A NOVEL HUMID ELECTRONIC NOSE COMBINED WITH AN ELECTRONIC TONGUE FOR ASSESSING DETERIORATION OF WINE

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Abstract: We report herein the use of a combined system for the analysis of the spoilage of wine when in contact with air. The system consists of a potentiometric electronic tongue and a humid electronic nose. The potentiometric electronic tongue was built with thick-film serigraphic techniques using commercially available resistances and conductors for hybrid electronic circuits; i.e. Ag, Au, Cu, Ru, AgCl, and C. The humid electronic nose was designed in order to detect vapours that emanate from the wine and are apprehended by a moist environment. The humid nose was constructed using a piece of thin cloth sewn, damped with distilled water, forming five hollows of the right size to introduce the electrodes. In this particular case four electrodes were used for the humid electronic nose: a glass electrode, aluminium (Al), graphite and platinum (Pt) wires and an Ag-AgCl reference electrode. The humid electronic nose together with the potentiometric electronic tongue were used for the evaluation of the evolution in the course of time of wine samples. Additionally to the analysis performed by the tongue and nose, the spoilage of the wines was followed via a simple determination of the titratable (total) acidity.

Keywords: Electronic tongue, electronic nose, wine quality

INTRODUCTION

The determination of wine quality has always been a dynamic field of research. The main constituents of wine are water, ethanol and acids, but the elements that distinguish one wine from another, namely, their quality, area of origin, vintage, etc are a large number of constituent components that are present in very small proportions. Besides, the wine can be considered as a living product because its chemical and organoleptic characteristics change over time. This makes the analysis of wine a rather difficult task because, in addition to the determination of key components in small proportions, analysis must be performed in different stages of its manufacture, storage and consumption. Another reason for the interest in wine analysis resides in the quality control and detection of possible adulterations or spoilage. Currently the basic technique to asses wine quality is the use of a panel of trained experts that carry out sensory analysis based on colour, taste and flavour. However this is often time-consuming and requires skilled personnel. Therefore, there is an increasing interest in the development of low-cost, easy-to-use analytical protocols able to *in situ* and *at site* monitoring wine quality. In this context the use of electronic tongues and noses is a timely research field and a good alternative to be used in the characterization of wines and other foodstuffs [1,2].

Electronic noses or tongues are inspired in the mode mammalians recognize samples via olfaction and taste senses. In this approach, sensors do not have to be selective but to respond unspecifically to a group of related chemical species. The sensors are then integrated in an array and their response is analysed by suitable pattern recognition procedures. These systems usually display comparative/qualitative rather than quantitative information. Several research groups have developed gas multisensor systems to determine the aroma of wine using electronic noses based on metal oxides, such as SnO_2 [3,4], WO_3 [5], surface acoustic wave (SAW) devices [6] or gas chromatography–mass spectrometry GC–MS [7] and compared their performance with sensory analysis [8]. In most cases electronic noses commonly use resistive sensors, whose impedance varies with the presence of certain gases. However it has been reported that the analysis of alcoholic beverages with semiconductor-based electronic noses is a difficult task due to the presence of high ethanol and water concentrations, which tend to mask the presence of other important volatile compounds and contribute to the shortening of sensor life [9]. In that sense, various solutions for dehydration and dealcoholisation of wine samples have been proposed. [10].

On the other hand, electronic tongues have also been used for the analysis of wines employing arrays of electrochemical Langmuir-Blodgett film sensors and voltammetry [11], impedance spectroscopy [12], amperometry [13] or potentiometry [14]. In relation to sensor technologies, thin-film electrodes have been used for the analysis of white wines and artificial wines [15]. Additionally it should be noted that some authors have studied the possibility of using a combination of electronic noses and tongues for wine analysis, [16,17] whereas more advanced systems combining electronic nose, electronic tongue and an electronic eye have also been reported [18].

Following our interest in the design of electronic tongues and noses [19] we report on the use of a combined system for the analysis of the spoilage of wine when in contact with air. The system consists of a potentiometric electronic tongue and a humid electronic nose. The latter, in contrast to resistive sensors employed in electronic noses, uses electrodes that are placed on a wet setting. This proposed system detects vapours that emanate from the wine and are apprehended by a moist environment. The design of such a humid electronic nose as far as we know, is new and allows the use of classical electrochemical techniques commonly employed in e-tongues for the analysis of volatile compounds. In this paper we report the use of such a humid electronic nose together with a potentiometric electronic tongue for the evaluation of the time evolution of wine samples.

MEASUREMENT SYSTEM

The measurement system used consists of two arrays of electrodes, for the humid electronic nose and for the electronic tongue, that are attached to a common measurement equipment. The measurement set is formed by a signal conditioning system, which comprises amplifiers with very high impedance and filters for rejecting the 50 Hz noise, a system for data acquisition and a multivariate data analysis engine (Fig. 1). This measurement system is self-built. Details of its construction have been reported elsewhere [20].

Insert here Figure 1

Electronic Tongue Electrodes

In order to make the electronic tongue, a potentiometric measurement system has been developed, which consists of electrodes built employing thick-film serigraphic techniques. The pastes are commercially available and commonly used in the manufacture of thick-film resistances and conductors for hybrid electronic circuits. Each one of these pastes has an active element, which we employed to obtain potentiometric electrodes. The active elements are: Ag, Au, Cu, Ru, AgCl, and C. Although in the electronic tongue these materials are used as non-specific electrodes, their properties as suitable surfaces sensitive to chemical species have already been studied [21]. Some materials have been duplicated on the multisensor system, finally obtaining 9 potentiometric electrodes. Fig. 2 shows the electrode distribution on the multisensor board and the tracks and pads for connecting the board using a flat wire. More details can be found elsewhere [22].

Insert here Figure 2

The Humid Electronic Nose

The humid electronic nose was inspired in biological olfaction which needs a wet medium for the absorption of volatile components. The humid electronic nose was constructed using a piece of thin cloth, sewn forming five hollow spaces of the appropriate size to introduce five different wire electrodes (i.e. four active electrodes and one reference electrode). Electrodes are tightly fit so a perfect contact between the electrode and the cloth is accomplished. In order to achieve a good conductivity between the active electrodes and reference electrode the cloth was damped with distilled water. Appropriate results were obtained using nylon textiles. Fig. 3 shows a scheme of the humid nose. Volatile compounds in wine will evaporate and will be dissolved in the damp fabric were the potentiometric electrodes are included. In this particular case four electrodes were used for the humid electronic nose: a glass electrode, aluminium (Al), graphite and platinum (Pt) wires and an Ag-AgCl reference electrode. All electrodes were placed in a glass container tightly closed to prevent contact with external vapours

Insert here Figure 3

EXPERIMENTS

Samples

Three Spanish table wines were analyzed with the humid electronic nose and the electronic tongue combined system; i.e. two red and one white wine. The red wines were labelled RA and RB and the white wine was labelled W. All the wine bottles were opened on the same day, and measurements were made on days 1, 5, 9, 15, 19, 22, 28, 36 and 48. During these days the bottles remained opened. Wines were stored at a constant temperature of 15ºC. Each working day the wines were measured using the humid electronic nose and the electronic tongue. Also each working day the total titratable acidity was measured for all three wines.

Acidity Determination

Titratable (total) acidity in wines was determined by simple acid–base titration using NaOH with either visual or potentiometric detection.

Measurement using the electronic tongue and the humid electronic nose

To perform the measurements with the electronic tongue system the multisensor board (see Fig. 2) containing an Ag-AgCl reference electrode, was dipped into a vessel containing the corresponding wine sample. Then the potential between each active electrode and the reference electrode was measured. Measurements were performed automatically by sampling every five seconds during a time of about ten minutes to achieve electrochemical stability.

To make measurements with the humid electronic nose the corresponding wine was poured into a container that comprised the set of electrodes wrapped by a damp fabric and the system was sealed. Thus, volatiles emanating from the wine permeated the wet cloth, changing the characteristics of the electrochemical cells formed by an active electrode and the reference electrode. Similar to the electronic tongue system, the potential between each electrode and the reference electrode was measured for ten minutes in order to reach electrochemical stability. After each measurement, the damp cloth was removed and the electrodes were careful cleaned with distillated water in order to remove all traces of previous experiences.

For both the electronic nose and the humid electronic nose a standard solution was prepared. Before measurements with the wine samples the set of electrodes were dipped in buffered water at pH 5 (standard solution) and the potential for each electrode was measured. This was set as a zero reference value. The data for the posterior analysis with the wine samples was taken as the difference between the zero reference and the measured potential for each sample.

The final data array contained of 27 rows (3 wines x 9 days) and 13 columns (electrodes from the humid electronic nose (4) and from the electronic tongue (9)).

RESULTS

As stated above, following our interest in the design of electronic tongues and noses for different applications, we attempted to apply the use of these devices to the analysis of the spoilage of wine when in contact with air. In the first step a potentiometric electronic tongue was used. The electronic tongue consisted of a set of electrodes built with thick-film serigraphic techniques. The active elements in the electrodes were: Ag, Au, Cu, Ru, AgCl, and C (see experimental section). Despite the fact that similar electronic tongues have been used by some of us in certain applications such as in fish freshness analysis, [23] in this case, the tongue barely was able to discriminate the evolution of the samples through time (data not shown) in the wine spoilage process. In this particular case, this low discrimination using the electronic tongue may be attributed to the possible masking ability of water and ethanol that are found in very high concentrations in wine samples. Therefore it occurred to us that a combination of tongue and nose might be more suitable for monitoring the evolution of wine through time due to the presence, after some time, of volatile derivatives usually associated to wine spoilage (vide infra). Additionally we were especially interested in the design of a humid electronic tongue as a suitable alternative to the use of classical electronic noses based on metal oxides. One advantage of this humid electronic tongue, that was designed to evaluate the presence of volatile compounds, is the possibility of using typical electrochemical electrodes such as those usually found in electronic tongues. The nose involves the use of potentiometric electrodes (wires of Al, C (graphite), Pt and a glass electrode) and a reference electrode (Ag-AgCl) that are placed in a damp cloth sewn. We used such humid electronic nose in combination with a potentiometric electronic tongue for monitoring the evolution of wine with time. As sated above for this set of experiments three wines were used; i.e. two red wines (RA and RB) and one white wine (W). The wine bottles were opened the same day and measurements were made at days 1, 5, 9, 15, 19, 22, 28, 36 and 48 after they were opened.

Insert here Figure 4

Wine is a complex mixture of compounds that usually derive from three major sources; i.e. grapes, microorganism and (if used) oak. Additionally wine spoilage is a rather complex process in which acetic acid bacteria play an important role because their metabolites result in disagreeable wine sensory characteristics. The concentration of acetic acid in wine is an important parameter because it is the head of the deterioration process of the wine, causing the spoilage effect that set the wine a vinegary taste. Acetic acid is the major volatile acid in wine and the main constituent of wine volatile acidity and is usually considered undesirable in wines. At high concentrations, acetic acid gives a sour flavour and a vinegar-like aroma. Acetic acid is produced by bacteria through the metabolism form ethanol to acetaldehyde to acetic acid. Both volatile intermediate metabolites acetaldehyde and ethyl ester of acetic acid also contribute to the sensory spoilage of wine. [24,25] Whereas in the spoilage of wine process other acids such as citric acid and malic acid remain at the same concentrations, the amount of acetic acid, ethyl acetate and acetaldehyde increases significantly. Therefore, as a simple control of wine spoilage as a function of time we determined the titratable (total) acidity in wines RA, RB and W by simple acid–base titrations at days 1, 5, 9, 15, 19, 22, 28, 36 and 48. The results are shown in Fig. 4. The acidity measurements reveal that, for all wine types, little variation occurs in the first days and a sharp increase in acidity is observed in the last days. Note also that the variation of acidity slightly depends on the type of wine.

Results independently of the electronic tongue and the electronic nose

A suitable mode to interpret the results obtained from the use of the electronic tongue and the humid electronic nose on the different wine samples is to use multivariate analysis which is a statistical method able to determine the contribution of various factors on a single event. To perform this type of analysis Matlab 2010 with the appropriate Toolbox (PLS_Toolbox and Statistics Toolbox) has been used. One of the methods most commonly used of multivariate analysis is Principal Component Analysis (PCA). For this purpose, new orthogonal directions in the variable space are searched, called Principal Components (PC). The representation of the first two principal components (PC1 and PC2) in a two-dimensional graphic often provides a fairly significant result of the actions and behavior of the system. [26]

PCA analysis of the results of the electronic tongue shows a good discrimination of the measures of the some days (1, 5, 9, 22, 28 and 36) but not discrimination on the last day (48). Comparing these results with those obtained in the measure of acidity it suggests that the cause of discrimination obtained by the electronic tongue is different from the change in the acidity of the wine. In contrast, in the PCA analysis of the results of the electronic nose stands out a clear discrimination measures for the last tested day (48). This suggests that the response of the electronic nose is related to the increase in acidity. Results independently of the electronic tongue and the electronic nose are shown in Fig. 5.

Insert here Figure 5

Result combining the electronic tongue and the electronic nose

The results obtained independently from the electronic tongue and the electronic nose suggest that from the combination of both results it could be possible to monitorize the evolution of wine as a function of the days elapsed since the bottle was opened. In fact is observed in Fig. 6 that shows the first two principal components of a PCA of data from the combined electronic tongue and humid electronic nose systems. Samples of three wines RA, RB and W of a given day appear close to each other. While the content of acetic acid in wine increases slightly (i.e., from day 1 to day 36), the scores of the wines tested move from right to left along the first principal component. On day 48, a strong variation in the second principal component is observed. This may be due to the sharp increase in the concentration of acetic acid 48 days after the bottles were opened but also to the occurrence of other compounds associated to wine degradation. It is interesting to note that the system is capable of distinguishing the measurements of the first days, despite the fact that acidity measurements of those days were almost identical. That is, the proposed system appears to be able to detect components that do not directly affect the acidity of wine. One of the main problems when using metallic electrodes is the possible occurrence of response or baseline drift that could lead to obtain irreproducible data or to mistakenly believe that drift variations are changes in wine spoilage. In order to control these possible drifts, prior to the measurement of the wine samples, the electrodes were immersed in an aqueous sample (25 ^{o}C buffered at pH 5, standard solution) and the data for the posterior analysis were taken as the difference between the zero reference and the measured potential for each wine sample.

Insert here Figure 6

In order to understand the relationship between the diverse electrodes used, the loads of each electrode in the first two Principal Components are shown in Fig. 7. This figure helps to verify the different significance of the electrodes in the electronic nose respect the ones used in the electronic tongue. The loads of the electronic tongue electrodes are on the left-hand side of the plot (loads on PC1 are negative), all of them with a homogenous activity.

Glass, Aluminium and Platinum electrodes of the humid electronic nose show very different loads with respect of the electronic tongue ones, that is to say, the former electrodes are independent of the latter. These electrodes, which appear in the upper side of Fig. 7, are responsible for the position of measurements performed the last day (48), which appear apart in the score plot (Fig. 6). A possible chemical interpretation of these results is that the last day (48) the wines give off aromas with a higher acidity than in previous days because wines are soured.

Fig. 7 also shows that the different electrodes significantly contribute to the first two principal components. Only the loads of the graphite electrode are close to zero. In fact this electrode had an erratic behaviour and could be removed from the set of electrodes without significant changes in the PCA scores plot.

Insert here Figure 7

By selecting the first two principal components in the principal component analysis, only 69.38% of the data variance (i.e. information) provided by the electronic tongue and humid electronic nose are actually used. This value is not very high, which means that there is not a high degree of correlation between the different electrodes employed. This fact is quite logical due to the different nature of the electrodes employed in the electronic tongue and humid electronic nose.

To achieve an analysis in which all the information (i.e. all data variance) from the electronic tongue and the humid electronic nose is used, a cluster analysis with dendrograms has been performed. A dendrogram acts as genealogical tree of the measurements. The measurements are associated to each other to complete the tree. To obtain a dendrogram different algorithms can be employed but the most commonly used is K-means clustering. This algorithm aims to partition *n* observations into *k* clusters in which each observation belongs to the cluster with the nearest mean [27]. Fig, 8 shows the dendogram obtained when a k-means clustering is applied to the wine data. Measurements performed at day 48 are clearly different from any other measurement performed before and appear grouped in a single cluster. Two other clusters can be easily inferred, which group together measurements performed between days 1 to 9 and from days 15 to 36, respectively. If we consider now the cluster grouping measurements from day 1 to day 9, measurements of the first day are clearly different from the others suggesting that early stages of wine evolution can be detected. For the cluster that groups measurements performed between days 15 and 36, the initial and last measurements within this group (i.e. those of day 15 and day 36) appear clearly discriminated in the dendogram. These results are consistent with those obtained in the PCA plot.

Insert here Figure 8

CONCLUSIONS

In summary we have combined a potentiometric electronic tongue with a humid electronic nose and have applied the joint electronic system to the analysis of the spoilage of wine. The potentiometric electronic tongue was designed using thick-film serigraphic techniques and commercially available pastes originally intended for resistances and conductors (i.e. Ag, Au, Cu, Ru, AgCl, and C). The designed humid electronic nose contained a glass electrode, aluminium (Al), graphite and platinum (Pt) wires and a Ag-AgCl reference electrode that were included in a damp fabric. The humid electronic nose responds to volatile compounds that evaporate from the wine samples and that dissolved and concentrated in the wet cloth were the potentiometric electrodes are included. The process of wine spoilage when in contact with air was followed with the combined electronic system with good results. Additionally, the spoilage was also assessed by using a simple determination of the titratable (total) acidity. To check the system, three Spanish table wines, two red and one white, have been analyzed. The wine bottles were all opened at the same time and measurements were made with the wines for 48 days. A clear discrimination as a function of time was achieved.

AKNOWLEDGEMENTS

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VITAE

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Figure 1

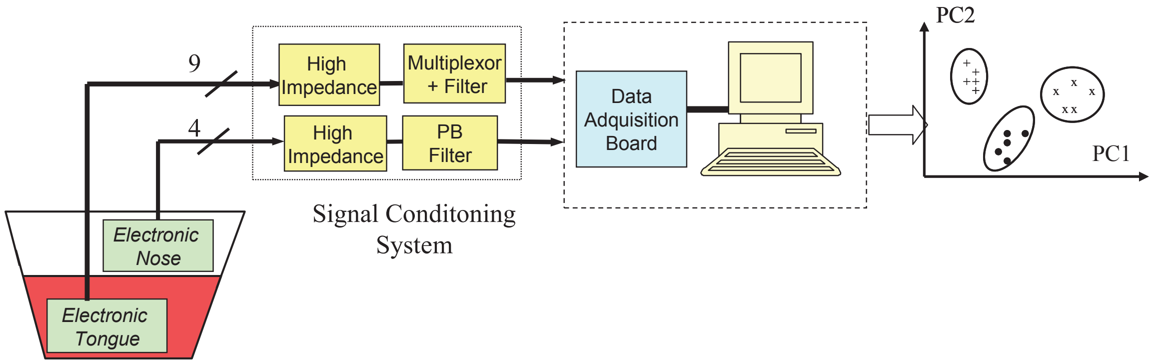

Fig. 1. Block diagram of the measurement system

Figure 2

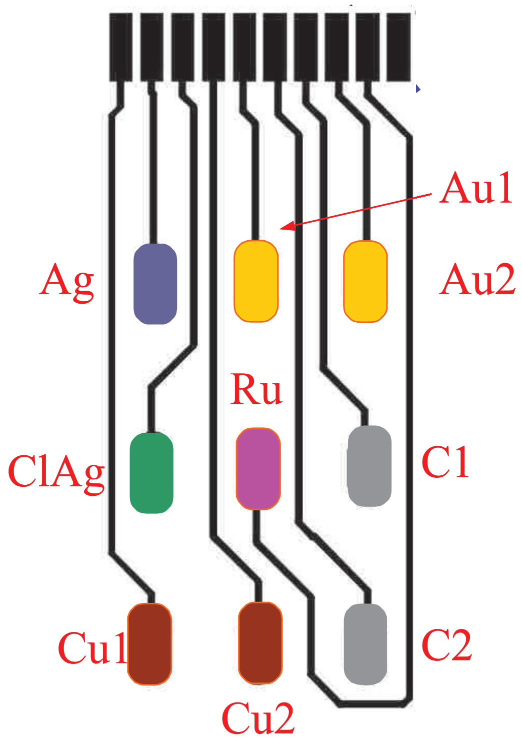

Fig. 2. Potentiometric sensors for electronic tongue

Figure 3

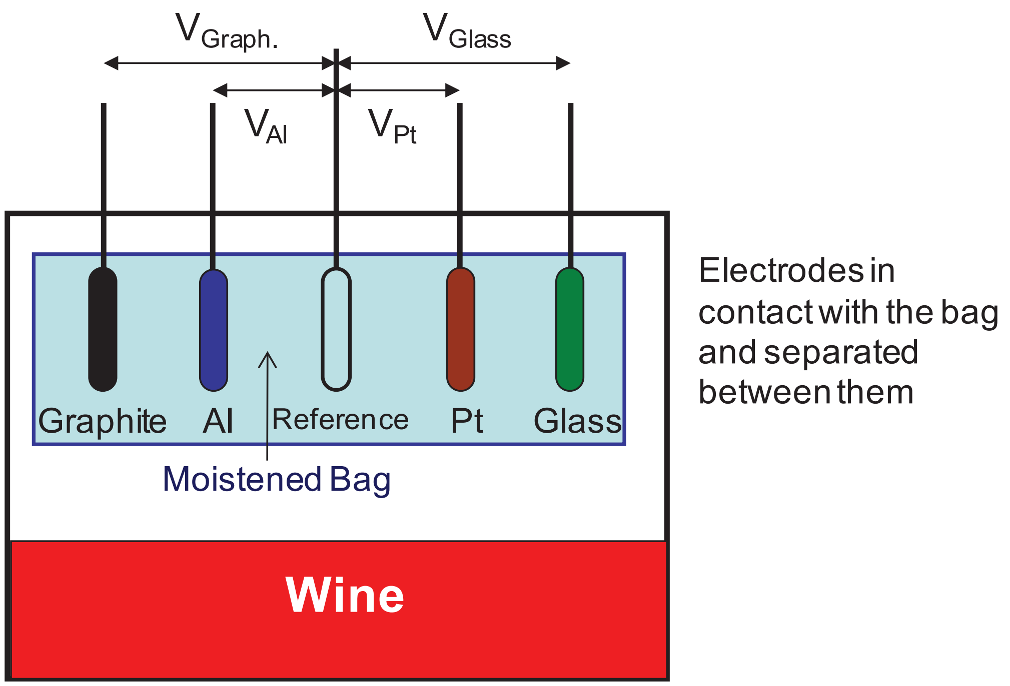

Fig. 3. Scheme of the humid electronic nose constructed using a set of electrodes closed in a piece of thin moistened cloth

Figure 4

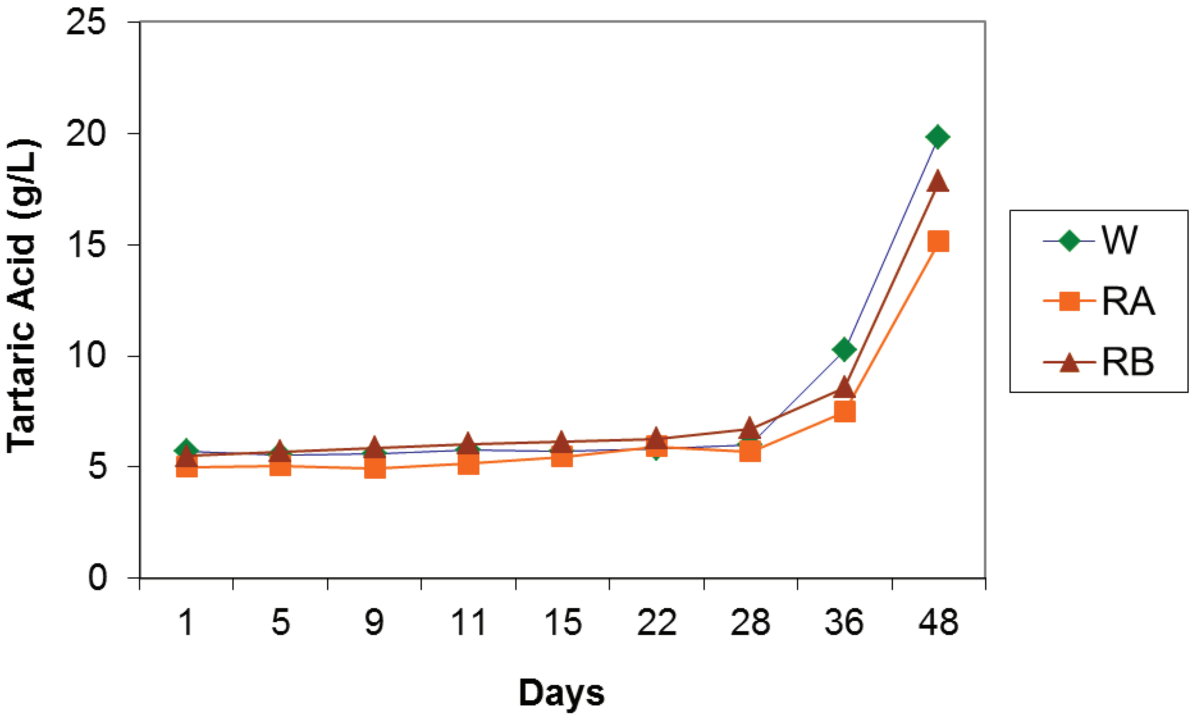

Fig. 4. Variation of acidity on two red wines (RA, RB) and a white wine (W)

Figure 5

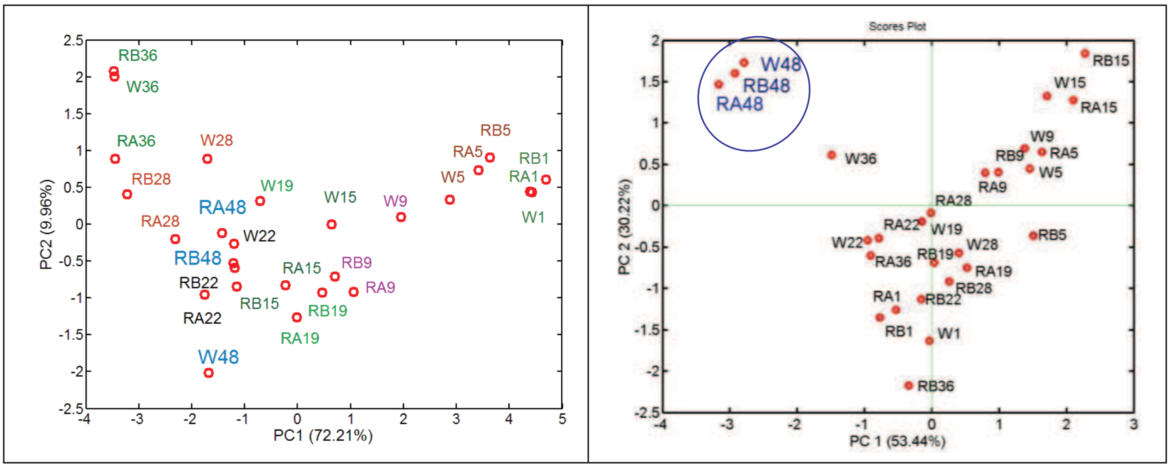

Fig. 5. PCA scores separately of the electronic tongue (left) and the electronic nose (right) on two red wines (RA, RB) and a white wine (W) using the experimental setup seen in Fig. 2 and Fig. 3. The number after RA, RB and W symbols represents the day the wines were measured after they were opened

Figure 6

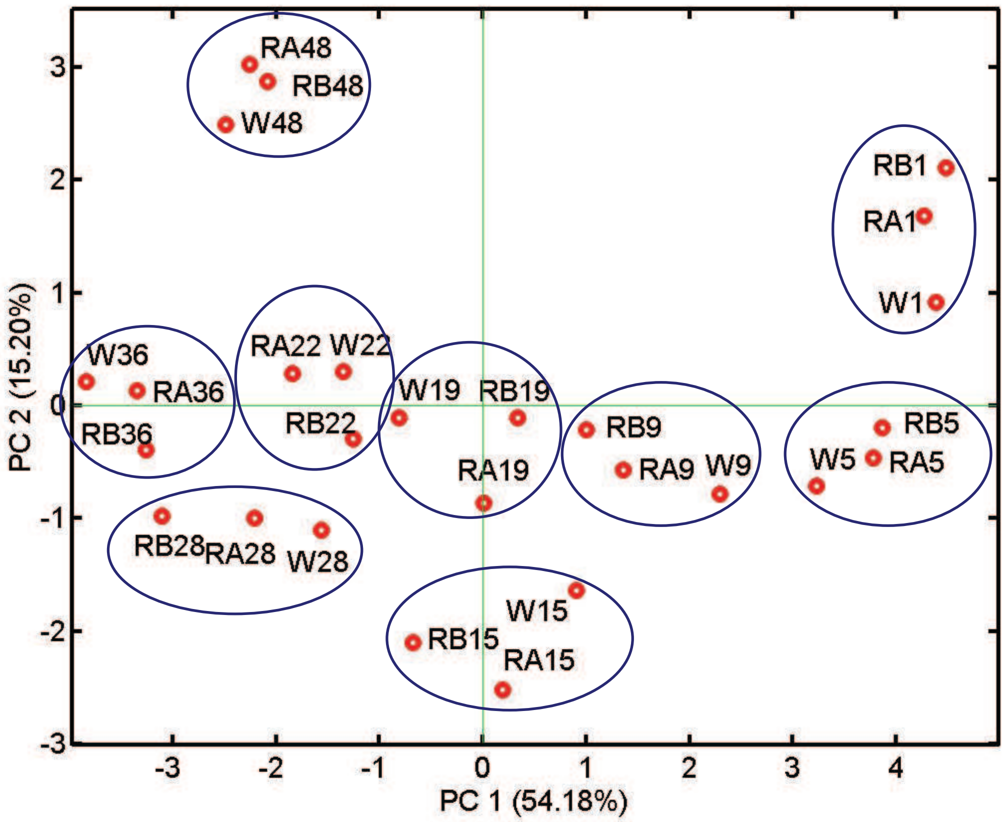

Fig. 6. Principal component analysis (PCA) score plot obtained by combination of measurements of the electronic tongue and the humid electronic nose on two red wines (RA, RB) and a white wine (W) using the experimental setup seen in Fig. 2 and Fig. 3. The number after RA, RB and W symbols represents the day the wines were measured after they were opened

Figure 7

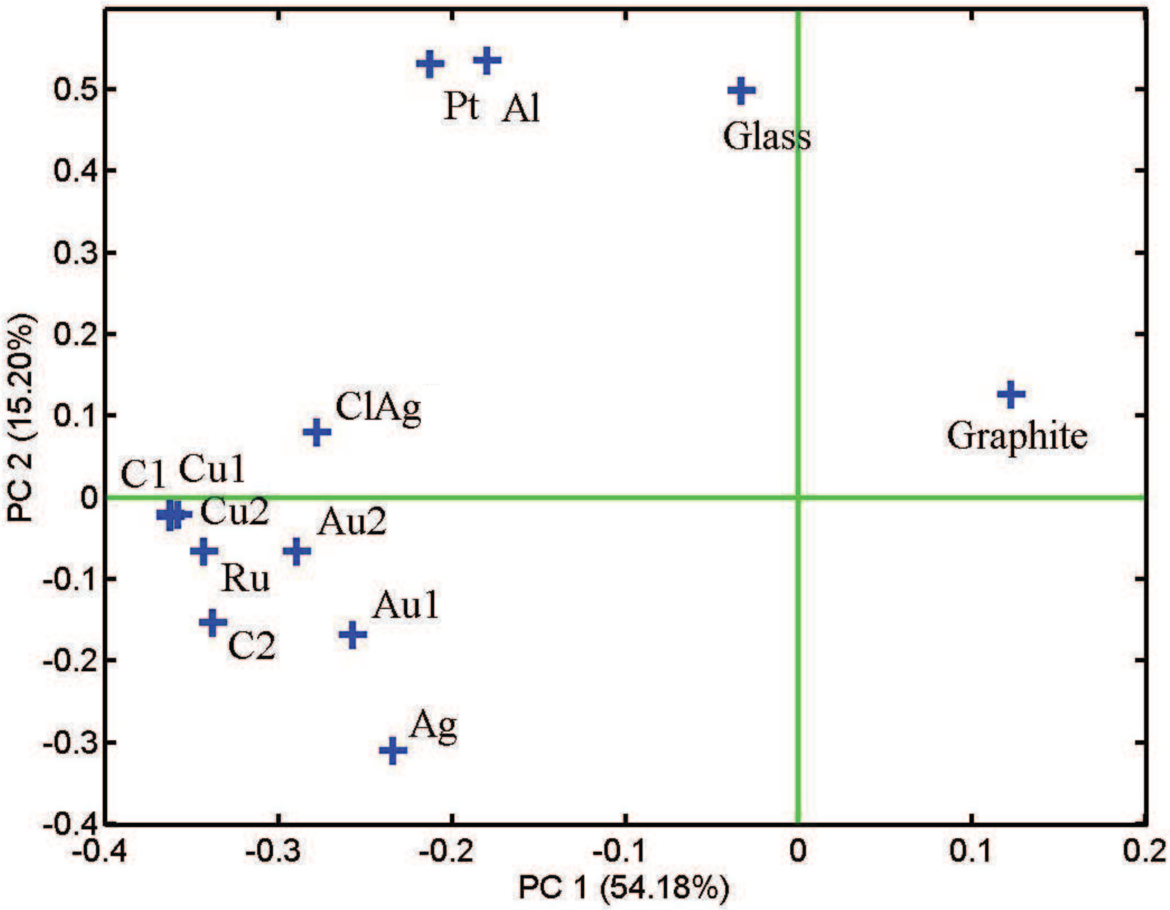

Fig. 7. PCA loads for data obtained by combination of measurements of the electronic tongue and the humid electronic nose on two red wines (RA, RB) and a white wine (W) using the experimental setup seen in Fig. 2 and Fig. 3. Symbols are related with the used electrodes; electronic tongue (see Figure 2): Ag, Au (two electrodes Au1 and Au2), Cu (two electrodes Cu1 and Cu2), Ru, AgCl, and C(graphite) (two electrodes C1 and C2); humid electronic nose (see Figure 3): C(graphite), Al, Pt and glass electrode

Figure 8

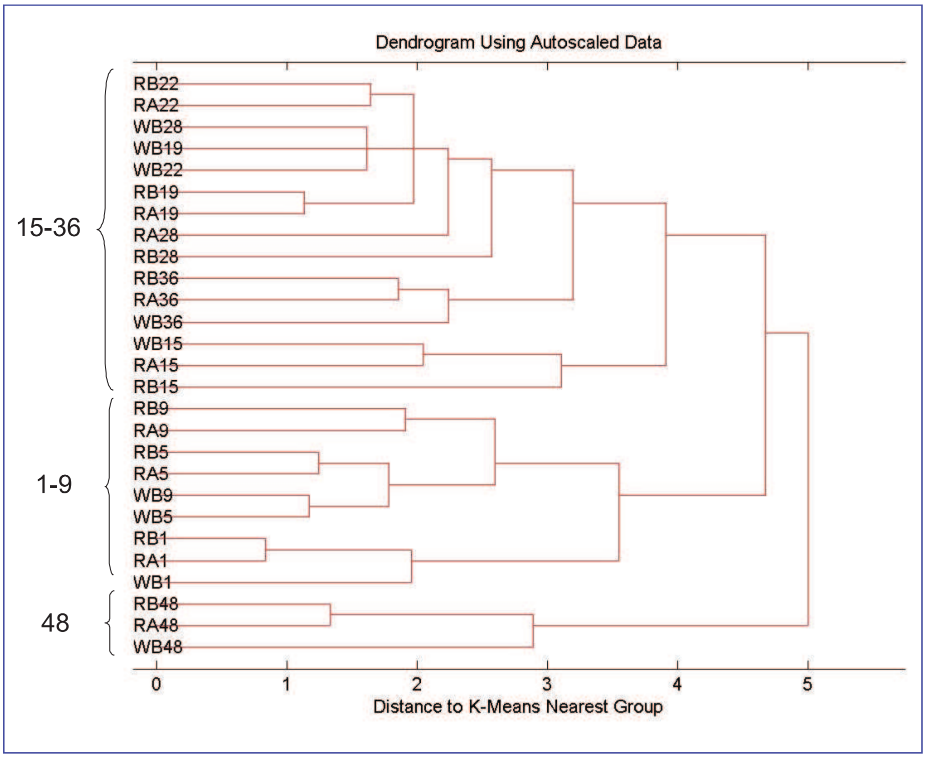

Fig. 8. Dendrogram using K-means on two red wines (RA, RB) and a white wine (W) using the experimental setup seen in Fig. 2 and Fig. 3. The number after RA, RB and W symbols represents the day the wines were measured after they were opened