



# Electronic nose and isotope ratio mass spectrometry in combination with chemometrics for the characterization of the geographical origin of Italian sweet cherries



F. Longobardi<sup>a,\*</sup>, G. Casiello<sup>a</sup>, A. Ventrella<sup>a</sup>, V. Mazzilli<sup>a</sup>, A. Nardelli<sup>a</sup>, D. Sacco<sup>a</sup>, L. Catucci<sup>a,b</sup>, A. Agostiano<sup>a,b</sup>

<sup>a</sup> Dipartimento di Chimica, Università di Bari "Aldo Moro", Via Orabona 4, 70126 Bari, Italy

<sup>b</sup> Consiglio Nazionale delle Ricerche, Istituto per i Processi Chimico-Fisici (IPCF-CNR), sez. di Bari, Via Orabona 4, 70126 Bari, Italy

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## ABSTRACT

Sweet cherries from two Italian regions, Apulia and Emilia Romagna, were analysed using electronic nose (EN) and isotope ratio mass spectrometry (IRMS), with the aim of distinguishing them according to their geographic origin. The data were elaborated by statistical techniques, examining the EN and IRMS datasets both separately and in combination. Preliminary exploratory overviews were performed and then linear discriminant analyses (LDA) were used for classification. Regarding EN, different approaches for variable selection were tested, and the most suitable strategies were highlighted. The LDA classification results were expressed in terms of recognition and prediction abilities and it was found that both EN and IRMS performed well, with IRMS showing better cross-validated prediction ability (91.0%); the EN–IRMS combination gave slightly better results (92.3%). In order to validate the final results, the models were tested using an external set of samples with excellent results.

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## 1. Introduction

The fruits of the sweet cherry tree (*Prunus avium* L.) are used for fresh consumption, and for the production of marmalades, juices, jams, jelly fruits, and also alcoholic beverages. Sweet cherries are widely appreciated for their taste and their nutritional qualities. In particular, they show a higher simple sugar content if compared to sour cherries, with glucose and fructose as main responsible for their sweetness; they contain a considerable amount of water-soluble (C, B) and fat-soluble (A, E and K) vitamins, carotenoids (such as  $\beta$ -carotene, lutein and zeaxanthin), minerals (calcium, magnesium, phosphorous and potassium), and volatile compounds, such as esters, alcohols, aldehydes, ketones, and terpenoid compounds (Ferretti, Bacchetti, Belleggia, & Neri, 2010; Girard & Kopp, 1998; Pérez-Sánchez, Gómez-Sánchez, & Morales-Corts, 2010; Qin, Cai, Zhang, Qi, & Geng, 2010; Serradilla et al., 2012). In addition, natural healthy antioxidant substances like anthocyanins and polyphenols are present in significant amounts (Liu et al., 2011).

The main producers of sweet cherries are Turkey, the United States, Iran, Italy, France, Spain and Russia (Doymaz & Ismail, 2011; Pérez-Sánchez et al., 2010), Italian production takes place mainly in the regions of Apulia, Campania, Veneto and Emilia

Romagna. The varieties principally cultivated in Italy are Bigarreau, Black, Anella, Giorgia and Ferrovia, and some of them are cultivated mainly in specific localities, so showing peculiar traits, that confer them with unique qualities, encouraging local producers to act with the purpose of obtaining European quality marks, such as "protected designation of origin" (PDO), "protected geographical indication" (PGI) and "traditional specialty guaranteed" (TSG), that, in general, help to protect and promote the brand names of Europe's traditional agricultural produce and foods.

Therefore, it is clear there is an economic basis to develop analytical methods able to certify the declared geographical origin of food products, in order to protect consumers and honest producers from fraud and unfair competition, respectively; consequently, during recent years, several food authentication techniques have been proposed (Cajka et al., 2010; Camin, Perini, Bontempo, & Giongo, 2009; Longobardi, Ventrella, Casiello, Sacco, Catucci et al., 2012; Longobardi, Ventrella, Casiello, Sacco, Tasioula-Margari et al., 2012; Longobardi et al., 2013; Torri, Sinelli, & Limbo, 2010).

Among the innovative analytical techniques, the electronic nose (EN) has proved highly useful in studies on food matrices (Benedetti, Buratti, Spinardi, Mannino, & Mignani, 2008; Pacioni, Cerretani, Procida, & Cichelli, 2014; Russo et al., 2013). Briefly, ENs are devices that mimic the sense of smell, on the basis of different technologies, to detect volatile analytes in complex matrices

\* Corresponding author. Tel.: +39 080 5442042; fax: +39 080 5443607.

E-mail address: [francesco.longobardi@uniba.it](mailto:francesco.longobardi@uniba.it) (F. Longobardi).

(Peris & Escuder-Gilabert, 2009). The application of the EN in the discrimination of the geographic origin or of the variety of food matrices is well documented (Cajka et al., 2010; Cynkar, Damberg, Smith, & Cozzolino, 2010; de las Nieves López de Lerma, Bellincontro, García-Martínez, Mencarelli, & Moreno, 2013).

Another innovative technique for the analysis of food matrices is isotope ratio mass spectrometry (IRMS), which investigates the ratios of the stable isotopes present in a sample, i.e. those isotopes that do not decay through radioactive processes over time. In the field of food authentication and, in particular, the discrimination of the geographical origin of food matrices, IRMS has great potential as demonstrated by numerous papers (Kelly, Heaton, & Hoogewerff, 2005; Longobardi, Casiello, Sacco, Tedone, & Sacco, 2011; Perini & Camin, 2013; Rossmann et al., 1999; Rummel, Hoelzl, Horn, Rossmann, & Schlicht, 2010; Sacco et al., 2009).

Examples of the use of EN and IRMS in cherry samples, to our knowledge, are few and mainly deal with the evaluation of fruit ripeness (Benedetti, Spinardi, Mignani, & Buratti, 2010).

In this work, sweet cherry samples coming from two different Italian regions devoted to cherry production, Apulia and Emilia Romagna, were analysed by EN and IRMS, in order to discriminate the samples on the basis of their geographic origin.

## 2. Materials and methods

### 2.1. Sample collection

A total of 112 commercial cherry samples from two different Italian regions, i.e. 56 Emilian samples and 56 Apulian samples, belonging to three different varieties, i.e. “Bigarreau”, “Giorgia” and “Ferrovia” were collected. Cherries were harvested during 2010, between May and June. Apulian samples came from an area close to the south-east of Bari whereas Emilian cherries were from an area within the provinces of Modena and Bologna. The fruits were harvested when ripe enough to eat, cooled for a few hours, and transported to the laboratory assuring the maintenance of the cold chain. Subsequently, the cherries were washed with tap water, carefully wiped with laboratory paper, and, for IRMS analyses, freeze dried (see below) while for EN analyses, samples were enclosed in polyethylene bags and stored at  $-70^{\circ}\text{C}$ .

### 2.2. EN apparatus and analyses

For the EN measurements the cherry samples were thawed at  $4^{\circ}\text{C}$  for 2 h, cut in small pieces, and then an aliquot of 2 g was placed into a 10-mL vial hermetically sealed with a cap having a Teflon septum and placed in a thermostatic bath at  $40^{\circ}\text{C}$  for 90 min in order to establish equilibrium between headspace and sample. The cherry headspace was pumped into a PEN3 Electronic Nose System (Airsense Analytics, Schwerin, Germany), equipped with an array of 10 metal oxide semiconductor (MOS) sensors, at a flow rate of  $400\text{ mL min}^{-1}$ , and the sensor responses were sampled every 1 s for 120 s. After each sample analysis, the system was purged for 200 s with filtered air prior to the next sample injection to allow re-establishment of the instrument baseline.

Each sample was analysed twice and the average of the results was used for subsequent statistical analysis.

### 2.3. IRMS apparatus and analyses

For stable isotope ratio analysis, cherry fruits were cut in half, pitted, frozen at  $-80^{\circ}\text{C}$  and then freeze dried for 48 h using a Heto Lyolab 3000 freeze dryer (Heto-Holten A/S, Allerød, Denmark). Freeze-dried cherries were powdered using a commercial blender and stored in sealed containers under vacuum until analysis.

For  $^{13}\text{C}/^{12}\text{C}$  analysis about 0.3 mg of freeze-dried sample were weighed into tin capsules and directly analysed, whereas for  $^{18}\text{O}/^{16}\text{O}$  and  $^2\text{H}/^1\text{H}$  analysis about 1.5 mg of sample were firstly weighed into silver capsules and then stored in a desiccator above  $\text{P}_2\text{O}_5$  for at least 72 h before analysis.

The analyses were performed using an isotopic ratio mass spectrometer (Finnigan Delta V Advantage IRMS; Thermo Fisher Scientific, Bremen, Germany) coupled with an elemental analyser (EA, FlashEA 1112 HT, Thermo Fisher Scientific). The EA was equipped with a combustion reactor (held at  $1020^{\circ}\text{C}$ ) for  $^{13}\text{C}/^{12}\text{C}$  determination and a pyrolysis reactor (a high-temperature conversion elemental analyser, held at  $1450^{\circ}\text{C}$ ) for  $^{18}\text{O}/^{16}\text{O}$  and  $^2\text{H}/^1\text{H}$  ratios. Samples were introduced into the pyrolysis/combustion column via the autosampler (MAS 200R; Thermo Fisher Scientific), equipped with a suitable cover, where dry conditions were ensured by flushing nitrogen continuously over the samples.

The EA was interfaced with the IRMS through a dilutor (Finnigan ConFlo III; Thermo Fisher Scientific) dosing the samples and reference gases. To separate the gases produced ( $\text{CO}_2$  during the combustion and  $\text{CO}$  or  $\text{H}_2$  during the pyrolysis) the elemental analyser was supplied with two Porapak QS gas chromatography columns.

The isotopic values were expressed using the conventional  $\delta$  notation in parts per thousand (‰) vs V-SMOW (Vienna-Standard Mean Ocean Water) for oxygen and hydrogen, PDB (Pee Dee Belemnite) for carbon, according to the following formula:

$$\left[\frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}}\right] \times 1000$$

where  $R$  represents the ratio between the heavy and light isotopes, in the sample and standard. Each sample was analysed twice and the isotopic value was reported as the mean of the two determinations. The values were calculated against reference gases (i.e.  $\text{CO}_2$ ,  $\text{CO}$  and  $\text{H}_2$ ) previously calibrated against International Standards supplied by IAEA (International Atomic Energy Agency, Vienna, Austria): USGS 40 for  $^{13}\text{C}/^{12}\text{C}$ , IAEA-CH-7 for  $^2\text{H}/^1\text{H}$ , and IAEA-601 for  $^{18}\text{O}/^{16}\text{O}$ . To check the accuracy, working in-house standards were analysed in each run. In particular, commercial casein and benzoic acid standards (Carlo Erba Reagents, Milan, Italy) were used for  $^{13}\text{C}/^{12}\text{C}$  and  $^{18}\text{O}/^{16}\text{O}$ , respectively. For  $^2\text{H}/^1\text{H}$ , supposing the possible exchange of hydrogen with water and/or ambient air moisture, the values were corrected against an Interlaboratory Comparison Material (ICM – casein reference material) according to the “comparative equilibration technique” (Wassenaar & Hobson, 2003). The precision of measurement, expressed as one standard deviation and obtained measuring a cherry sample 10 times, was  $\pm 3\text{‰}$  for  $\delta\text{D}$ ,  $\pm 0.3\text{‰}$  and  $\pm 0.2\text{‰}$  for  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$ , respectively.

### 2.4. Chemometrics

For the multivariate data analyses, the dataset was divided into two subsets by exploiting the Kennard and Stone Duplex design (Kennard & Stone, 1969): a modelling set and an external set, containing 78 (39 Emilia Romagna and 39 Apulian samples, i.e. about 70% of total samples), and 34 (17 Emilia Romagna and 17 Apulian samples, i.e. about 30% of total samples) cherry samples, respectively.

The modelling subset was processed by univariate statistics ( $t$ -test) and by the following multivariate techniques: PCA for an exploratory overview, and supervised discriminant techniques (LDA) for building statistical models able to discriminate cherries according to their geographic origin. In the model-building step, each supervised pattern recognition model was evaluated in terms of non-error classification rate, both on the whole modelling set (recognition ability), and on the test set obtained by  $k$ -fold cross-validation (CV prediction ability) with a  $k$  value equal to 5. Finally, the validation and comparison of the models were executed

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