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STUDY OF THE METHANOL CONCENTRATION IN COMMERCIAL WINES AND ITS INFLUENCE ON THE DETECTION OF QUALITY AND POSSIBLE ADULTERATION OF WINES

Ana L. Paredes-Doig
Faculty of Sciences, National University of Engineering, Lima, Perú

Maria R. Sun-Kou
Department of Sciences, Pontifical Catholic University of Peru, Lima 32, Perú

Elizabeth Doig-Camino
Department of Sciences, Pontifical Catholic University of Peru, Lima 32, Perú

Gino Picasso
Faculty of Sciences, National University of Engineering, Lima, Perú

Adolfo La Rosa-Toro Gómez
Faculty of Sciences, National University of Engineering, Lima, Perú

Abstract: In the present study, the variation of the sensitivity of the sensors prepared from SnO_2 doped with Pt, in contact with different concentrations of methanol present in Peruvian wines using an array of sensors (electronic noses), in order to find which sensors were the most appropriate to differentiate commercial wines from adulterated ones, it was found that methanol It is found in a higher percentage in adulterated wines than in commercial ones. sensors Pt-SnO_2 coated with zeolite Y were the ones that presented a higher detection of this alcohol. Zeolite can act as a selective element, especially in platinum-doped sensors. In the principal component analysis (PCA) obtained, a good total variance was observed (the value is missing) in the results for both **Nose 1** and **Nose 2** (greater than 70%) with correlations close to zero, which indicates the independence of the observations. With **Nose 1**, built by sensors based on Pt-SnO2, a good differentiation of Peruvian wines of known brands was achieved with respect to those of unknown brands (possible adulterated wines) when applying the PCA method. Through the cluster analysis and the Factorial Analysis, the results obtained from the PCA were corroborated. Additionally, with the Factorial Analysis a high value was obtained in the variance (99.26%) of the two factors.
Keywords: Wines, possibly adulterated wines, alcohols in wines, multivariate analysis.

INTRODUCTION

In medical research it has been determined for many years that the breath of a living being contains substances that serve as specific markers of diseases. For example, a sequel to a liver disease can profoundly increase the concentration of dimethyl sulfide (bad breath), just as in kidney conditions there is an increase in ammonia (NH3) concentrations, etc. [Erase, J.A.; Duran, C.M. & Gualdrón, O.E. (2016)]

On the other hand, the possible presence of some substances such as NH3, benzene that can be toxic or dangerous, can be detected through the human nose in the environment. Likewise, the aroma of food and beverages can be perceived to determine if they are suitable for consumption and assess their quality through the aroma they emit (examples: coffee, alcoholic or aromatic beverage, among others) [NiuY.; Yao Z.; Xiao Q.; Xiao Z.; Ma N. & Zhu J. (2017)]

The wine is the result of a process of total or partial alcoholic fermentation of the grape [] Katalinic, V., Milos, M., Modun, D., Music, I., & Boban, M. (2004, Avalos Llano, K. R. (2003).] Its last aromatic level of the wine is carried out in oak barrels, in the stainless steel of the tank or in the bottle.These processes characterize the wine in such a way that the resulting qualities are used to understand its quality. sensory, the analysis of the chemical components that make up the aroma of the drink, serves to identify, differentiate and classify wines.The experts who can make this sensory appreciation only with it are the so-called sommeliers.

Another way to examine the quality of wines is by gas chromatography (GC) and high performance liquid chromatography (HPLC). Although these instrumental techniques are used in the wine industry, they have their limitations. For example, analytical methods only focus on the analysis of certain components of the beverage but not in its entirety. In addition, the high cost of testing and the long analysis time periods make it difficult to apply at each stage of wine production [Cetó, X.; González-Calabuig, A.; Capdevila, J.; Puig-Pujol, A. & del Valle, M. (2015)].

Another limitation of the latter is the little information that can be correlated with the sensory appreciation of the sommelier who has a sommelier staff who can evaluate each stage of the winemaking process [Cetó, X.; González-Calabuig, A.; Capdevila, J.; Puig-Pujol, A. & del Valle, M. (2015)]. Another alternative To solve this problem, this work proposes the implementation of a monitoring system for volatile organic compounds (VOCs) present in the aroma of wine by means of an array of chemical sensors called electronic nose, which, when interacting with the volatile organic compounds that are present in the aroma of a drink generate a response signal that modifies the electrical conductivity of the sensor.

The most commonly used chemical sensors are based on metal oxide semiconductors (MOS) due to their moderate thermal and chemical stability. Previous studies revealed that doping MOS with some transition metals allows them to improve their sensitivity and selectivity [Lee, J. H. (2018)].

The idea of using changes in electrical conductance of metal oxides for gas detection dates from around 1962. Jordao et al. [Jordao A., Vilela A. & Cosme F., (2015)], Wilkinson et al. [Wilkinson K. & Jiranck V. (2013)] and Panighel et al. [Panighel A. & Flamini R. (2014)] reported that the main component in wines, in addition to water, is ethanol, in a range of 9 to 14.5%, depending on the type of wine (red, rosé or white), in contrast to other volatile components of wine. such as methanol, n-propanol, n-butanol, acetic acid, among others, which are found in most cases in very low concentrations [Alam, H., & Saeed, S. H. (2012).] However, in wines adulterated, the methanol content increases.

Ahmadnia et al. [Ahmadnia, S.; Khodadadi, A.; Vesali, M. & Mortazavi, Y. (2012)], studied the detection of trichlorethylene, toluene, ethanol, acetaldehyde and acetone using SnO_2-based sensors with carbon nanotubes. The results revealed that the use of carbon nanotubes significantly improved the amplitude of the sensing signal of each of these compounds and favored the selectivity towards ethanol, acetaldehyde and acetone compared to trichlorethylene and toluene, which was attributed to a higher surface area and the presence of regular pores in the system. Janga et al. [Janga B., Landaub O., Choia S., Shina J., Rothschildb A. & Kima I. (2012)] prepared sensors based on tin oxide nanofibers doped with Pt nanoparticles, which improved the sensitivity and selectivity of the sensor towards certain volatile compounds.

In a previous job, Paredes-Doig et al. [] Paredes, A. L.; Tovar, O.; Càrcamo, H. A.; Hurtado, M.; Sun, M. D. R.; Doig, M. E.; Picasso, G.; Comina, G. & La Rosa-Toro, A. (2019).] studied the synthesis and physicochemical characterization of MOS sensors based on SnO_2 and ZnO to detect volatile compounds in Peruvian wines such as ethanol, propanoic acid, acetic acid and 1-phenyl ethanol, the work presented a selection of the best sensors with the highest response signal, which allowed a differentiation of the wines.

In the present investigation, tin oxide-based sensors without and with zeolite Y coating have been developed to quantify two of the main components of wines: ethanol (around 12% content) and methanol (around 3% of content). In this research work, it was considered important to modify the tin oxide sensor by adding small amounts of a noble metal (Pd or Pt) to improve the semiconductor properties of the oxide and increase the sensitivity and selectivity of the sensor towards the different concentrations of ethanol and methanol. with the aim of detecting what would be the characteristics of the sensors studied to find the differences between a commercial wine and an adulterated one.

METHODOLOGY

Table 1 presents the nomenclature of the wines used in this study.

Nomenclature	Commercial wine brands
CB1	Ocucaje Borgoña
CB2	Tabernero Borgoña
CR1	Tabernero Rose
CR2	Santiago Queirolo Rose
CR3	Tabernero Gran Rose
CT1	Santiago Queirolo Magdalena
Nomenclature	**Unknown wines**
DB1	Unknown 1
DB2	Unknown 2
DB3	Unknown 3
DM1	Unknown 4

Table 1. Nomenclature of the wines analyzed in this study.

The procedure followed for the preparation of the tin oxides consisted of weighing 30mg of the sample and adding 200uL of 1,2-propanediol as a dispersant.

The doped samples:

Pt-SnO_2 y Pd-SnO_2 were prepared using the wet impregnation technique used in previous works. [Paredes-Doig, A.L.; Cárcamo, H.; Hurtado Cotillo, M.; Sun Kou, M.R.; Doig Camino, E.; Picasso, G. & La Rosa-Toro Gómez, (2019)]. Doping ratios for each sensor were 0.1; 0.2; 0.3 and 0.5%

In addition, interdigital platinum electrodes were prepared on alumina substrates of dimensions 16 x 5 x 0.625 mm by assisted screen printing with a Trotec model 300 laser cutter, located in the VEO - PUCP Room.

Subsequently, the metal oxide samples were dispersed under ultrasound for 15min, using a DCG-200H Scientific Instruments brand. This way, 10μL of these dispersions were deposited on the alumina substrates with the platinum electrodes. Finally, they were dried at 110°C.

And calcined at 450°C for 2h. The nomenclature and description of the prepared sensors are shown in tables 2 and 3.

Additionally, for the coating with zeolite-Y on the sensors, a dispersion of 250mg of zeolite-Y in 500μL of 1,2-propanediol was prepared under ultrasound, for 15min. The coating was carried out by depositing 10μL of the dispersion on the sensors of the samples previously deposited on the alumina substrate using the microdropping technique following the procedure described by Vilaseca et al. [Vilaseca, M.; Coronas, J.; Cirera, A.; Cornet, A.; Morante, J.R. & Santamaria, J. (2008)]. The samples coated with zeolite-Y were dried at 80°C for 1h and finally, they were calcined at 450°C for 2h. Zeolite-coated samples were identified using the following nomenclature:xx% Pt/SnO_2–Z (Tables 2 and 3). The physical-chemical characterization of the sensors was reported in a previous work [Paredes, A. L.; Tovar, O.; Càrcamo, H. A.; Hurtado, M.; Sun, M. D. R.; Doig, M. E.; Picasso, G.; Comina, G. & La Rosa-Toro, A. (2019).].

Nomenclature -Sensors	Description
SnO_2	tin oxide
0,1%Pd/SnO_2	0.1% palladium doped tin oxide
0,2%Pd/SnO_2	0.2% palladium doped tin oxide
0,3%Pd/SnO_2	0.3% palladium doped tin oxide
0,5%Pd/SnO_2	0.5% palladium doped tin oxide
SnO_2-Z	Zeolite Coated Tin Oxide
0,1%Pd/SnO_2-Z	0.1% palladium-doped tin oxide with zeolite coating
0,2%Pd/SnO_2-Z	0.2% palladium-doped tin oxide with zeolite coating
0,3%Pd/SnO_2-Z	0.3% palladium-doped tin oxide with zeolite coating
0,5%Pd/SnO_2-Z	0.5% palladium-doped tin oxide with zeolite coating

Table 2: Description of palladium-doped tin oxide sensors with and without zeolite coating.

Nomenclature -Sensors	Description
SnO_2	tin oxide
0,1%Pt/SnO_2	0.1% platinum doped tin oxide
0,2%Pt/SnO_2	0.2% platinum doped tin oxide
0,3%Pt/SnO_2	0.3% platinum doped tin oxide
0,5%Pt/SnO_2	0.5% platinum doped tin oxide
SnO_2-Z	Zeolite Coated Tin Oxide
0,1%Pt/SnO_2-Z	0.1% platinum-doped tin oxide with zeolite coating
0,2%Pt/SnO_2-Z	0.2% platinum-doped tin oxide with zeolite coating
0,3%Pt/SnO_2-Z	0.3% platinum-doped tin oxide with zeolite coating
0,5%Pt/SnO_2-Z	0.5% platinum-doped tin oxide with zeolite coating

Table 3. Description of platinum-doped tin oxide sensors with and without zeolite coating.

Prior to the sensing measurements, the major components in wines were determined using a gas chromatograph coupled to a mass detector in an external laboratory. The results of the analysis indicated that the methanol content in the wines of recognized brands was between 2 - 3% and in the possibly adulterated wines it was approximately 4%. The ethanol content in all the wines varied between 10 - 20%.

The sensing system used was divided into two parts: the first, referring to sampling, made up of a 100 mL capacity glass bubbler, and the second, made up of a closed stainless steel sensing chamber, inside which was placed a resistance, a contact thermocouple to control the working temperature and additionally, up to a maximum of 10 different sensors were placed, which made up the electronic nose (Figure 1). Air was used as the carrier gas for the tests.

To carry out the tests, the sensor signal was first stabilized by passing a constant flow of air through the sensing chamber and maintaining the chamber temperature at 220°C for approximately 2 h, until achieving a stable baseline, which also ensured the stability of the working temperature.

Subsequently, 100 mL of the methanol solution to be analyzed was placed in the bubbler. Work was carried out in prepared concentrations of 1, 3, 5, 7 and 10%, simulating the contents detected in the tested wines. The tests were repeated later with the wines under study.

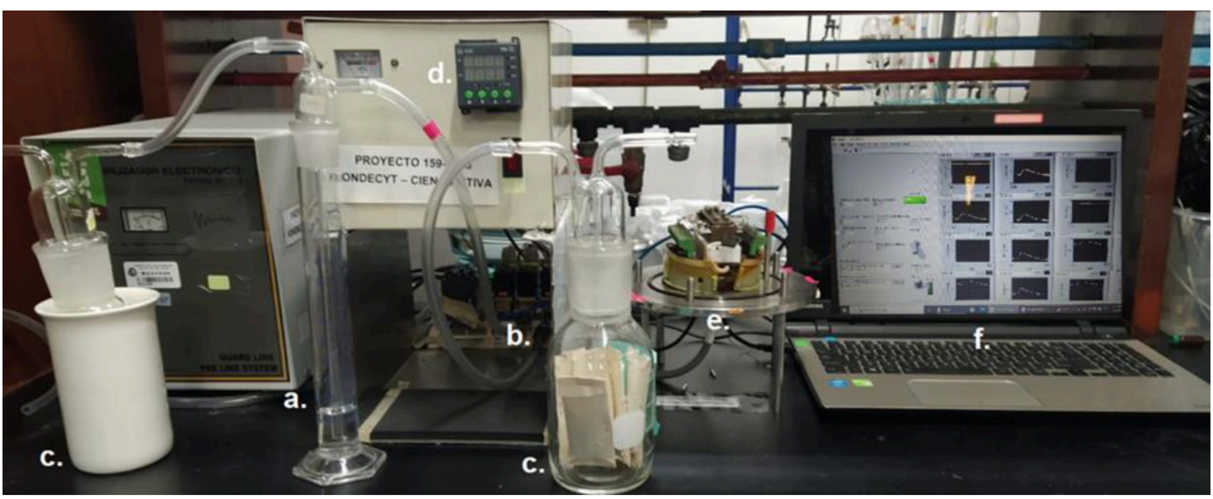

Figure 1. Electronic nose system. (a) Methanol sample in the bubbler during sensing. b. Hydraulic system. c. Desiccators with silica gel. d. Temperature controller. and. Sensor arrangement. F. Labview 2018 software interface.

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At the beginning of the test, a constant air flow is passed through the bubbler and, with the help of a vacuum pump and two solenoid valves, the gaseous mixture of air saturated with the methanol solution or with the volatile components of the wine is transported to the chamber. sensing at a flow less than 2 L/min.

All the tests were carried out at the working temperature of 220°C, with data collection periods of 80s (time in which methanol or volatile components of the wine were in contact with the sensors), followed by a purge of the system with air for 400 s, before proceeding to the next test. For each solution containing methanol or wine, the tests were carried out in quintuplicate.

The sensors were connected by cables to a National Instruments USB 6213 analog/digital converter (ADC) that records the change in conductivity (expressed in voltage), which is produced by the interaction of each sensor with the volatile component of the sample. This signal was recorded with a sampling frequency of 1 Hz. The LabView 2018 software allowed the control of the entry and exit of gases in the chamber, by opening and closing the solenoid valves. Additionally, the recording of the responses of the sensors was carried out with the help of a digital computer.

The voltage data obtained during the sensing was transformed into resistance values, which in turn were converted into the sensing response signals (V/Vr). For the analysis of the effect of the methanol content, this response was plotted against the measurement time, where "V" is the measurement of the voltage obtained from the sample in relation to the reference voltage "Vr" of the signal used in the equipment that was tested. from 5.2V. Subsequently, the responses were processed using the following mathematical statistical analysis methods: Principal Component Analysis (PCA), Cluster and Factor Analysis. The same procedure was carried out with the volatile components contained in the aroma of each studied wine.

The PCA allowed to visualize the differentiation between the wine varieties, as well as the differentiation against a possible wine adulterated with methanol. Each repetition is represented by a point and the data collected corresponding to the same type of wine are shown within a confidence ellipse assuming that they follow a normal distribution.

The approach or the distance between the ellipses allows to visualize with greater ease the capacity of separation or differentiation between different varieties of a sample. The total explained variance is also obtained, which indicates the confidence level of the results. It is recommended that said variance be greater than 70%.

RESULTS AND DISCUSSION

DETECTION OF SENSOR RESPONSE IN CONTACT WITH METHANOL SOLUTIONS AT DIFFERENT CONCENTRATIONS

From the graphs of the response of the sensor versus time, obtained for the measurements of methanol at different concentrations, using the **sensors of SnO_2 palladium-doped without zeolite coating** (Figure 2, series located on the left), it was observed that as the methanol concentration increased, the response signals present a slight increase in the intensity of all the sensors in this series, due to the fact that the surface of the sensor interacts with a larger number of methanol molecules apparently without becoming saturated.

The maximum intensity value reached is around 4, the sensors being 0.1% Pd/SnO2 and 0.2% Pd/SnO_2 those who presented a greater response; this may be due to the low metallic content and the greater dispersion

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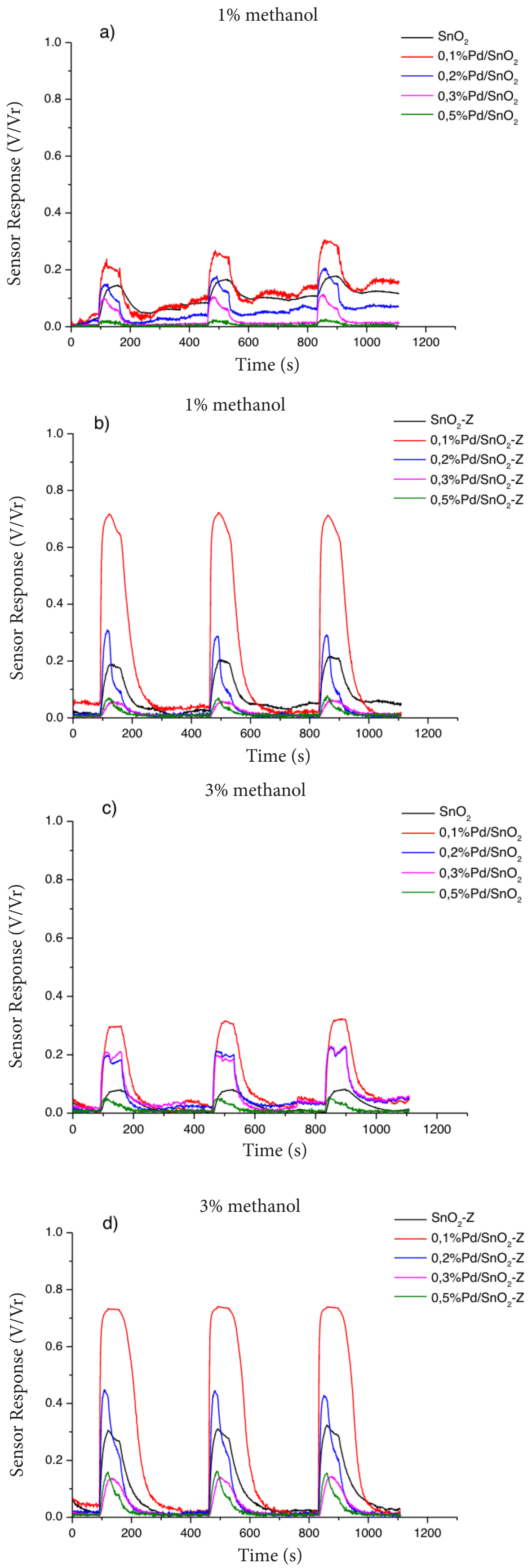
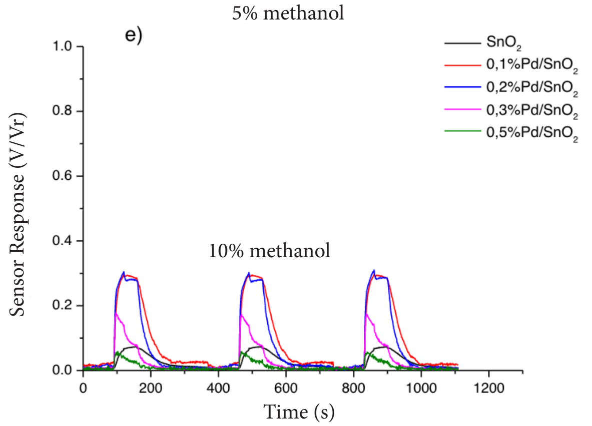
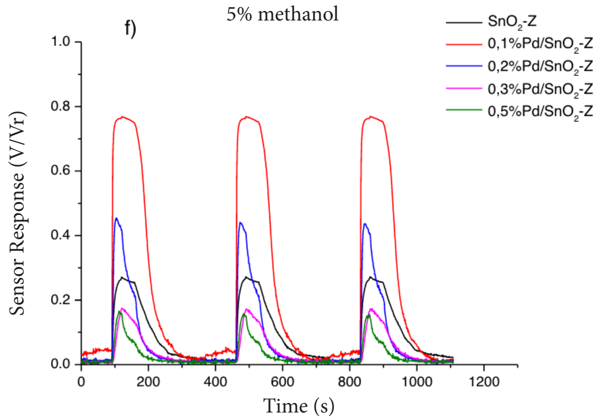
of the metal on the oxide that allows a better interaction of the volatile compound with the sensor surface.

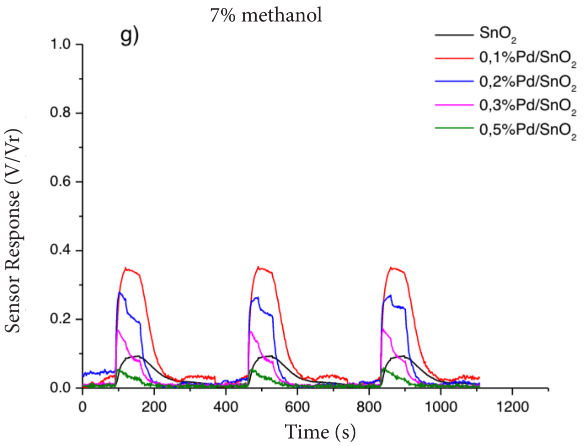
And this occurs in a humid environment [] Yamazoe, N.; Sakai, G. and Shimanoe, K. (2003)]. Tianjiao Qi et al. [Qi, T.; Sun, J.; Yang, X.; Yan, F. and Zuo, J. (2019)] evaluated the behavior of Pd/SnO_2 at different calcination temperatures, determining that, at T > 450°C, the selectivity and sensitivity are better for the detection of H_2, because in this range of T the presence of Pd is ensured. It is possible that the presence of PdO produces less interaction with volatile compounds. Sensor response plots obtained for methanol measurements at different concentrations using the **sensors of SnO_2 palladium-doped with zeolite coating** (Figure 2, series located on the right), shows a clear increase in the intensity of the sensing signal as the methanol concentration increases, reaching values between 7 and 8 with the sensor:0,1%Pd/SnO_2-Z, the response signal of the other sensors is also gradually increased in relation to the same sensors without zeolite coating, this effect is also noticeable with the sensor of SnO_2-Z. This may be due to the fact that certain volatile compounds, which may cause interference, are retained by the Y zeolite, which, having regular-sized pores, acts as a molecular sieve, favoring the interaction of the sensor with methanol [Trevejo Pinedo Jorge, 2019].

Additionally, this fact may also be due to the fact that the zeolite layer interacts with alcohol, catalyzing the formation of a product from methanol inside its structure, with which Pd-doped tin oxide is more sensitive, increasing thus the intensity in the signals. As in the previous case, it is observed that the sensor that presents the greatest intensity in the response is:









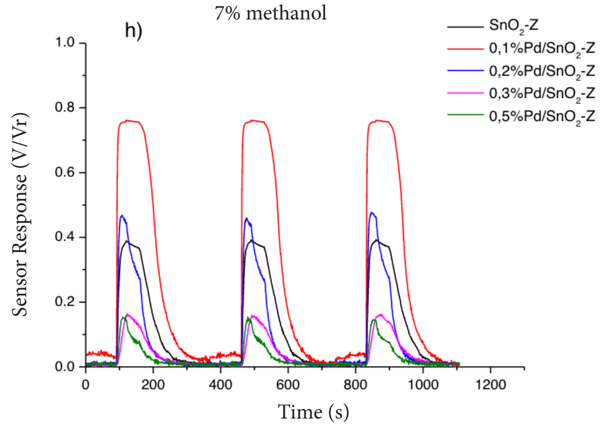
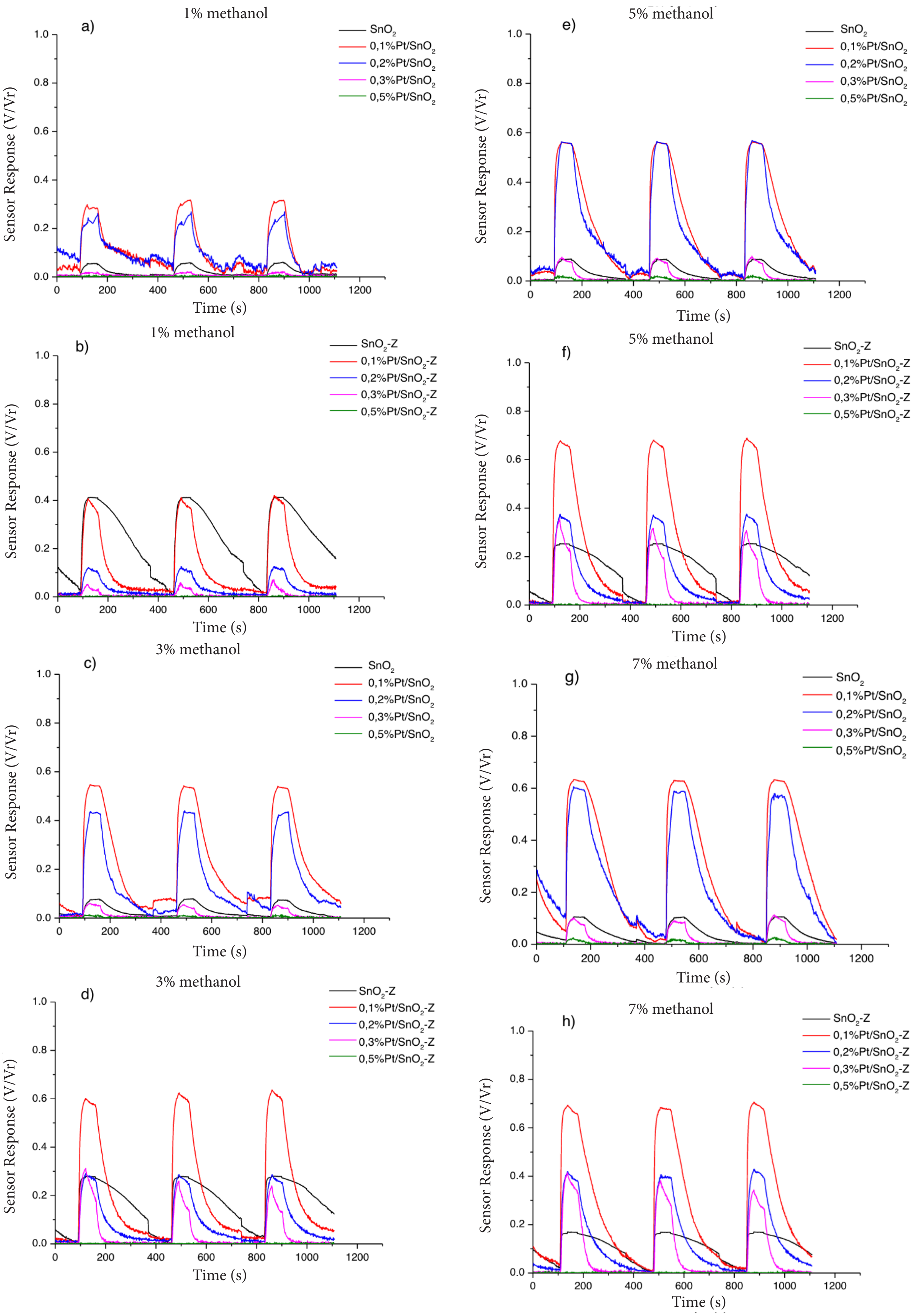
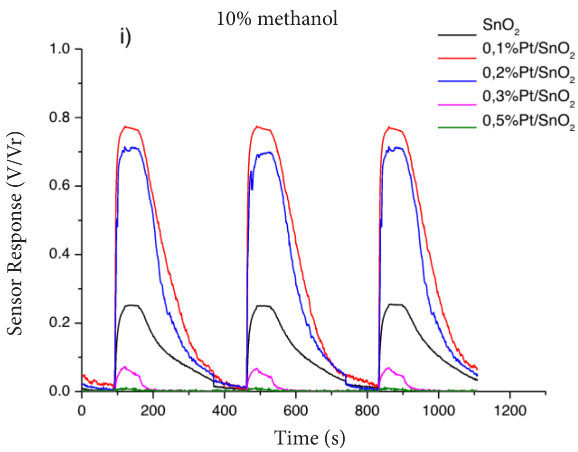


Figure 2. Response of the sensors of **palladium-doped tin oxide** without zeolite (left side) and with zeolite (right side) in contact with **different concentrations of methanol** and at a working temperature of 260 °C.

Figure 3, series located on the left side, shows the response of the **Platinum-doped tin oxide sensors without zeolite coating** in contact with different concentrations of methanol, comparatively it is observed that the intensity of the response signal is greater in relation to its homologues doped with palladium (Figure 2, series located on the left side), which would indicate a greater selectivity of platinum towards the methanol. This better behavior in the sensors of SnO_2 doped with Pt can be explained considering that platinum can also act as an active center for the oxidation reactions that occur when the sensor comes into contact with a reducing gas. This fact favors a greater interaction and, therefore, doping with Pt would be generating more charge density or more oxygen vacancies or charge carriers, which is subsequently reflected in the PCA analyses. The strongest response signals were obtained with the sensors: 0,1%Pt/SnO_2 followed by 0,2%Pt/SnO_2



1% methanol
a)
SnO2
0,1%Pt/SnO2
0,2%Pt/SnO2
0,3%Pt/SnO2
0,5%Pt/SnO2
Sensor Response (V/Vr)
Time (s)
1% methanol
b)
SnO2-Z
0,1%Pt/SnO2-Z
0,2%Pt/SnO2-Z
0,3%Pt/SnO2-Z
0,5%Pt/SnO2-Z
Sensor Response (V/Vr)
Time (s)
3% methanol
c)
SnO2
0,1%Pt/SnO2
0,2%Pt/SnO2
0,3%Pt/SnO2
0,5%Pt/SnO2
Sensor Response (V/Vr)
Time (s)
3% methanol
d)
SnO2-Z
0,1%Pt/SnO2-Z
0,2%Pt/SnO2-Z
0,3%Pt/SnO2-Z
0,5%Pt/SnO2-Z
Sensor Response (V/Vr)
Time (s)
5% methanol
e)
SnO2
0,1%Pt/SnO2
0,2%Pt/SnO2
0,3%Pt/SnO2
0,5%Pt/SnO2
Sensor Response (V/Vr)
Time (s)
5% methanol
f)
SnO2-Z
0,1%Pt/SnO2-Z
0,2%Pt/SnO2-Z
0,3%Pt/SnO2-Z
0,5%Pt/SnO2-Z
Sensor Response (V/Vr)
Time (s)
7% methanol
g)
SnO2
0,1%Pt/SnO2
0,2%Pt/SnO2
0,3%Pt/SnO2
0,5%Pt/SnO2
Sensor Response (V/Vr)
Time (s)
7% methanol
h)
SnO2-Z
0,1%Pt/SnO2-Z
0,2%Pt/SnO2-Z
0,3%Pt/SnO2-Z
0,5%Pt/SnO2-Z
Sensor Response (V/Vr)
Time (s)



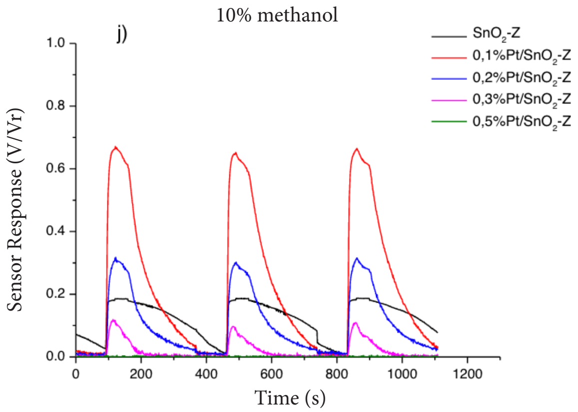


Figure 3. Response of the sensors of **platinum doped tin oxide** without zeolite (left side) and with zeolite (right side) in contact with **different concentrations of methanol** and at a working temperature of 260 °C.

Related to Pt-SnO_2 **with zeolite coating** (Figure 3, series located on the right side), it is observed that the intensity of the response signal increases with the higher percentage of methanol and is greater when compared with the same sensor without zeolite coating. This effect is greater with the sensors :0,1%Pt/SnO_2-Z; 0,3%Pt/SnO_2-Z y SnO_2-Z, however, the signal strength is reduced for the sensor: 0,2%Pt/SnO_2-Z with increasing methanol concentration, this indicates that the presence of zeolite can generate a selective effect (positive or negative) in platinum-doped sensors that does not occur with palladium-doped sensors.

MATHEMATICAL STATISTICAL ANALYSIS WITH THE PCA, CLUSTER AND FACTORIAL ANALYSIS METHODS OF THE RESULTS OBTAINED WITH THE ELECTRONIC NOSES MADE UP OF THE ARRANGEMENT OF THE SENSORS STUDIED

From the results collected from each sensor, all the data was ordered in a database built for the electronic nose. Subsequently, all this information was processed using the Principal Component Analysis (PCA), Cluster and Factor Analysis methods. In the case of the PCA, from this statistical analysis it was possible to reduce the dimensionality of the data that characterize each sample and transform them into principal components (ordered by the variation of the data set), which allow groupings of similar samples to be made in the form of of ellipses, based on the different profiles of the sensors used. This way, the results of the Total Explained Variance and a biplot graph that allows visualizing the relationship of the variables were obtained.

NOSE 1: Electronic nose made up of 10 platinum-doped SnO2 sensors (0.1; 0.2; 0.3 and 0.5% Pt) with and without zeolite coating.

a) Application of the PCA for the Nose 1:

Figure 4 shows the PCA of the sensing results of nose 1, where it can be seen that the ellipse that groups the signals of well-known brand wines appears to the left of the graph, while the ellipse that groups signs for unknown brand wines appear on the right. The Total Explained Variance obtained was 88.42%

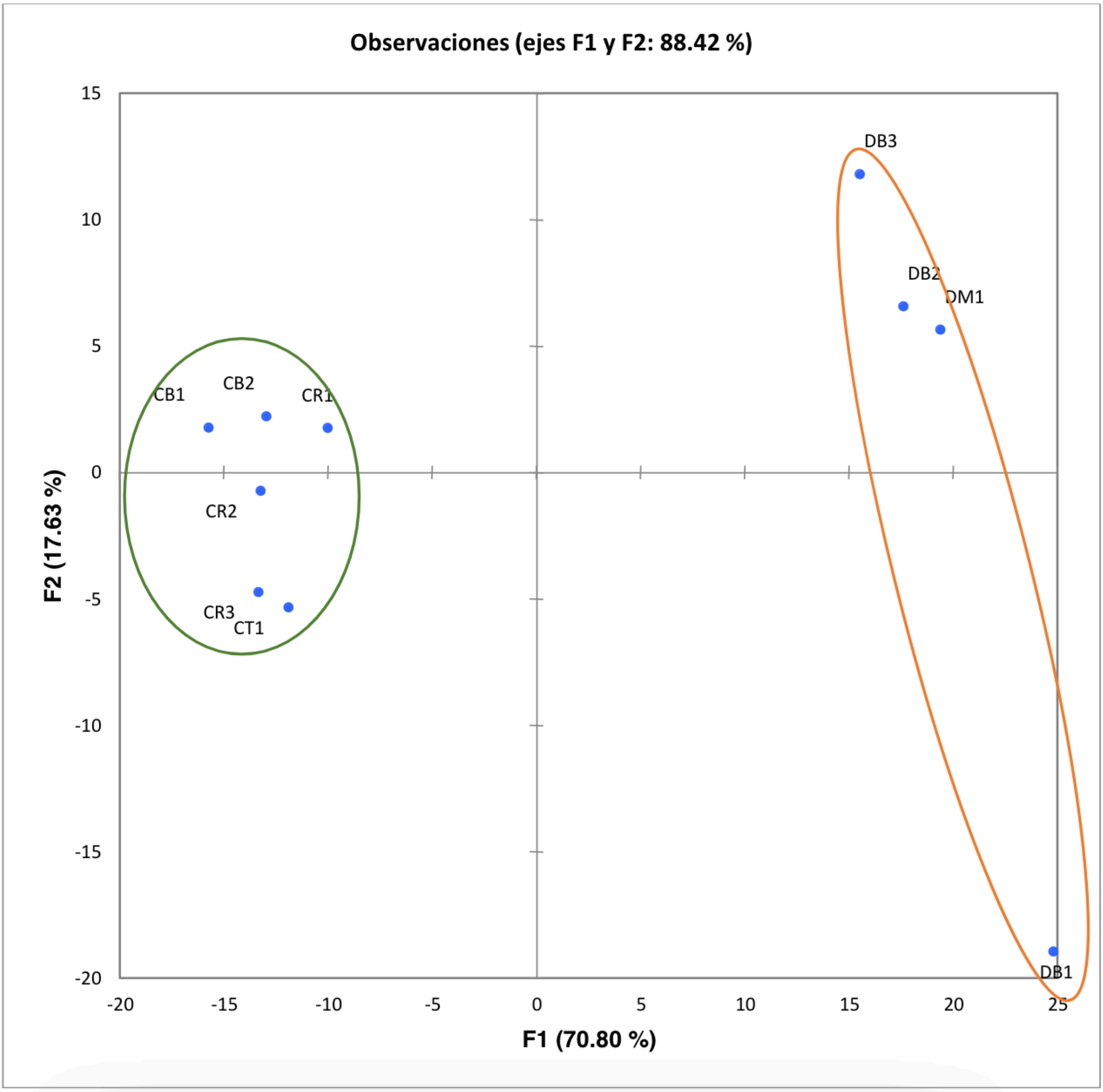


Figure 4. PCA applied to the sensing results obtained with **Nose 1.**

b) Application of Cluster Analysis for the Nose 1:

Using the information obtained from the database, the cluster method was applied to the results to achieve the partition of the elements of Nose 1.

From the graph obtained not shown, known as dendrogram, it was possible to observe that despite the fact that there are three groups of agglomerates found, basically two are significant. From the cluster analysis it is inferred that there is greater inter-class heterogeneity and there is also intra-class homogeneity, that is, it is observed that there is a similarity between the wines of the same class.

c) Application of Factor Analysis for the Nose 1:

Making use of the collected data, Factorial Analysis was applied to the results obtained with Nose 1, in order to group the wines. Figure 5 shows the results presented with the Factor Analysis.

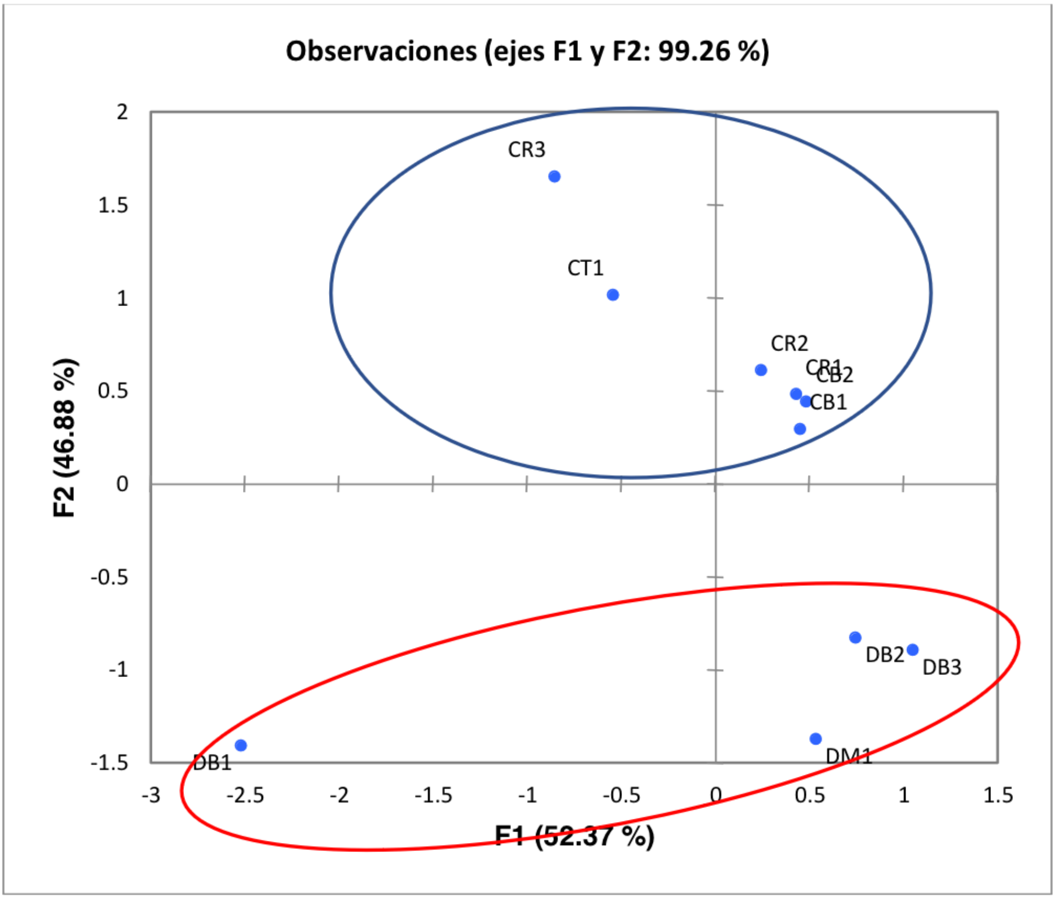


Figure 5. Factorial Analysis applied to the results obtained with **Nose 1.**

It is clearly observed that **Nose 1** separates the wines into two well-differentiated groups: the ellipse that groups the signs of the wines of well-known commercial brands and the difference of the other ellipse that groups the wines of unknown brands or those wines that possibly they are adulterated. It is also observed that the value of the variance of the two factors is quite high (99.26%).

NOSE 2: Electronic nose made up of 10 SnO2 sensors doped with different proportions of palladium, with and without zeolite coating.

a) PCA Application for Nose 2:

En la Figura 6 se presenta el PCA de los resultados de sensado utilizando los sensores que conforman la **Nariz 2**. From the biplot graph, it can be seen that the ellipses that group the response signals of the wines studied in known brands and unknown or adulterated brands are not grouped as visibly as in the case of **Nose 1**, although it is observed that there is a separation between the ellipses. On the other hand, it is observed that the signals of the four wines of unknown brands are closer to each other. Among the wines of well-known commercial brands, these are grouped according to the type of wine; that is to say, one has that those that are of the Burgundy type and those of the Rosé type are closer to each other. In the case of the sign of the only Red wine, it is located a little further from the previous ones. The Total Explained Variance obtained was 89 %.

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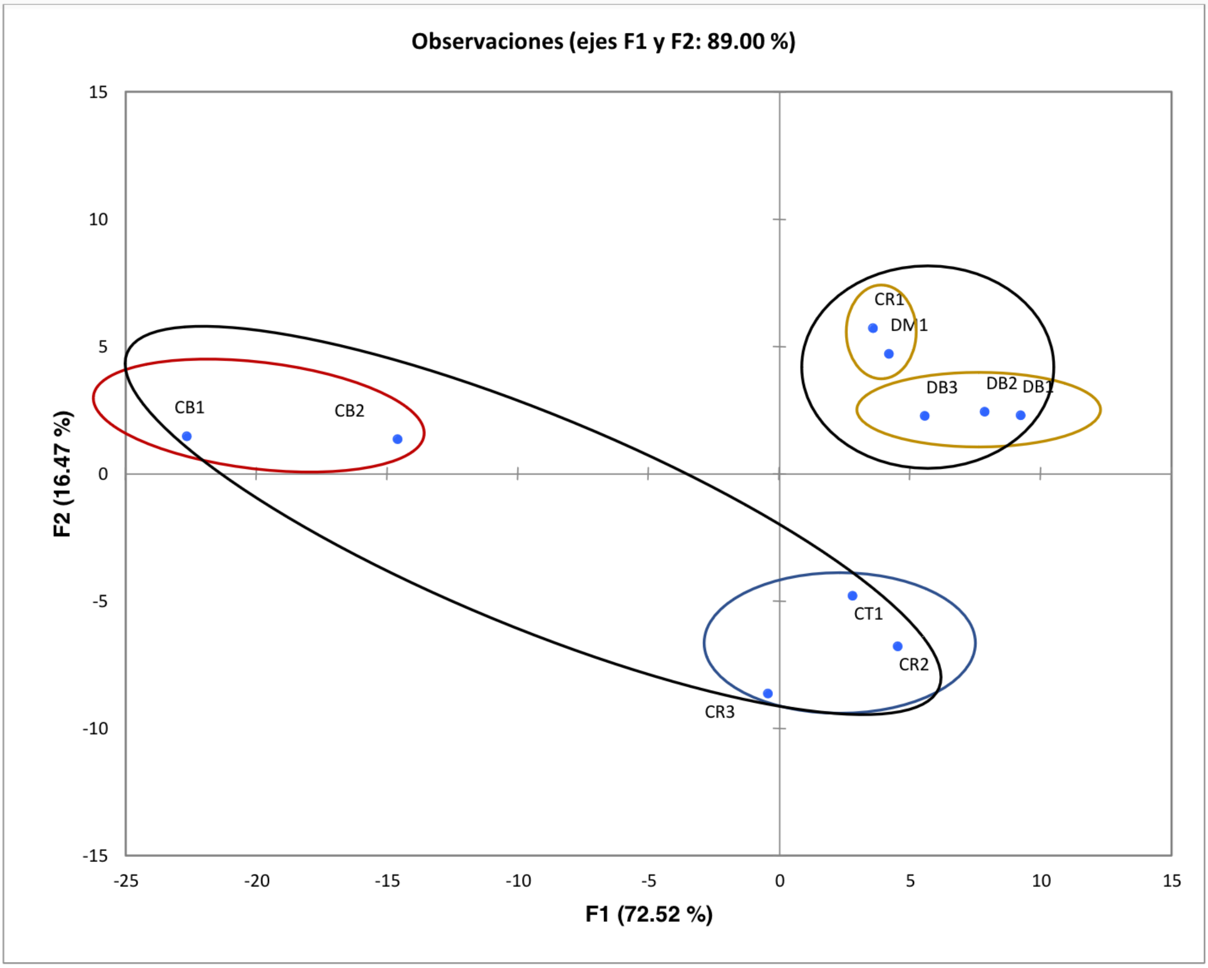

Figure 6. PCA applied to the results obtained by **Nose 2.**

b) Aplicación del análisis Clúster para la Nariz 2:

As in the previous case, the cluster method was applied to the results to partition the elements of **Nose 2**.

From the dendrogram of **Nose 2** (not shown) it was possible to verify the formation of three agglomerates (ellipses): one that includes wines of unknown brand, another that includes Rosé type wines, and the last one that includes Burgundy type wines. Although there are two that are located outside the true type of wine that corresponds to them.

As in Nose 1, good results are observed in the differentiation between classes and the intra-class similarity. It is corroborated that three significant classes would be forming; in this case, it also coincides with the PCA obtained for **Nose 2**.

c) Aplicación del Análisis Factorial para la Nariz 2:

With the data obtained, Factorial Analysis was applied to the results obtained with **Nose 2**, in order to group the wines studied. Figure 7 shows the results corresponding to this statistical technique:

It is clearly observed that **Nose 2** separates the wines into two groups: known commercial wines and unknown ones, although not in the same way as differentiated as in the case of **Nose 1**. It is also observed that the value of the variance of both factors is quite high (93.98%).

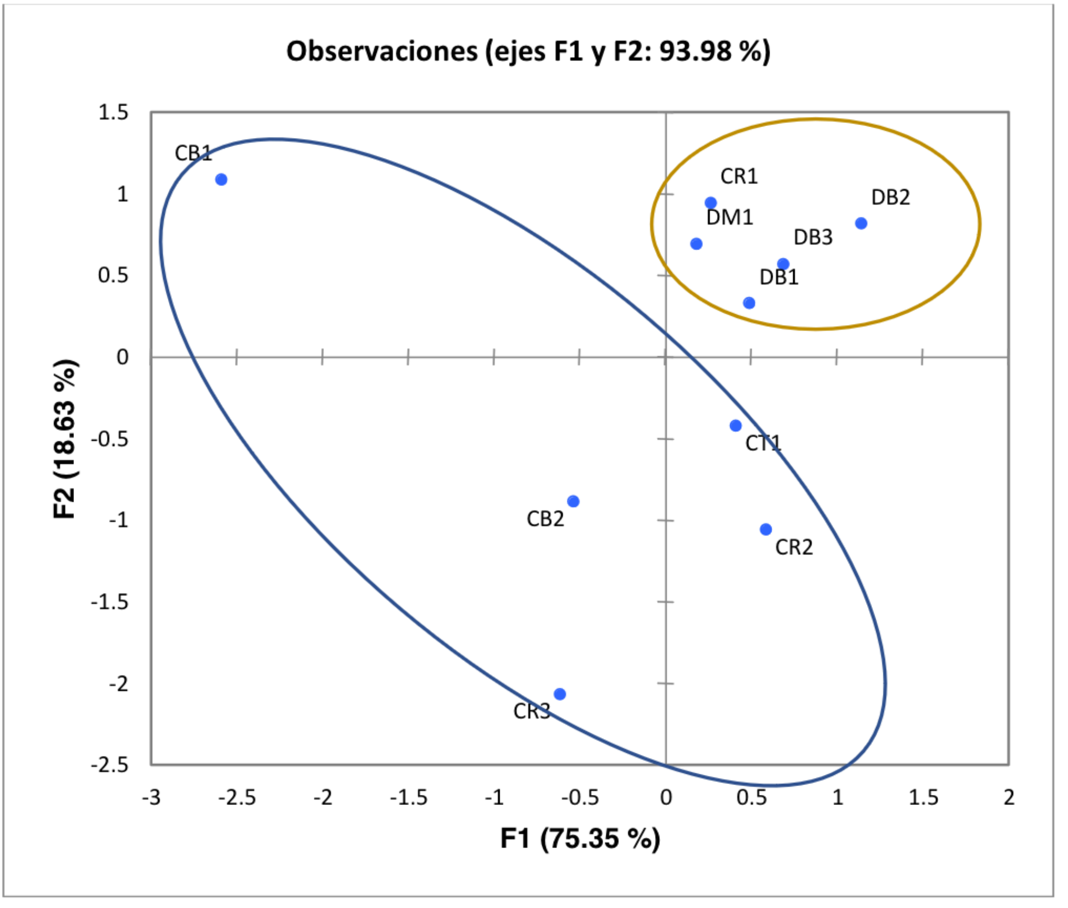

Figure 7. Factorial Analysis applied to the results obtained with **Nose 2.**

CONCLUSIONS

- In this research, 10 wines of known and unknown commercial brands were studied. For their sensing, they prepared SnO_2 doped with Pt or Pd by the wet impregnation method. Subsequently, the vast majority of the prepared sensors were coated with zeolite Y.

- The intensity of the sensor response increased as the concentration of alcohol (methanol) increased.

- The Pt-doped SnO2 sensors generated signals with greater intensity compared to the signals obtained with their palladium-doped counterparts, evidencing a greater interaction of methanol with these sensors.

- The sensors that presented the highest sensitivity and stability were the sensors with low dopant metal content without and with zeolite coating, following the following order: 0,1%Pd/SnO_2-Z > 0,1%Pt/SnO2-Z > 0,1%Pt/SnO_2 > 0,2%Pt/SnO_2

- The intensity of the response of the sensors: 0,1%Pd/SnO_2-Z y 0,1%Pt/SnO_2-Z with zeolite coating was higher compared to their counterparts without zeolite. However, the signal strength is reduced in the case of the sensor: 0,2%Pt/SnO_2-Z with increasing alcohol concentration, this indicates that the presence of zeolite can generate a selective effect (positive or negative) in platinum-doped sensors that does not occur with palladium-containing sensors.

- From the results analyzed, it is established that with **Nose 1**, made up of sensors based on tin oxide doped with platinum, without and with zeolite coating, a good differentiation of Peruvian wines of well-known commercial brands was achieved with respect to those of brands unknown when applying the PCA method. Through Factorial and Cluster Analysis it was possible to differentiate the wines in a similar way, corroborating the results by three different methods.

- In the case of **Nose 2**, made up of palladium-doped tin oxide-based sensors with and without zeolite coating, it was not possible to differentiate as visibly as in the case of **Nose 1**, Peruvian wines from known brands of wines of unknown brands when applying the PCA method. Something similar happens when the Cluster method is applied to the results, however, with **Nose 2**, it manages to make a good separation according to the type of wine (red, Rosé, Burgundy).

- The **Factor Analysis** that was applied to complete the statistical mathematical analysis leads to similar results found with the two previous statistical methods.

- In general, a good Total Explained Variance was observed in the results for both electronic noses (greater than 70%) with correlations close to zero, which indicates the independence of the observations.

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