

Determination of Safranal Concentration in Saffron Samples by Means of VE-Tongue, SPME-GC-MS, UV-Vis Spectrophotometry and Multivariate Analysis

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Abstract— An experimental investigation has been carried out to characterize and discriminate seven saffron samples and to verify their declared geographical origin using a voltammetric electronic tongue (VE-tongue). The ability of multivariable analysis methods such as Principal Component Analysis (PCA), Hierarchical Cluster Analysis (HCA) to classify the saffron samples according to their geographical origin have been investigated. A good discrimination has reached using PCA and HCA in the VE-tongue characterization case. Furthermore, cross validation and Partial Least Square (PLS) techniques were applied in order to build suitable management and prediction models for the determination of safranal concentration in saffron samples based on SPME-GC-MS and UV-Vis Spectrophotometry. The obtained results reveals that some relationships were established between the VE-tongue signal, SPME-GC-MS and UV-Vis spectrophotometry methods to predict safranal concentration levels in saffron samples by using the PLS model. In the light of these results, we can say that the proposed electronic system offer a fast, simple and efficient tool to recognize the declared geographical origin of the saffron samples.

Keywords— Voltammetric electronic tongue; SPME-GC-MS; UV-Vis Spectrophotometry; Saffron; Geographic differentiation; Chemometrics.

I. INTRODUCTION

Since ancient times, dehydrated stigmas of the saffron flower (*Crocus sativus* L.) is commonly used as spice and food colorant, and less extensively, as a textile dye, perfume and as cosmetics. Saffron has been considered the most precious and expensive of spices. The price of this spice greatly depends on the country of origin, not only because of the different labour costs but also because of its different capacity to transmit the three main characteristics of saffron aroma [1], taste [2] and colour [3]. Indeed, saffron's commercial quality is determined by specifications recommended by the ISO/TS-3632 standard [4]. The compounds responsible for such attributes are crocins, a group of glycoside derivate from the carotenoid crocetin; terpenic aldehydes known as safranal (2,6,6-trimethyl-1,3-cyclohexadiene-1-carboxaldehyde) and a glycoside terpenoid,

picrocrocin, respectively (picrocrocin for flavour and safranal for aroma) [1]. Like almost all foodstuff products, the price of saffron is directly depending on its quality, which is also related to the geographical origin of the production area. The Protected Designation of Origin (PDO) for agricultural products has been introduced with official European regulations, which allow the labelling of some products with the names of the geographical area of production. Moreover, the problem of geographic identification of food becomes more attractive when it concerns to restricted production areas. To deal with this subject, a lot of methods have been employed for the determination of the geographical origin of saffron, such as Liquid Chromatography-Diode Array Detector Coupled with Electron Spray Mass Spectrometry (LC-DAD/MS/MS ESI) [2], Thermal Desorption-Gas Chromatography-Mass Spectrometry (TD-GC-MS) [1], Gas Chromatography equipped with a Flame Ionization Detector (GC-FID) [5], Near-Infrared Spectroscopy [6], and High-Performance Liquid Chromatography (HPLC) [7]. Analysis of electrochemical species has been proposed as rapid patterns screening of several products [8,9]. The E-tongue have widely been suggested for the monitoring of food quality. The E-tongue is a sensor array combined with pattern recognition system for liquid analysis using both several non-specific, low-selective, chemical sensors with high stability, cross-sensitivity and ion-selective sensors [10]. It could represent a convenient alternative for screening due to their rapidity, simplicity and low cost to classify products with a different chemical "fingerprint".

Due to high demand for knowledge the saffron quality, the request to develop a rapid and low cost method that can be used for routine quality control of saffron spice was under investigation. The proposed VE-Tongue in correlation with SPME-GC-MS and UV-vis spectrophotometry was used, to establish a model able to predict the safranal as the major compound responsible for saffron's bitter taste.