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Analytical Methods

Evaluation of apple juice quality using spectral fluorescence signatures

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ABSTRACT

In current work the method of *in vivo* evaluation of apple juice degree of naturalness based on Spectral Fluorescence Signature (SFS) is proposed. SFS spectra of intact apple juice were measured as excitation-emission matrix by specially designed compact spectrofluorimeter with front-face optical layout – Instant Screener Compact (LDI AS, Estonia). The data were analysed using PCA method with a view to evaluate the information of polyphenol's content in different commercial juices. Results of PCA analysis have shown a clear separation of juice reconstituted from concentrate, unclarified pasteurised juice and personally squeezed apple juice at the two dimensional PCs space. For implementation of apple juice analysis into spectrofluorimeter software the k-Nearest Neighbor (kNN) Search technique was used. The implemented model was tested using 19 different samples of apple juice. Results of test demonstrate that SFS–PCA–kNN method can provide quick nondestructive analysis of naturalness degree of commercial apple juice.

1. Introduction

Apples constitute an important part of the human diet, as they are a source of monosaccharides, minerals, dietary fibre, and various biologically active compounds, such as vitamin C, and certain phenolic compounds which are known to act as natural antioxidants (Sluis, Dekker, Skrede, & Jongen, 2002).

Phenolic compounds have a number of healthy properties for human, such as anticancer, antibacterial and anti-inflammatory effects. Apples have been associated with a decreased risk of chronic diseases such as cardiovascular disease and asthma (Boyer & Liu, 2004).

The concentration of apple polyphenolics may depend on many factors, such as cultivar of the apple, harvest and storage of the apples, and processing of the apples (Otto, 2005).

Apple polyphenolic content is not greatly affected by storage but processing of apples has been found to affects phytochemical content considerably. Through chemical and physical impacts on the product during the manufacturing processes the amount of polyphenols and other natural substances are reduced (Otto, 2005). This aspect negatively affects the juice quality.

Common methods of analysing the polyphenols content require long and complicated preparation of sample. Before polyphenols are extracted, samples containing these compounds must be collected, reserved and prepared properly. Care must be taken to minimise the loss of compounds of interest during transportation and preservation of the samples. To avoid degradation of native polyphenols, samples are often dried, frozen or lyophilized before extraction because high moisture or water content aids enzyme activities (Stalikas, 2007). Heating and exposure to light and oxygen may affect the polyphenolic composition in many cases; therefore high-temperature drying should be avoided as much as possible. Antioxidants such as butylated hydroxytoluene (BHT) and ascorbic acid are often added to samples to avoid oxidation of the polyphenols. Sample pre-treatment may be done by filtration and centrifugation as well (Naczk & Shahidi, 2006). Many different extraction methods are available for different types of samples. For the majority of plant originated food samples, solvent extractions such as liquid/liquid partitioning and solid/liquid extraction are most frequently employed in the laboratory (Manach, Scalbert, Morand, Rémésy, & Jiménez, 2004; Naczk & Shahidi, 2004).

Spectrophotometric methods are still used for the estimation of total phenolic, total flavonoid and total anthocyanins contents (Hollman, 2001; Scalbert & Williamson, 2000). Reversed-phase high performance liquid chromatography (HPLC) coupled with a diode array detector (DAD) and/or mass spectrometric detector (LC–MS) is the most widely use analytical tool for quantification of polyphenols, although occasionally polyphenols such as isoflavones are derivatized to methyl esters and analysed by gas chromatography (GC), or normal phase column for the separation of procyanidins (Kahle, Huemmer, Kempf, Erk, & Richling, 2007).

Owing to the chemical complexity and the frequent occurrence of polyphenols in plants, extraction, separation, identification and analysis of polyphenols remain as challenging as ever, despite the recent advances in new instrumentation.

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The native composition of polyphenols in apple as a measure of the juice quality is proposed to use. It can be assumed that any high-quality juice, as a liquid extract from the fruit or vegetable, should contain not destructive complex of the polyphenols as the fresh product has. In this research the Spectral Fluorescence Signature (SFS) method was used that allows to receive the result of juice analysis rapidly and without any additional treatment of sample before measurement. The SFS method is based on the measurement and analysis of 3-dimensional fluorescent matrixes, where the intensity I is a function of excitation, emission wavelengths and concentration of substances of interest: $I(\lambda_{ex}, \lambda_{em}, C)$. The SFS peculiarity can be considered as a "fingerprint", which characterises the substances in sample, the fluorescence intensity displays the concentration of compounds. Recognition of individual components in SFS allows one to identify the substances in sample; the determination of fluorescence intensity provides information about its quantity. This analysis does not require additional actions (e.g. extracting of components) and therefore can be carried out on-line.

SFS can be presented in 3-dimensional spectral format or in 2-dimensional format, where the fluorescence intensity at constant level is indicated by definite colours (or gray tone).

SFS method has repeatedly proved its ability in a variety of industrial and environmental applications (Babichenko, Orlov, Persiancev, Poryvkina, & Rebrik, 1996; Babichenko, Poryvkina, Orlov, Persiatsev, & Rebrik, 1998). This method is widely used for real-time analysis of various organic compounds in different environments: aromatic compounds in beverages, natural ingredients and contaminants in the aquatic environment, vital components in food (Christensen, Nørgaard, Bro, & Engelsen, 2006; Poryvkina, Babichenko, Kaitala, Kuosa, & Shalapjonok, 1994).

2. Materials and instruments

2.1. Samples preparation

The samples were prepared using four different types of apple products: commercial juice reconstituted from concentrate, commercial unclarified pasteurised juice, personally squeezed juice and apple pulp. In the period from June 2010 to July 2011 59 samples were examined, including 17 commercial juices (11 reconstituted from concentrate and 6 commercial unclarified pasteurised) and 42 homemade products. Homemade samples are 21 personally squeezed juices and 21 apple pulp substances, they were prepared using 12 different apple cultivars. All studied material was bought from retail shops in Tallinn, Estonia. Commercial apple juices were packed in 1 and 2 L Tetra Pak containers.

A manual household juicer (Moulinex) was used to make personally squeezed juices. Apples were cleaned from seeds, cut into pieces and juiced together with peel. After each juice sample preparation juicer was cleaned and washed with distiled water. Apple pulp samples were measured as the pieces of apple directly placing into optical cell.

The volume of each prepared sample was 5 ml. All homemade samples were measured immediately after the preparation. The experiments were carried out in two replicates using one sample per trial.

2.2. Instrument description

All measurements were performed by Instant Screener Compact (ISC) analyser (LDI AS, Estonia). The optical system of ISC is aimed to induce the fluorescence of the sample in front-face mode by monochromatic light at different wavelength in spectral range from 230 to 350 nm with 5 nm step and record the spectrum of fluorescence in spectral range from 250 to 565 nm by detector. For fluorescence excitation 5 W pulse Xe-lamp is used. The time of SFS matrix measurement is less than one minute. By default the SFS matrix consists of 25 fluorescence emission spectra. Every fluorescence emission spectrum in the SFS matrix is normalised by the reference channel signal to correct the fluorescence intensity on the spectral distribution of lamp and eliminate it's possible fluctuations.

3. Results and discussion

If consider that SFS matrix is a set of features $f_1(x)...f_i(x)$ where x is excitation-emission coordinate, the applicable dissimilarity measure for SFS objects space is weighted Minkowski metric. The dimension of SFS feature space is high ($25 \times 40 = 1000$) thus the selected metric is exposed to the detrimental effects of curse of the dimensionality, a term introduced by Bellman in 1961 (Beyer, Goldstein, Ramakrishnan, & Shaft, 1999).

It is proposed to use feature extraction method to extract the relevant information from SFS data and thereby suppress dimensionality effect.

It is assumed that for the selected dataset of juice products the needed information is carried in the variance of the features. Thereby Principal Component Analysis (PCA) was selected as method to extract the relevant features from data. The linear transformation employed by PCA method is based on preserving the most variance in the data using reduced to a minimum number of dimensions. Using linear transformation the high-dimensional data is embedded in low dimensional Principal Component (PC) space where the new uncorrelated features have the best represent of entire data (Shlens, 2009). As will be shown later two first PCs with highest variance provide robust classification of juice product type and also have clear interpretation within the bounds of SFS terms.

Average SFS spectra of four studied groups of juices are depicted on Fig. 1. The colour map represents the fluorescence intensity in arbitrary units. The value of fluorescence of polyphenolic content marked with arrows rapidly attenuates if to look at SFS in the direction from pulp (Fig. 1, upper left) to juice from concentrate (Fig. 1, bottom right). This behaviour agrees with known fact that any processing of apples influence polyphenolic content of product (Mayer-Miebach, Adamiuk, & Behsnilian, 2012).

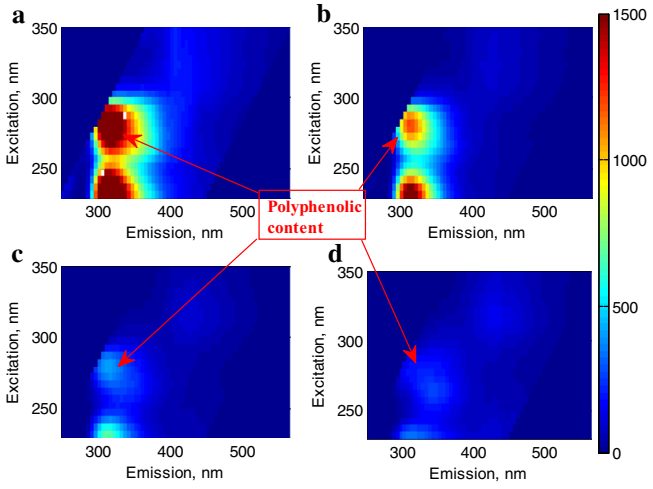

Fig. 1. Average SFS spectra of juice samples. (a) apple pulp, (b) personally squeezed juice, (c) unclarified pasteurised juice, (d) reconstituted from concentrate juice.