

1 **DETERMINATION OF INTERNAL APPLE QUALITY BY NON-**
2 **DESTRUCTIVE VISIBLE AND NIR SPECTROSCOPY**

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7
8 *Abstract*

9 *The goal of this study is the development of a grading machine capable of classifying apples*
10 *according to their internal quality. For this purpose a DA 7000 NIR spectrometer from*
11 *Perten Instruments was used. This post dispersive polychromator generates spectra from 400*
12 *to 1700 nm with a spectral resolution of 5 nm. The non-destructive reflectance spectrum was*
13 *taken along the equator on the whole apples. Apples from three years were measured (1996-*
14 *1998). Samples were selected among the main varieties commercialised in Belgium and cover*
15 *most of the variability of studied parameters. Modified partial least square regression method*
16 *based on the NIR spectra (math treatment 2,3,3,1) and lab values, gave good results.*
17 *Determination coefficients and standard errors of prediction obtained for a set of 800 apples*
18 *are : 0.89/0.49 for brix, 0.75/1.39 for titrable acidity, 0.86/0.78 for dry matter, 0.78/0.09 for*
19 *pH, 0.70/0.83 for firmness, 0.80/0.20 for diameter. In order to meet the expectations of*
20 *package storage houses and store markets, the feasibility of on-line application of the method*
21 *was investigated. To fulfil these requirements, the instrument was installed above a conveyer*
22 *belt and the scanning speed was increased to obtain a spectrum in 0.03 second.*

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24 Keywords: apple grading, near-infrared, diode array, internal quality, non destructive quality
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1. 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 the 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 reflectance NIR 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 0.96⁷. The Cemagref team of Montpellier developed an NIR spectrometer coupled with optical fibres to determine sugar at the speed of three apples per second. Standard error of prediction 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 commercialised by Mitsui Mining and Smelting Co., LTD. Three apples were sorted per second ⁹.

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

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54 **2. Material and method**

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56 2.1. Instrument

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58 A DA 7000 NIR spectrometer from Pertten Instruments was used in this study (Figure 1a).

59 The polychromatic beam falls onto the sample. Part of the beam enters into the sample,

60 undergoes multiple scattering and exits the sample. The reflected light is sent to the grating,

61 split into wavelengths and then collected by the diode array detectors. Diode array detectors

62 are made of silicium detectors for the visible and the beginning of NIR range (400 to 1098

63 nm) and of gallium arsenite for the NIR range (1100 to 1700 nm) with a spectral resolution of

64 5 nanometers. With these kinds of detectors the whole signal is acquired within 1 second.

65 Each spectrum is the average of 600 scans. Moreover the large area illuminated by the

66 spectrometer allows to measure non homogeneous samples like fruits.

67 Spectralon[®] was used as the reference.

68 For the on line measurement, the instrument is positioned above the conveyor belt (Figure

69 2b).

70 The spectral data are processed by the DA 7000 software and ISI V4 (Foss-Infrasoft

71 International).

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73 2.2. Sampling

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75 Samples were collected over a three years (1996-1998) period just before harvest, at harvest
76 and during storage in order to cover most of the variability of the studied parameters. The
77 apples were selected among the main varieties growing in Belgium (Jonagold, Golden
78 delicious, Boskoop, Jonagored, Granny Smith...). The fruits were obtained directly from the
79 orchards during the harvest and otherwise, were purchased in big store markets.

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81 2.3. Physical and chemical analyses

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83 Fruit firmness measurements were achieved with a penetrometer (QTS 25, Quality and
84 testing systems) which monitors the maximum force to compress the apple flesh with a probe
85 of 1 cm² surface area at the speed of 100 mm/min. The four measurements performed around
86 the apple, were averaged to obtain a global reference value. The brix value was determined by
87 a manual refractometer, Atago N20, DBX-55 (accuracy : ±0.1 Brix) on the juice extracted
88 from the whole fruit. Apple juice acidity was titrated by a solution of NaOH 0.1N to pH 8.2.
89 Dry matter content was measured by drying chopped flesh of the apple at 65°C during 24
90 hours. pH and diameter were determined by a pHmeter WTW (Wissenschaftlich-Technische-
91 Werkstätten, GmbH) and a gauge.

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94 **III. Results and discussion**

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96 3.1. Non homogeneity inside the apple

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

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105 3.2. Apple set

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

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112 3.3. Apple spectra

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

117 Figure 2 illustrates the classification results obtained with the two first dimensions calculated
118 in the PCA. The set of samples was mainly composed by the Jonagolds. This explains the

119 rather large area covered by this variety. Golden and Boskoop spectra occupy specific areas.

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121 3.4. Calibration results

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123 Calibrations are conducted by the modified partial least square (MPLS) method¹⁰ which uses
124 all the wavelengths to develop the equation. The calibration routine runs automatically cross
125 validations (4 groups) and gives the standard error of cross validation (SECV) and the
126 determination coefficient of validation (R^2V).

127 The raw spectral data are corrected by a standard normal variate and detrend treatment
128 (SNVD). This mathematical treatment combines the detrending (elimination of the increasing
129 level of the $\log 1/R$ reflectance values over the range 1000 to 1700 nm) and the standard
130 normal variate corrections (decreasing the effect of particle size).

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

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136 **III. Conclusions**

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138 Calibration results were obtained by using a Modified Partial Least Square (MPLS)
139 regression method on the second derivative of the spectra. The statistical performances of the
140 predictive models were: $R^2V=0.89$ and $SECV=0.49$ for brix, $R^2V=0.78$ and $SECV=0.09$ for
141 pH, $R^2V=0.75$ and $SECV=1.39$ for titrable acidity, $R^2V=0.67$ and $SECV=0.83$ for hardness,
142 $R^2V=0.84$ and $SECV=0.78$ for dry matter and $R^2V=0.80$ and $SECV=0.20$ for diameter. If the
143 ratio $SD/SECV$ is superior to 3, quantitative predictions can be achieved. This was the case
144 for brix (3.12), acidity (3.52) and dry matter (3). The ratio for the other parameters was

145 inferior to 3 and allowed only classifications. The results of this study, demonstrated that
146 several quality attributes can be measured on each whole apple allowing the use of DA 7000
147 for practical commercial sorting and therefore apples can be easily graded into homogeneous
148 batches of quality.

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151 **Acknowledgment**

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154 Ministry, research and development DG6.

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157 **References**

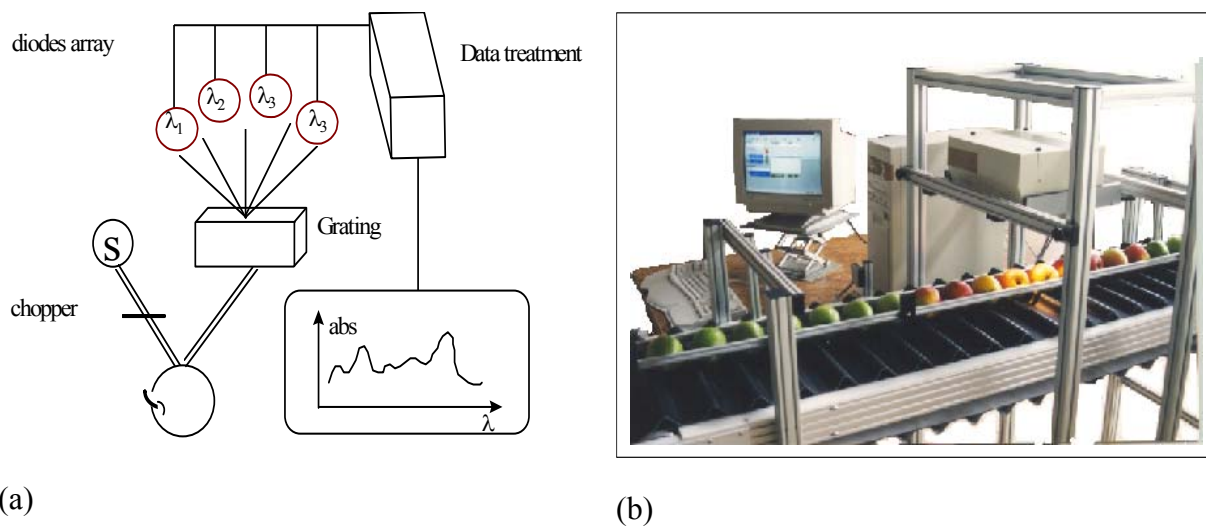
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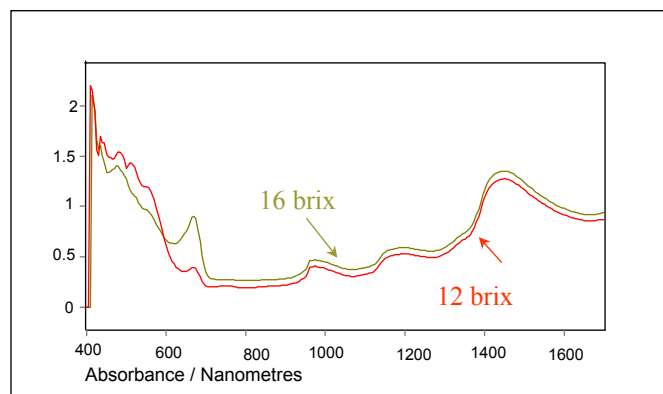
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177 **Figures**



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



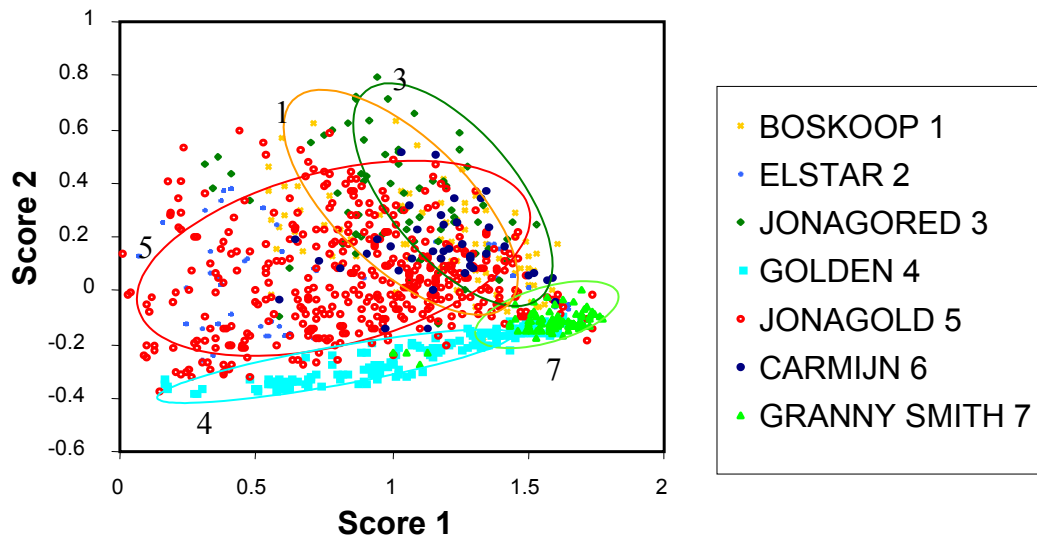
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Figure 2: Spectra of apples with different level of brix

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

185 **Table 1** : Chemical and physical reference values of a 30 Jonagold set for the study of spatial
 186 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

187 N : number of sample

188 **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 NaOH0.1N/ 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

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193 **Table 3:** Calibration and cross validation results for the determination of quality parameters.

	SEC	RSQ	SECV	RSQV	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

194 SEC: Standard error of calibration SECV: Standard error of cross validation (4 groups)

195 RSQ: Determination coefficient of calibration RSQV: Determination coefficient of cross validation

196 PLST: Number of PLS terms

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