Brix in 69% of the samples. Results were not good instead for the prediction of firmness, with only 50% of the samples with a difference from the reference values of less than 3 Joules.
Fig. 6 - Frequency of error for predicted data compared to reference results on ‘Stark Red Delicious’ samples for Firmness (penetration energy of apple pulp). Different colors show acceptability threshold corresponding to an estimation error of about 10%

CONCLUSION

In this work, a desk sorting system based on Vis/NIR technology was tested with the aim of selecting homogeneous lots of apples in a non destructive way to optimize the apple storing.

Models based on spectral data of Vis/NIR device show, for both varieties, good prediction ability for TSS and firmness. Seven monthly samplings were done during the whole storage time, in order to analyze apples shelf-life. Every month, TSS and firmness predictions carried out with Vis/NIR device were compared with analytical data obtained by standard destructive analysis. The 72% of the analyzed samples of Golden Delicious and the 69% of Stark Red Delicious show a difference from reference value lower than 1° Brix. Encouraging results were obtained for firmness evaluation too.

The system was able to classify in a quick and non-destructive way fruits both at harvest and during storage. This study based on non destructive class selection with QS 200 system point out the possibility to select homogeneous lots of fruits in order to optimize cold store management and plan their opening sequence on fruits features.

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