



Can Sensory Analysis and E-Noses Support the Assessment Work behind DOC and DOCG Wines?

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Protected Denominations of Origin (PDO) DOC/DOCG labelling is a key factor in qualifying wines for premium positioning and requires a batch-level institutional approval based on chemical and physical analyses and a gustative assay by a commission of experts.

The highly standardised products required by international markets requires a critical assessment of the quality of the process generating the assaying commission counsel so that well-known denominated wine products, hold and possibly expand, their market position.

The present study was carried out to investigate the relations between electronic nose analysis and judge-based sensory analysis and the assaying commission counsel to address possible ways to 'inject' quality assurance tools and concepts in the pipeline of the 'institutional filter' of the Prosecco-area DOC/DOCG. Chemical analysis and of chemometrics proved good predictors of the assaying commission counsel, while significant deviations between the outcomes of the panel and commission evaluations. The role of the electronic nose detection and of chemical/physical analyses in helping resolve such discrepancies is discussed.

1. Introduction

Protected Denominations of Origin (PDO) are a key factor in qualifying food products for premium positioning, and claiming origin denomination is especially rewarding for wines. Awarding a bottle the precious DOC/DOCG labelling is the end point of a process which begins at the winery, where grapes are pressed and then fermented to become wine under the oenologist's control, but each finished wine batch must actually pass a critical step of 'institutional' approval based on chemical and physical analyses and a gustative assay by a commission of experts. The 'institutional' approval is entrusted to a designated qualified body, which may be a Consortium, or a private Company.

Wine commercialisation puts a lot of pressure on top of wineries because of the different expectations of the various markets. International markets require highly standardised products, where normal batch-to-batch variations, which would be denoted as 'typical' in the domestic market, are not acceptable. Therefore, a critical assessment of the quality of the process generating the assaying commission counsel is of paramount importance in the endurance of the market grip of well-known, denominated wine products. However, the fluctuations in market capacity following the opening of new high capacity markets, or the strong fluctuations of market trends, may put the whole production chain under pressure (because of the high number of submitted batches, or the dominance of specific markets) and may inject a negative bias into quality assessment because of the effort to satisfy the commercial requirements. Arguably, the weakest step of the whole institutional quality assessment is the only non-instrumental assessment, that is the gustative assessment, which relies entirely on large groups of experts operating in small groups where different experts alternate without a specifically established planning.

Researchers and instrument producers have been developing instruments that possess a limited number of non-specific sensors for well above 20 years now. Such instruments that mimic Nature's senses which derive

a large number of sensations from a limited number of receptors justify naming their use in combination with data processing algorithms 'artificial sensory analysis': the sensor mimics the biologic receptor, while a mathematical algorithm mimics the brain functions of recognition and judgement.

The so-called 'Electronic noses' (E-Noses) fall within the class of artificial sensory analytical tools. E-noses have found two main fields of application: environmental monitoring (for environmental quality assurance, investigation, and liability; Dentoni et al., 2012) and food product characterisation (Peris and Escuder-Gilabert, 2009); in this latter domain inter- (Alexandre et al., 2009) and intra-varietal (López de Lerma et al., 2013) identification, and real-time process monitoring (Pinheiro et al., 2002; Lozano et al., 2014). In winemaking, on-line fermentation monitoring has been proposed by density measurement, ethanol concentration and CO₂ evolution. Attempts have been made at the on-line measurement of specific by-products (e.g. by biosensors) and quality markers or of several simultaneous products (by FT-IR or E-noses). This objective is highly ambitious, but not unrealistic (Sablayrolles, 2009). However, to the best of the authors' knowledge, no significant implementations of such a system has ever been established in any large scale facility as a production aid tool.

Recently, Franceschi et al. (2015) investigated the capability of hybrid analytical systems to early warn against a 'likely non conformant' verdict of the assaying commission for sparkling wines belonging to the "Prosecco DOC" and the Prosecco Superiore DOCG" protected denominations, while Franceschi et al. (2016) investigated the conditions that permit the diagnosis of 'Brett' (i.e., produced by *Brettanomyces* spp. yeasts) taints in Valpolicella red wines by the exclusive use of an electronic nose.

The present study was carried out to investigate the relations between assessable sensory analysis instruments and the assaying commission counsel to address possible ways to 'inject' quality assurance tools and concepts in the pipeline of the 'institutional filter' of the Prosecco-area DOC/DOCG.

The E-nose responses, with the help of the chemical analysis and of chemometrics, have proved to be good predictors of the assaying commission counsel and of the aroma level of wine. At the same time, parallel, double-blind runs by a trained sensory panel and by the charged assaying commission reveals significant deviations between the outcomes of the two man-based evaluations. The role of the electronic nose detection and of chemical/physical analyses in helping resolve such discrepancies is discussed.

2. Materials and Methods

2.1 Experimental Design

The analysed samples belonged to the 'Prosecco DOC' PDO and were supplied anonymously by Valorigalia, the body in charge of assigning DOC and DOCG certifications for Prosecco wines based on their sensory identity. 25 batches submitted to the commission were analysed by chemical, gustative, and by the E-Nose. 15 of them were also analysed by the sensory panel.

Valorigalia commissions are composed by 5 expert members, which intervene on a rotative basis, and is not subjected to internal validation protocols. Upon tasting, the Valorigalia Commission either approves the batch or suspends the judgement (on the product batch) and states the need of repeating the assessment (MIPAAF, 2011a, 2011b and 2011c). Therefore, samples from re-assessable batches technically failed the sensory test. Blind (for the commission) witnessing to the commission's sessions was performed by an expert person that took notes concerning the adopted procedures and in any comment made during the session and taking part in its outcome, be it passing mode (unanimity pass, pass with taint note, that is with a contrary vote, simple majority pass, that is with two contrary votes, rejection, without notion of any possible favourable votes). The conformity notes were transformed into a multi valued index by taking the average of the commission votes, calculated attributing '+1' to each positive evaluation and '-1' to each negative evaluation. Therefore, in correspondence to the four listed possible outcomes the index may assume the following values: -1 (non conformity), +0.2 (simple majority conformity), +0.6 (conformity pass with taint note) and +1 (unanimity conformity). This index will be called Degustative Average Conformity Index (DACI) in the following. Wines samples were then transferred to the laboratory for the electronic nose analysis and, during the second part of the investigation, to the sensory panel.

The sensory panel was made up by 10 members, familiar with Prosecco wines and trained and managed by University of Padua / CIRVE personnel in conformity to the ISO 8586 1 and 2 norms. The members were asked to provide a quantitative evaluation of the following characters of Prosecco: colour intensity, olfactive intensity, white flowers flavour, lemon flavour, apple flavour, fresh vegetable flavour, tropical fruit flavour, gustative intensity, acid taste, salty taste. An overall mark was then calculated as the sum of each individual mark of the preceding list. Finally, each member of the panel was asked whether he/she would approve or reject that batch and the average aggregate conformity index was calculated as indicated above, i.e. attributing '+1' to each positive evaluation and '-1' to each negative evaluation and an average was calculated (Sensory Panel Average Conformity Index, SPACI). The sensory panel was kept in the dark of the assaying

commission's work and the authors of this paper were kept in the dark of every operational detail of the assaying commission's work until data analysis time.

2.2 Experimental Setup

The artificial sensory analyses were carried out in a stream of pure nitrogen (cylinder), which was used both as a carrier stream (brushing the free surface of the sample in an Erlenmeyer flask), and as the reference substance (Figure 1 and 2). In order to avoid the stripping of aromas and volatile taints the artificial sensory analyses were carried out in a stream of pure nitrogen (cylinder) in a special aroma-preserving gas circuit permitting the full recycle of the equilibrated gas mixture stream (carrier gas + volatiles) during the measurement part of the overall sample analysis management procedure and avoid errors due to the coupling of desorption kinetics and the duration of the measurement. The three-way valve has two positions: 1-2 and 2-3. 1-2 is used during the loading of the carrier gas; the gas previously filling the circuit is discharged through the hydraulic guard. 2-3 is used during the active phase of the measurement. During this phase the gas is recirculated from the outlet port of the electronic nose to the sampler and back to the electronic nose inlet port. During the analysis phase of the carrier gas, which is also used as the reference standard stream, the gas sampled from the carrier gas line leaves the circuit through the hydraulic guard. An excess of carrier gas, signalled by a continuous leakage from the specific outlet port, avoids an unwanted leakage of ambient air into the measurement circuit.

The electronic nose used throughout the experimentation was a Libra Nose rev. 2.1, featuring multiple quartz micro-balance technology by Tor Vergata University of Roma. The steady state readings of the 8 E-nose sensors on the reference gas were subtracted to the sensor response to the reading with the sample wine. Following that, the deviations of the steady state readings obtained on the relevant sample obtaining the raw data ready for subsequent chemometric analysis. The steady state value of the measured relative humidity of the circulating sample was added to the 8-dimension array of sensor data so that each experimental run was described by a 9-number array.

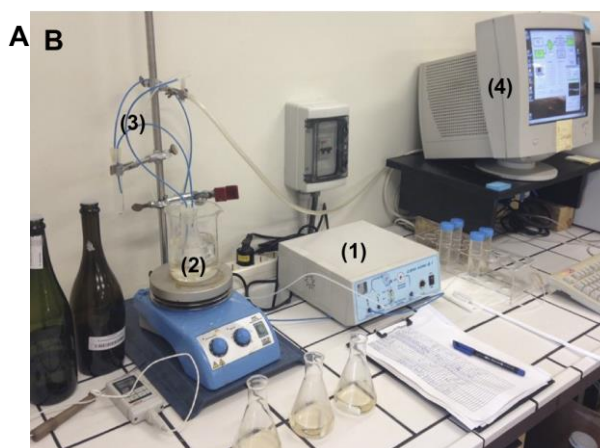
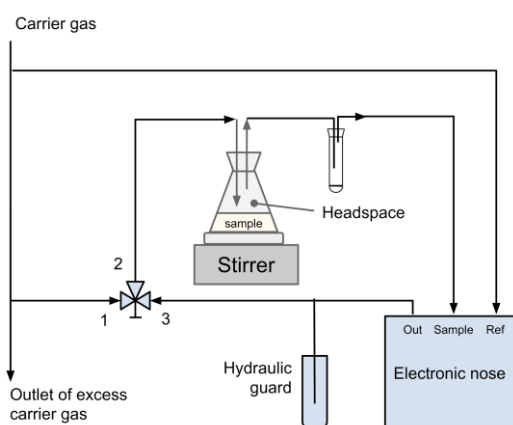


Figure 1: (A) Scheme of the measuring set-up including the sample holder, the piping, mode switching valves and guards. (B) View of the electronic nose sparkling wine sample assaying setup showing (1) the E-nose; (2) the sample assaying chamber (b); the carrier gas and mixture gas piping and the ancillary gas management devices (3); the personal computer deputed to E-nose control (4).

2.3 Chemometric Analysis

Classification was carried out in non supervised and supervised manner by using Octave (<http://www.gnu.org/software/octave/>) on an Ubuntu Linux personal computer.

The responses of the 8 E-nose sensors underwent time shift-neutral time-domain filtering to identify the steady state responses of the sensors and blank reference by subtracting the sensor response on the reference gas to the reading with the sample wine. Following that, the deviations of the sensor responses with respect to the blank were joined with the 4 variables of the chemical analysis related to the condition of the gas phase in contact with the product (volatile acidity, SO₂, CO₂ overpressure and effective ethanol concentration) and the whole set of information was subjected to standardisation and classification analysis.

Prior to data analysis, the whole data set was standardised, that is, each variable (e.g., relative humidity and

sensor 1 to eight) was mean centered and standardised (e.g., transformed into unit variance). Then, non supervised classification was carried out by Principal Component Analysis (by retaining the topmost 2 and 3 components), while supervised classification was carried out by (Fisher) two-dimensional Linear Discriminant Analysis and Partial Least Squares (again, by retaining the topmost 2 and 3 component PLS) were performed by using the additional keying information provided by the aggregate conformity index calculated for the assaying commission and the sensory panel (Franceschi et al., 2015).

3. Results and Discussion

The first observation that is worth giving account concerns the relation that can be found between the overall sensory mark issued by the sensory panel and the conformity advice by the sensory panel itself. As it can be observed in Figure 2A, the advice is roughly proportional to the overall sensory mark. The main factors contributing to this outcome are the sensory marks in the 'White flowers' and 'Apple' flavours, which are also maximally correlated to the sensory panel average conformity index (SPACI vs 'White flowers' trait, $R = 0.87$; SPACI vs 'Apple' trait, $R = 0.82$). Such correlation factors are normally judged weak when dealing with strictly 'physical' dependencies, but this is an incorrect point of view in this case, where a subjective 'suitability' parameter is related to the quantitative assessment of several sensory traits. To give the reader a different point of view of this dependency, one may state that the p-value that SPACI depends on the 'White flowers' and 'Apple' traits with a p-value $< 6 \cdot 10^{-5}$, while the p-values for the remaining traits are much higher.

Electronic nose data were related to sensory analysis and chemical analysis data to find whether individual factors could be related to one another. For the sensory analysis, only a weak positive correlation was found for the 'Tropical fruit' trait and a weak negative correlation with the 'Salty' trait, possibly related to the depression of vapour pressure of the liquid phase as an effect of salinity.

In order to find whether non linear, rather than linear, relations were present quantitative sensory traits was modelled with the Stevens' law (Stevens, 1962) and e-nose sensor data with the Freundlich isotherm, both of the power law form, obtaining

$$I = k \cdot S^n \quad (1)$$

where I and S stand for 'quantitative sensory evaluation' and 'e-nose sensor datum' respectively; applying physical considerations it can be seen that n may lie slightly below or above unity. The frequency shift data set was transformed by raising each datum to the square and by taking the square root of it, but the correlation matrix did not improve. Furthermore, no linear correlations were found between e-nose data and chemical analysis data.

The assaying commission aggregated conformity index was then related to the sensory panel conformity advice (Figure 2B). It should be first noted that if the two evaluation groups had substantially equivalent decision criteria, the chart should show an interpolating line passing through the origin. However, the interpolation line rather intercepts the ordinata (DACI) at about 0.4. This translates into saying that when the sensory panel is split between accepting and rejecting (SPACI = zero), the assaying commission evaluates the batch with a mark that is better than a "majority conformity pass".

Once this skewness was observed, the operation procedure of the assaying commission was carefully examined and it was found that the commission had a "verticised" operation where the commissioners observations and verdicts were not withdrawn before the beginning of the "open" part of the session, which was in turn initiated by the commission's president that would take the floor and set forth his opinion concerning the flavour and gustative traits. Normally, other opinions would follow, before the final vote during which contrary voices would normally show up.

It is clear that a number of weak points affect this procedure. First, the inconsistent recruiting mode, which does not exclude specific subjects (for instance, using perfumes is not permitted to sensory panel members, and panelists are temporarily excluded from their duties when their health impairs sensory accuracy) and does not foresee any internal statistical validity test. Secondly, the verticised operating mode where the president starts talking without the other commission's members having delivered their notes and verdicts introduces a clear bias toward an appeasing attitude with the producers.

The possibility of predicting the assaying commission's verdict based on the electronic nose and chemical analysis data only was tested by resorting to chemometry. Unsupervised techniques (PCA) failed, signifying that the information related to this is not clearly represented by the raw physical data. Supervised techniques, namely PLS (Figure 3A) and LDA (Figure 3B), instead, were more capable of highlighting more classificatory and descriptive points of view. In particular, LDA shows well aggregated clusters showing all the four categories that the aggregate average conformity index of the assaying commission can assume (full reject, majority pass, taint note pass, full pass).

While it is understandably difficult for an institutional panel having to carry a significant workload to be fully assessed and statistically validated, the lack of horizontality (lack of a previous blind note-taking time when all the commissioners are free from any external influence and independence of the final verdict from anything that happens after the blind note-taking time) appears to be the single, most important and easy to correct weakness.

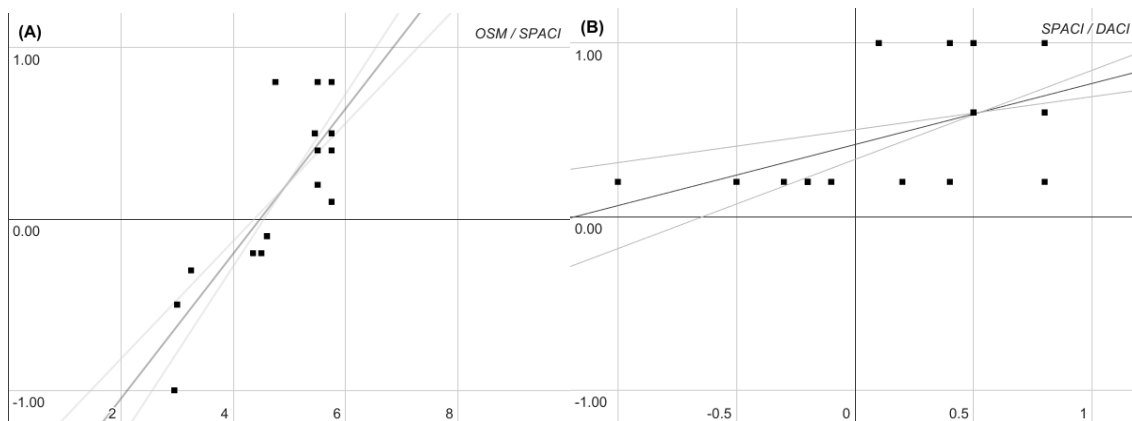


Figure 2: (A) Relation between overall sensory mark (OSM) and conformity advice by the sensory panel (SPACI); (B) Relation between conformity declared by the assaying board (DACI) and conformity advice by the sensory panel (SPACI). Axis meaning and units are given as x-quantity / y-quantity at the upper right of each chart. Upper and lower gray lines indicate confidence intervals at ± 1 standard deviation from the maximum likelihood estimate.

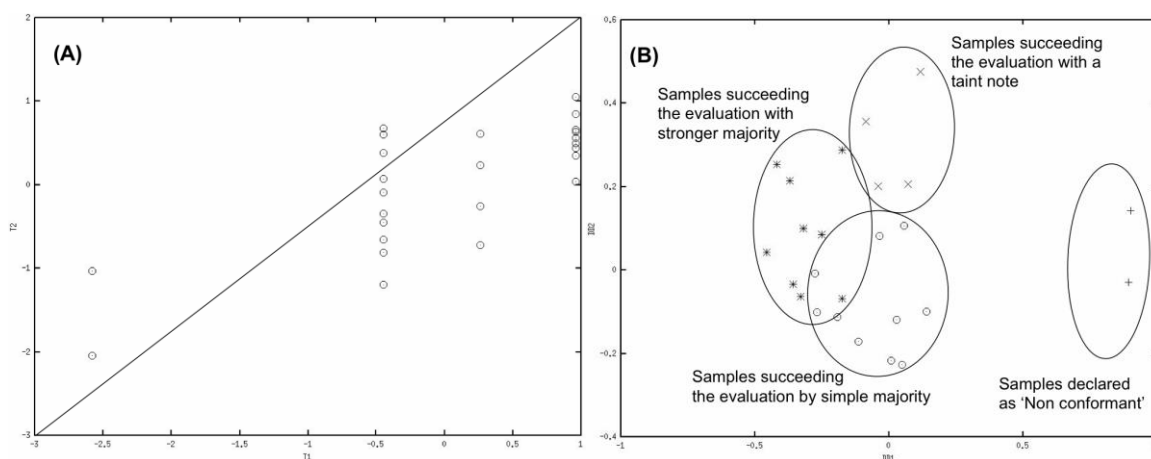


Figure 3: A: Score plot of 2-D PLS correlation of DACI prediction based on electronic nose + chemical analysis vs actual DACI. B: Score plot of 2-D LDA correlation of DACI prediction based on electronic nose + chemical analysis vs actual DACI.

4. Conclusions

Selected chemical analysis data from the routine base together with electronic nose analysis constitutes a sufficient base to infer the Prosecco DOC commission's verdict if a supervised algorithm is used, such as, for instance, LDA. For the Prosecco DOC, the conformity declaration by the assaying commission is significantly more forgiving than the conformity advice produced by the sensory panel. A simple correction to the customary operation would be to make members' advices really independent from one another.

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