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Evaluation of Italian wine by the electronic tongue: recognition, quantitative analysis and correlation with human sensory perception

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Abstract

The electronic tongue based on a sensor array comprising 23 potentiometric cross-sensitive chemical sensors and pattern recognition and multivariate calibration data processing tools was applied to the analysis of Italian red wines. The measurements were made in 20 samples of Barbera d'Asti and in 36 samples of Gutturnio wine. The electronic tongue distinguished all wine samples of the same denomination and vintage, but from different vineyards. Simultaneously the following quantitative parameters of the wines were measured by the electronic tongue with precision within 12%: total and volatile acidity, pH, ethanol content, contents of tartaric acid, sulphur dioxide, total polyphenols, glycerol, etc. The electronic tongue is sensitive to multiple substances that determine taste and flavour of wine and, hence, the system was capable of predicting human sensory scores with average precision of 13% for Barbera d'Asti wines and 8% for Gutturnio wines.

Keywords: Evaluation; Italian wines; Electronic tongue

1. Introduction

Rapid and low-cost methods enabling quality assessment of food and raw products, including measurements on-site, are of urgent interest for industry. Traditionally used analytical techniques of food analysis and wine in particular include HPLC, different versions of GC, various types of spectroscopy, etc. (e.g. [1–3]). These techniques can be highly selective and reliable, but they require expensive instrumentation, sample preparation, and experienced operators and can hardly be fully automated. Neither such instruments are mobile. On the other hand there is a need to assess food flavour and integral food quality, which are the most important characteristic from the customer's point of view. Only trained sensory panel consisting of experience tasters can reliably evaluate food flavour, taste and aroma. Food flavour assessment is a time-consuming and expensive procedure since an extensive training of panellists is necessary for reproducible results and even the trained panel can perform only a limited number of analyses per day. Different panels often use different parameters for flavour description and the results can neither be compared explicitly nor properly generalised in most cases. Application of traditional analytical techniques for this task is also hardly possible because the relationship between chemical composition of food and

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its flavour is not established even for many important common products.

Sensor systems are one of the most promising ways of developing rapid and low-cost methods for foodstuff quality control [4,5]. The electronic tongue sensor system can be applied to food flavour assessment and these results may be correlated to the marks of a taste panel. On the other hand the electronic tongue also can be used for multi-component analysis of the content of the most important food nutrients.

The idea of the electronic tongue is based on the utilisation of the specially designed non-specific potentiometric chemical sensors with enhanced cross-sensitivity to as many different components in solution as possible. These non-specific sensors are comprised into sensor arrays producing multidimensional response, which contains information about various substances or group of substances in the complex analytes. Response of the sensors of the array can be related to ionic, redox or molecular interactions at the sensor/solution interface. Pattern recognition and/or multivariate calibration methods are used to interpret complex signals from such sensor arrays thus producing qualitative and quantitative information about multi component solutions. Thus, electronic tongue concept suggests the possibility of both qualitative recognition and distinguishing between integral chemical images and quantitative determination of the content of substances or taste or flavour characteristics. The overview of the existing electronic tongue systems can be found in [4,5].

Despite numerous attempts of using the electronic noses for the wine analysis (e.g. [6–9]), application of the electronic tongues for this purpose remains scarce.

Combined artificial olfaction and taste systems were used for wine discrimination [10]. Four different wines, two red and two white, were discriminated using such system. This work should be considered as a demonstration rather than an analytical application.

Preliminary data of the electronic tongue application to the analysis of Italian red wines were reported by our group [11,12]. A combined electronic nose and tongue system based on metalloporphyrines sensors was reported in [12] for quantitative wine analysis. One of the findings was that the best regression models were obtained for compounds mostly correlated with the electronic tongue output. Worse regression models were obtained for the compounds, which concentrations were mostly correlated with the electronic nose output. Thus, the electronic tongue likely produces more relevant information about wine composition. Furthermore, enhancing the sensor array of the electronic tongue by incorporating the sensors based on different sensitive materials, besides metalloporphyrines, may ensure better recognition capabilities of the system and provide for additional information about wine composition and taste properties.

The present paper deals with the detailed results of the electronic tongue application to the recognition (classification, identification), quantitative analysis and flavour assessment of Italian produced wines.

2. Experimental

2.1. Wine samples

Measurements with the electronic tongue were performed in three types of Italian wine during two measuring sessions. Firstly, the measurements with the electronic tongue were made in red and white wines of Castelli Romani denomination. Optimal measurement time and other details of methodology were determined at this stage. It was found that all sensors of the array would reach the stable potential (changing less than 0.1 mV/min) in the wine within 10 min. After the methodology study, the same 2 samples of the wine of Castelli Romani denomination, 20 samples of red wine of the Barbers denomination and 36 samples of red wine of Gutturnio denomination were measured. Wines of each denomination were produced essentially from the same typical grapes of the same vintage but at different vineyards and by different farmers. Barbera d'Asti wine samples were divided into three portions. Between measurements the samples from each set were hermetically closed without free headspace to prevent oxidation. In the same way Gutturnio wine samples were divided into four portions and hermetically closed. Three and four replica measurements were made in all Barbera d'Asti and Gutturnio wine samples, correspondingly, each time in a fresh portion of the wine.

Authentic Barbera d'Asti and Gutturnio wine samples were obtained from Italian Enological Institute in Asti (Italy). Along with the wine samples the results of determination of major wine components using

Table 1
Components and parameters determined in Gutturnio and Barbera d'Asti wine samples by conventional analytical methods and typical ranges

Component	Minimum content	Maximum content
Gutturnio		
Extract (g/l)	21.9	44.2
Density	0.9913	1.0005
Sugar (g/l)	1.62	5.28
Alcohol (vol.%)	11.88	14.42
pH	3.16	3.53
Total acidity (g/l)	4.90	8.60
Volatile acidity (g/l)	0.22	0.67
Tartaric acid (g/l)	1.26	2.75
Malic acid (g/l)	1.28	3.27
Lactic acid (g/l)	1.24	3.54
SO_2 total (mg/l)	59	131
Glycerol (g/l)	6.69	10.52
Total polyphenols (mg/l)	783	2209
Antocianins (mg/l)	126	445
Ca (mg/l)	41	89
K (mg/l)	593	1243
Mg (mg/l)	64	104
D.O. 420	1.361	5.115
D.O. 520	1.683	10.100
Barbera d'Asti		
Extract (g/l)	29.3	52.6
Density	0.9939	1.0037
Sugar (g/l)	0.80	1.98
Alcohol (vol.%)	9.94	13.74
pH	3.19	3.61
Total acidity (g/l)	8.78	10.95
Volatile acidity (g/l)	0.27	0.66
Tartaric acid (g/l)	3.17	5.74
Malic acid (g/l)	2.36	4.44
Shicimic acid (mg/l)	17	59
Citric acid (g/l)	0.31	1.45

conventional analytical techniques were also obtained from the Enological Institute. The components and parameters determined in wine samples and their typical quantitative ranges are shown in the Table 1. Also the Institute provided for the results of wine sensory assessments made by the trained taste panels. Tasters utilised 14 parameters describing different aspects of wine taste and flavour. Some of these parameters were different for Barbera d'Asti and Gutturnio wines, some of them were identical or close. The results of chemical analysis and the marks of sensory panels were used as reference data for calibration of the electronic tongue for respective tasks.

2.2. Sensor array

Sensor array used for measurements in the wine comprised 23 potentiometric chemical sensors. For wine experiment the sensors displaying cross-sensitivity to inorganic cations and anions such as potassium, calcium, chloride, etc. and organic substances such as phenols, organic acids, alcohols, etc. were chosen. Results of cross-sensitivity evaluation of different classes of sensing materials to inorganic and organic substances were reported earlier [13–15]. Sensor array included 14 sensors with chalcogenide glass and crystalline (for Cl^-) membranes, 2 metallic (Pt and Sb) and 6 with plasticised polymer membranes and pH glass electrode. Details of sensor preparation and composition of materials are given elsewhere [13–15].

Potentiometric measurements with the electronic tongue were made using a specially designed multi channel digital voltmeter with high input impedance. Sensor potential values were measured versus conventional Ag/AgCl reference electrode with precision of 0.1 mV and written into PC data files. The measurements were done directly in the wine samples without any sample preparation or treatment. Sensors were washed with distilled water between measurements for several minutes to reach steady readings in water.

2.3. Data processing

The processing of the data from the sensor arrays was performed using principal component analysis (PCA), partial least squares regression (PLS) and artificial neural network (ANN), namely back-propagation neural network (BPNN). All these methods are widely referred to in the literature (e.g. [16–18]) as the tools for multivariate data processing. The following computer software was used: NeuroSolutions (v.3.02 by NeuroDimensions Inc., USA) for ANN and the Unscrambler (v.6.0, 1997, CAMO ASA, Trondheim, Norway) for PCA and PLS. The analysis of the experimental data was aimed at: (1) classification and recognition of the samples; (2) quantitative determination of the content of multiple substances in wines; and (3) prediction of human sensory scores for wine samples.

The first task was to study the capability of the electronic tongue to distinguish between different sorts of wines and between different samples of the wine of the same denomination but from different vineyards. The distinguishing ability of the "electronic tongue" was investigated using PCA. The same method was also used for visualisation of the results.

Classification of wines of different denominations was also performed using soft independent modelling of class analogy (SIMCA) method. SIMCA consists in building models by PCA for each class separately and using these models afterwards for prediction of class memberships. Two parameters defining class boundaries are used: sample to model distance, which is Euclidean distance from class centre to the sample, and leverage, which is considered as a measure of similarity of the sample to all samples of the given class. An unknown new sample is assigned to the given class if it falls within described class boundaries. The details about numerical calculations in SIMCA method can be found elsewhere [16]. Validation of all classification models was performed using independent test sets. Test set comprising about one-fifth of all the data was used for validation of classification models. Samples for the test sets were chosen randomly. All replicas of each given sample were included either in the calibration set or in the test set but not into both of them.

In quantitative analysis the content of different components in the wine was determined. Concentrations of different inorganic and organic components that were determined by standard analytical methods were used as reference data in the calibration process. Another task was prediction of sensory scores related to wine flavour using the electronic tongue. In this case human scores of wine flavour and taste produced by trained taste panels were used as the reference data for system calibration. The calibration models were made using PLS and back-propagation neural network.

Validation of all PLS calibration models was performed using independent test sets. Test set of about one-third of all the data was used for validation of PLS calibration. Samples for the test sets were chosen randomly. All replicas of a given sample were included either in the calibration set or in the test set but not into both of them. Thus, samples used for testing of calibration models can be considered as really unknown and prediction results represent an adequate estimate of the electronic tongue performance. On the other hand, prediction results for replicated measurements in the same sample give an adequate estimate of the electronic tongue reproducibility.

A three-layer back-propagation neural network was applied in this work. Hyperbolic tangent was used as transfer function of hidden layer nodes. Neural network was trained using back-propagation algorithm with momentum and batch weight update [18]. Neural network contained 23, 8 and 1 neuron in the input, hidden and output layers, respectively. Responses of all 23 sensors of the array were used as network input. Modelling of multiple independent variables simultaneously might be used either if they are highly correlated or for screening purposes. It was observed earlier [16,19] that modelling of only one independent variable at the time allows obtaining better fit of the data and, thus, better calibration models. Therefore, in this work separate calibration model was produced for each parameter using either ANN or PLS. According to the literature data [19] and earlier gained experience the networks with multiple hidden layers are more prone to overfitting while not providing better data fit at least for sensor array data. For this reason the network architecture with a single hidden layer was chosen. Number of hidden neurons was optimised with the aim to obtain the lowest prediction errors for cross-validation dataset. Eight neurons were found to be optimal number of hidden nodes.

Cross-validation was performed for ANN to avoid overfitting using ca. one-third of the calibration dataset. Each neural network was calibrated several times to avoid local minima and to obtain the best fit of the data, i.e. the lowest prediction errors for cross-validation dataset. The best network configuration giving the smallest errors for the cross-validation dataset was further used for test runs. Calibration and test sets were completely independent. The test samples were never used in the calibration and should be treated as the samples unknown for the system. All analytical results of the electronic tongue presented in this paper were obtained only during the test sessions as predicted values for unknown test samples.

3. Results and discussion

The ability of the electronic tongue to discriminate wines from different regions as well as wines from the same geographical area and of the same denomination

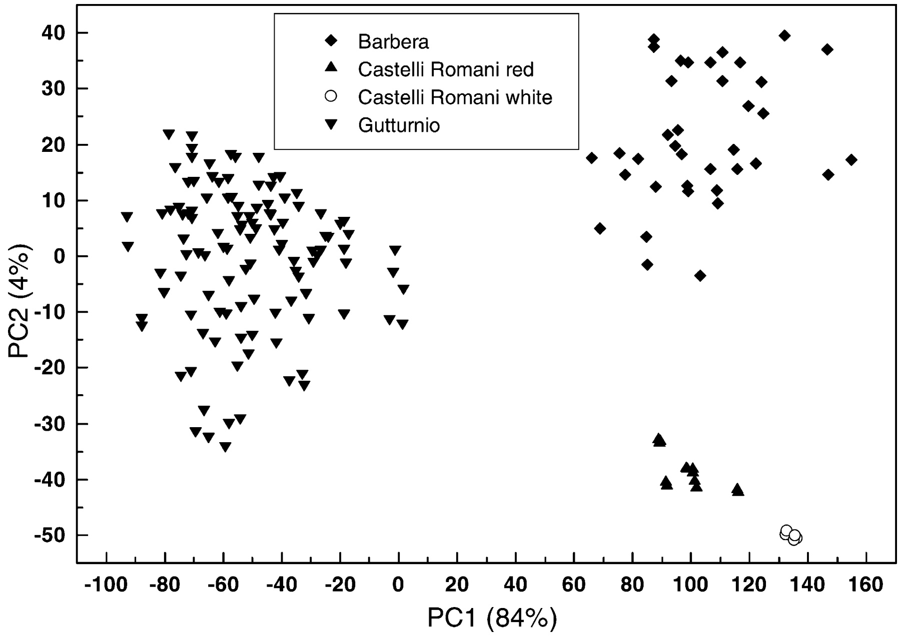

Fig. 1. Discrimination of Italian wines using the electronic tongue. Data were processed by PCA.

was studied on the Italian wines of Castelli Romani, Barbera d'Asti and Gutturnio types. Barbera d'Asti is produced in the north of Italy, two others in different areas in the middle part of the country. Discrimination of all wines, namely of red and white samples of Castelli Romani, 20 samples of red Barbera d'Asti and 36 samples of red Gutturnio by the electronic tongue is shown in the Fig. 1. Three different types of Italian wines can be easily separated from each other. Obviously, red and white wines even from the same geographical area differ very significantly.

Discrimination of wines of different denominations and identification of the wines from the same geographical region might be necessary to control quality and authenticity of the origin of wines [20,21]. Therefore, numerical classification of wines of the different denominations was performed with the help of SIMCA. The classes corresponding to each of the wines of the three types were modelled. The resulting plots of samples to model distance versus leverage for each wine are shown in the Fig. 2a–c. A sample is assigned to the given class if it falls within class boundaries defined by Sample to Model Distance and Leverage. The area corresponding to the given class is shown on each plot as the rectangle in the low left corner. As shown on the plots, all wine samples were assigned correctly to the corresponding class. That means that the electronic tongue is capable, after an appropriate calibration, of identifying correctly at least the denomination of the red wine.

The electronic tongue could distinguish all samples of different wines (Fig. 1). Furthermore, the system was capable of distinguishing red wines of the same denomination (either Barbera d'Asti or Gutturnio) that were very close in terms of origin, taste and chemical composition. The results of recognition of Gutturnio and Barbera d'Asti wine samples by the electronic tongue are shown in the Figs. 3 and 4 correspondingly. Two replicas of each wine are shown. It should be noted that reproducibility of the measurements with the electronic tongue in Barbera d'Asti wines was better then in Gutturnio wines. In most cases the wines from the different vineyards can be correctly distinguished and identified by the electronic tongue though some of the samples are located quite close to each other. Thus, the instrument can be used for fast identification of wines.

The possibility to use the electronic tongue for measuring the content of different inorganic and organic substances in the wine was evaluated. Earlier the results of determination of the main wine characteristics such as total and volatile acidity, content of ethanol, tartaric and shicimic acids and pH in the Barbera d'Asti wine were reported [11].

The number of substances and parameters determined by conventional analytical methods for the Gutturnio wine samples was bigger in comparison

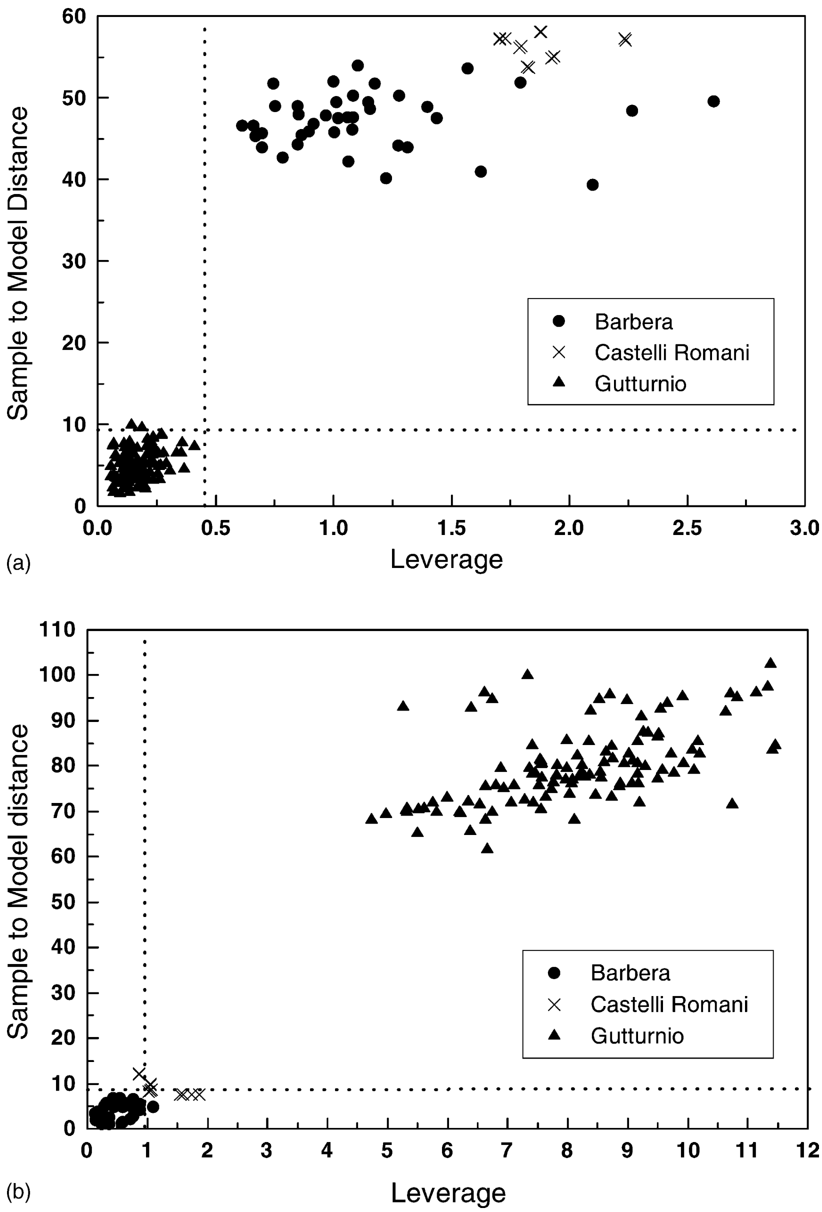

Fig. 2. SIMCA results of class membership prediction of the wine samples by the electronic tongue. The Sample to Model Distance and Leverage determined the class boundaries (low left corner). Modelled classes are: (a) Gutturnio; (b) Barbera d'Asti; and (c) Castelli Romani, respectively.

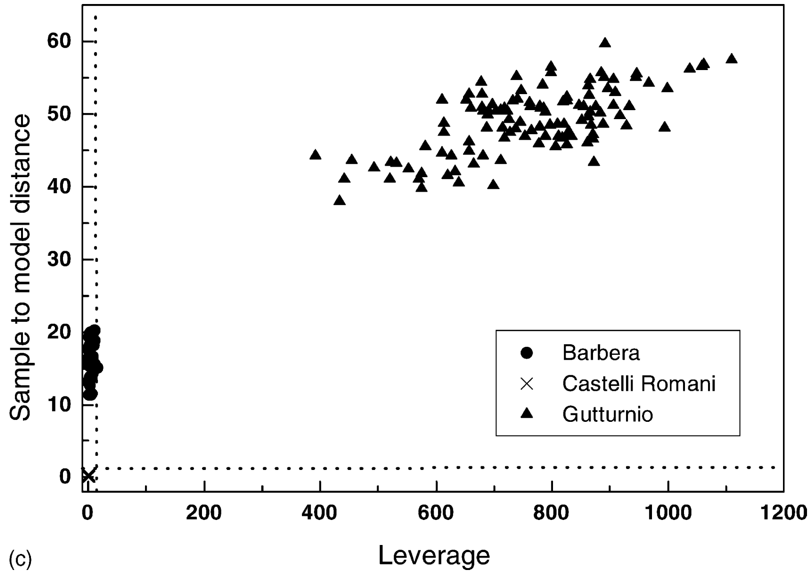

Fig. 2. (*Continued*).

with those for Barbera d'Asti wine samples (Table 2). Moreover, chemical composition of these two wines differs significantly at least according to the content of main components. Typical ranges of concentrations or values of parameters of the most main wine nutrients do not coincide or only slightly overlap for Barbera d'Asti and Gutturnio (Table 2). Thus, the calibration models obtained for a single wine type may not be easily transferable to another one since the models will not account for a part of concentration range for many compounds. Application of the calibration model produced using, e.g. Gutturnio wine samples

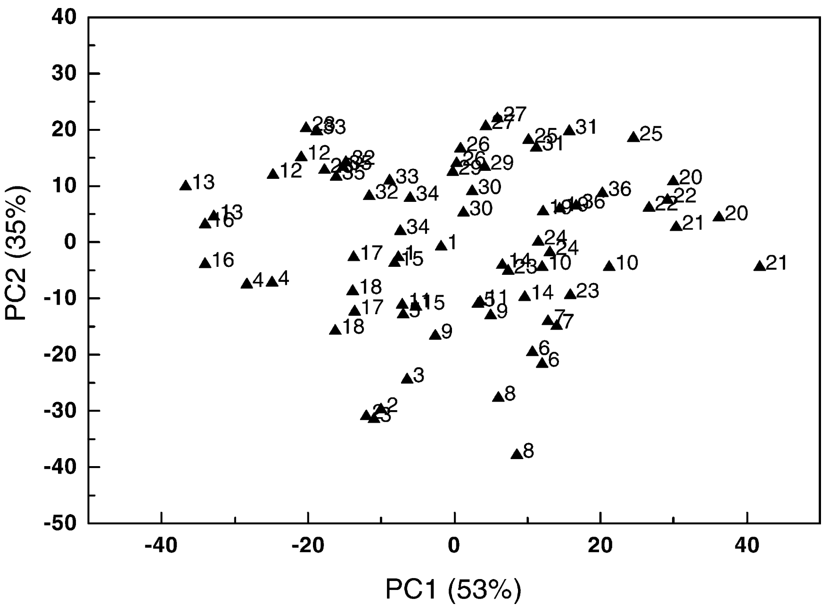

Fig. 3. Recognition (PCA score plot) of 36 samples of Gutturnio red wine obtained using the data from the array of 23 sensors.

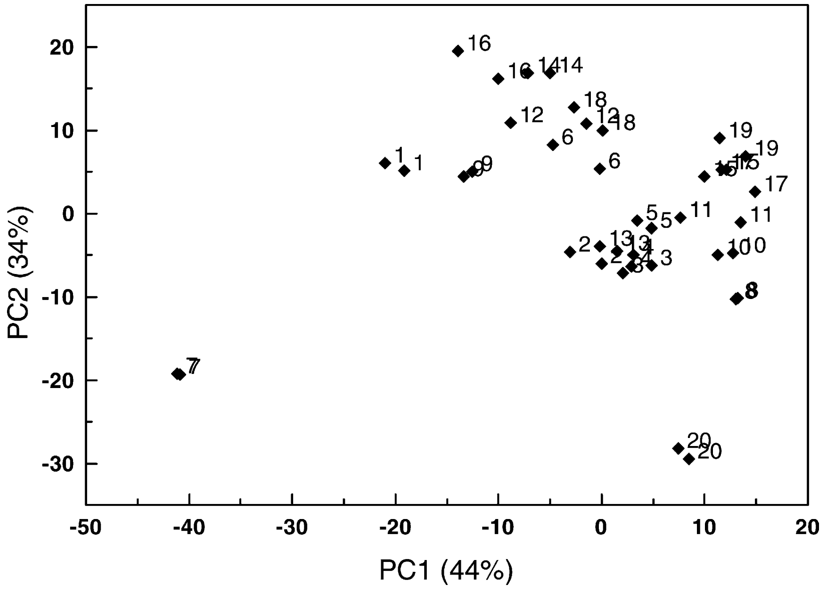

Fig. 4. Recognition (PCA score plot) of 20 samples of Barbera d'Asti red wine obtained using the data from the array of 23 sensors.

to Barbera d'Asti ones will require extrapolation that normally should give poor results. However, the universal (applicable to different wines) calibration of the electronic tongue system is possible if the whole concentration range for the given compound is taken into account. Thus, a feasible universal calibration should be produced using the data obtained for the both wines or, generally speaking, for all wines under study.

Considering this, the universal calibrations applicable for both Barbera d'Asti and Gutturnio wines were produced and tested using the samples of both wines. When the reference data were available for only one wine, e.g. Gutturnio, the calibration and consequent testing were performed only with the samples of this wine. Such characteristics as extract, density, pH, total and volatile acidity, content of sugar, ethanol, tartaric and malic acids were determined by conventional analytical techniques and were made available for both types of the wine. The results of determination of some of these components in test samples together with the standard deviations and mean relative errors and reference values (chemical analysis) for both types of wines are summarised in the Table 2. The calibrations of the electronic tongue for total acidity and tartaric and malic acids content were made separately for each

Table 2
The results of determination of total acidity, tartaric and malic acids contents in the samples of Barbera d'Asti and Gutturnio wines by the electronic tongue

Samples	Chemical analysis	Electronic tongue	S.D.	Mean relative error (%)
Total acidity (g/l)				
Barbera d'Asti 5	9.60	9.45	0.2	5
Barbera d'Asti 7	10.65	10.71	0.3	
Barbera d'Asti 20	9.23	9.2	0.2	
Gutturnio 1	6.50	6.6	0.9	
Gutturnio 10	7.58	7.3	0.2	
Gutturnio 25	7.04	7.2	0.2	
Tartaric acid (g/l)				
Barbera d'Asti 1	4.41	4.4	0.1	7
Barbera d'Asti 12	4.17	4.1	0.2	
Barbera d'Asti 20	3.30	3.5	0.1	
Gutturnio 1	2.22	2.4	0.2	
Gutturnio 5	1.86	1.9	0.1	
Gutturnio 8	1.73	1.7	0.1	
Malic acid (g/l)				
Barbera d'Asti 5	3.31	3.5	0.2	12
Barbera d'Asti 7	2.36	2.4	0.2	
Barbera d'Asti 10	3.32	3.7	0.2	
Barbera d'Asti 20	3.57	3.5	0.2	
Gutturnio 10	1.14	1.2	0.7	
Gutturnio 12	1.89	1.4	0.4	

Universal calibration models were produced using PLS.

parameter or component using PLS regression. Test set validation was performed on an independent dataset as described in the Section 2. It can be concluded that the electronic tongue is capable of measuring the content of different organic acids (also of total acidity and pH) in the wine with a good precision. This was primarily ensured by incorporating the sensors with direct sensitivity and cross-sensitivity to organic acids [15] into the electronic tongue sensor array. On the other hand, such parameters as extract or density were not determined by the system, because the electronic tongue did not include any sensors that may produce useful information for prediction of these parameters.

Furthermore, we also aimed at the determination of polyphenols, antocyanins, glycerol, sulphur dioxide, potassium and calcium content in the Gutturnio wine samples. Polyphenols, antocyanins and glycerol are substances naturally occurring in wine as a result of different processes taking place during fermentation and ageing [1]. These substances strongly influence different aspects of wine quality therefore their content is usually determined in the standard chemical analysis. Particularly important are polyphenols and antocyanins that contribute to the wine colour, body (mouth feel) and astringency and some flavour nuances. Sulphur dioxide is widely added to the wines as the most common antioxidant. Concentration of sulphur dioxide in the wine should be strictly controlled below permitted values established by the law in the most of wine-producing countries. Also it may be useful to follow-up the evaporation of free SO_2, occurring during wine storage, to learn how much of sulphur dioxide should be added. Glycerol content is also essential for texture and mouth feel of the wine and determination of the concentration of glycerol is a typical part of the standard chemical analysis of wines.

The results of determination of the content of these components in the test samples of Gutturnio wine are summarised in the Table 3. Calibration was done using PLS with the test set validation. The sensitivity of the electronic tongue to these substances may be explained as follows. We found out earlier [14] that several different sensors with both chalcogenide glass and polymer membranes were directly sensitive to different phenols and also to primary and higher alcohols. A sub-set of such sensors included into the sensor array of the electronic tongue ensured the possibility of determining the content of glycerol, polyphenols and antocyanins. Sulphur dioxide exists in aqueous media in the form of inorganic and organic bisulphites, sulphites and dissolved SO_2. There is equilibrium between these forms in the wine depending on the total SO_2 concentration and pH value. Reproducible response of another sub-set of anion-sensitive sensors present in the array to sulphites and bisulphites along with sensitivity of multiple sensors to pH allowed reliable quantitative determination of total SO_2 in the wine by the electronic tongue.

Table 3
The results of determination of different components in Gutturnio wine samples by the electronic tongue

Samples	Chemical analysis	Electronic tongue	S.D.	Mean relative error (%)
Glycerol (g/l)				
2	8.27	8.1	0.2	2
3	8.12	8.2	0.1	
7	7.70	7.7	0.1	
17	8.47	8.6	0.1	
Antocianins (mg/l)				
7	193	200	29	7
10	204	204	7	
11	206	220	13	
17	310	318	20	
Total polyphenols (g/l)				
3	1.99	1.7	0.1	8
5	1.18	1.3	0.1	
7	1.37	1.4	0.1	
16	1.71	1.6	0.1	
Sulphur dioxide (mg/l)				
1	91	96	8	11
13	97	103	8	
15	74	81	7	
35	100	96	8	
19	74	87	7	
Potassium (g/l)				
3	1.06	0.98	0.06	6
4	1.03	1.01	0.09	
12	0.83	0.79	0.03	
14	0.99	0.92	0.02	
Calcium (mg/l)				
7	62	65	4	7
11	70	64	2	
12	63	61	0	
17	50	56	3	
25	80	76	2	

Calibration models were made using PLS.

Successful application of conventional analytical techniques to the evaluation of sensory properties of foodstuffs is very difficult, primarily because the relationship between chemical composition and flavour is not properly known and also due to high complexity and variability of food composition. Some studies were earlier performed with the aim to quantify the taste using a taste sensor system [22–25]. Calibrations of the taste sensor were done in the individual or mixed solutions of reference taste substances and afterwards applied for determination of the basic taste in beverages. However, such an approach poses big problems in many practical applications. The most important issue is that the substances of different nature may induce the same taste (e.g. sweet) in human perception. For example, a calibration of the sensor system produced using glucose as a reference, might be not applicable to evaluation of sweetness in the foodstuffs that contain artificial sweeteners or even other natural sugars such as sucrose or lactose. Generalised calibrations of the sensor systems with respect to any of the basic tastes, e.g. sweet, were not yet reported. Thus, a calibration based on reference taste substances can be done only for the certain type of foodstuff and only if its composition was well known and could be adequately modelled. This is surely not the case of the wine, which is an extremely complex media containing up to a thousand of various compounds and components whose relationship with flavour might be not well established [1,26].

Another problem is that many parameters used for human evaluation of taste and flavour of wine, as well as of many other foodstuffs, were chosen subjectively, on the basis of tradition. These parameters might be quite accidental and unclear from chemical point of view. For example, typical parameters for assessment of the white wine flavour are images named by analogy after light coloured fruits and other objects [26]. On the other hand, sensory parameters of the red wine flavour are also images but mainly named after dark coloured fruits and objects. Many flavour compounds are however, identical in white and red wines from chemical point of view, but human assessment scales can hardly be comparable. Furthermore, the sets of flavour parameters of different taste panels often do not coincide and the same property or flavour nuance can be named and described differently depending on the wine type, national winemaking traditions, taste panel selection and training and numerous minor local peculiarities. This was also true for our study. Different number of parameters was used for flavour assessment of Barbera d'Asti and Gutturnio wines and these parameters were only partly overlapping (see the first column of the Table 4 for the list of parameters). One can suppose that some parameters differing in names were designed for the evaluation of the same or very similar wine flavour characteristics.

Table 4
Mean error of prediction of sensory parameters' values by the electronic tongue in the samples of Barbera d'Asti and Gutturnio wines

Parameter	Mean relative error (%)
Gutturnio	
Gradevolezza (general acceptance)	7
Rosso rubino (ruby red)	6
Riflessi violacei (violet reflects)	8
Viola (violet)	7
Speziato chiodi di garofano (spice clove)	13
Lampone (raspberry)	9
Ciliegia (cherry)	7
Prugna essiccata (dry plum)	8
Confettura marmellata (jam–marmalade)	9
Mandorla (almond)	8
Erbaceo fresco (fresh grass)	10
Acidita (acidity)	5
Astringenza (astringency)	5
Struttura (body)	6
Persistenza (persistency)	4
Barbera d'Asti	
Riflessi violacei (violet reflects)	16
Viola–rosa (violet–rose)	19
Struttura (body)	6
Pepe–chiodi di garofano (pepper–clove)	11
Ciliegia (cherry)	14
Bacce more (mulberry)	8
Prugna essiccata (dry plum)	13
Caramelizzato (caramel)	27
Trito d'erba-raspo (chopped grass)	14
Acidita (acidity)	6

Data were processed by back-propagation neural network.

Furthermore, flavour assessments made by humans are often rather badly reproducible. All these features result in the difficulty of establishing explicit relationship between chemical composition of the wine and its consumer properties though some aspects are commonly accepted. It is known, for example, that polyphenols are mainly responsible for astringency and colour intensity of red wines.

Considering this complicated situation it looks promising to try evaluating flavour of the wine using an analytical instrument capable of producing a number of signals related to the content of multiple different compounds (and their combinations) in the wine and then correlating the output of such a system to the taste panel scores. The electronic tongue, which combines a set of really cross-sensitive sensors, responding to various chemical features of the wine seems to be an appropriate device for such a task. Modelling in this case was performed using back-propagation neural network capable to approximate non-linear functional dependencies.

A wide cross-sensitivity of the sensors of the electronic tongue to the multiple wine components including those determining taste and flavour of wines ensures a possibility of extracting of essential "chemical images" from the sensor array signals. This property might be successfully used for predicting and quantifying complex scores such as human sensory assessments of wine produced by trained panellists. Mean relative errors of prediction of flavour parameters by the electronic tongue in the test samples of Barbera d'Asti and Gutturnio wine are shown in the Table 4. Selected wine flavour parameters (in Italian) and the errors of their determination (prediction) by the electronic tongue are shown in the Table 5. The errors of prediction of taste and flavour parameters are within 6–27% for Barbera d'Asti wine variety and 4–13% for Gutturnio wines.

Though the sensor array included no optical sensors, directly sensitive to the colour intensity (optical absorption at the certain wavelength), the system included chemical sensors directly sensitive to the compounds giving rise to wine colour such as polyphenols (Table 2). Therefore, some parameters describing wine colour such as rosso rubino and rosso violetto were also correctly predicted (Table 4).

Table 5
The results of prediction of sensory parameters by the electronic tongue in the samples of Gutturnio wine

Sample	Sensory panel			Electronic tongue	S.D.
	Minimum	Maximum	Median		
Gradevolezza (general acceptance)					
19	4.7	10	7.2	7.3	0.2
12	2.3	10.3	7.3	7.4	0.2
29	5.4	9.8	7.8	7.7	0.2
2	2	10.7	7.3	7.2	0.2
11	2.2	11.4	7.7	7.8	0.2
Riflessi violacei (violet reflects)					
1	1.7	6.5	4.8	4.8	0.2
27	3.3	6	5.2	5.2	0.2
33	3.6	6.8	5.0	5.0	0.2
11	2	6	4.8	4.9	0.2
28	3.3	6.4	5.1	5.0	0.2
Prugna essicata (dry plum)					
10	0.5	4.4	2.8	2.8	0.2
1	0.5	5	2.8	2.8	0.2
27	0.5	5.7	3.1	3.1	0.2
14	1	4.9	2.9	3.0	0.2
17	0.5	4.9	3.1	3.1	0.2
Confettura marmellata (jam–marmalade)					
24	1.2	5.1	3.0	3.1	0.2
18	1.4	4.8	2.7	2.8	0.2
27	0.5	4.6	2.9	2.9	0.2
14	1.5	5.9	3.0	2.9	0.2
12	1.3	6	3.0	2.9	0.2

Data were processed by back-propagation neural network.

4. Conclusion

The electronic tongue comprising an array of 23 potentiometric chemical sensors was developed and applied to discrimination and qualitative analysis of Italian wines of Barbera d'Asti and Gutturnio denominations. The electronic tongue was capable of distinguishing the wines from different geographical areas as well as the wines of the same vintage and denomination but produced at different vineyards. Quantitative determination of sulphur dioxide, glycerol and total polyphenols content in Gutturnio wine was also carried out. The electronic tongue can determine concentration of these substances (or group of substances, e.g. polyphenols) with an average prediction error not exceeding 12%. Calibration of the system in this case was performed using the results of standard analytical methods as the reference data. Furthermore, the electronic tongue could quantify taste and flavour parameters of the wine in terms of complex scores typically produced by human tasters. After an appropriate calibration versus sensory panel data the system was capable of predicting human scores with the average error of 13% for Barbera d'Asti wines and 8% for Gutturnio wines. The system may be put forward as an untraditional but yet promising instrument for multi component quantitative analysis of the wine and also for qualitative judgements about the identity of the wines, features of their flavour and hence quality of the wine.

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