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DETERMINATION OF THE WORKING TEMPERATURE OF THE MOS SENSORS FOR DETECTION OF ETHANOL AND METHANOL

Ana L. Paredes-Doig
Faculty of Sciences, National University of Engineering. Rímac, Lima, Perú
https://orcid.org/0000-0002-7180-2823

Henry Cárcamo
Chemistry Section, Department of Sciences, Pontifical Catholic University of Peru
San Miguel, Lima, Perú
https://orcid.org/0000-0003-2229-2115

Elizabeth Doig-Camino
Mathematic Section, Department of Sciences, Pontifical Catholic University of Peru
San Miguel, Lima, Perú
https://orcid.org/0000-0002-2407-0738

Gino Picasso
Faculty of Sciences, National University of Engineering. Rímac, Lima, Perú
https://orcid.org/0000-0002-5553-5278

Adolfo La Rosa-Toro Gómez
Faculty of Sciences, National University of Engineering. Rímac, Lima, Perú
https://orcid.org/0000-0001-8143-9936

Maria R. Sun-Kou
Chemistry Section, Department of Sciences, Pontifical Catholic University of Peru
San Miguel, Lima, Perú
https://orcid.org/0000-0002-0432-3013

Abstract: In this work, some peruvian red wines were analyzed using gas chromatography coupled to mass spectrometry (GC-MS) and it was determined that ethanol was the major volatile component present in the aroma (12 % in volume). followed by methanol (2-3 % in volume). Some MOS sensors based on SnO_2 doped with Pd and Pt were prepared by wet impregnation with metallic charges from 0.1 to 0.5% and were tested with the same Peruvian wines. The stability and reproducibility of the sensing signal was analyzed at different working temperatures (200, 220, 240, 260 and 280 °C). The best working temperature at which the highest intensity of the response signal of the sensors was obtained at 260 °C. In most of the cases studied, the sensing signal of the sensors was in general repetitive and stable, maintaining its amplitude and shape during long periods of the analysis. However, at the temperature of 280° C the signal loses intensity and in contact with methanol the signal is distorted.
Keywords: Sensors MOS, Working Temperature, Ethanol, Methanol

INTRODUCTION

The idea of using the changes in electrical conductance of metal oxides for gas detection dates from about 1962. Jordao et al. [1], Wilkinson et al. [2] and Panighel et al. [3] reported in their respective investigations that the main component in wines, in addition to water, is ethanol, in the range of 9 to 14.5%, depending on the type of wine (red, rosé or white), in contrast with the 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.

According to Ahmadnia et al. [4], the detection of trichlorethylene, toluene, ethanol, acetaldehyde, and acetone was studied: using sensors based on SnO2 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 in comparison with trichlorethylene and toluene, which was attributed to a higher surface area and the presence of regular pores in the system. Janga et al. [5] prepared sensors based on tin oxide nanofibers doped with Pt nanoparticles, thus improving the sensor's sensitivity and selectivity towards certain volatile compounds.

In the present research, palladium or platinum doped tin oxide sensors have been used to detect two of the main components in wines: ethanol (12%) and methanol (3%) to find the optimal temperature of the operation of these sensors in working conditions. To this aim, the components of the aroma in wines have been previously determined by means of the gas chromatography technique.

MATERIALS AND METHODS

1. Sensors Preparation

In a previous work [6], the sensors based on SnO_2 doped with palladium (0.1, 0.2, 0.3 and 0.5% Pd) or platinum (0.1, 0.2, 0.3 and 0.5% Pt) were prepared by wet impregnation method. To increase the sensitivity of the sensors to contact with volatile chemicals present in the aroma for the evaluation of Peruvian wines, some sensors were coated with Zeolite Y. Many combination arrays of sensors were made to obtain electronic noses, using at least 10 sensors.

2. Detection of the major components in wines

In the present work, an Agilent Technologies 7890A gas chromatograph was used coupled to an Agilent Technologies 5975 mass selective detector. An HP-FFAP

polar capillary column (30 m × 250 μm × 0.25 μm) was used.

3. Preparation of samples

A template was formed with the adhesive tape to define the area that would cover the SnO_2 doped with metal (Pd or Pt) on the surface of one alumina plates. Subsequently, 0.1 gram of doped tin oxide was combined with (0.1, 0.2, 0.3 and 0.5%) Pd or Pt with 0.02 g of ethylcellulose and 32 μL of α-terpineol, forming a paste, which was deposited on the one substrate of alumina, and then a heat treatment was carried out in the oven for 15 min at 60°C.

4. Sensors with zeolite Y coating.

In a beaker containing 0.05 g of tin oxide doped with Pt or with Pd, 0.01 g of ethylcellulose and 16 μL of α-terpineol were added, these substances were mixed uniformly to form a paste, which that was deposited on a surface of alumina containing two gold electrodes, and then it was calcined at the 600 ° C for 10 min using a heating ramp of 3°C/min.

To prepare a thin layer of zeolite Y, 1,2-propanediol was used as a solvent following the procedure described by Vilaseca et al. [7]. Each mixture was constantly stirred until the zeolite Y was dispersed in the solvent. Later, with the help of a micropipette, a small quantity was extracted, which was deposited by microdripping on the surface of the tin oxide previously placed on the alumina sheet. Subsequently, it was evaluated the sensor signal obtained in the presence of volatile compounds.

5. Sensitivity of Sensors.

Sensitivity was measured by calculating the difference between the two signals, the signal of baseline and the signal of the plateau. The sensing of wine aroma compounds was measured following these steps:

(a) The sample was placed in a container

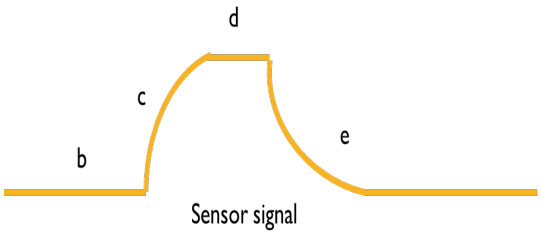
(b) Vacuum was made with a pump and the aroma compound (sample) was carried to container through a pneumatic system

(c) The sample reached the sensor surface and was detected

6. Tests at different working temperatures.

The tests of the sensors were carried out at different working temperatures (200, 220, 240, 260 and 280^{0}C). Some solutions of 3% methanol and 12% ethanol in volume (100ml) were prepared. The concentration of ethanol and methanol in the solutions were fixed in accordance with the values found in the Peruvian wines.

In this investigation, two electronic noses were studied, each one was made up of an arrangement of 10 sensors. The first one (NOSE 1) consists in sensors based on tin oxides doped with Pd with different percentage volume concentrations: 0.1, 0.2, 0.3 and 0.5, with and without zeolite coating. The second one (NOSE 2) consists in sensors based on similar compositions of the first one but doped with Pt.



7. The following parameters were chosen for each trial:

a) Sensing Temperature: 200, 220, 240, 260 and 280 ^{0}C

b) Initial purge time: 120 seconds

c) Sample carryover time: 30 seconds

d) Reading time: 40 seconds

e) Final purge time: 240 seconds

Cycle time: 430 seconds

The following describes the sensors based on palladium doped tin oxide (Table 1) or with platinum (Table 2) with and without zeolite coating.

RESULTS

In a previous work, the results of the analysis of 10 red wines were presented (Table 3) using gas chromatography coupled to a mass spectrometer (GC-MS) and it was determined that ethanol was the major volatile component contained in the aroma of the wines, followed by methanol (Table 4).

As is observed, the methanol content in the wines of recognized brands is between 2 to 3% and in the possibly adulterated wines is around 4%. Additionally, the ethanol content in all wines is ranging from 10 to 20%.

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	Tin oxide with zeolite coating
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 1. Composition of palladium-doped tin oxide sensors and the same sensors but coated with zeolite (assigned with Z).

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	Tin oxide with zeolite coating
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 2. Composition of platinum-doped tin oxide sensors and the same sensors but coated with zeolite (assigned with Z).

Nomenclature	Description of well-known brand wines
CB1	Ocucaje Borgoña
CB2	Tabernero Borgoña
CR1	Tabernero Rose
CR2	Santiago Queirolo Rose
CR3	Tabernero Gran Rose
CT1	Santiago Queirolo Magdalena
Nomenclature	**Description of unknown brand wines**
DB1	Unknown 1, burgundy type
DB2	Unknown 2, burgundy type
DB3	Unknown 3, burgundy type
DM1	Unknown 4, mixtela

Table 3. Description of the Peruvian wines used in this research.

		% in the sample (relative areas)									
Compounds	**tR (min.)**	**CR3**	**CR1**	**CT1**	**CR2**	**DM1**	**CB2**	**CB1**	**DB1**	**DB2**	**DB3**
Ethanol	2,8	10-20	10-20	10-20	10-20	10-20	10-20	10-20	10-20	10-20	10-20
Methanol	2,6	2,0	2,0	2,0	2,0	2,0	2,0	2,0	4.0	4.0	2,0
1-butanol	11,7	12,2	13,5	11,1	15,7	13,1	20,6	4,4	3,7	4,3	4,4
1-propanol	23,9	---	0,2	0,1	0,2	0,1	0,1	---	---	---	---
1-octanol	18,9	---	---	---	---	---	---	---	0,01	---	---
Phenylethanol	29,1	3,3	8,4	4,7	4,9	5,6	6,2	4,0	2,1	2,2	2,5
Nerol	71,2	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1
Geraniol	14,6	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1
Propanoic acid	16,0	1,4	7,5	5,1	5,7	7,9	4,5	20,6	14,3	10,1	---
Ascorbic acid	27,5	5,4	6,3	2,7	8,4	2,9	4,4	1,5	---	---	1,8
Ethyl succinate	31,2	4,2	11,4	9,3	8,0	8,9	6,3	1,6	---	---	4,7
Butanedioic acid	31,7	0,9	2,0	1,7	1,4	1,4	1,0	0,5	0,4	0,2	---
2-Butanone	10,2	---	---	---	---	---	---	---	4,4	0,8	0,3
Benzoic acid	31,1	---	---	---	---	---	---	---	3,4	8,2	1,2
Pentane cycle	11,9	---	---	---	---	---	---	---	1,4	0,3	0,2
Butane cycle	8,7	---	---	---	---	---	---	---	---	3,0	2,2
Octadecanoic acid	58,9	---	---	---	---	---	---	---	0,7	1,3	1,1
n-Hexadecanoic acid	56,7	---	---	---	---	---	---	---	1,4	2,4	2,3

Table 4. Major compounds in Peruvian wines.

Below are two chromatograms (Figure 1 and Figure 2) of two wines: one from a known brand (CR3) and the other from an unknown brand (DB1).

DETECTION OF THE SENSOR RESPONSE IN CONTACT WITH 3% METHANOL SOLUTIONS AND AT DIFFERENT WORKING TEMPERATURES

In contact with 3% methanol and using the electronic nose formed by the SnO_2 sensors doped with palladium with and without zeolite coating (Figure 3), it was observed that as the sensing temperature increases from 200°C to 240°C, the intensity of the response from all sensors increases.

This is possibly due to the semiconductor nature of tin oxide. Because SnO_2 is an n-type semiconductor, it causes the species that are more easily adsorbed to be those that tend to attract electrons from the semiconductor, this implies that the surface of SnO_2 is mostly covered by species from oxygen and water [8].

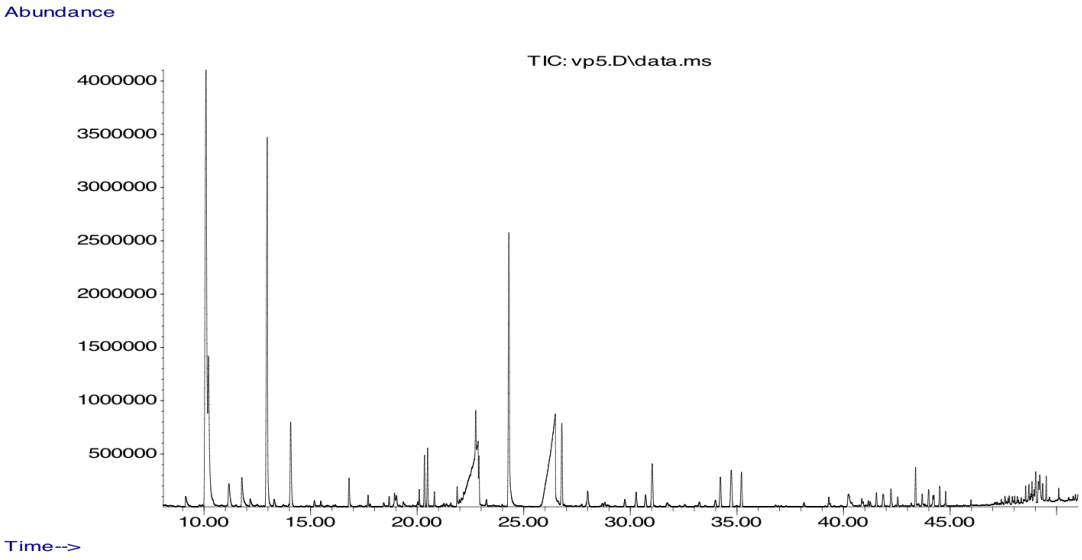


Figure 1. GC-MS chromatogram of a tinto wine (CR3).

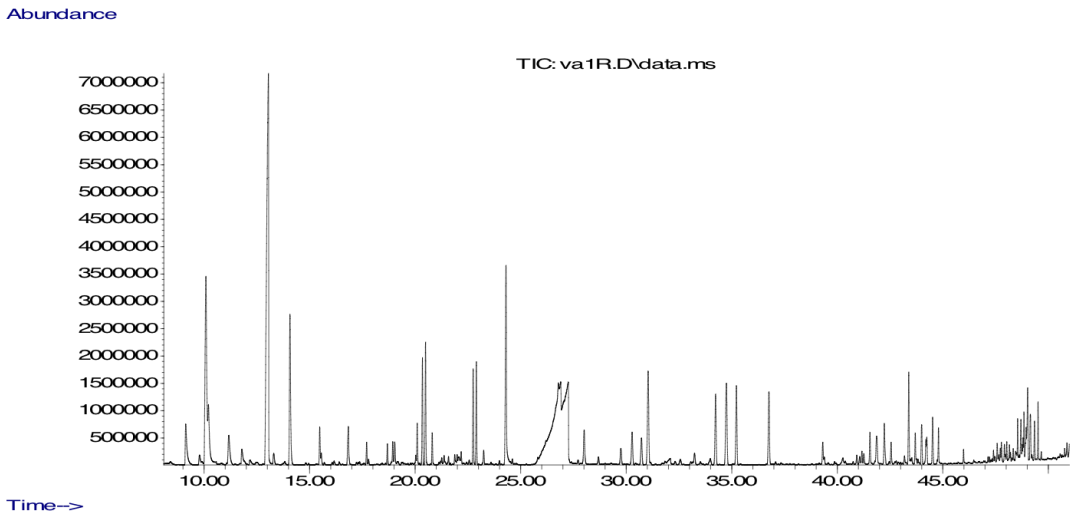


Figure 2. GC-MS chromatogram of a burgundy wine DB1.

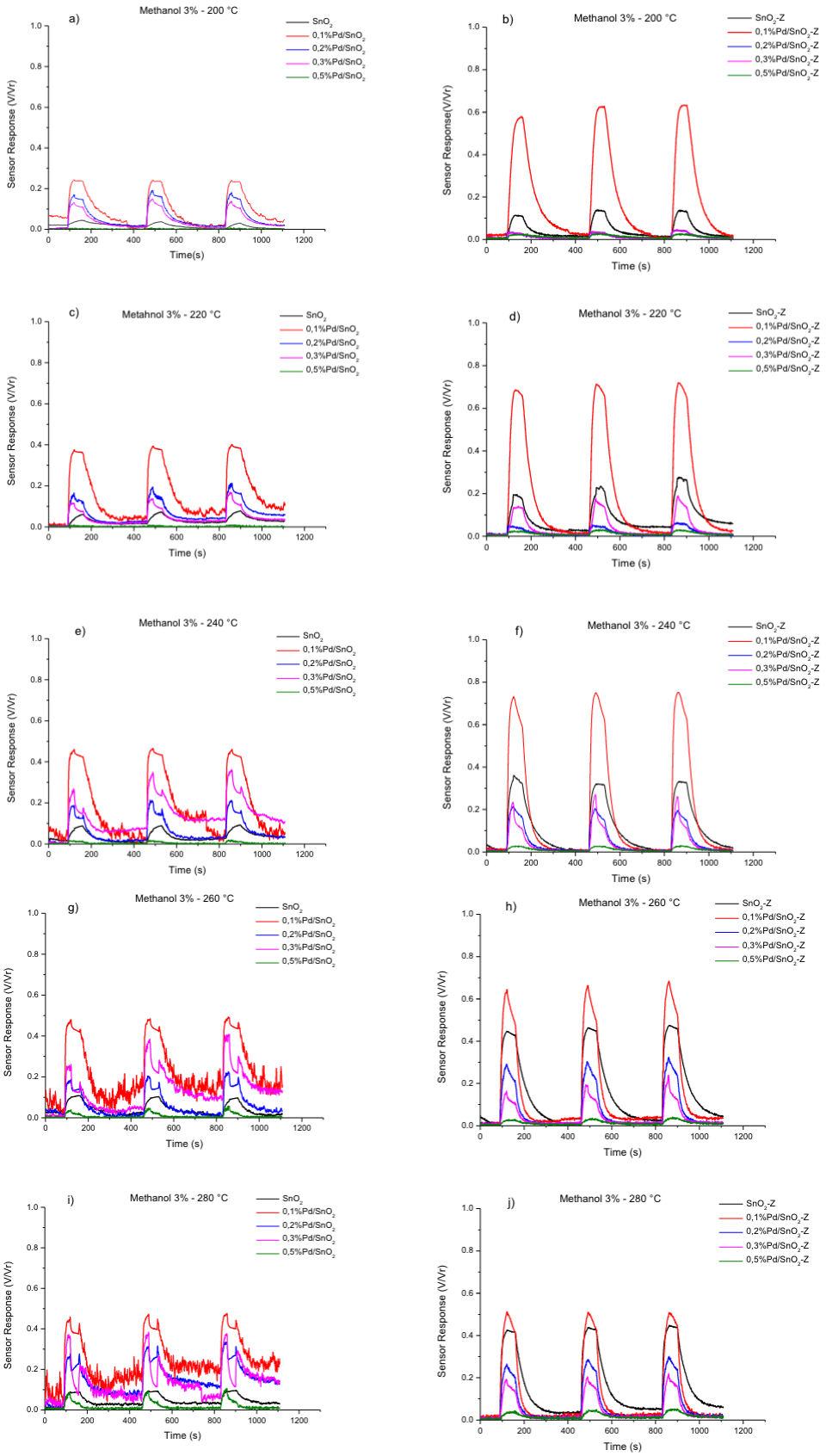


Figure 3. Response signal from Palladium-doped sensors. No zeolite coating (left side series). Zeolite coated (right side series). In the presence of 3% methanol and at different working temperatures.

Following the ionosorption model [9], in which it was assumed that the thermally stimulated processes of oxygen adsorption, dissociation and charge transfer involve only electrons from the conduction band (BC), it has that the adsorbed oxygen species they are transformed into the oxide surface according to the following general scheme:

$$O_{2(gas)} \rightleftarrows O_{2(ads)} \quad physisorption \quad Ec.1$$
$$O_{2(ads)} + e^{-}(BC) \rightleftarrows O^{-}_{2(ads)} \quad ionosorption \quad Ec.2$$
$$O^{-}_{2(ads)} + e^{-}(BC) \rightleftarrows 2O^{-}_{(ads)} \quad ionosorption \quad Ec.3$$
$$O^{-}_{(ads)} + e^{-}(BC) \rightleftarrows O^{2-}_{(ads)} \quad ionosorption \quad Ec.4$$
$$O^{2-}_{(ads)} \rightleftarrows O^{2-} \quad (1^{st}\ bulk\ layer) \quad Ec.5$$

With which it is explained that the surface of the semiconductor becomes richer in electrons. The oxygen ion induces electrical changes in the SnO_2 layers in the temperature range 500 to 800 K. The nature of the ionized oxygen species depends on the adsorption temperature. At low temperatures (150-200°C), oxygen is adsorbed on the surface of SnO_2 in molecular form (as charted ions of O_{2ads}^{-}).

At high temperatures (between 200 and above 400°C) it dissociates to atomic oxygen (charted ions of O_{ads}^{-} or O_{ads}^{2-}) [9]. The atomically charged oxygen ion (O_{ads}^{-}) is of particular importance in gas detection because it is the more reactive of the two possibilities and therefore more sensitive to the presence of organic vapors or reducing agents, producing a flow of electrons that increase the conductivity of the sensor [5, 8-9].

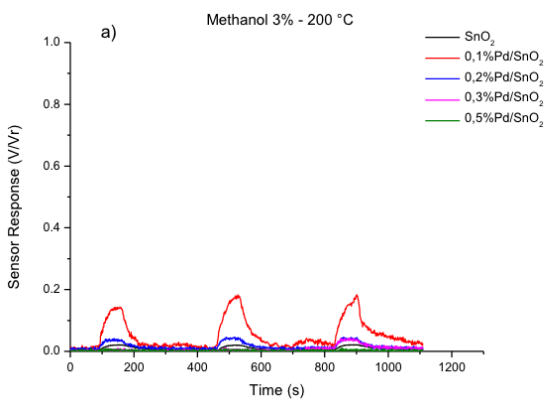
In Pd-doped sensors without zeolite coating, as the temperature increases from 240 °C to 280 °C the signal intensity decays, the signal becomes distorted and unstable. This also happens with the other sensors.

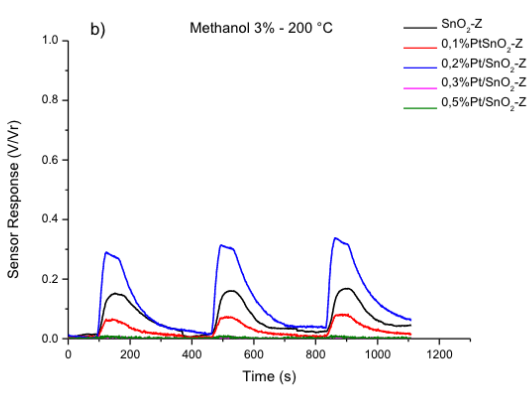
Additionally, it was observed that the tin oxide with the lowest doping ratio (0.1% Pd) showed the highest response with respect to the sensors with the highest degree of doping. This can occur because, at a lower degree of doping, the dispersion of the metal improves and the contact area of the metal is greater, promoting a better interaction with the volatile components analyzed.

As in the previous case, it was observed for NOSE 2 that as the sensing temperature increases from 200 ° C to 260 ° C, the intensity of the response signal of the sensors increases. This increase is higher for platinum-doped sensors coated with zeolite (Figure 4).

The increase in the electronic conductivity of tin oxide may also be due to the fact that when the water dissociates, the hydroxyl group binds to the tin atoms and the remaining hydrogen ions reduce the oxygen atoms, thus creating donor centers in the oxide tin.

The sensors that presented the sensing signals with the highest intensity were: 0.1%





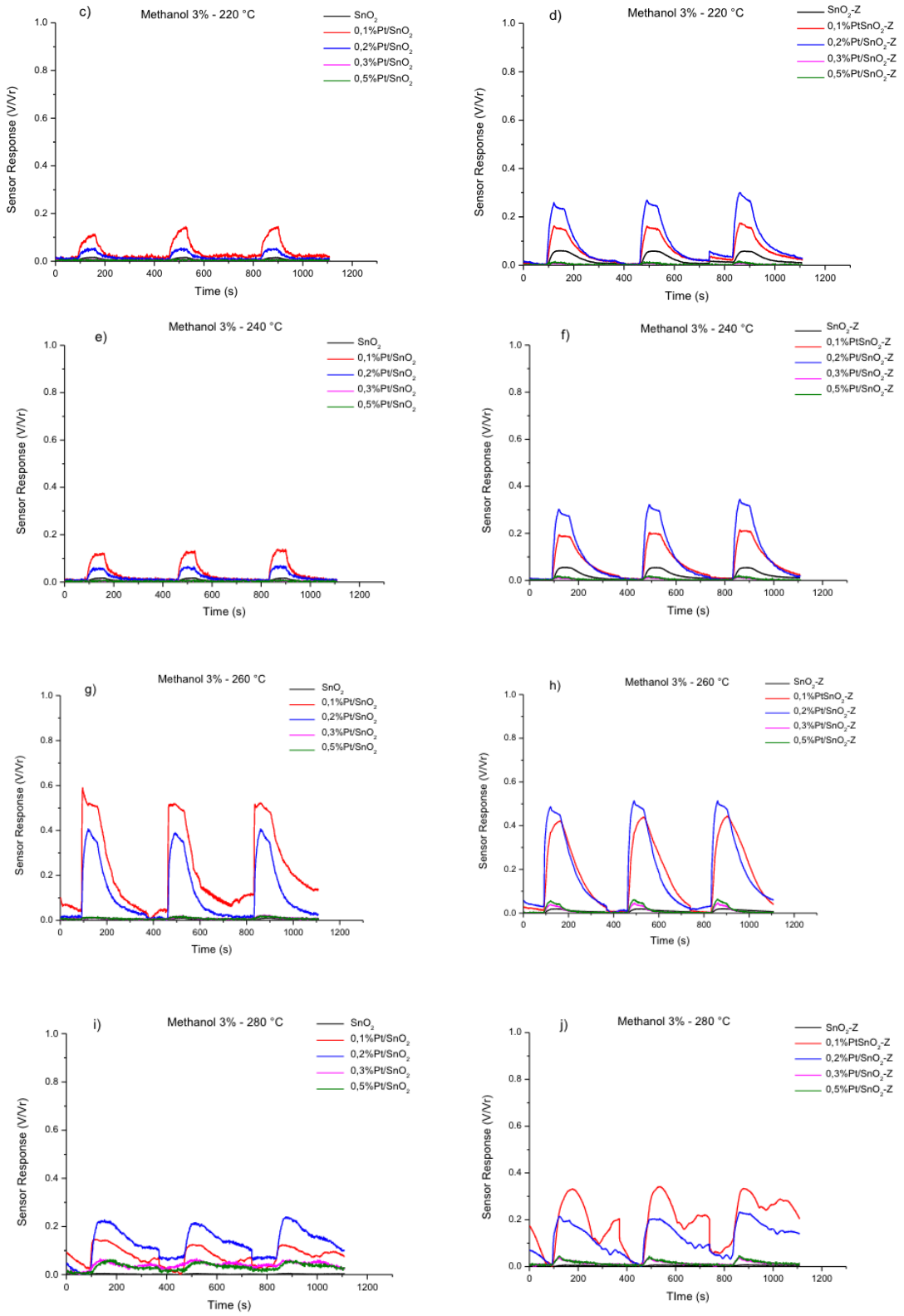


Figure 4. Response signal from Platinum-doped sensors coated with zeolite (right side series) and the same but without zeolite (left side series) using 3% methanol as model molecule at different working temperatures.

Pt / SnO_2; 0.1% Pt / SnO_2-Z and 0.2% Pt / SnO_2-Z.

Additionally, in all platinum-doped sensors it is observed that the response signal of the sensors was stable and reproducible at working temperatures of 200°C to 260°C, maintaining its intensity and shape during the analysis.

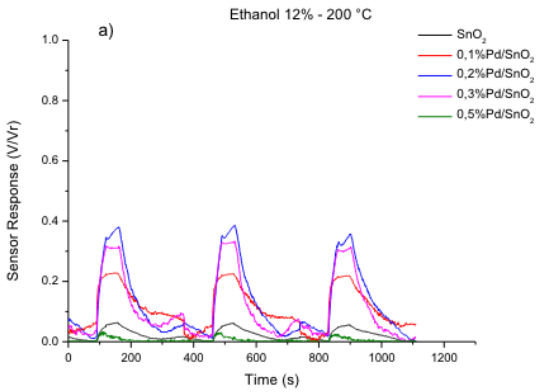
This behavior pattern is altered at a temperature of 280 ° C, where the sensing signal is distorted and becomes unstable, possibly due to a desorption of adsorbed oxygen (O-) on the sensor surface, causing a negative effect on the signal [8-9].

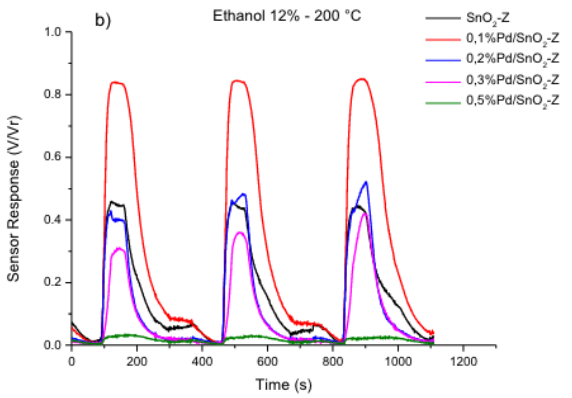
It may also be due to the fact that at temperatures from 250 ° C there is the loss of the physiosorbed water molecules on the surface of the tin oxide, this loss occurs in the form of desorption of the OH^- groups.

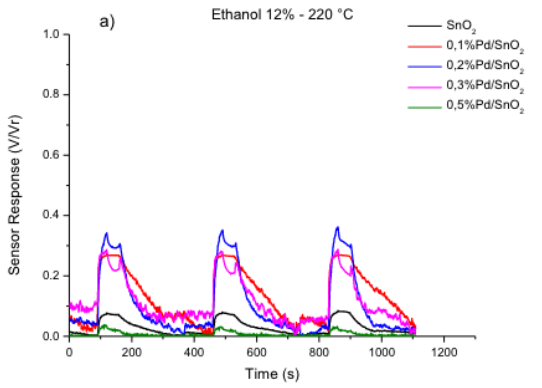
DETECTION OF THE SENSOR RESPONSE IN CONTACT WITH 12% ETHANOL SOLUTIONS AND AT DIFFERENT WORKING TEMPERATURES

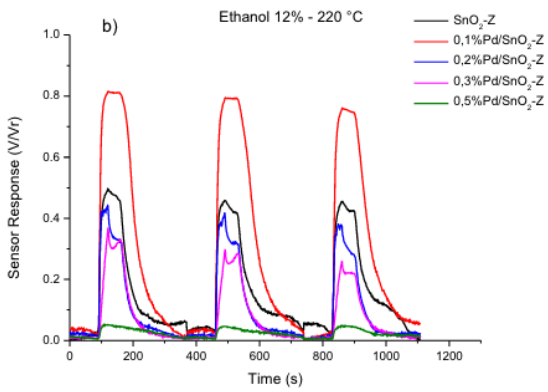
The Figure 5 shown response signal from palladium-doped sensors with and without zeolite coating in contact with 12% ethanol. It is observed that the sensitivity of the sensors is higher compared to those obtained with the same sensors but in contact with 3% methanol, which would indicate a greater selectivity of these sensors towards ethanol or the obvious, that when the ethanol is in a higher concentration, an increased signal is achieved.

As the sensing temperature increases from 200 ° C to 260 ° C, the sensitivity of sensors doped with Pd increases with respect to SnO_2 and this effect is higher in sensors coated with zeolite.









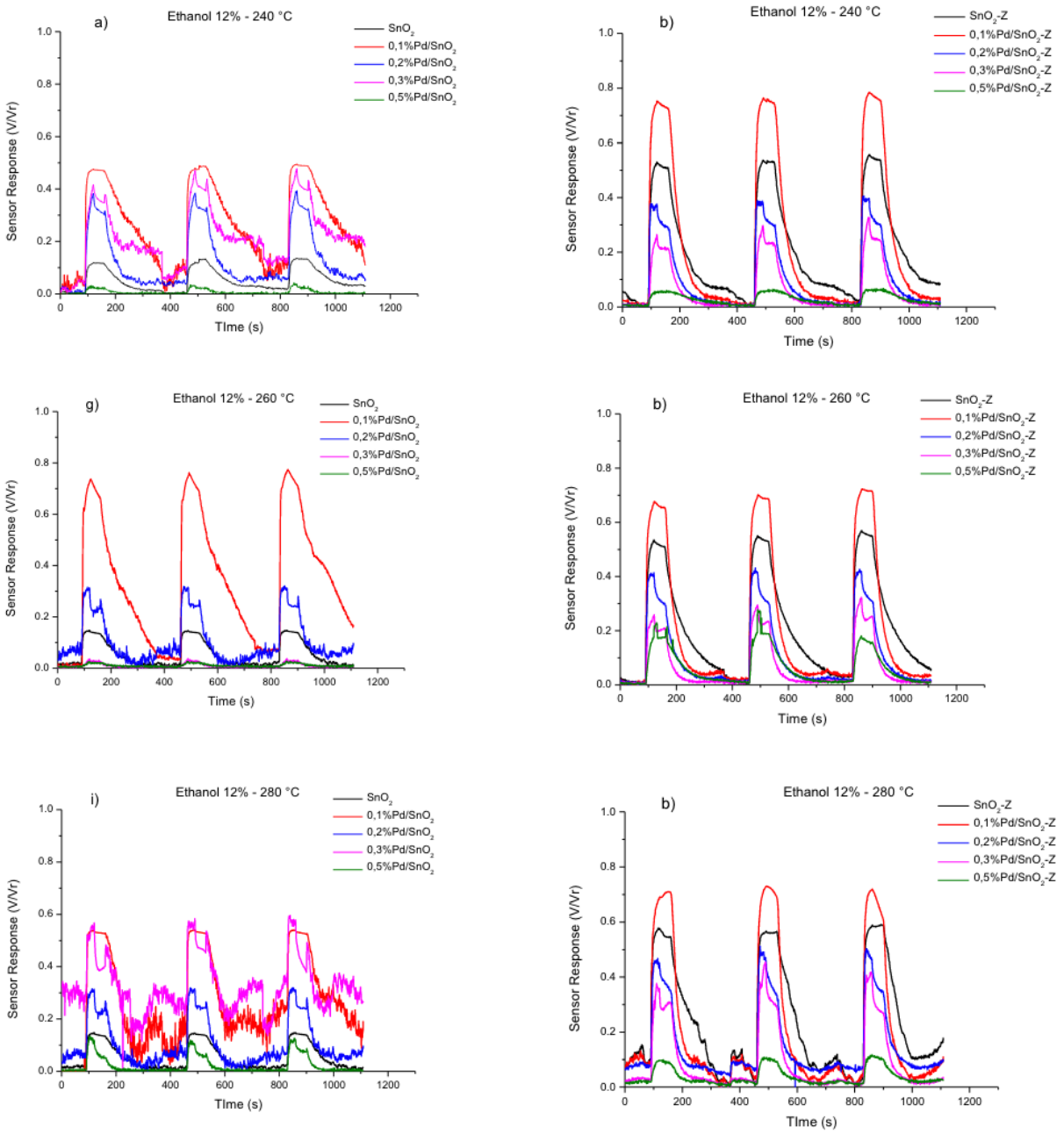


Figure 5. Response signal from Palladium -doped sensors coated with zeolite (right side series) and the same but without zeolite (left side series) using 12% ethanol as model molecule and at different working temperatures.

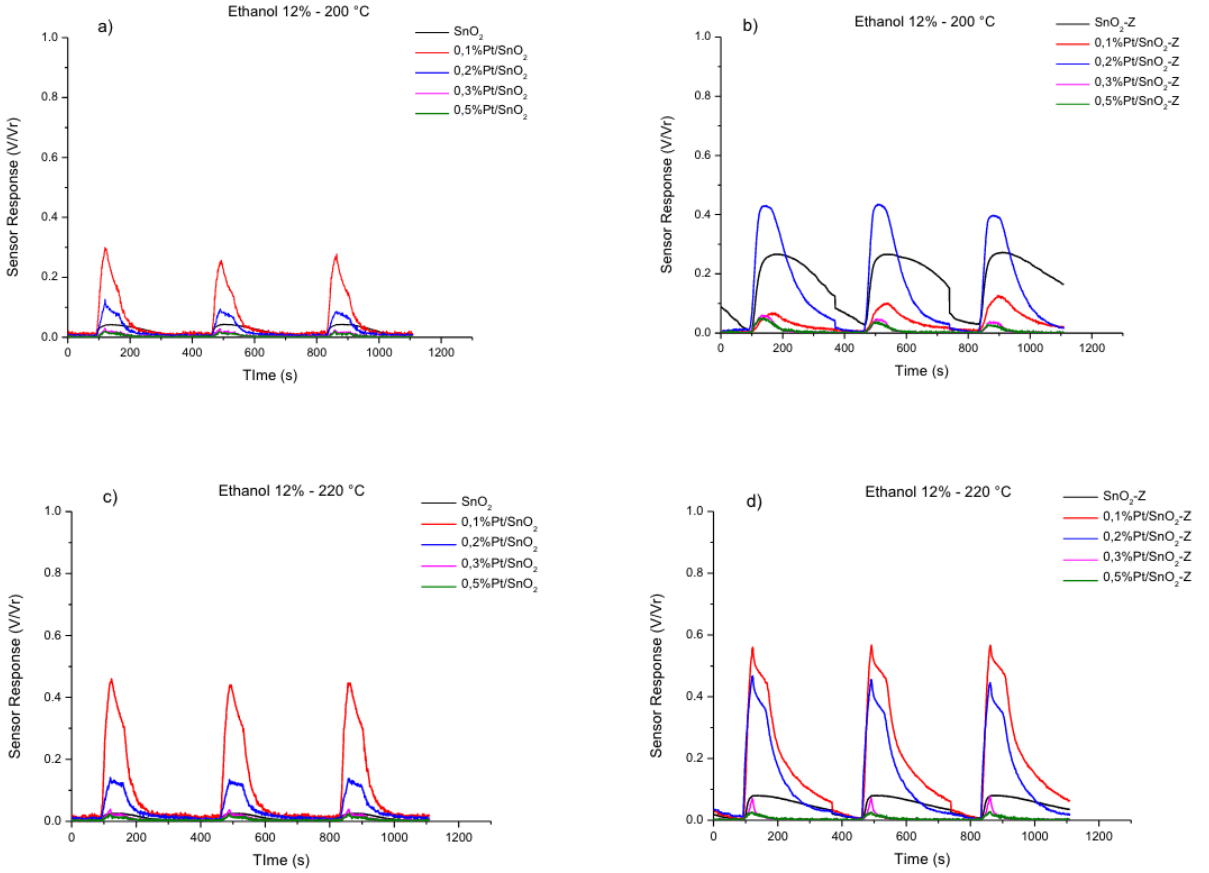
This is possibly due to the semiconducting nature of tin oxide and the doped with palladium, which, as its surface temperature increases, becomes richer in electrons due to the increase in the O^- adsorbed species. This adsorption occurs by the ionosorption mechanism, which reacts with reducing substances, in this case ethanol, producing a flow of electrons that increase the conductivity of the sensor [8-9].

For the sensors without zeolite coating, the highest value in sensitivity was obtained at 260 ° C and for the sensor 0.1% Pd/SnO_2–Z. The sensing signal is not very stable, and the distortion is greater than obtained at 280 ° C, where there is also a decrease in the intensity of the sensor response.

Considering the sensors with zeolite coating, the signal is more stable and reproducible, and the highest intensity is observed at 200 ° C and for the sensor 0.1% Pd/SnO_2–Z. As the working temperature is increased, the intensity of the signal drops a little. The value obtained was approximately similar to the temperature of 280 ° C, where some instability of the sensing signal was also observed.

It was also observed that by increasing the metal content (> 2% Pd) in the doping of tin oxides, the sensitivity of the signal was reduced, which could be due to the fact that is not achieved a good dispersion of the metal onto the oxide surface, affecting the sensitivity of the sensor in a negative way.

The Figure 6 shown response signal from the electronic nose made up of SnO_2 sensors doped with platinum with and without zeolite coating in contact with 12% ethanol.



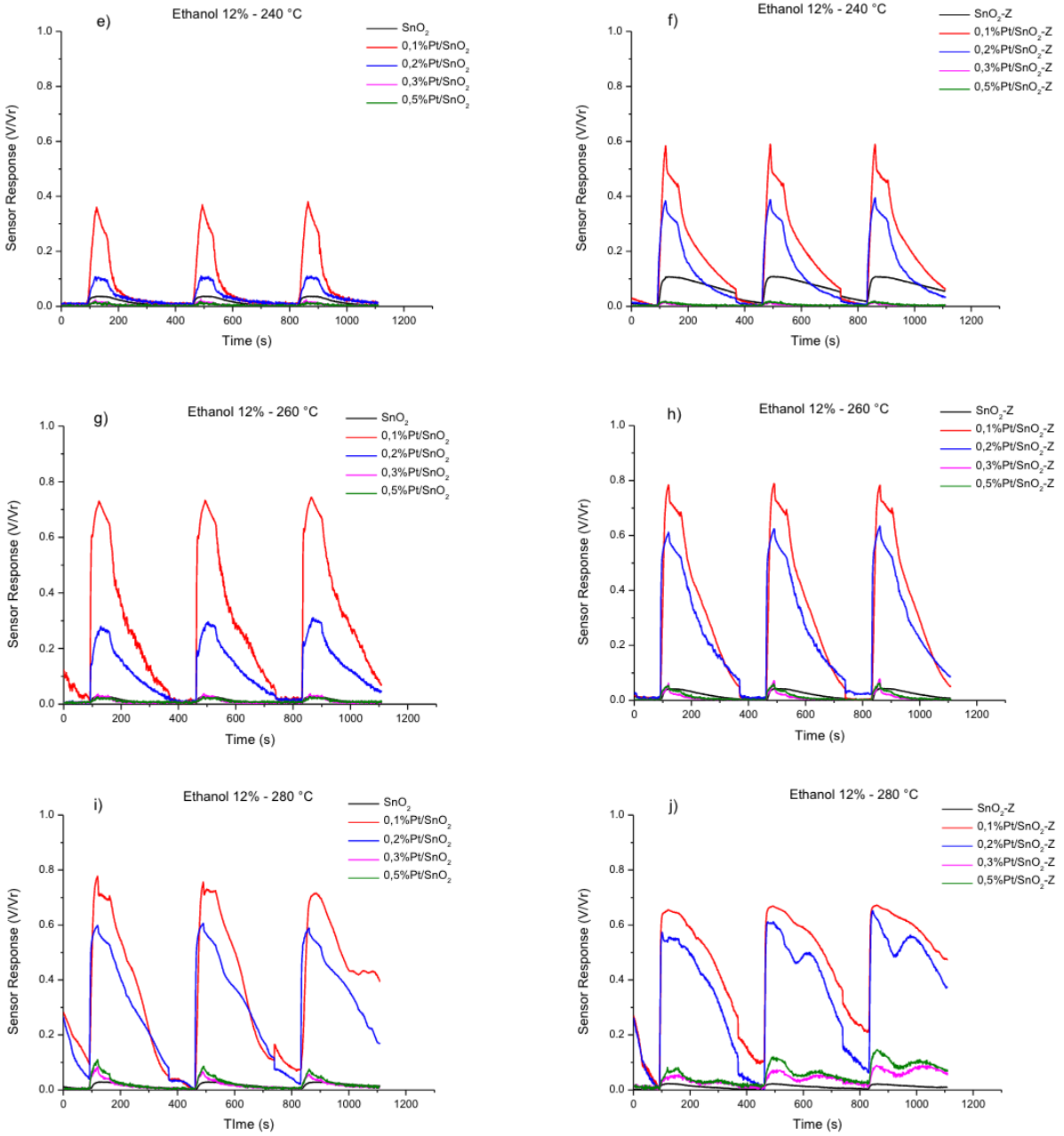


Figure 6. Response signal from Platinum-doped sensors. No zeolite coating (left side series). Zeolite coated (right side series). In the presence of 12% ethanol and at different working temperatures.

As is observed, the response signal in all platinum-doped sensors was stable and reproducible at working temperatures of 200 °C to 260 ° C, maintaining its intensity and shape during the analysis. However, the signal widens and distorts a little bit at 280 ° C.

The highest value for the sensors without zeolite in sensitivity was observed around 0.7 V/Vr at the temperature of 260°C and for the sensor 0.1% Pt/SnO_2. The signal strength is practically kept at 280°C for this sensor.

It should be noted that the sensing signal increases to 0.6 V/Vr for the sensor 0.2% Pt/SnO_2 at a temperature of 280°C, the reasons why this effect occurs in this sensor is unknown.

Considering the sensors with zeolite coating, the highest intensity in the signal was observed around 0.8 V/Vr the temperature of 260°C and for the sensor 0.1% Pt/SnO_2-Z. At the working temperature of 280°C the signal is distorted and drops to 0.6 V/Vr.

In the case of the 0.2% Pt/SnO_2-Z sensor, the intensity of the signal increases to 0.6 V/Vr at a temperature of 260°C, then the signal is slightly distorted at 280°C and its intensity decreases slightly.

CONCLUSIONS

In this work, it was studied the composition of wine aroma of some Peruvian wines with electronic noses. The noses were composed of an array of 10 sensors based on Pd and Pt doped-SnO2, the 50% of them coating with zeolites. The stability and reproducibility of the response signal of the sensors was analyzed at different working temperatures and in contact mainly with 3% methanol and 12% ethanol solutions (the two most important components of the Peruvian brands analyzed by GC). Sensitivity is higher in Pt-doped sensors compared to their Pd-doped counterparts, and this effect is higher in zeolite-coated sensors. By increasing the metal content (> 2% Pt or Pd) in the SnO_2 doping, the sensitivity of the signal was reduced.

The working temperature with which the highest intensity in the response signal is obtained was 260 ^{0}C, at this temperature the sensors with the best results were:

0.1% *Pd/SnO_2;* 0.1% *Pd/SnO_2–Z;* 0.2% *Pd/SnO_2–Z;* 0.1% *Pt/SnO_2;* 0.2% *Pt/SnO_2;* 0.2% *Pt/SnO_2–Z and* 0.2% *Pt/SnO_2–Z.*

In most of the cases studied, it was observed that the sensing signal was repetitive and stable, maintaining its amplitude and shape during the analysis. However, at the temperature of 280 ° C the sensor response signal loses intensity and becomes distorted, probably attributed to the loss of dispersion because of sintering of particles. Comparatively, the response signals of the zeolite-coated sensors presented a higher intensity and stability than those obtained with the same sensors without zeolite coating and the ones consisted in only tin oxide sensors.

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