



## Quality assessment of the saffron samples using second-order spectrophotometric data assisted by three-way chemometric methods via quantitative analysis of synthetic colorants in adulterated saffron



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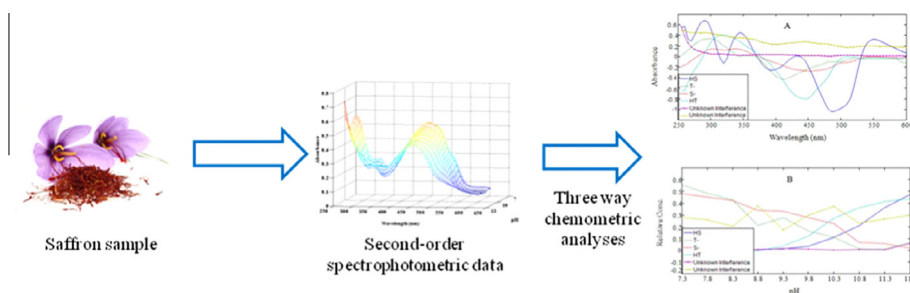
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### HIGHLIGHTS

- Quality assessment of saffron using multivariate processing of second-order data.
- Non separative methods for determination of synthetic colorants in saffron.
- Modeling the system through the unique decomposition of the three way data array.

### GRAPHICAL ABSTRACT

Quality assessment of the saffron with spectrophotometric method using multivariate processing of pH-spectra matrices in the presence of unexpected interference.



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### ABSTRACT

Saffron is a valuable culinary spice that can be used not only for dyes and cooking, but also for many medical purposes. Due to its high price and restriction of its production, various fraud manners in its production have been growing. Addition of synthetic colorants to saffron is the most common way for adulteration. In this work, chemometric methods are proposed to resolve the three-dimensional absorbance spectra–pH data for simultaneous determination of the two colorants Tartrazin and Sunset yellow, in adulterated saffron. The rank deficiency in the concentration mode impaired the system. Therefore, to extirpate the ambiguity, which results from rank deficiency, three-way variation array  $\mathbf{V}$  was generated by subtracting the first pH spectrum from each spectrum at each pH. This allows the extraction of extent reaction profile and mixture reaction spectral profiles, as well as the relative concentrations of the analytes.

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### Introduction

Saffron, a plant from the family *Iridaceae*, is produced from dried stigmas of *Crocus sativus* and is considered as the highest priced spice in the world [1]. Saffron contains more than 150 volatile

and aroma-yielding compounds and also has many nonvolatile active components, which are carotenoids, such as zeaxanthin, lycopene, and various  $\alpha$ - and  $\beta$ -carotenes [2]. Saffron has been used in traditional medicine for a long time. The modern studies show the carotenoid compounds in the saffron could inhibit growth of tumors. The active constituents in saffron have significant roles to alleviate gastric problems, heart disease, depression, premenstrual syndrome, insomnia and anxiety. Consumption of saffron also

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seems to benefit for vision by retarding the degeneration of the retina that occurs with [3–6].

The quality of saffron depends on the concentration of its three important and major metabolites that responsible for supplying the distinctive color and flavor to the stigmas. These components are crocin, picrocrocin and safranal present in commercial saffron. Saffron's golden yellow-orange color is the result of  $\alpha$ -crocin that is hydrophilic carotenoid, and easily dissolves in water to provide an orange-red solution. Picrocrocin is responsible for saffron's flavor. Safranal is the most volatile oil in the stigmas of saffron that is less bitter than picrocrocin and the distinctive aroma of saffron comes from this oil [7–9]. Saffron types are graded by quality according to laboratory measurement of these components present in commercial saffron. The colorants are the most significant additives that are found in food because they allow one to capture the desirable tinge and organoleptic qualities of foodstuff, and this is the main reason for using colorants in food industry. Natural colorants are replaced by synthetic ones due to their high cost and instability. Synthetic dyes often contain azo (N=N) functional groups and aromatic ring structures, which are known of their high risk on human health.

Although such attempts on the quality control of saffron sample have been done but adulterated saffron is being sold. Typical methods of saffron adulteration include mixing of extraneous substances like beets, pomegranate fibers, and red synthetic dyed such as Sunset yellow, Tartrazine, Ponceau4R, Methylene orange and Erythrosine. Saffron adulteration with addition of synthetic colorants or even other extraneous materials is a most common way with the aim of misleading of the consumer for improving the appearance of the dried stigmas and to give rise to the coloring strength of the aqueous extract. Sometimes saffron is used as a therapeutically plant to cure illnesses and some synthetic colors may be pathogenic, especially when they are consumed in excess. For this reason, adulterations make it completely harmful [10–12].

The method of saffron quality control that was recommended by the international standardization organization is UV-Vis spectrophotometry because it is quick, easy and low cost. Unfortunately, this method is non-specific and unable to adequately separate between genuine and adulterated saffron due to overlapping of the signal, and thus unable to provide a quality category on the international market [13]. The determination of two colorants Tartrazin (TA) and Sunset yellow (SY) in adulterated saffron have been done by separation techniques such as high performance liquid chromatography (HPLC) [14]. In the case of the complex matrix, such methods are often laborious, very expensive and in most cases are time-consuming. In addition unwanted constituents are usually present in real sample which contain overlapping signals with the signal of the analyte, and give false positive results on the signal of the analyte. In most cases, these problems are associated with the removal of the undesirable components without affecting the concentration and prototype of the analytes, but these separation methods are expensive and in some cases are not available [12].

Multivariate spectroscopic methods in combination with chemometric data analyses are used widely for quality control of food [15]. Chemometrics is an approach based on the idea of indirect observation. Measurements related to the chemical composition of a substance are taken, and the value of a property of interest is inferred from them through some mathematical relation without need a prior knowledge which increases the understanding of chemical information. Some data are arranged in a three-way matrix, i.e. a data cube or high order data matrices. When a spectral three-dimensional landscape is collected for each sample, three-way data array is gained. This is the case when a spectrum of the identical sample is measured under several different conditions, such as varying pH and dilution, or, in case of fluorescence

to obtain excitation-emission fluorescence matrices [16–20]. Trilinear decomposition methods are implemented for the quantification of analytes in a complex matrix in the presence of unknown and uncalibrated interferences. This feature is commonly called the second order advantages. Three-way chemometric approaches such as parallel factor analysis (PARAFAC), alternating penalty trilinear decomposition (APTLD) and self-weighted alternating trilinear decomposition (SWATLD) can be used to perform analysis of these kinds of data that are called "second-order calibration" methods [21–23]. The analytical methods such as the UV-Vis molecular absorption spectrophotometry can be considered as the simple technique for analysis of food products. The absorbance spectra obtained from UV-Vis spectrophotometer is unsuitable for second-order calibration, because the UV-Vis spectrophotometers give a first-order absorbance data. A second-order data can be achieved, when the absorbance spectra of the sample containing the analyte with acid-base property are obtained at varying pHs. So a three-way structure of data array by second order advantage feature is found. Standard methods for second-order data analysis are second-order multivariate algorithms, often achieving the unique decomposition of three-dimensional arrays [24].

In this study, we developed a selective and non-separative method, without need a prior knowledge, for quality control of saffron samples. For this purpose, we focused on simultaneous determination of two colorants Tartrazin (TA) and Sunset yellow (SY), with high degree overlapping spectra in adulterated saffron. Due to the presence of unknown interferences, three-way chemometric methods for analysis of the three-dimensional absorbance spectra-pH gradient data are used.

## Experimental section

### Materials

All the used chemicals were prepared from analytical grade reagents and distilled water. Sodium hydroxide and hydrochloric acid were provided from Merck (Darmstadt, Germany). SY and TY were purchased from Proquimac (Spain). The analyzed commercial samples were purchased from the local market.

### Preparation of standard and real samples

Stock solutions of SY and TY with a concentration of  $1.0 \times 10^4 \text{ mg L}^{-1}$  were prepared by dissolving 1.000 g of these reagents in 100.0 mL distilled water. Standard solutions of lower concentrations were prepared by appropriate dilution of the stock solutions with distilled water. Then the samples containing different amounts of SY and TY were magnetically stirred and titrated in the pH range from 7.3 to 11.8 with NaOH. To keep sample dilution effects negligible, NaOH was used as concentrated as possible. The absorbance spectra of the resulted solutions were recorded over the wavelength range of 250–600 nm with 5 nm intervals every 0.5 pH unit when the selected pH value was reached. To evaluate the performance of this model, two saffron samples were studied. These samples were prepared by dissolving 1.000 g of saffron samples in distilled water and diluted to final volume of 100.0 mL.

### Instrumentation and software

The UV-Visible spectra were recorded using Optizen 3220UV which equipped with a 10-mm quartz cuvette. For each sample, absorbance spectrums were generated at 5 nm intervals from 250 to 600 nm. The pH value was measured using a Metrohm 691 pH-Meter with a combined glass electrode. Calculations were

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