Food Chemistry 115 (2009) 1133–1140

Contents lists available at ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

Analytical Methods

Application of ATR-FTIR for a rapid and simultaneous determination of sugars and organic acids in apricot fruit

Sylvie Bureau [a,*], David Ruiz [b], Maryse Reich [a], Barbara Gouble [a], Dominique Bertrand [c], Jean-Marc Audergon [b], Catherine M.G.C. Renard [a]

[a] UMR408 Sécurité et Qualité des Produits d'Origine Végétale, INRA, Université d'Avignon, Site Agroparc, F-84000 Avignon, France
[b] Unité de Génétique et d'Amélioration des Fruits et Légumes, INRA, Domaine Saint Maurice, BP94, F-84143 Montfavet, France
[c] UMR1124 Sensométrie Chimiométrie, ENITIAA, INRA, F-44300 Nantes, France

ARTICLE INFO

Article history:
Received 1 July 2008
Received in revised form 12 September 2008
Accepted 24 December 2008

Keywords:
Mid-infrared
PLS
Prunus armeniaca L.
Cultivars
Fruit quality
Maturation
PCA

ABSTRACT

A simple, fast and accurate Fourier transform mid-infrared spectroscopy method was developed for simultaneously determining sugar and organic acid contents in apricot fruit slurries using the attenuated total reflectance. The potential of this method coupled with chemometric techniques based on partial least squares was assessed by comparison with currently used enzymatic determination of sucrose, glucose, fructose, malic acid and citric acid. Fruits of eight contrasted cultivars harvested at different ripening stages were used in this study and randomly divided in a calibration set (505 apricots) and in a validation set (252 apricots). The most suitable region was found in the range between 1500 and 900 cm^{-1}. Good prediction performances were obtained ($R^2 \geqslant 0.74$ and RMSEP $\leqslant 18\%$). Results concerning the prediction of other quality traits such as firmness, skin colour, ethylene production, soluble solids content and titratable acidity were discussed.

1. Introduction

Apricot fruit quality is a multicomponent concept, defined by physical, physiological and biochemical attributes such as firmness, skin and flesh colour, ethylene production, respiration rate, sugars, organic acids, pigments, phenolic compounds and volatiles (Audergon, Souty, Breuils, Reich, & Duffillol, 1989; Guillot et al., 2006; Gurrieri, Audergon, Albagnac, & Reich, 2001; Marty et al., 2005; Ruiz, Egea, Gil, & Tomas-Barberan, 2005). Most instrumental techniques currently required for measuring these parameters are long, expensive and involve a considerable amount of manual work. Therefore, there is a demand for new and rapid analytical methods for assessing quality attributes. Recently, Fourier transform mid-infrared (FT-MIR) spectroscopy has become a well-accepted method for the determination of food constituents since it achieves high analysis speed and requires little or no sample preparation. FT-MIR spectroscopy often coupled with chemometrics has been used to study different quality attributes in many food samples including fruits, vegetables or beverages e.g. epicuticular wax of apple (Veraverbeke, Lammertyn, Nicolaï, & Irudayaraj, 2005), olive pulp cell-wall polysaccharides (Coimbra, Barros, Rutledge, & Delgadillo, 1999), polymethoxylated flavone of orange oil residues (Manthey, 2006), vitamin C in powdered mixture and liquid (Yang & Irudayaraj, 2002). FT-MIR spectroscopy has been widely used for must and wine analysis (Fernandez & Agosin, 2007; Patz, Blieke, Ristow, & Dietrich, 2004; Urtubia, Pérez-Correa, Pizarro, & Agosin, 2008). Moreover, it has become an alternative method for sugar analysis (Bellon-Maurel, Vallat, & Goffinet, 1995), in food such as mango juices (Duarte, Barros, Delgadillo, Almeida, & Gil, 2002), cane juices (Cadet & Offmann, 1997), soft drinks and fruit juices (Ramasami et al., 2004). More recently, this technique has been applied for the analysis of acids in fruits, and in particular apple and tomato (Beullens et al., 2006; Irudayaraj & Tewari, 2003). On the other hand, FT-MIR has been used for the authentication or for the detection of adulteration of many fruit-based products (Defernez, Kemsley, & Wilson, 1995) and for the discrimination or classification of foods such as wine and honey according to their origin (Bertelli, Plessi, Sabatini, Lolli, & Grillenzoni, 2007; Edelmann, Diewok, Schuster, & Lendl, 2001).

Abbreviations: FT-MIR, Fourier transform mid-infrared; ATR, attenuated total reflectance; SSC, soluble solids content; TA, titratable acidity; RMSEP, root mean square error of prediction; LV, latent variables; RMSEC, root mean square error of calibration; RMSEP, root mean square error of prediction.

* Corresponding author. Tel.: +33 432722509; fax: +33 432722492.
E-mail address: sylvie.bureau@avignon.inra.fr (S. Bureau).

0308-8146/$ - see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.foodchem.2008.12.100

A precedent paper presents the usefulness of ATR-FTIR reflectance spectroscopy to accurately predict the content of individual sugars and organic acids in apricot fruits using a small number of samples (50 samples) and the "leave-one-out" cross-validation test (Bureau, Reich, Marfisi, Audergon, & Albagnac, 2006). On a larger variability of apricot fruits and a larger number of samples, the prediction of soluble solids content and titratable acidity using the external cross-validation was shown in apricot fruit using the non-destructive near-infrared spectroscopy (Bureau et al., 2009). Here, the objective was to evaluate the potential of the ATR-FTIR as a fast technique to predict the main traits involved in organoleptic quality of apricot fruit. The prediction has been evaluated for individual sugars, organic acids and complementary quality traits such as fruit firmness, skin colour, ethylene production, soluble solids and titratable acidity through the comparison with standard techniques. A large diversity of fruits covering genetic factor and physiological stages was used in this work. The sample set was designed to be representative of the variability observed in the apricot species. Samples belonging to eight cultivars harvested at different stages of ripening were used as a calibration set. The prediction models for each quality parameters were developed with partial least square (PLS) technique using the external cross-validation.

2. Materials and methods

2.1. Selection of apricot fruit samples

Eight apricot cultivars or hybrids, named 'Moniqui', 'Goldrich', 'Bergeron', 'Iranien', 'Badami', 'Ravicille', 'Ravilong' and 'A4034' were chosen for their contrasted fruit quality traits such as colour, taste, physiological behaviour. To obtain a wide range of fruit composition, apricot fruits were collected from June 22nd to August 2nd, during the maturation period, from the beginning of ethylene production to the full maturity. A total of 757 fruits were collected in 2005. Fruits came from two INRA experimental orchards (Amarine (Gard) and Gotheron (Drôme), South of France) for 'Moniqui', 'Goldrich', 'Iranien', 'Badami', 'Bergeron' and 'A4034', and from a traditional private orchard (Donzère, Drôme, South of France) for 'Ravicille' and 'Ravilong'.

2.2. Experimental procedure

Immediately after harvest, fruits were transported in an air-conditioned car to the laboratory where they were carefully selected to ensure that fruits were free of defects. Non-destructive measurements were performed the day of picking. ATR-Mid-infrared reflectance measurements and conventional destructive measurements (SSC, TA, individual sugars and organic acids) were carried out a few days later on frozen materials. Each apricot was individually characterised for its quality traits and spectral data.

2.3. Determination of quality traits using reference analyses

Fruit firmness was determined by the pressure (kPa) required to achieve a 3% deformation of fruit height with a multipurpose texture analyser (Pénélaup®, Serisud, Montpellier, France). The skin colour (un-blushed and blushed sides) was determined using a CR-400 chromameter (Minolta, Osaka, Japan) and expressed in the CIE 1976 $L^*a^*b^*$ colour space (illuminant D65, 0° view angle, illumination area diameter 8 mm). Ethylene production rate was measured after 1 h of confinement of each fruit in a hermetically closed jar by gas chromatography (IGC 121FL model, IGC Instruments, France) equipped with a flame ionization detector (FID) at 150 °C and fitted with a Porapak Q column (3 m, particle size 80/100 mesh, Sigma–Aldrich, St. Louis, MO) operated at 120 °C. The carrier gas was nitrogen with a flow rate of 30 mL min^{-1}. After these non-destructive measurements, fruits were cut and frozen at −20 °C for a few days until biochemical analyses. Fruit pieces were ground with an Ultraturrax T25 equipment (Ika Labortechnik, Staufen, Germany) to obtain a slurry. Soluble solids content (SSC) was determined with a digital refractometer (PR-101 ATAGO, Norfolk, VA) and expressed in % Brix at 20 °C. Titratable acidity (TA) was determined by titration up to pH 8.1 with 0.1 N NaOH and expressed in meq 100 g^{-1} of fresh weight using an autotitrator (Methrom, Herisau, Switzerland). Sugars (glucose, fructose, sucrose) and organic acids (malic acid and citric acid) were quantified using an enzymatic method with kits for food analysis (Boehringer Mannheim Co., Mannhein, Germany) and expressed in g 100 g^{-1} of fresh weight for sugars and meq 100 g^{-1} of fresh weight for acids. These measurements were performed with an automatic analyser BM-704 (Hitachi, Tokyo, Japan).

2.4. ATR-Mid-infrared reflectance measurements

FT-IR spectra were recorded on a Tensor 27 spectrometer (Bruker Optics, Wissembourg, France) with a deuterated triglycine sulphate (DTGS) detector. It was equipped with a horizontal attenuated total reflectance (ATR) accessory composed of a zinc

Table 1
Mean, standard deviation (SD) and range of the observed apricot quality traits in both calibration and validation sample sets (an example of a random split of the fruits).

	Calibration (n = 505)			Validation (n = 252)		
	Mean	SD	Range	Mean	SD	Range
Weight (g)	59	12	28–116	60	13	31–97
Pressure (kPa)	121	91	5–508	118	97	6–537
L^* blush	54.1	11.4	29–76	53.8	11.5	30–77
a^* blush	20.8	12.6	−9–43	20.6	12.7	−8–43
b^* blush	32.1	10.5	9–52	31.8	10.5	5–52
L^* un-blush	64.8	6.6	39–81	64.6	7.0	41–81
a^* un-blush	8.6	12.2	−13–41	8.5	12.4	−14–42
b^* un-blush	42.7	7.4	17–57	42.4	7.6	14–55
Ethylene (nmole h^{-1} kg^{-1})	276	871	0.6–6322	312	952	1–5294
Ethylene (ln(nmole h^{-1} kg^{-1}))	3.7	0.2	2.7–4.0	3.7	0.2	3.2–4.0
SSC (% Brix)	12.3	2.4	6.6–21.7	12.5	2.5	6.9–22.2
TA (meq 100 g^{-1} FW)	23.2	8.1	4.4–42.5	23.5	8.1	5.6–40.6
Glucose (g 100 g^{-1} FW)	2.2	0.7	0.7–4.9	2.2	0.7	0.6–5.1
Fructose (g 100 g^{-1} FW)	0.8	0.3	0.3–1.9	0.8	0.3	0.2–1.7
Sucrose (g 100 g^{-1} FW)	4.8	2.0	0.5–10.7	4.9	2.0	0.3–11.7
Citric acid (meq 100 g^{-1} FW)	15.8	10.2	0.3–44.4	16.0	10.1	0.1–41.5
Malic acid (meq 100 g^{-1} FW)	10.6	7.0	0–30.1	10.4	6.9	0–27.7

SSC: soluble solids content, TA: titratable acidity, FW: fresh weight.

selenide (ZnSe) crystal with six internal reflections (crystal area: 60 × 10 mm). The depth of penetration in apricot slurry was 0.5 μm at 4000 cm^{-1} and 3 μm at 650 cm^{-1}. The spectrometer was completely software-controlled by the OPUS software version 5.0 provided by Bruker Optics. The spectrum of each sample was obtained by taking the average of 32 scans at a resolution of 4 cm^{-1}. It was acquired between 4000 and 650 cm^{-1}, with scanner velocity of 10 KHz and a background of 32 scans. The reference spectra were recorded using a blank ATR crystal every twenty samples. The time required to achieve a spectral measurement was 30 s. The measurements were performed on apricot slurries prepared for the standard analyses of SSC, TA, sugars and organic acids. Each slurry was put on the ZnSe crystal for measurements. Between measurements the crystal was carefully cleaned using distilled water and dried with filter paper.

For determining the spectra of pure compounds, aqueous solutions were prepared at 0.1 g mL^{-1}. The solution was put on the ZnSe crystal for measurements with the same conditions used for apricot slurries.

2.5. Spectra processing and statistical treatment of data

The ATR-FTIR reflectance data were transformed with standard normal variate (SNV) to correct multiplicative interferences, variations in baseline shift and curvilinearity (Barnes, Dhanoa, & Lister, 1989). Before the calibration, the spectral variation was analysed

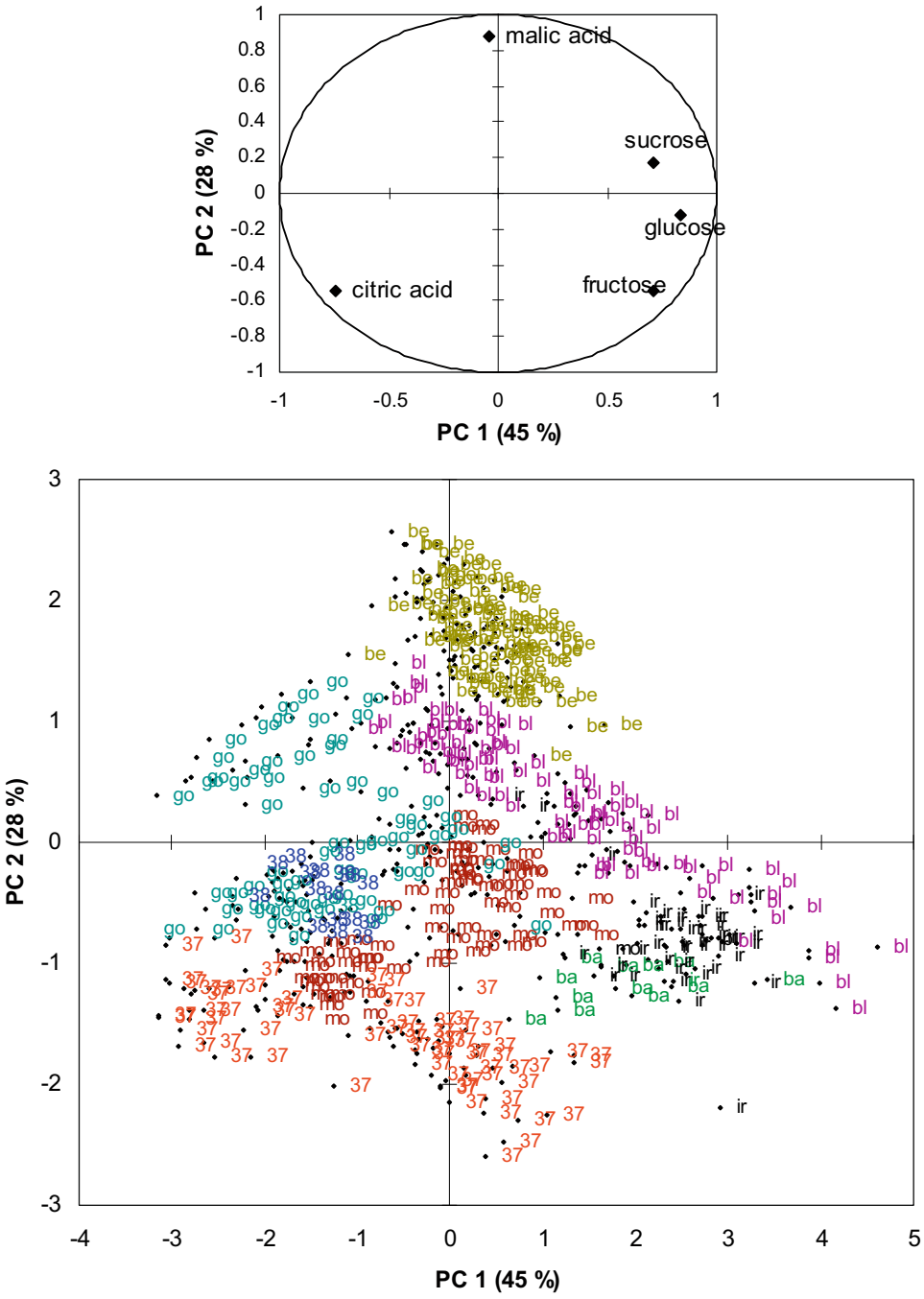


Fig. 1. Results of principal component analysis (PCA) based on enzymatic measurements of individual sugars and organic acids in eight apricot cultivars harvested at different ripening stages. Bi plot of the two first PCs. mo: Moniqui; go: Goldrich; be: Bergeron; ir: Iranien; ba: Badami; 38: Ravicille; 37: Ravilong and bl: A4034.

by principal component analysis (PCA) and defective spectra were eliminated (only aberrant spectra due to a problem of acquisition).

The PLS regression method was used to develop models for predicting the composition of apricot fruits (Haaland & Thomas, 1988). In PLS, both the spectral matrix *X* and the reference data in the data matrix *Y* are used for the calibration. The *X* and *Y* matrices are reduced to a few factors (latent variables) using all of the available information.

The whole spectral collection eventually included 757 spectra, each corresponding to a single fruit. In order to carry out a validation test, the data set was randomly split, with no repeat, into two subsets: two third of the fruits (505 observations) were used for calibration and one third (252 observations) was used for validation. This procedure was repeated 10 times, in order to select the appropriate dimension of the PLS model.

The performance of the calibration models and the number of latent variables (LV) (up to a maximum of 15) were evaluated by the root mean square error of calibration (RMSEC), the root mean square error of prediction (RMSEP) and the determination coefficient (R^2) between the predicted and the measured parameters. Acceptable models should have low RMSEC and RMSEP, high R^2 and small differences between RMSEC and RMSEP. Large differences indicate the introduction of too many PLS factors (latent variables) in the model.

The pre-processing (SNV) and calculations were carried out under SAISIR environment (Bertrand, 2008) and DESIR interface (Lecomte, 2007) in MatLab software package (version 7.2, MathWorks, USA).

3. Results and discussion

3.1. Diversity of apricot fruits

A synthetic view of the observed physical, physiological and biochemical traits is presented (Table 1). Chosen apricot fruits were contrasted for their colour (from white to red apricot skin), their firmness in relation with the ripening changes, their physiological activities (diversity in ethylene production in relation with ripening and genetic factor) and their biochemical characteristics (more or less sweet and acidic with particular composition in sugars and organic acids). According to the already known variability on apricot species (Audergon et al., 1989; Gurrieri et al., 2001), the data set appeared representative of the expected variation on the related quality traits and well adapted for this study. A principal component analysis (PCA) of the individual sugars and organic acids in apricot slurries was carried out (Fig. 1). The PC-plot of PCA illustrates the large variability of the eight apricot cultivars. The correlation plot (Fig. 1, top) shows that the first PC-score (PC1) is highly correlated with glucose, sucrose and fructose. This component is thus related to the variation of these sugars and probably to the degree of ripeness, their content increasing during fruit ripening. The second PC-score (PC2) is highly positively correlated with malic acid and negatively correlated with citric acid. This component opposes apricot fruit compositions dominated by malic acid from those dominated by citric acid. Moreover, the contents of malic acid and citric acid decrease during fruit ripening. The scattering of the fruits on the PC-plot (Fig. 1, bottom) is thus related to their sugar and organic acid composition and ripeness. For example, on the left, the cultivar 'Goldrich' coded *go* appeared to be less sweet than 'Iranien' cultivar coded *ir*, on the right. According to their respective composition (results not shown), at full maturity, the soluble solids content of 'Goldrich' cultivars is about 11% Brix whereas the one of 'Iranien' cultivar is about 16% Brix. The change of fruit composition during ripening (from the left to the right) can be clearly observed with 'A4034' cultivar coded *bl*. In these apricots, the soluble solids content increases from about 10 to about 15% Brix, the content of malic acid (the dominant acid) decreases from about 18 to about 9 meq 100 g^{-1} FW and the content of citric acid decreases from about 11 to about 6 meq 100 g^{-1} FW. Moreover, the acid composition is opposed between 'Bergeron' coded *be* and 'Ravilong' coded *37*. Indeed, 'Bergeron' composition is dominated by malic acid (about 16 meq 100 g^{-1} FW), its content in citric acid being about 7 meq 100 g^{-1} FW. Inversely, the composition of 'Ravilong' is dominated by citric acid (about 19 meq 100 g^{-1} FW), its malic acid content being about 6 meq 100 g^{-1} FW.

3.2. ATR-FTIR spectra analysis

The spectra of apricot slurry observed between 4000 and 650 cm^{-1} show three absorption zones: 3700–2800 cm^{-1}, 1800–1470 cm^{-1} and 1500–900 cm^{-1}. The first two are assigned to water. The third corresponds to the absorption region of the apricot major components, particularly sugars and organic acids. Sucrose, glucose, fructose, malic and citric acids show intense and characteristic bands in the region between 1500 and 900 cm^{-1} (Fig. 2a). The bands in the region 1500–1200 cm^{-1} are assigned to deformation of $-CH_2$ and angular deformation of C–C–H and H–C–O (Hineno, 1977). Those in the region 1200–950 cm^{-1} are explained by stretching modes of C–C and C–O (Pawan, Birch, & Green, 1973). The variations observed in the spectral region range from 1500 to 900 cm^{-1} are shown for different apricot cultivars (Fig. 2b).

Preliminary examinations of apricot slurry spectra were performed by PCA applied on the SNV corrected spectra in the range

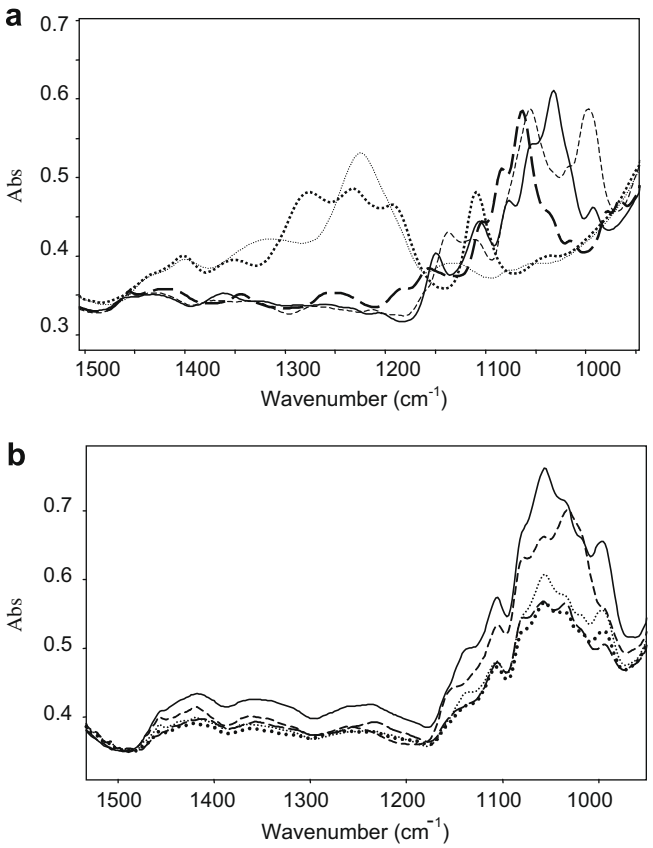


Fig. 2. ATR-FTIR spectra (1500 and 900 cm^{-1}) of standard aqueous solutions (a) and different apricot slurries (b) recorded using ZnSe six reflectance ATR cell. (a) Aqueous solutions at 0.1 g mL^{-1} of: Citric acid, Malic acid, Sucrose, Glucose, Fructose (b) apricot slurries of different cultivars: Badami, Iranien, Moniqui, Ravilong, Bergeron.

1500–900 cm^{-1}. We wanted to know if this technique allows the discrimination of apricot samples according to their ripening stages or to their genetic characteristics. So, data corresponding to the ripening of the 'A4034' cultivar and data corresponding to fruits harvested at full maturity of the eight cultivars ('Moniqui', 'Goldrich', 'Bergeron', 'Iranien', 'Badami', 'Ravicille', 'Ravilong' and 'A4034') are used and illustrated (Figs. 3 and 4).

The PCA of ATR-FTIR spectra acquired on 'A4034' apricots allows the visualisation of the change of apricot composition during their ripening between the first stage coded 1 (just before the beginning of ethylene production) and the fourth stage coded 4 (the full maturity) (Fig. 3). The groups 3 and 4 appeared to be not well separated according probably to the large variability of the fruits harvested at an interval of eight days. The PC loadings show the spectral variations responsible for this apricot discrimination. Region between 900 and 1450 cm^{-1} corresponding to the organic acid and sugar absorption is negatively correlated to the first component with a less contribution of the region between 1150 and 1300 cm^{-1} corresponding to a part of malic and citric acid absorptions. The same region between 1150 and 1300 cm^{-1} appears also to be the main contributor of the second component. So, the first axis discriminates A4034 apricots according to the change during ripening of their sugar and organic acid contents with the increase of sucrose, glucose and fructose and the decrease of malic and citric acids. The second axis discriminates these apricots in relation with their organic acid content and in particular with the citric acid content, which was measured to increase between the first and the second ripening stages and decrease after.

Moreover the PCA performed on the eight apricot cultivars at full maturity is shown in Fig. 4. Regions between 900 and 1150 cm^{-1} and between 1300 and 1500 cm^{-1} corresponding to the sugar absorption and a part of organic acid absorption are positively correlated to the first component. The main contributor of the second component is the region between 1150 and 1300 cm^{-1} corresponding to the citric acid absorption. So, the first axis separates apricots according to their sugar levels, cultivars 'Badami', 'A4034' and 'Iranien' being the richest in the three sugars. The second axis separates apricots according to their citric acid content. At the top of the graph, cultivars 'Ravilong', 'Ravicille', 'Goldrich' and 'Badami' have the highest citric acid content up to 18 mg 100 g^{-1} FW whilst at the bottom, its level is the lowest with less than 15 mg 100 g^{-1} FW in the cultivars 'Bergeron', 'A4034', 'Moniqui' and 'Iranien'. Thus, some separation of apricot cultivars can be observed on the basis of FTIR spectral characteristics in relation with the biochemical fruit quality. This separation could probably be increased by using a discriminant method such as canonical discriminant analysis, taking the cultivars as qualitative groups. Apricots rich in the three sugars (sucrose, glucose, fructose) are distinguished from the others and apricots rich in malic acid are separated from the others. The technique that consists in acquiring spectra on fruit slurries and performing PCA on spectra between 900 and 1500 cm^{-1} could be very useful for accessing a

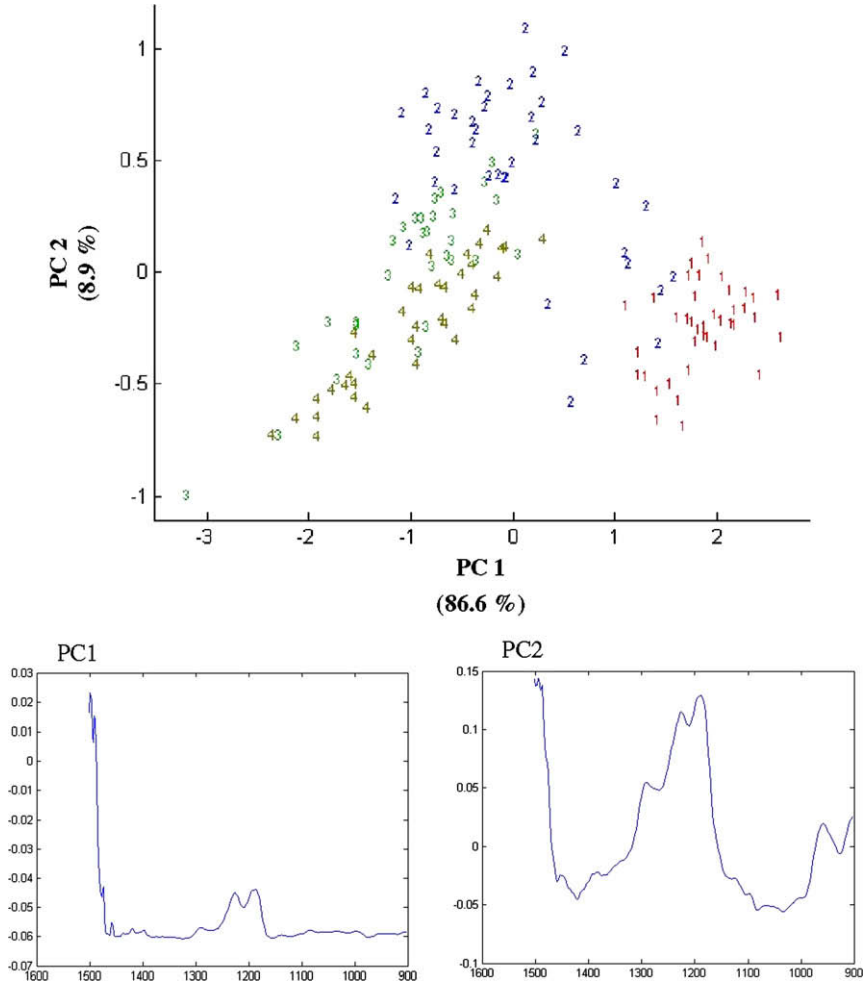


Fig. 3. Results of PCA of the apricot slurry FTIR spectra between 1500 and 900 cm^{-1}: example of A4034 apricot during ripening from (1) unripe and (4) full maturity. (a) scores plot of the first two PCs and (b) Loading plot of PC1 and PC2.

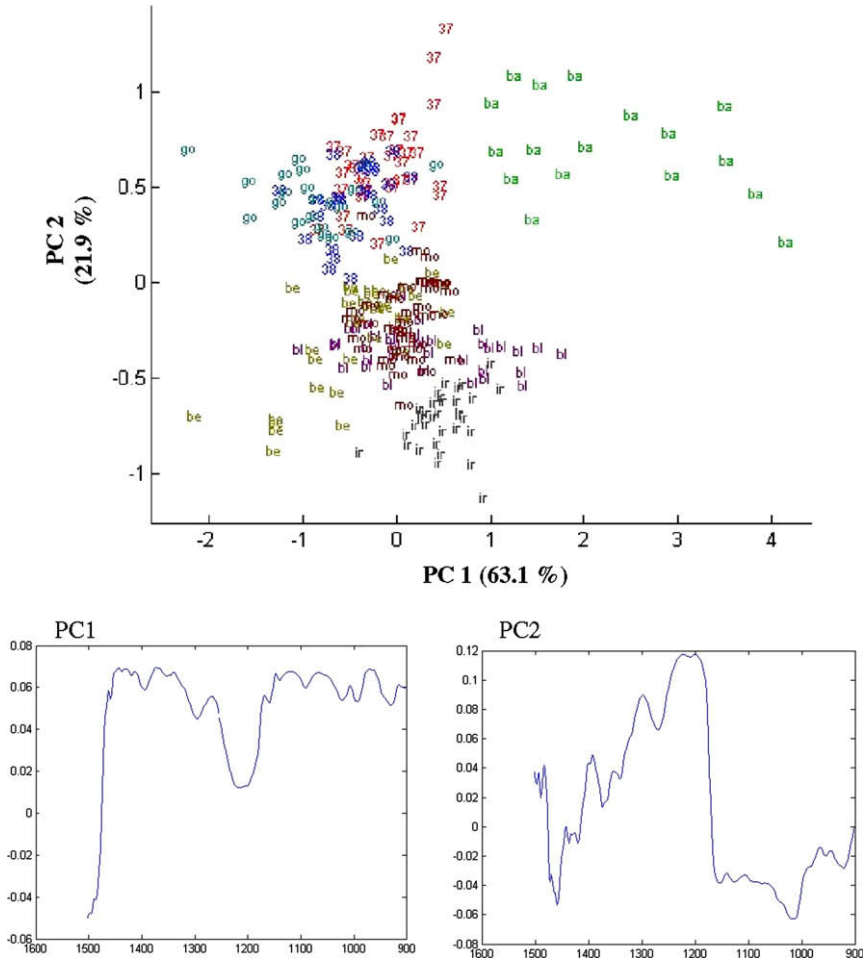


Fig. 4. Results of PCA of the apricot slurry FTIR spectra between 1500 and 900 cm^{-1}: example of eight apricot cultivars at full maturity. (a) Scores plot of the first two PCs and (b) Loading plot of PC1 and PC2. mo: Moniqui; go: Goldrich; be: Bergeron; ir: Iranien; ba: Badami; 38: Ravicille; 37: Ravilong and bl: A4034.

rapid global selection of genotypes with interesting fruit quality amongst a very large population in observation.

3.3. Prediction of individual sugars and organic acids

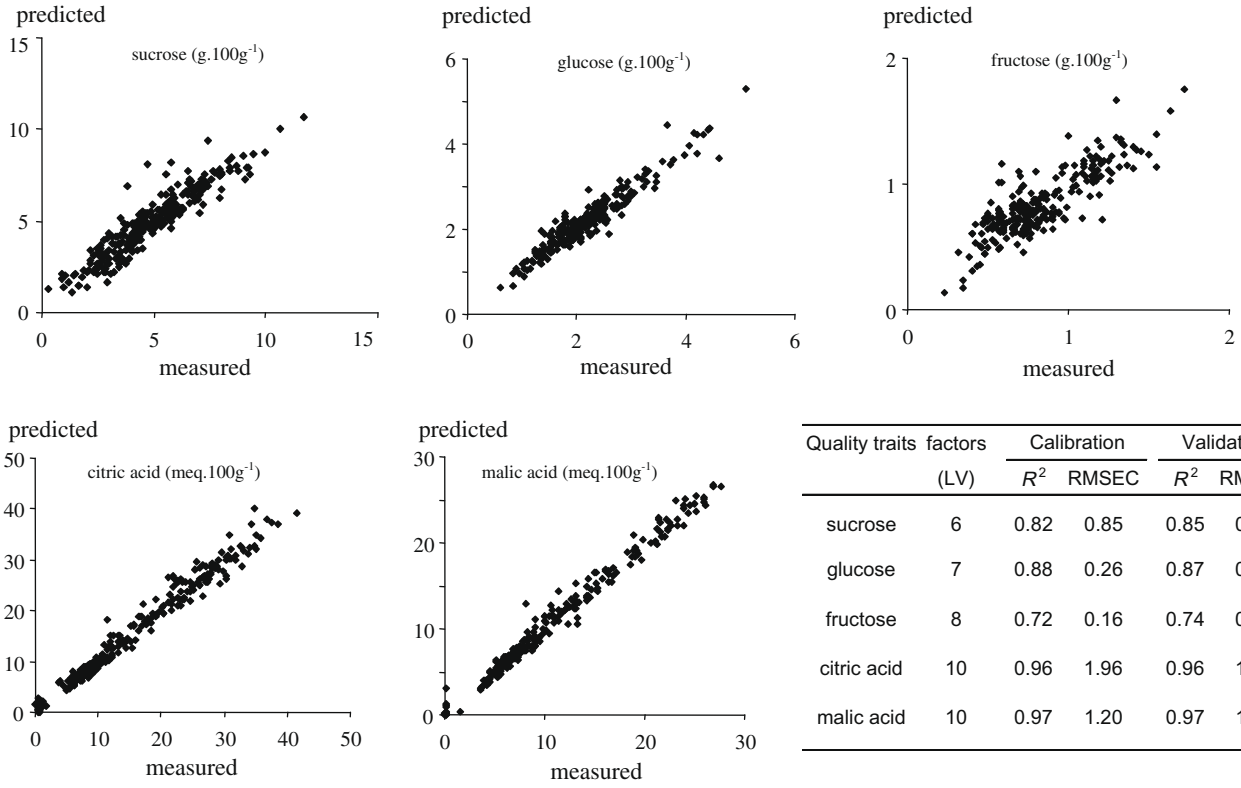
The spectral region between 1500 and 900 cm^{-1}, the most suitable region to quantify sugars and organic acids, was therefore used. The calibration models were built using the PLS method from data of 757 apricot slurries (505 for calibration and 252 for validation) for predicting apricot fruit contents of sucrose, glucose, fructose, malic acid and citric acid. Good correlations of calibration were found between ATR-FTIR spectra and content of sucrose, glucose, malic acid and citric acid with a determination coefficient (R^2) $\geqslant$ 0.82. When the model was applied to predict 252 other apricot slurries, the prediction results were similar with $R^2 \geqslant 0.85$ (Fig. 5). The root mean square error of calibration (RMSEC) was close to the root mean square error of prediction (RMSEP) for each compound. The errors of prediction represented about 12% for glucose, malic acid and citric acid and 16% for sucrose. The worst results were obtained for fructose, the minor sugar in apricot, with R^2 of prediction of 0.74 and an error of prediction of 18% (Fig. 5). The prediction equations, which link individual components to the spectral data, were established using between six and ten factors according to the compound.

So, determination of individual sugar and organic acid content in apricot could be considered simultaneously using the ATR-FTIR prediction equations obtained in this work.

The PLS-FTIR method has been shown to be suitable for predicting sucrose, glucose and fructose in soft drinks and food beverages with prediction errors ranged from 0 to 15.6% using calibration models performed on sugar aqueous mixtures (Sivakesava & Irudayaraj, 2000). The same method was used for the determination of sucrose, glucose and fructose changes in Mango of the 'Tommy Atkins' cultivar during a storage at 22 °C (Duarte et al., 2002). Sucrose and fructose were accurately quantifiable whereas glucose, remaining in low level, was predicted with an error of 25%. These authors have used a triangular model of standard sugar solutions for the calibration. A similar work has been performed on apple (Irudayaraj & Tewari, 2003). Calibration models to predict sucrose, glucose, fructose, sorbitol, citric and malic acid, were obtained on synthetic apple juice using PLS or PCR (Principal component regression) and then successfully validated on apple juices in comparison with the HPLC measurements (determination coefficient R^2 = 0.998). Using the PLS-FTIR and the cross-validation on four tomato cultivar juices, the best correlations with compound concentrations measured by HPLC were obtained for malic acid, fumaric acid, glucose, fructose and sucrose with coefficients of correlation of, respectively, 0.78, 0.89, 0.86, 0.77 and 0.73 (Beullens et al., 2006).

3.4. Prediction of complementary fruit quality traits

As for sugars and organic acids, the calibration models were built using the PLS method from data of 757 apricot slurries and



Quality traits	factors	Calibration		Validation	
	(LV)	R^2	RMSEC	R^2	RMSEP
sucrose	6	0.82	0.85	0.85	0.80
glucose	7	0.88	0.26	0.87	0.26
fructose	8	0.72	0.16	0.74	0.15
citric acid	10	0.96	1.96	0.96	1.99
malic acid	10	0.97	1.20	0.97	1.28

LV: latent variables or factors, R^2: coefficient of determination, RMSEC: root mean square error of calibration, RMSEP: root mean square error of prediction

Fig. 5. Prediction of individual components (sucrose, glucose, fructose, malic and citric acids) in apricot slurries (validation set: 252 apricots) using ATR-FTIR: measured values by enzymatic methods vs. ATR-FTIR predicted values.

the spectral region between 1500 and 900 cm^{-1}, for predicting ethylene production rate, firmness, colour, SSC and TA

High correlations were found for calibration between ATR-FTIR spectra and global biochemical data: soluble solids content (SSC) and titratable acidity (TA) values with R^2 of 0.94 and 0.97 and RMSEC of 0.84% Brix and 1.32 meq 100 g^{-1}, respectively (Table 2). When the models were applied to predict 252 other apricot fruits, the prediction results were similar with prediction errors of 4% and 4.7% respectively. The PLS models appeared to be robust with 6 and 7 factors respectively. ATR-FTIR method using the cross-validation have been used for determination of titratable acidity and soluble solids content in pomegranate juice concentrates with coefficients of determination of 0.91 and 0.99, respectively (Vardin, Tay, Ozen, & Mauer, 2008).

The physical parameters such as firmness (pressure required to achieve a 3% deformation of fruit height) and skin colour (a^* of the un-blushed side of fruit), are considered (Table 2). These two quality traits are commonly used to observe the fruit changes (softening and degreening) during ripening. The ATR-FTIR technique appears not suitable for their prediction. Good correlations for calibration and validation (R^2 = 0.80 and 0.84, respectively) were obtained for firmness but the error of prediction was high (29%). For the skin a^* value, the correlation were low ($R^2 \leqslant 0.70$) and the error of prediction was particularly high (75%). So, the substitution of compression test and colour measurement by the ATR-FTIR technique is not conceivable. These measurements are relatively rapid but require several fruit manipulations because of the use of the different techniques.

On the other hand, surprisingly good results are obtained for the prediction of ethylene production rate (ln(nmol kg^{-1} h^{-1})). Good correlations for calibration and validation (R^2 = 0.81 and 0.83, respectively) and acceptable errors of validation and prediction (0.86 and 0.84 nmol kg^{-1} h^{-1}, respectively) were obtained. An explanation could be that the prediction of ethylene production rate on apricot slurries using ATR-FTIR would be due to the correlation with a compound involved in the ethylene biosynthesis

Table 2
Results of ATR-FTIR calibration and validation performance for quality assessment of apricot fruits (Spectra performed on fruit slurries).

Quality traits	Range	Factors	Calibration (n = 505)		Validation (n = 252)	
		(LV)	r	RMSEC	r	RMSEP
SSC (%Brix)	1500–900	6	0.94	0.84	0.96	0.49
TA (meq 100 g^{-1}FW)	1500–900	7	0.97	1.32	0.98	1.10
Ethylene (ln(nmol h^{-1} kg^{-1}))	1500–900	9	0.81	0.86	0.83	0.84
Pressure (kPa)	1500–900	8	0.80	43.66	0.84	35.05
a^* un-blush	1500–900	10	0.70	6.23	0.68	5.42

SSC: soluble solids content, TA: titratable acidity, FW: fresh weight, LV: latent variables or factors, R^2: coefficient of determination, RMSEC: root mean square error of calibration, RMSEP: root mean square error of prediction.

pathway. The direct precursor of ethylene is 1-aminocyclopropane-1-carboxylic acid (ACC) and presents two major absorptions in the studied spectral region, at 1255 and 1410 cm^{-1}. But, according to some results obtained in our team (not published), the variation of ACC content would be between 0 and 1 mg 100 g^{-1} of FW in apricot fruits of hybrids issued from the crossing between 'Goldrich' and 'Moniqui' cultivars. The ACC content appears very low in apricot making its prediction using ATR-FTIR probably impossible. So, the prediction of ethylene production rate on apricot slurries using ATR-FTIR must be due to an internal correlation with ripeness and further work is thus needed to validate this predictive model. Concerning the fruit characterisation, ethylene production rate is an important quality trait because it is a marker for the maturity state of apricots. Moreover, compared to the method of reference, ATR-FTIR has been shown to be fast and easy applicable. So, its prediction may have an important practical use even if the prediction errors represented 22%.

4. Conclusion

In this paper we have established the possibility of using ATR-FTIR technique for determining soluble solids content, titratable acidity, individual sugars (sucrose, glucose, fructose) and organic acids (malic and citric acids) in apricot slurry. The time of analysis was considerably reduced compared to the current method using enzymatic assays for individual sugars and organic acids. The method was calibrated and cross-validated on fruits representative of the variability observed in apricot species. In fact, fruits of eight contrasted cultivars were used to establish pluri-cultivar models. We plan to check the robustness of these models on other apricot fruits, including different cultivars, harvested over years and issued from different orchards. The ATR-FTIR technique can be easily adapted to routine analysis in apricot industries.

Acknowledgment

This study was supported by department for Science and Process Engineering of Agricultural Products (CEPIA) of INRA and by Region Provence-Alpes-Côte d'Azur (PACA).

References

Audergon, J. M., Souty, M., Breuils, L., Reich, M., & Duffillol, J. M. (1989). Biochemical and physicochemical characterization of 400 apricot varieties. Consequences in the apricot selection and improvement process. *Acta Horticulturae, 293*, 111–120.

Barnes, R. J., Dhanoa, M. S., & Lister, S. J. (1989). Standard normal variate transformation and detrending of near infrared diffuse reflectance spectra. *Applied Spectroscopy, 43*, 772–777.

Bellon-Maurel, V., Vallat, C., & Goffinet, D. (1995). Quantitative analysis of individual sugars during starch hydrolysis by FT-IR/ATR spectrometry. 1. Multivariate calibration study-repeatability and reproducibility. *Applied Spectroscopy, 49*, 556–562.

Bertelli, D., Plessi, M., Sabatini, A. G., Lolli, M., & Grillenzoni, F. (2007). Classification of Italian honeys by mid-infrared diffuse reflectance spectroscopy (DRIFTS). *Food Chemistry, 101*, 1565–1570.

Bertrand, D. (2008). Dominique Bertrand, Unité de Sensométrie et de Chimiométrie ENITIAA-INRA, Rue de la Géraudiére – BP 82 225, 44322, Nantes, France. SAISIR©, Free procedures using MATLAB® for chemometrics. Available from: <http://easy-chemometrics.fr>.

Beullens, K., Kirsanov, D., Irudayaraj, J., Rudnitskaya, A., Legin, A., Nicolaï, B., et al. (2006). The electronic tongue and ATR-FTIR for rapid detection of sugars and acids in tomatoes. *Sensors and Actuators B, 116*, 107–115.

Bureau, S., Reich, M., Marfisi, C., Audergon, J. M., & Albagnac, G. (2006). Application of Fourier-Transform Infrared (FT-IR) spectroscopy for the evaluation of quality traits in apricot fruits. *Acta Horticulturae, 717*, 347–349.

Bureau, S., Ruiz, D., Reich, M., Gouble, B., Bertrand, D., Audergon, J. M., et al. (2009). Rapid and non-destructive analysis of apricot fruit quality using FT-Near-Infrared spectroscopy. *Food Chemistry, 113*, 1323–1328.

Cadet, F., & Offmann, B. (1997). Direct spectroscopic sucrose determination of raw sugar cane juices. *Journal of Agriculture and Food Chemistry, 45*, 166–171.

Coimbra, M. A., Barros, A., Rutledge, D. N., & Delgadillo, I. (1999). FTIR spectroscopy as a tool for the analysis of olive pulp cell-wall polysaccharide extracts. *Carbohydrate Research, 317*, 145–154.

Defernez, M., Kemsley, E. K., & Wilson, R. H. (1995). The use of infrared spectroscopy and chemometrics for the authentication of fruit puree. *Journal of Agriculture and Food Chemistry, 43*, 109–113.

Duarte, I. F., Barros, A., Delgadillo, I., Almeida, C., & Gil, A. M. (2002). Application of FTIR spectroscopy for the quantification of sugars in mango juice as a function of ripening. *Journal of Agriculture and Food Chemistry, 50*, 3104–3111.

Edelmann, A., Diewok, J., Schuster, K. C., & Lendl, B. (2001). Rapid method for the determination of red wine cultivars based on mid-infrared spectroscopy of phenolic wine extracts. *Journal of Agriculture and Food Chemistry, 49*, 1139–1145.

Fernandez, K., & Agosin, E. (2007). Quantitative analysis of red wine tannins using Fourier-Transform Mid-Infrared spectrometry. *Journal of Agriculture and Food Chemistry, 55*, 7294–7300.

Guillot, S., Peytavi, L., Bureau, S., Boulanger, R., Lepoutre, J. P., Crouzet, J., et al. (2006). Aroma characterization of various apricot varieties using headspace-solid phase microextraction combined with gas chromatography-mass spectrometry and gas chromatography-olfactometry. *Food Chemistry, 96*, 147–155.

Gurrieri, F., Audergon, J. M., Albagnac, G., & Reich, M. (2001). Soluble sugars and carboxylic acids in ripe apricot fruit as parameters for distinguishing different cultivars. Use of principal component analysis to characterize apricot fruit quality. *Euphytica, 117*, 183–189.

Haaland, D. M., & Thomas, E. V. (1988). Partial least-squares methods for spectral analyses. 1. Relation to other quantitative calibration methods and the extraction of qualitative information. *Analytica Chimica Acta, 60*, 1193–1202.

Hineno, M. (1977). Infrared spectra and normal vibrations of D-glucopyranose. *Carbohydrate Research, 56*, 219–227.

Irudayaraj, J., & Tewari, J. (2003). Simultaneous monitoring of organic acids and sugars in fresh and processed apple juice by Fourier transform infrared-attenuated total reflection spectroscopy. *Applied Spectroscopy, 57*, 1599–1604.

Lecomte, A. (2007). Alain Lecomte, Plantes et Systèmes de culture Horticoles, INRA-Avignon, Domaine St Paul, 84914, Avignon, France.

Manthey, J. A. (2006). Fourier transform infrared spectroscopic analysis of the polymethoxylated flavone content of orange oil residues. *Journal of Agriculture and Food Chemistry, 54*, 3215–3218.

Marty, I., Bureau, S., Sarkissian, G., Gouble, B., Audergon, J. M., & Albagnac, G. (2005). Ethylene regulation of carotenoid accumulation and carotenogenic gene expression in colour-contrasted apricot varieties (Prunus armeniaca). *Journal of Experimental Botany, 56*, 1877–1886.

Patz, C. D., Blieke, A., Ristow, R., & Dietrich, H. (2004). Application of FT-MIR spectrometry in wine analysis. *Analytica Chimica Acta, 513*, 81–89.

Pawan, G. L. S., Birch, G. G., & Green, L. F. (1973). *Molecular structure and function of food carbohydrates*. London: Applied Science Publishers. p. 65–80.

Ramasami, P., Jhaumeer-Laulloo, S., Rondeau, P., Cadet, F., Seepujak, H., & Seeruttun, A. (2004). Quantification of sugars in soft drinks and fruit juices by density, refractometry, infrared spectroscopy and statistical methods. *South African Journal of Chemistry, 57*, 24–27.

Ruiz, D., Egea, J., Gil, M. I., & Tomas-Barberan, F. A. (2005). Characterization and quantification of phenolic compounds in new apricot (*Prunus armeniaca* L.) varieties. *Journal of Agriculture and Food Chemistry, 53*, 9544–9552.

Sivakesava, S., & Irudayaraj, J. (2000). Determination of sugars in aqueous mixtures using mid-infrared spectroscopy. *Applied Engineering in Agriculture, 16*, 543–550.

Urtubia, A., Pérez-Correa, J. P., Pizarro, F., & Agosin, E. (2008). Exploring the applicability of MIR spectroscopy to detect early indications of wine fermentation problems. *Food Control, 19*, 382–388.

Vardin, H., Tay, A., Ozen, B., & Mauer, L. (2008). Authentification of pomegranate juice concentrate using FTIR spectroscopy and chemometrics. *Food Chemistry, 108*, 742–748.

Veraverbeke, E. A., Lammertyn, J., Nicolaï, B. M., & Irudayaraj, J. (2005). Spectroscopic evaluation of the surface quality of apple. *Journal of Agriculture and Food Chemistry, 53*, 1046–1051.

Yang, H., & Irudayaraj, J. (2002). Rapid determination of vitamin C by NIR, MIR and FT-Raman techniques. *Journal of Pharmacy and Pharmacology, 54*, 1247–1255.