Determination of internal apple quality by non-destructive visible and near infrared spectroscopy

E. Moons and P. Dardenne

CRAGx, Département Qualité des Productions Agricoles, Chaussée de Namur 24, B-5030 Gembloux, Belgium.

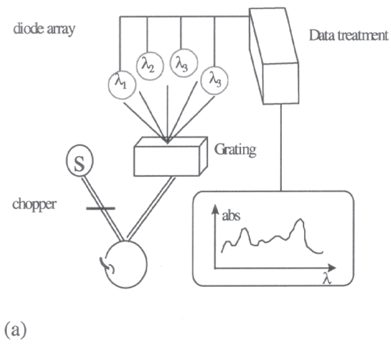
Introduction

At the present time, grading apples is only based on the external aspect. Fruits are sorted visually and manually according to their size and colour. Apples with surface defects such as scabs, breaks and bruises are discarded. But fruit eating quality is mainly related to chemical parameters like sugars, acidity, dry matter and to physical parameters like firmness. For non-destructive determination of these parameters, infrared techniques proved successful in several cases: determination of dry matter in onions,[1] potatoes[2] and whole dates,[3] internal quality in peaches, nectarines,[4] raisins[5] and pineapples.[6]

Some non-destructive near infrared (NIR) reflectance methods have been specially applied to predict sugar content in apple. On a data set of 320 apples sugar content could be predicted with an error of prediction of 6.8 g L^{-1} and a correlation coefficient of 0.96.[7] The Cemagref team in Montpellier developed an NIR spectrometer, coupled with optical fibres, to determine sugar at the speed of three apples per second. The standard error of prediction (*SEP*) was 2.4 g L^{-1} of glucose.[8]

In Japanese packing sheds, NIR spectroscopy is used for the determination of sugar and acidity in apples, pears and peaches. The sensors, called Multi Purpose Sensor (MPS) are manufactured by Mitsui Mining and Smelting Co. Ltd. Three apples were sorted per second.[9]

The aim of our study is to develop a grading machine capable of classifying apples according to the prediction of their internal quality parameters.



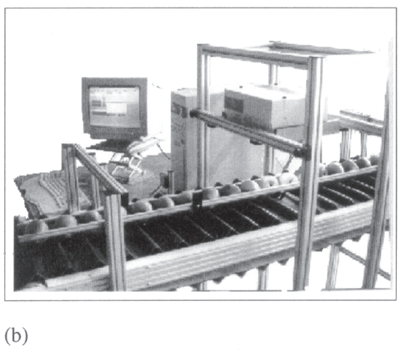


Figure 1. Schematic view (a) and picture (b) of the post dispersive diode array instrument.

Materials and methods

Instrument

A DA 7000 NIR spectrometer from Perten Instruments was used in this study [Figure (1a)]. The polychromatic beam falls onto the sample. Part of the beam enters into the sample, undergoes multiple scattering and exits the sample. The reflected light is sent to the grating, split into wavelengths and then collected by the diode array detectors. Diode array detectors are made of silicium detectors for the visible and the beginning of the NIR range (400–1098 nm) and of gallium arsenite for the NIR range (1100–1700 nm) with a spectral resolution of 5 nm. With these kinds of detectors the whole signal is acquired within one second. Each spectrum is the average of 600 scans. Moreover the large area illuminated by the spectrometer allows measurement of non-homogeneous samples like fruits. Spectralon@ was used as the reference. For the on-line measurement, the instrument is positioned above the conveyor belt [Figure 1(b)]. The spectral data are processed by the DA 7000 software and ISI V4 (Foss-Infrasoft International, Port Matilda, PA, USA).

Sampling

Samples were collected over a three year (1996–1998) period just before harvest, at harvest and during storage in order to cover most of the variability of the studied parameters. The apples were selected among the main varieties growing in Belgium (Jonagold, Golden delicious, Boskoop, Jonagored, Granny Smith). The fruits were obtained directly from the orchards during the harvest or, otherwise, were purchased in large supermarkets.

Physical and chemical analyses

Fruit firmness measurements were achieved with a penetrometer (QTS 25, Quality and testing systems) which monitors the maximum force to compress the apple flesh with a probe of 1 cm^2 surface area at the speed of 100 mm min^{-1}. The four measurements performed around the apple were averaged to obtain a global reference value. The brix value was determined by a manual refractometer, Atago N20, DB-55 (accuracy: ± 0.1°Brix) on the juice extracted from the whole fruit. Apple juice acidity was titrated with a solution of NaOH 0.1 N to pH 8.2. Dry matter content was measured by drying chopped flesh of the apple at 65°C for 24 hours. pH and diameter were determined by a pHmeter WTW (Wissenschaftlich-Technische-Werkstätten GmbH) and a gauge.

Results and discussion

Non-homogeneity inside the apple

The different parameters vary according to their location inside the apple: radially, from base to apex and from sunned to shaded sides of the fruit. The NIR *SEP* takes this factor into account and cannot be more accurate than this variability. To get an idea of the intra fruit variability, four measurements of the same parameter were made around the same apple for a set of 30 Jonagolds. Mean, maximum, minimum and standard deviations are reported in Table 1.

Apple set

In order to increase variability in the calibration set and to gain robustness, some apples were measured three times at different temperatures from 4°C to room temperature (20°C). The number of samples (*N*), mean, standard deviation (SD) minimum and maximum levels (range) of the parameters under investigation are given in Table 2.

Table 1. Chemical and physical reference values of a 30 Jonagold set for the study of spatial variation within apple.

Jonagold	*N*	Mean	*SD*	Min.	Max.
Brix	30	13.0	0.34	11	17
Hardness	30	5.6	0.38	4	9
pH	30	3.7	0.10	3	7
Acidity	30	7.0	0.88	3	12
Dry matter	30	15.5	0.50	6	34

N: number of samples
SD: Standard deviation

Table 2. Chemical and physical reference values of studied parameters of apple set.

	N	Range	Mean	*SD*	Unit
Brix	793	9.20–19.4	13.64	1.53	%
pH	719	2.40–4.17	3.53	0.25	
Acidity	773	2.83–21.99	8.49	4.90	ml of NaOH/1N 10 ml of juice
Hardness	828	3.43–11.38	6.04	1.44	Kg cm^{-2}
Dry matter	537	7.37–20.64	15.20	2.34	%
Diameter	759	6.54–9.73	7.69	0.45	cm

Apple spectra

The apple spectrum (Figure 2) exhibits three major absorption bands of water in the vicinity of 955, 1155 and 1460 nm. The other less visible bands of sugar show near 885, 1380 and 1435 nm.

Figure 3 illustrates the classification results obtained with the two first dimensions calculated by PCA. The set of samples was mainly composed by the Jonagolds. This explains the rather large area covered by this variety. Golden and Boskoop spectra occupy specific areas.

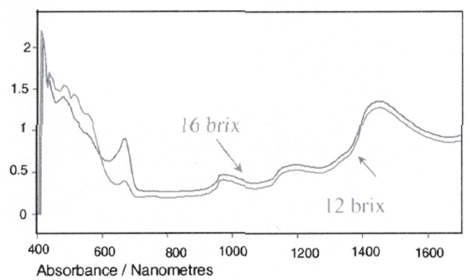


Figure 2. Spectra of apples with different levels of brix.

Calibration results

Calibrations are carried out using the modified partial least square (MPLS) method[10] which uses all the wavelengths to develop the equation. The calibration routinely automatically runs cross-validations (four groups) and gives the standard error of cross-validation (*SECV*) and the determination coefficient of validation (R^2V).

The raw spectral data are corrected by a standard normal variate and detrend treatment

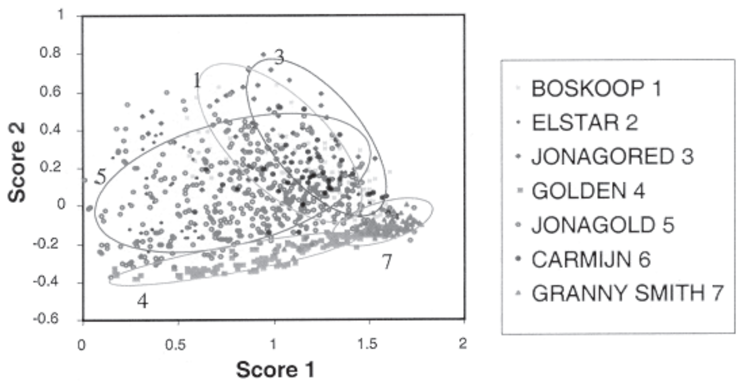


Figure 3. Representation of different apple varieties spectra in the PCA space.

(*SNVD*). This mathematical treatment combines the detrending (elimination of the increasing level of the log 1/*R* reflectance values over the range 400 to 1700 nm) and the standard normal variate corrections.

The highest correlations between the spectra and the reference values are found by using the second derivative spectra. This method reduces spectral variations due to radiation scattering and sample size. Calibration results obtained are shown in Table 3.

Conclusions

Calibration results were obtained by using an MPLS regression method on the second derivative spectra. The statistical performances of the predictive models were: $R^2V = 0.89$ and $SECV = 0.49$ for brix, $R^2V = 0.78$ and $SECV = 0.09$ for pH, $R^2V = 0.75$ and $SECV = 1.39$ for titrable acidity, $R^2V = 0.67$ and $SECV = 0.83$ for hardness, $R^2V = 0.84$ and $SECV = 0.78$ for dry matter and $R^2V = 0.80$ and

Table 3.Calibration and cross-validation results for the determination of quality parameters.

	SEC	R^2	*SECV*	R^2V	PLST
Brix	0.48	0.89	0.49	0.88	11
pH	0.09	0.78	0.09	0.77	9
Acidity	1.32	0.77	1.39	0.75	11
Hardness	0.79	0.70	0.83	0.67	11
Dry Matter	0.73	0.86	0.78	0.84	8
Diameter	0.19	0.82	0.20	0.80	8

SEC: Standard error of calibration
RSQ: Determination coefficient of calibration
SECV: Standard error of cross-validation (4 groups)
RSQV: Determination coefficient of cross validation
PLST: Number of PLS terms

SECV = 0.20 for diameter. If the ratio SD/*SECV* is superior to 3, quantitative predictions can be achieved. This was the case for brix (3.12), acidity (3.52) and dry matter (3). The ratio for the other parameters was lower than 3 and only allowed classifications. The results of this study demonstrated that several quality attributes can be measured on each whole apple allowing the use of DA 7000 for practical commercial sorting and, therefore, apples can be easily graded into homogeneous batches of quality.

Acknowledgment

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