Comparison of two electronic tongue’s sensor arrays during wine measurement

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Abstract

The objective of this work was to determine the applicability of two different sensor array of electronic tongue (ET) to discriminate wine samples originated from different wine regions and/or made from different grape variety in order to facilitate the selection of suitable sensor array for future applications.

The ET was equipped with seven ISFET based potentiometric sensors from two different sensor array. All measurements were performed either with sensor array “A” developed for specific taste screening or sensor array “B” developed for usual food analyses.

Further aim was to determine which sensor array can predict the chemical attributes with closer correlation. The results of classification models build by Linear discriminant analysis (LDA) obtained by the sensor array ”B” showed 100% correct classification both in calibration and validation (cross-validation) set evaluating the discrimination of the wine regions and the wine types. The LDA results obtained by the sensor array ”A” showed somewhat weaker but also good classification with low misclassification error.

Partial least squares (PLS) regression models were built to predict ‘acid content’, ‘alcohol content’, ‘ash content’, ‘sugar free extract’ and ‘volatile acid content’ based on ET results. The results showed good correlation (R²>0.85) in each attributes except in case of volatile acid content (R²=0.40) by the sensor array developed for usual food analyses (“B”). The results based on the ET measurements with sensor array developed for specific taste screening showed better correlation in case of sugar free extract (R²=0.95) and volatile acid content (R²=0.61).

Both sensor arrays were able to discriminate the wine samples originated from different wine regions and made from different grape variety and both of them can be useful tool to predict the chemical attributes. In case of discrimination the sensor array ”B” showed better differentiations while sensor array ”A” showed better correlations to predict the chemical attributes of the wine samples.

Keywords: electronic tongue, sensor arrays, wine, chemical attributes
1 Introduction

In order to protect consumers and producers, every aspects of winemaking are accompanied by strict laws and governmental regulations. The use of electrochemical sensors could greatly help and speed up the work of audit institutions, the analysis and the control processes. The electronic tongue (ET) can be a useful tool in this field. The ET concept emerged first in the middle of the nineties (Legin et al., 1999). The principle of the system is to apply cross-sensitive and partially selective sensors (Kovács et al., 2009). The ET usually consists of an array of non-specific chemical sensors combined with appropriate data acquisition systems and chemometric tools. During sample assessment the ET sensor array produces an unresolved electrochemical signal, which correlates with the chemical composition of the sample.

Comprehensive information on the quality and composition of food products is becoming increasingly important for consumer choice. Geographical origin, agricultural practices and chemical composition, together with sensory qualities play a vital role in the purchase decision of consumers. These factors are even more important if we are talking about wines. From the point of view of wine quality, the chemical compositions play important roles. Chemical analysis of wine is a mature field of research and almost every type of modern advanced analytical techniques have been applied to wine.

The result that we can obtain with ET is a chemical pattern characteristic for the definite sample. The similarities or even more the dissimilarities can be easily evaluated by the use of appropriate multivariate statistics. Therefore, ET is a useful tool for comparative measurements e.g. comparison to a reference sample or validating the origin of a sample (Kirsanov et al., 2012).

The correlation of ET data with sensory descriptors provided by an expert human panel (Buratti et al., 2007 and Soós et al., 2013) has been also evaluated. However, until now the effect of origin, grape varieties and chemical components in Hungarian white wines have not been reported.

The objective of this work was to determine the applicability of two different sensor array of electronic tongue to discriminate the wine samples originated from different wine regions and/or made from different grape variety in order to facilitate the selection of suitable sensor array for future applications.

Further aim was to determine, which sensor array can predict the chemical attributes with better correlation.
2 Materials and methods

2.1 Wine samples

Nine white wine samples were analyzed during the experiment. The tested wine samples were originated from three different Hungarian wine regions such as Balaton, Mátra, Villány. From each wine region there were three different wine samples. These wine samples were produced from different grape variety groups: Cserszegi fűszeres, Pinot Gris and Sauvignon Blanc.

2.2 Electronic tongue measurement

Alpha ASTREE II (Alpha M.O.S., Toulouse, France) potentiometric electronic tongue was used to measure the white wine samples. The ET was equipped with seven ISFET based potentiometric sensors. The measurements were performed either with sensor array “A” developed for specific taste screening (named SRS, GPS, STS, UMS, SPS, SWS and BRS according to the producer) or sensor array “B” (named ZZ, BA, BB, CA, GA and two HA according to the producer) developed for usual food analyses. These chemical sensors were potentiometric sensors with organic membrane coating that gives each sensor specific sensitivity and selectivity (Alpha M.O.S., 2003). The sensors were preconditioned before the tests performed by the electronic tongue. The preconditioning included the actual conditioning and the calibration by the AlphaSoft software. For conditioning we used 0.01M HCl solution (recommended by the manufacturer.). The conditioning was performed according to AlphaSoft (Standard analysis). The calibration was performed with the mixed samples containing the 9 wines in the same percentage. Every sample was measured in nine replications. All measurements including both conditioning and calibration were performed at room temperature. The detailed description of the instrument was introduced by Várvölgyi and co-workers (2012).

2.3 Statistical analysis

The steady state of ET sensor signals was used as variable for the statistical evaluation. Principal component analysis (PCA) was used for the preliminary evaluation of the results of electronic tongue tests. Stepwise Discriminant Analysis was used to select the sensors for the discrimination. Linear discriminant analysis (LDA) was used to build models to separate white wine samples based on wine regions and grape variety as well. The LDA was supported by cross-validation. The cross-validation (CV) was applied to confirm the LDA (2/3 of the data was the training set, the other 1/3 was the test set). Partial least squares (PLS) regression was used to predict the chemical attributes of the wine samples. The PLS regressions were supported by leave-one-out (LOO) validation. The program R (3.0.1, R Foundation for Statistical Computing, Vienna, Austria) was applied for the statistical evaluation and visualization.
3 Results and Discussions

3.1 Classification by Linear Discriminant Analysis

The corresponding LDA-classification matrix (data not shown), which includes the calibration and the validation (CV), was used in both cases of the discrimination of the wine region and the wine variety.

3.1.1 Sensor array “A”

The sensor selection showed that five sensors could describe the most of differentiation in both cases. The ET results obtained by the sensor array “A” (which was developed for specific taste screening) showed relatively good classification in case of discrimination of wine regions (Figure 1a) and wine varieties (Figure 1b).

![Figure 1. LDA score plots of electronic tongue measurement obtained by sensor array “A” to discriminate wine regions (a) and wine varieties (b)](image)

In case of discrimination of wine regions (Figure 1a) some wine samples from each region were misclassified. The misclassification error of the calibration was 21.11% and in the case of the validation it was 35.56%

The discrimination of wine variety (Figure 1b) showed better differentiation. The misclassification error of the calibration was 3.33% and during the validation it was 11.11%. The LDA plot showed that the group of Pinot Gris shows the best separation along Root1 having more than 90% of the variance.

3.1.2 Sensor array “B”

The sensor selection from sensor array “B” showed that five sensors could describe the most of differentiation in case of wine region. But in case of wine variety only four sensors were enough for the discrimination. The ET results obtained by the sensor array “B” (developed for usual food analyses) showed really good classification in case of discrimination of wine regions (Figure 2a) and wine varieties (Figure 2b).
In case of discrimination of wine regions (Figure 2a) each wine region were discriminated. The misclassification error of the calibration was 0% and in the case of the validation it was also 0%. The discrimination of wine variety (Figure 2b) showed similar differentiation. The results of classification models showed 100% correct classification as well as the calibration and the validation.

3.2 PLS regression models to predict main chemical attributes of the wine samples

The determination coefficient and the prediction error values of the PLS regression models are shown in Table 1. The RMSEP % values were indicated by the normalized value of the RMSEP. The PLS regression models showed good correlation ($R^2>0.85$) in each attributes with both sensor arrays except in case of volatile acid content. However, the ET measurements performed with sensor array developed for specific taste screening showed better correlation in case of sugar free extract ($R^2=0.95$) and volatile acid content ($R^2=0.61$). In case of the prediction of Ash content and Alcohol content the results were more similar with both sensor arrays.

Table 1. Parameters of ET performance for prediction of chemical attributes

<table>
<thead>
<tr>
<th>Sensor array &quot;A&quot;</th>
<th>Sensor array &quot;B&quot;</th>
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<tbody>
<tr>
<td>$R^2$</td>
<td>RMSEP</td>
</tr>
<tr>
<td>Acid content</td>
<td>0.89</td>
</tr>
<tr>
<td>Alcohol content</td>
<td>0.85</td>
</tr>
<tr>
<td>Ash content</td>
<td>0.88</td>
</tr>
<tr>
<td>Sugar free extract</td>
<td>0.95</td>
</tr>
<tr>
<td>Volatile acid content</td>
<td>0.61</td>
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</table>
4 Conclusions

The results of classification models build by LDA obtained by the sensor array developed for usual food analyses showed 100% correct classification. The calibration and the validation (CV) set evaluated the discrimination of the wine regions and the wine types. In both discriminations this sensor array showed much better classification. The LDA results obtained by the other sensor array showed somewhat worse but also good classification with low misclassification error. Both sensor arrays were able to discriminate the wine samples originated from different wine regions and made from different grape variety and both of them can be useful tool to predict the chemical attributes.

PLS regression models built to predict ‘acid content’, ‘alcohol content’, ‘ash content’, ‘sugar free extract’ and ‘volatile acid content’ based on ET results showed good correlation ($R^2>0.85$) in each attributes. But in case of volatile acid content ($R^2=0.40$) by the sensor array developed for usual food analyses the ET results showed the worst correlation. The results based on the ET measurements with sensor array developed for specific taste screening showed better correlation in case of sugar free extract ($R^2=0.95$) and volatile acid content ($R^2=0.61$).

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6 References


