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Detection of orange juice frauds using front-face fluorescence spectroscopy and Independent Components Analysis

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ABSTRACT

The aim of this study was to find simple objective analytical methods to assess the adulteration of orange juice by grapefruit juice. The adulterations by addition of grapefruit juice were studied by 3D-front-face fluorescence spectroscopy followed by Independent Components Analysis (ICA) and by classical methods such as free radical scavenging activity and total flavonoid content. The results of this study clearly indicate that frauds by adding grapefruit juice to orange juice can be detected at percentages as low as 1%.

1. Introduction

Production of fruit juices is one of the fastest developing industries in the world. Although many kinds of fruit juice are available, orange juice remains the most produced and most widely consumed (Wass-Garcia, Hammond, Mottram, & Gutteridge, 2000). However, this popularity makes orange juice a common target for adulterations and frauds.

Fruit juice adulteration presents an economic and regulatory problem. The most common adulteration methods for fruit juice include dilution with water, addition of sugars, addition of pulp-wash solids, or addition of a less expensive fruit juice (Brause, 1998; Nagy, 1997; Ebeler & Takeoka, 2007; Muntean, 2010).

Several methods have been proposed for the qualitative and/or quantitative analysis of adulteration of fruit juices. The most established approaches that have been successfully used to determine the authenticity of fruit juices are based on profiling of carbohydrates, phenols, carotenoids, amino acids, or other organic acids using different chromatographic techniques such as high-performance liquid chromatography (HPLC) and gas chromatography (GC) (Muntean, 2010; Gómez-Ariza, Villegas-Portero, & Bernal-Daza, 2005; Abad-García, Berrueta, Garmón-Lobato, Gallo, & Vicente, 2009; Ehling & Cole, 2011; Pan, Kilmartin, Smith, & Melton, 2002; Hammond, 2001; Catillo, Caja, & Herraiz, 2003; Low, McLaughlin, Hofsommer, & Hammond, 1999).

Some studies quantify naringin and hesperidin, which are the major flavonoid in grapefruit and orange respectively, to characterise these juices. Widmer (2000) used the naringin/neohesperidin ratio obtained by HPLC to indicate the presence of grapefruit juice in orange juice.

However, these chromatographic techniques are destructive, laborious, time-consuming and necessitate the use of potentially hazardous solvents.

In this study, in contrast to chromatographic techniques that focus on detecting and quantifying specific compounds, 3D-front-face fluorescence spectroscopy was used. This technique can generate a global signal containing information concerning all the fluorescent compounds within the sample. The acquisition of fluorescence spectra can be performed quickly, and is suitable for on-line controls. The total duration of the analysis largely depends on the spectrofluorometer used. In the present case, a relatively slow instrument was used and a complete spectrum took around 30 min.

Classical fluorescence spectroscopy has been used for the characterisation of different fruit juices such as apple and tomato juices (Petrus, 1988). It was also used for the detection of adulteration (Petrus & Attaway, 1980; Petrus, Fellers, & Anderson, 1984).

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The interpretation of fluorescence spectral data is complex due to the presence of many fluorophores and by changes caused by variation in the sample matrix, etc. In this paper, Independent Components Analysis (ICA) was applied to the unfolded 3D-front-face fluorescence spectra to facilitate the detection of signals indicating the presence of adulterants in orange juice samples.

ICA is a data analysis technique that aims to extract the underlying source signals and their proportions from a set of mixed signals based on the assumption that these source signals are statistically independent (Comon, 1994). The general ICA model is given by (Guoping, Quingzhu, & Zhenyu, 2008; Stone, 2004):

$$\mathbf{X} = \mathbf{A}.\mathbf{S}$$

where **X** is the matrix of observed spectra, **S** is the matrix of unknown "pure" source spectra and **A** is the mixing matrix of unknown coefficients, directly related to the corresponding proportions.

Classical methods such as free radical scavenging activity and total flavonoid content were also used to differentiate adulterated samples from authentic ones.

2. Material and methods

2.1. Juice samples

Various commercial brands of juices: orange (O) and grapefruit (G) were purchased in the French marketplace. These juices have no added sugar and are with or without pulp.

Some samples were also prepared in the laboratory in order to compare the commercial juices with the pressed juices.

Several mixtures were prepared by adding different percentages (0%, 1% and 2%, 4%, 6% up to 20%...) of grapefruit juice to the orange juices. For comparison, two commercial juices labeled as containing 55% grapefruit juice and 45% orange juice were also analysed.

2.2. Chemicals

DPPH (2,2-diphenyl-1-picryl hydrazyl), $AlCl_3$_$6H_2O$ and quercetin were purchased from Sigma (Saint-Quentin Fallavier, France).

2.3. Fluorescence spectroscopy

All the samples: adulterated juices (the different mixtures), the authentic orange and grapefruit juices as well as laboratory-pressed juices were all analysed by 3D-front- face fluorescence (3D-FFF) spectroscopy in the same conditions. Two different preparations were performed for each sample.

Fluorescence landscapes (3D spectra) were measured directly on the samples without prior preparation, using a Xenius spectrofluorometer (SAFAS, Monaco) equipped with a xenon lamp source, excitation and emission monochromators and a front-face sample-cell holder. Measurements were carried out using acryl cuvettes. The instrumental settings were: bandwidths 10 nm, excitation wavelengths 270–600 nm (every 4 nm) and emission wavelengths 290–700 nm (every 4 nm). A photomultiplier (PM) voltage of 470 V was used to avoid detector saturation. The "Forcing" option was also used in order to limit the emission range so that data acquisition started 25 nm beyond the excitation wavelength, thus avoiding interference from Rayleigh scattering. The data consisting of

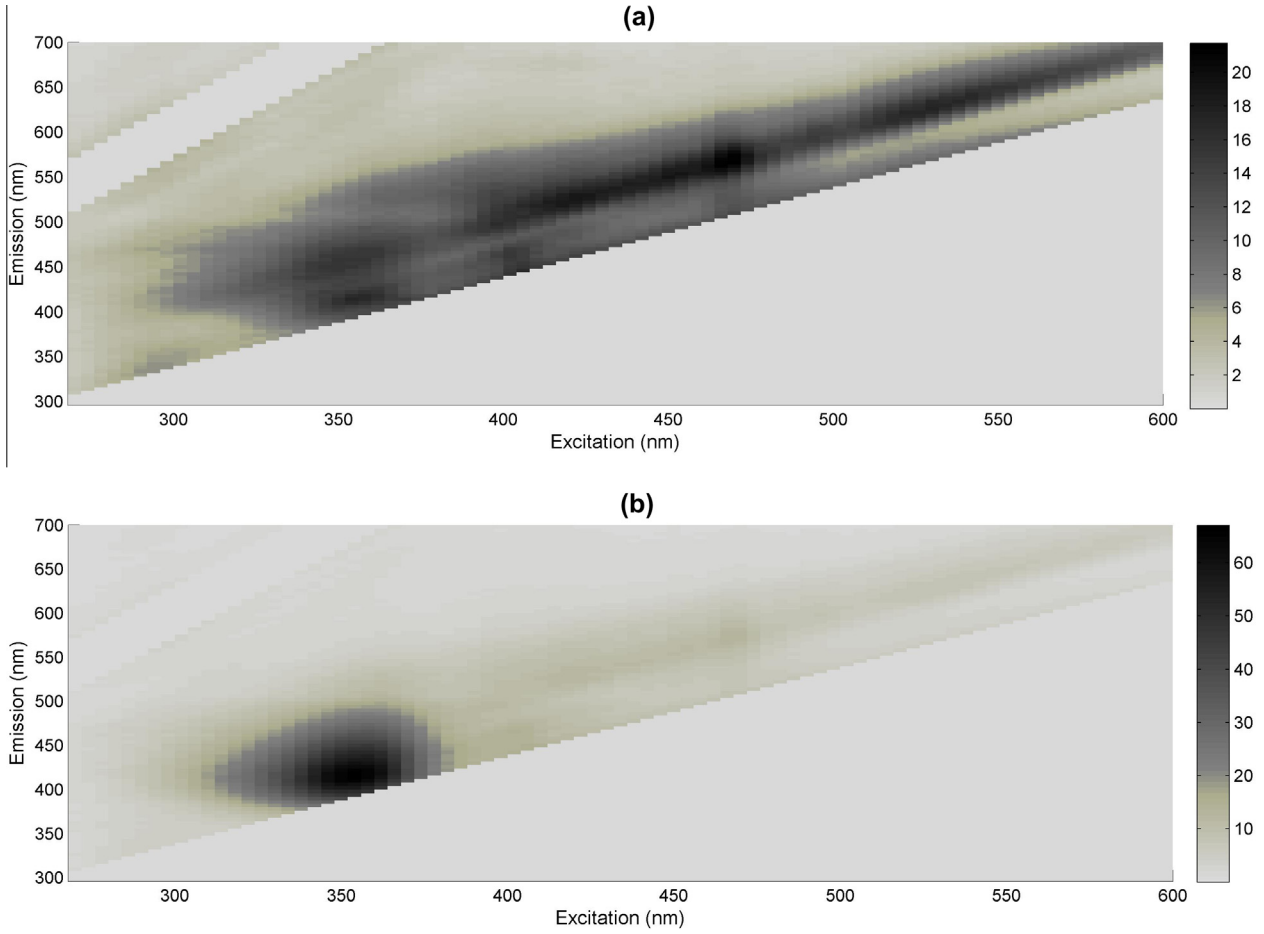

Fig. 1. A typical fluorescence excitation–emission matrix (EEM) obtained by 3D-FFF spectroscopy for orange juice (a) and for grapefruit juice (b).