The Detection of Quality Deterioration of Apple Juice by Near Infrared and Fluorescence Spectroscopy

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Abstract. Processing and storage of apple juice often triggers quality deterioration regarding nutritional valuable compounds and unfavourable color changes resulting from browning. Fluorescence and near-infrared (NIR) spectroscopy were applied to detect such quality loss in apple juice. Juice samples were produced from Malus x domestica 'Pinova', stored at 20 ℃ for 4 days or heated at 80 ℃ for 10 min and stored at the same conditions. The quality of apple juice was measured by standard parameters such as soluble solids content, pH, CIE L*, a*, and b* values. Juice fluorescence spectra were recorded with fluorescence excitation at 250, 266, 355, and 408 nm and emission at 280-899 nm resulting in an excitation-emission-matrix (EEM) of 1240×4 for each sample. The NIR transmittance spectra were recorded in the wavelength range 900-1350 nm. The often used color b*-value for monitoring browning was correlated with the EEM variation and a reasonable calibration was built by means of n-way partial least squares (N-PLS) regression. The correlation coefficients were >0.9 in all treatments. NIR spectra were sensitive for predicting soluble solids content, but had poor capability to measure the color deterioration. Results indicated that the combination of NIR spectra and fluorescence EEM can be used to monitor the quality deterioration of apple juice.

Keywords: near infrared spectroscopy, fluorescence spectroscopy, EEM, N-PLS, apple juice.

1 Introduction

Apple juice is very popular due to its beneficial health effect and pleasant flavor. However, quality deterioration temporarily appears during the processing and storage. Enzymatic browning of damaged tissues of fruits during postharvest handling and processing is one of the main causes for quality loss of fresh fruit produce [1]. Enzymatic browning in fruit juice starts after the mechanical breakage of the apple

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cell integrity during the juice extraction procedure [2]. It is influenced by the substrate, which are phenolic compounds, polyphenoloxidases and influencing factors (ascorbic acid and peroxidases). The reaction is characterized by an initial enzymatic oxidation of phenols into slightly colored quinones and following polymerization. Non-enzymatic browning occurs mainly in thermal processing, which involves caramelization, ascorbic acid degradation and Maillard reaction [3].

Since quality is supremely important for apple juice, deterioration has to be controlled during processing and storage. Therefore, the fast and real-time detection of the extent of quality changes would provide a valuable tool. Conventionally, the quality of apple juice was measured by enzymatic and chromatographic methods [4], which are time-consuming and laborious. The browning degree has been formerly measured by colorimetry and the result expressed as CIE L*a*b* color system. However, all these methods have some disadvantages such as the tristimulus data is often influenced by physical changes [5].

As a fast, non-destructive and environmentally safe analyzing method, near infrared (NIR) spectroscopy was applied for measuring the quality of fresh juice with respect to sugar and water content [6,7]. Fluorescence spectroscopy was introduced to measure, e.g., bitterness in beer [8] or other parameters related to the content of auto fluorescent compounds. In the present study, NIR and fluorescence spectroscopy were applied to detect the quality deterioration of apple juice during processing and storage. The quantitative relation between variation in the NIR spectra, fluorescence spectra and the quality parameters of apple juice such as soluble solids content, pH, and color were investigated.

2 Materials and Methods

2.1 Preparation and Processing of Apple Juice

Malus x domestica 'Pinova' apples with differences in color and size for capturing a wide range of pigments and soluble solids contents were picked from an orchard in Germany and preserved at 4 ℃. The juice was extracted with a home juice extractor (Bifinett, Kompernass GmbH, Bochum, Germany). Two or three apples with similar color were consider as one sample and extracted. Totally, 30 samples were prepared. The core was eliminated, while the skin was reserved. The juice was centrifuged for 10 min with a speed of 3600 rpm and room temperature (16 ℃) (Sigma 4K 15, SIGMA Laborzentrifugen GmbH, Germany). Subsequently the juice was filtered and each sample was separated into two portions. One portion was measured immediately (marked as 'Fresh') and stored at 20 ℃ for 4 days (marked as 'stored'). The other portion was heated in a water bath (Victor Rector, Krankenhaus-Laborbedarf GmbH, Germany) at 80 ℃ for 10 min. The juice was cooled rapidly with an ice-water bath, and stored at 20 ℃. On the forth day, the spectra and reference values were measured (marked as 'heated-stored'). Resulting, three juice states were obtained.

2.2 Spectroscopic Readings

NIR spectra were measured using a UV-VIS-NIR scanning spectrophotometer (Lambda 950, PerkinElmer, USA). Because higher wavelength regions had significant noise and

the lower wavelength regions were almost flat, only the wavelength range of 900-1350 nm was collected. Spectral resolution was 1 nm. Distilled water was used as zero reference.

Fluorescence emission spectra were measured using a fluorescence spectrophotometer (LS55, PerkinElmer, USA) in front-face geometry at four excitation wavelengths (250 nm, 266 nm, 355 nm, and 408 nm). The corresponding emission spectra ranged from 280-899 nm, 296-899 nm, 385-899 nm, and 438-899 nm, respectively. Spectral resolution was 0.5 nm. Therefore, an EEM with the size of 1240×4 (emission×excitation) was obtained for each sample. Appropriate cut-off filters were used to prevent the influence of direct reflectance from the excitation light. Each sample was measured twice and the average spectra were considered as the output.

2.3 Measurement of Laboratory Reference Values

Soluble solids content (SSC) was measured with a digital refractometer (PR-1, Atago Co., Ltd, Japan). The pH was measured with a pH-meter (pH340i, WTW, Germany). Color measurement was made using a colorimeter (CM-2600d, Konica Minolta Sensing, Inc. Japan) based on the CIE L*a*b color system. SCI mode was selected because it considered the influence of specular component. The colorimeter was calibrated with dark and white references. A glass cell containing the apple juice was placed against the head of the colorimeter and the three color parameters, namely L*, a*, b*, were recorded. Each sample was measured three times and the average values were calculated. The color degradation (ΔL*, Δa*, Δb*) were calculated as the difference between the processed juice and fresh juice. Also, the total color change was calculated as follows:

$$\Delta E = ((\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2)^{0.5} \quad (1)$$

2.4 Data Processing

Partial least squares (PLS) regression was used to construct the calibration model between NIR spectra and reference values. Here, the optimal number of factors were selected by leave-one-out cross validation. For each model, the reference value was arranged with an ascending order, and then every third sample was selected as calibration set, and the remaining part provided the prediction set. The correlation coefficient and standard error for the prediction set were used to measure the model quality. The n-way partial least squares (N-PLS) analysis [9] was applied to build regression models between the fluorescence excitation-emission matrices (EEM) and laboratory reference values. Mean centering was used as data preprocessing for all spectra.

2.5 Software

PLS_Toolbox 3.0 (Eigenvector Research, Inc. Manson, WA, USA) was used for PLS calculation and N-PLS were constructed with the N-way toolbox [10]. All calibrations were carried out in the environment of MATLAB (2006a, The Math Works Inc., USA).

3 Results and Discussion

3.1 Characteristics of Spectra

The three dimensional EEM of the fresh juice (Fig. 1a) mainly represents the fluorescent polyphenols (such as hydroxycinnamic acid derivates) and chlorophyll. However, chlorophyll is mostly located in the skin and although apple juice was extracted from both skin and flesh, the chlorophyll content was low. Using the spectrophotometric analysis after acetone/diethyl ether extraction [11], the chlorophyll concentration was below the detection limit. The emission spectra with excitation wavelength of 250 nm and 266 nm have show peaks with maximum at 350 nm and 630 nm. The two peaks are possibly related to polyphenols. The excitation wavelength of 355 nm yields a peak with maximum at 450 nm and a relatively smaller peak at 715 nm. The 450 nm peak is related to polyphenols, while the 715 nm peak is possibly related to chlorophyll residues [12]. The excitation wavelength of 408 nm yields one broad peak at 500 nm, which is possibly related to 5-hydroxymethylfurfural (HMF) [13]. The present study focused on the correlation between fluorescence spectra and the quality of apple juice by means of laboratory reference data SSC and colour, while the investigation of specific fluorophores in apple juice will be studied in further experiments. The NIR spectra of original fresh juice (Fig. 1b) appear with broad absorption peaks as reported earlier [14]. One spectrum that is obviously different from others was considered as outlier according to the criterion of general Mahalanobis distance [15]. Resulting, this sample was deleted and the remained 29 samples were used for NIR analysis. In the fluorescence readings, no outlier appeared (n=30).

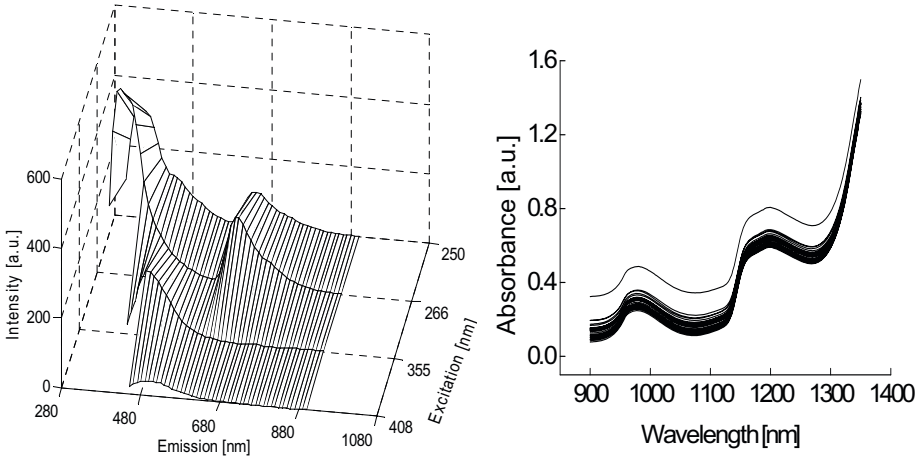

Fig. 1. (a) The mean excitation-emission matrix (EEM) for fresh juice; (b) The NIR transmission spectra of the 30 original fresh juice samples. Absorption was calculated by log (I/I0) from transmittance readings.

3.2 Characteristics of Laboratory Reference Values

The quality of juice was characterized by means of five reference parameters: SSC, pH, CIE L*, a*, and b*. Changes during heating and storage are presented in figure 2. The SSC was almost stable in all juice variants, suggesting that caramelization did not occur to a high extend due to relatively low temperature impact. In addition, heating at 80℃ for 10 minutes inactivated polyphenol oxidase [16]. Therefore, the color change observed in stored juice was mainly due to enzymatic browning. While in heated and stored juice, Maillard reaction or ascorbic acid degradation might provide the main reason for quality loss. The pH value decreased slightly during storage. The L* hardly changed during storage, but increased after heating and storage. The color

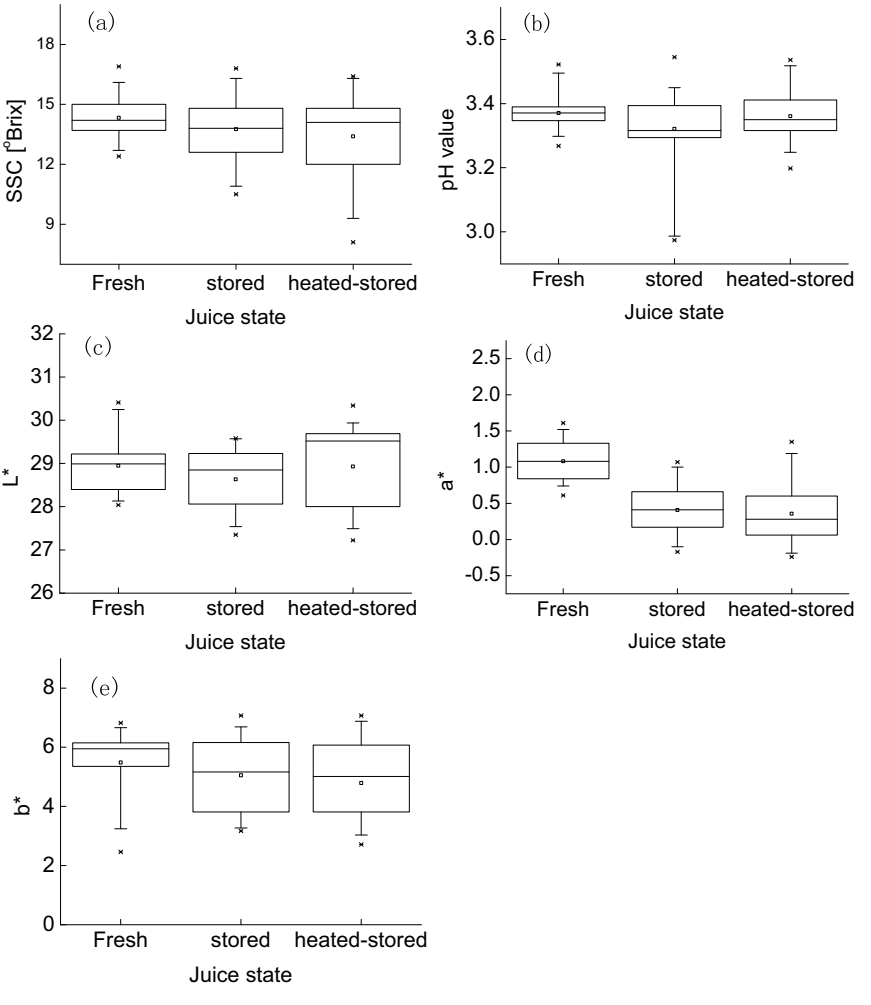

Fig. 2. Box-whisker plots of laboratory reference values

parameters a* and b* had similar changes: both values decreased after heating or storage. This indicated that SSC, pH and L* were not applicable as indicators for quality deterioration due to browning, while a* or b* can be used for this purpose.

3.3 Calibration Models

In order to see the potential ability to describe the quality of browning juice by fluorescence and NIR spectra, N-PLS was used to construct the multi-way calibration model with fluorescence EEM, and PLS was applied to construct model with NIR spectra. The quality of juice during the browning process was measured by SSC, pH, L*, a*, b*, ΔL*, Δa*, Δb*, ΔE (Table 1). The absolute NIR spectra and fluorescence EEM were used to build calibration models for SSC, pH, L*, a* and b*, while the different spectra were used to build calibration models for ΔL*, Δa*, Δb*, and ΔE. For detection of SSC, NIR showed high correlation and low measuring uncertainty, which was consistent with previous research for measuring fresh juice published by many working groups. In contrast, the correlation coefficient of models based on fluorescence EEM was low. This is consistent with the result of Seiden et al. (1996), who reported a correlation coefficient of 0.804 for 'Elstar' apple juice predicted by fluorescence spectra. Both fluorescence EEM and NIR spectra had low correlation with pH as no direct information can be expected in the spectral data. For L*, NIR had better results than fluorescence EEM. Both data sets had poor correlation for a* and Δa*.

The models based on fluorescence EEM had high correlation for both b* and Δb* prediction. Among the three parameters of colorimetric method, Krapfenbauer et al. (2006) reported that b* values changed to a greater extent in comparison to a* and L* values for cloudy apple juice. Resulting, b* is considered as being more important than other two for describing the browning extent of apple juice. Fluorescence EEM has shown a high correlation with colorimetric method and can be applied to predict

Table 1. The correlation coefficients for N-PLS model of fluorescence EEM and PLS model of NIR spectra

		SSC	pH	L*	a*	b*
Fresh juice	EEM	0.7079	0.5006	0.6963	0.4816	**0.9087**
	NIR	**0.9827**	0.5237	**0.8000**	0.7902	0.7069
Stored juice	EEM	0.6576	0.1906	0.6976	0.5998	**0.9052**
	NIR	**0.8976**	0.4024	**0.9010**	0.7693	0.6127
Heated-stored juice	EEM	0.8172	0.944	**0.8892**	0.7876	**0.9280**
	NIR	**0.9528**	0.6092	**0.9511**	0.2876	0.7921
		ΔL*	Δa*	Δb*	ΔE	
Difference between fresh and stored juice	EEM	0.6754	0.6499	**0.9610**	0.7446	
	NIR	**0.9258**	0.3465	0.7338	0.8741	
Difference between fresh and heated-stored juice	EEM	0.7833	0.3612	**0.8769**	0.4912	
	NIR	**0.8787**	0.3148	**0.9501**	0.7132	

the b*. Therefore, fluorescence EEM can be used to detect the quality change of apple juice during browning, encouraging further studies on developing a standardized method. On the other hand, NIR spectra, although high correlation was obtained for prediction of lightness parameter L* and ΔL*, showed no information for the browning color a* and b*.

4 Conclusions

During heating and storage of apple juice, the quality and color changed due to enzymatic browning and non-enzymatic browning. NIR spectra can be used to detect SSC and L* and ΔL*, while fluorescence spectra were feasible for predicting b* and Δb*. Both spectral readings had poor ability for measuring pH and a*. The results indicated that the combination of NIR spectra and fluorescence EEM provided a fast and non-invasive method for detecting quality deterioration of apple juice during storage and heating.

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