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NIR and UV–vis spectroscopy, artificial nose and tongue: Comparison of four fingerprinting techniques for the characterisation of Italian red wines

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ABSTRACT

Four rapid and low-cost vanguard analytical systems (NIR and UV–vis spectroscopy, a headspace-mass based artificial nose and a voltammetric artificial tongue), together with chemometric pattern recognition techniques, were applied and compared in addressing a food authentication problem: the distinction between wine samples from the same Italian oenological region, according to the grape variety.

Specifically, 59 certified samples belonging to the Barbera d'Alba and Dolcetto d'Alba appellations and collected from the same vintage (2007) were analysed.

The instrumental responses, after proper data pre-processing, were used as fingerprints of the characteristics of the samples: the results from principal component analysis and linear discriminant analysis were discussed, comparing the capability of the four analytical strategies in addressing the problem studied.

1. Introduction

In recent decades, there has been an exponential increase in the availability of analytical instrumentation capable of acquiring huge amounts of data in a short time and, as a consequence, the need for advanced and efficient strategies for the analysis of the data has emerged.

Examples of such instrumentation are NIR and UV–vis spectrophotometers, artificial noses and tongues, which are employed in the so-called "without identification", "blind" or "fingerprinting" procedures. In fact, these techniques are able to provide non-specific information, meaning that they generate complex signals or often combinations of measurements (*e.g.* spectral fingerprints, multi-sensor array fingerprints, etc.). They are not used to verify the existence or absence of particular chemical compounds, nor to measure individual chemical/physical properties, but to obtain a comprehensive, multivariate description of the samples.

For this reason, an increase in the use of multivariate statistical analysis (chemometrics) for the elaboration of such amounts of data and for the evaluation and interpretation of useful information has been reported.

In the case of the wine sector, studies that apply chemometric methods to non-specific data (fingerprints) can be classified into *quantitative* and *qualitative studies.*

The former are widely referenced in the literature: for example, the *quantitative* determination of different analytes, mainly ethanol, glycerol and sugars, has frequently been performed using especially NIR spectroscopy [1,2].

Urbano Cuadrado et al. [3] developed a method based on the joint use of NIR and MIR spectroscopy for the determination of several oenological parameters: alcoholic degree, volumic mass, total acidity, pH, volatile acidity, glycerol, total polyphenol index, reducing sugars, lactic, malic, tartaric and gluconic acids, colour, tone, total sulphur dioxide and free sulphur dioxide.

Buratti et al. [4] used innovative analytical techniques such as an artificial tongue and an artificial nose, together with spectrophotometric methods, to predict sensorial descriptors of Italian red wines and used a genetic algorithm to select variables and build regression models.

The combination of a mass spectrometry-based artificial nose and visible and near-infrared spectroscopy was explored as an objective tool to measure sensory attributes in commercial Riesling wines from Australia, by Cozzolino et al. [5]; in order to reach this goal, calibration models between instrumental data and sensory scores were developed using PLS.

On the contrary, supervised and non-supervised pattern recognition techniques have been applied less to non-specific data for *qualitative* wine problems, *e.g.* to distinguish samples according to the grape variety or the geographical origin.

Armanino et al. [6] used a headspace-mass spectrometry (HS-MS, artificial nose) instrument for analysing wine headspace and for distinguishing between Italian red wines from Barbera, Dol-

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cetto and Chianti cultivars, by means of their aroma. In this study, the Barbera and Dolcetto samples came from different oenological regions (Alba, Asti, Langhe, Monferrato and Ovada), so that factors other than grape variety might be involved in the differentiation. Acevedo et al. [7] distinguished wines according to the denomination of origin using UV–vis spectroscopy combined with support vector machines. Pigani et al. [8] classified Italian red wines on the basis of their variety by chemometric analysis of voltammetric signals (artificial tongue). Buratti et al. [9] elaborated artificial nose and artificial tongue data together to characterise and classify four types of Barbera wines (same grape variety) with different denominations of origin and produced in northern Italy in enclosed geographical areas. Cozzolino et al. [10] distinguished between white wines differing in botanical origin (Riesling and Chardonnay cultivars, respectively), using vis–NIR (200–2500 nm) spectral data. Visible and NIR regions were also used by Liu et al. [11] to verify the geographical origin of commercial Tempranillo wines from Australia and Spain.

Given the demand for easy and fast analytical methods, fingerprinting techniques represent an interesting alternative to the traditional analytical techniques [12] for carrying out the characterisation of the wine. However, no studies in the literature compare different techniques for the characterisation of wine.

In the present study, the capabilities of four fingerprinting techniques, NIR and UV–vis spectroscopy and artificial nose and tongue, for distinguishing between two Italian red wines from different grape varieties (Barbera d'Alba and Dolcetto d'Alba) have been compared. The evaluation was performed taking into consideration both the classification results achieved and economic factors (time required and cost). The aim was to identify which of the four fingerprinting techniques, investigated, is the most efficient in addressing the problem of grape cultivar identification. Such an achievement may be of great interest for both wine protection consortia and consumer associations.

2. Experimental

2.1. Samples

All 59 wine samples come under the Italian trademarks of Barbera d'Alba and Dolcetto d'Alba. The wines were collected from the same vintage (2007) and from the same production area, in order to avoid significant variability factors other than the grape variety. They were produced by different, known and reliable wine makers: the wine samples and their respective grape variety are listed in Table 1. Two samples (D03 and D08) were produced by the same vintner but they came from different lots.

Barbera and Dolcetto are produced in Piedmont, from two homonymous cultivars of *Vitis vinifera,* indigenous to Piedmont. The authenticity of the 23 samples of Barbera and the 36 samples of Dolcetto was guaranteed by the DOC ("denominazione di origine controllata" *i.e.* controlled denomination of origin) status, which certifies their provenance from a defined region around Alba.

In fact, the DOC status (EEC Regulation 823/1987) clearly defines a delimited geographic zone, identified by the oenological name of the territory (Alba in this case), which authenticates the origin of a wine and its basic characteristics. In order to obtain DOC status, wines must be made under specific conditions: with pre-determined yields per hectare, and using clearly defined grape varieties and traditional wine-making methods. According to the respective DOC regulations, Barbera d'Alba wine is produced entirely from Barbera cultivar, and Dolcetto d'Alba wine, is entirely produced from the homonymous grape variety.

Table 1
Wine samples with the respective grape variety.

Codex	Grape variety	Trade name
B01	Barbera	TERREDAVINO
B02	Barbera	TERRE DEL BAROLO
B03	Barbera	CA' DEL PLIN
B04	Barbera	DAMILIANO
B05	Barbera	CANTINA CLAVESANA
B06	Barbera	VIGNOTA
B07	Barbera	BORGOGNO
B08	Barbera	NEGRO
B09	Barbera	SANMICE'
B10	Barbera	RENATO RATTI
B11	Barbera	CA' VIOLA
B12	Barbera	PIETRO RINALDI
B13	Barbera	BERA
B14	Barbera	CONTERNO FANTINO
B15	Barbera	VITICOLTORI ASSOCIATI RODELLO
B16	Barbera	GIANFRANCO ALESSANDRIA
B17	Barbera	PAOLO SCAVINO
B18	Barbera	PIRA
B19	Barbera	ELIO ALTARE
B20	Barbera	MAURO VEGLIO
B21	Barbera	PARUSSO
B22	Barbera	CORDERO DI MONTEZEMOLO
B23	Barbera	ENZO BOGLIETTI
D01	Dolcetto	FONTANAFREDDA
D02	Dolcetto	LA MORRA
D03	Dolcetto	DUCHESSA LIA
D04	Dolcetto	MARCHESI DI BAROLO
D05	Dolcetto	CA' DEL PLIN
D06	Dolcetto	TOSO
D07	Dolcetto	ENRICO SERAFINO
D08	Dolcetto	DUCHESSA LIA
D09	Dolcetto	BRICCO BASTIA
D10	Dolcetto	BORGOGNO
D11	Dolcetto	LE COSTE
D12	Dolcetto	CA' VIOLA
D13	Dolcetto	PRUNOTTO
D14	Dolcetto	PIRA LUIGI
D15	Dolcetto	MARCARINI
D16	Dolcetto	MAURO VEGLIO
D17	Dolcetto	FRATELLI REVELLO
D18	Dolcetto	DAMILIANO
D19	Dolcetto	ENZO BOGLIETTI
D20	Dolcetto	SERRABOELLA
D21	Dolcetto	SORI' PAITIN
D22	Dolcetto	RIZZI
D23	Dolcetto	CASCINA MORASSINO
D24	Dolcetto	BARTOLO MASCARELLO
D25	Dolcetto	PAOLO SCAVINO
D26	Dolcetto	BRUNO GIACOSA
D27	Dolcetto	PIO CESARE
D28	Dolcetto	MADONNA DI COMO
D29	Dolcetto	ELIO ALTARE
D30	Dolcetto	SURI' VIGNAZZA
D31	Dolcetto	BRICCO BASTIA
D32	Dolcetto	PIETRO RINALDI
D33	Dolcetto	TENUTA CARRETTA
D34	Dolcetto	PARUSSO
D35	Dolcetto	RENATO RATTI
D36	Dolcetto	TRE VIGNE

2.2. Apparatus and procedure

Wine samples were analysed using NIR and UV–vis spectrophotometers, artificial nose and tongue. All four analytical techniques allowed measurements to be taken directly from the wine samples, without any physical-chemical pre-treatment, resulting in a significant reduction in time and costs. Two series of measurements were taken for all the samples, randomising the order of analysis. Finally, each sample was identified with the average of the two replicated signals, acquired from each instrumental technique.

NIR measurements were taken with an FT near-infrared spectrometer based on a polarisation interferometer (Buchi NIRFlex