Noise spectroscopy-based gas identifying methods to improve the selectivity of MOX gas sensors.

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***Abstract*—Air quality monitoring and analysis have become a major issue in recent years. Metal oxide gas sensors are very sensitive due to high variability of its resistivity in presence of gas. However, they are not selective. It is not possible to determinate the both gas nature and concentration using sensors resistance variation. Noise spectroscopy is one of solution to improve the selectivity. In this paper, we apply the recent developed noise spectroscopy-based gas identifying methods in order to show the possibility of each method to discriminate the nature of different gases. Noise measurements have been carried out on metal-oxide gas micro-sensors with tungsten trioxide (WO_3) sensing layer, under several NO_2, O_3 and CO concentrations in dry air. The obtained results have demonstrated that a selective sensing of the studied gases is possible using a single MOX gas micro-sensor.**

Keywords—noise spectroscopy, adsorption-desorption noise, selectivity, metal oxide gas sensors

I. INTRODUCTION

Nowadays, there is a growing need for low-cost, low-power miniaturized gas sensors mainly due to the connectivity of sensing devices on global network (internet of things) enabling immediate sharing of information in a variety of fields such as portable and connected devices for domestic and industrial air quality control, security and defence, food quality control … In this context, a great deal of research and development work is being carried out to design small and cheap gas sensors with high sensitivity, selectivity and stability, with respect to a given application. Metal oxide (MOX) gas sensors are readily available and widely used in portable and low cost gas monitoring devices because of their high sensitivity, stability, and attractive life time. However, this type of gas sensor suffers an inherent lack of selectivity, because the gas detection mechanism is rather unspecific and more or less any type of reducing or oxidizing gas is detected.

Due to this poor selectivity, MOX gas sensors are more often assembled into a multi sensor array that forms the core of an electronic nose. Electronic nose is a complex system used in the identification of gas mixtures. It consists of a multi sensor array, an information-processing unit, software with digital pattern-recognition algorithms and reference-library databases [1-2]. The sensor array is composed of different sensors chosen to respond to a wide range of chemical classes. The output of individual sensors are collectively assembled and integrated to generate a distinct digital response pattern. Identification and classification of an analyte mixture is accomplished through recognition of this unique chemical signature (electronic fingerprint) of collective sensor responses. The challenge in miniaturizing devices and lowering power consumption is to minimize the number of sensors required for a given application. To do this, we must try to increase the amount of information provided by one sensor using advanced measurements, like temperature modulation or fluctuation enhanced sensing (FES). [3,4].

The FES principle uses the fluctuations of the gas sensors' response as an information source. This experimental technique is based on noise spectroscopy: the measurement and the analysis of the power spectral density (PSD) of the fluctuations measured at the terminals of sensors in the presence of one or more gases. Measuring these fluctuations caused by adsorption–desorption and diffusion noise provides enhanced selectivity and sensitivity. Several studies have shown that noise spectroscopy is a relevant signal-processing tool able to extract selective informations on multiple gases with a single sensor [4-6].

II. GASES IDENTIFICATION METHODS

In MOX gas micro sensors, noise depends strongly on the oxygen stoichiometry and oxygen motion. The adsorption-desorption process of oxygen atoms, the presence of defects and grain boundaries in metal-oxide cause fluctuations of the oxygen density and, thus fluctuations of the sensing layer electrical conductance. In a gaseous environment, the sensing layer conductance fluctuations due to free carrier's number and mobility fluctuation are related to concentration and distribution fluctuations of adsorbed chemical species.

A. Noise current spectral decomposition

In earlier work [7], we presented a model of adsorption–desorption (A-D) noise in MOX gas sensors, developing the idea that the fluctuation of the gas sensor resistance is, among others noise sources, due to the fluctuation of the density of gas molecules on the surface of the sensing film. The modeling was developed by taking into account the polycrystalline structure of the sensing layer and the effect of the adsorbed molecule's density fluctuation on the grain boundary barrier height.

If the gas sensor resistance R_{sensor} is biased by a voltage V_0 and the measured noise is a current fluctuation, the PSD of the fluctuations of the total terminal current across the gas sensor resistance writes [7]:

$$S_{\delta I_{sensor}}(f) = \frac{V_0^2}{R_{sensor}^4} \sum_{i=1}^{g} S_i \frac{1}{1+\left(\frac{f}{f_{ci}}\right)^2} + \frac{4kT}{R_{sensor}} \quad (1)$$

The first term in (1) is a sum of lorentzians having a cut-off frequency f_{ci} and a low frequency magnitude S_i. Their expressions are given in [7], and they depend on the nature of the detected gas, and on the grain size. g is the number of most prevalent grain sizes involved in the sensing layer, T is the temperature and k is the Boltzman constant.

B. *First derivative of noise current spectral density*

In our recent work [8], we calculated the theoretical expression of the first derivative of the PSD of the gas sensor noise, and showed that it admitted a minimum which depends on the nature of the detected gas.

Using "(1)", the expression of the first derivative of the PSD of the gas sensor noise can be written as follows:

$$\frac{dS_{\delta I_{sensor}}(f)}{df} = -2\frac{V_0^2}{R_{sensor}^4} \sum_{i=1}^{g} \frac{S_i}{f_{ci}^2} \frac{f}{\left[1+\frac{f^2}{f_{ci}^2}\right]^2} \quad (2)$$

First derivative of each single Lorentzian has a minimum at the frequency $f_{ci}/\sqrt{3}$ that depends on the nature of the detected gas. We have demonstrated that the complete expression of the first derivative of the PSD of the gas sensor noise had a minimum at a frequency between $f_{c1}/\sqrt{3}$ and $f_{cg}/\sqrt{3}$ [8].

C. *Product of the noise current spectal density by the frequency*

Another gas identification method is based on the product $f \cdot \left(S_{\delta I_{sensor}}(f) - S_{Th}(f)\right)$ where f is the frequency, $S_{\delta I_{sensor}}(f)$ is the PSD of gas sensor noise current as (1) and $S_{th}(f) = \frac{4kT}{R_{sensor}}$. This product writes as follows:

$$f \cdot \left(S_{\delta I_{sensor}}(f) - S_{Th}(f)\right) = I_0^2 \sum_{i=1}^{g} S_i \frac{f}{1+\left(\frac{f}{f_{ci}}\right)^2} \quad (3)$$

with $$I_0^2 = \frac{V_0^2}{R_{sensor}^4} \quad (4)$$

The product of frequency by the PSD of the gas sensing layer resistance fluctuations often has a maximum which is characteristic of the gas and, that is the combination of maxima of each term [9].

III. Experimental

The experimental protocol used in the present work is the same one used in our recent paper [9]. Indeed, the noise measurements have been performed on WO_3 based gas sensors. For more details concerning the experimental setup (see figure 1) and the preparation of the WO_3 based sensing layer, one can see the descriptions given in [9].

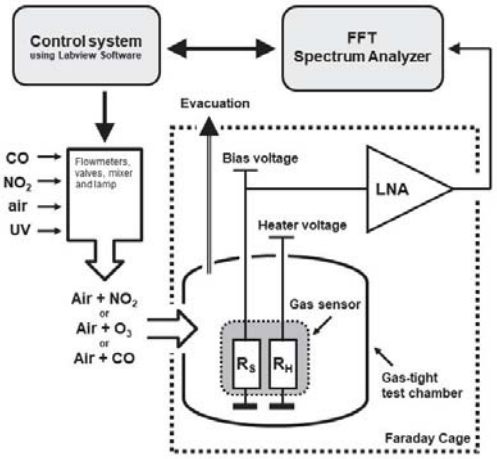

Fig. 1. General diagram of measurements setup used to characterize microsensors noise responses

The gas microsensor was exposed to 4 concentrations of three different gases characteristic of the air quality (see Table I), diluted in dry air. These are ozone and nitrogen dioxide, which are oxidizing gases, and carbon monoxide, which is a reducing gas.

TABLE I. VARIOUS GASES CONCENTRATION USED IN EXPERIMENTAL SET UP

Gases	Concentrations			
	C1	C2	C3	C4
NO_2	1ppm	2ppm	5ppm	10ppm
O_3	80ppb	110ppb	160ppb	240ppb
CO	5 ppm	10 ppm	20ppm	40 ppm

IV. Results

The developed gas identification methods are based on precise spectral decomposition of measured noise responses. To extract useful information from the measured noise across the sensor in the presence of gas, we take into account the characteristics of low noise amplifier by:

$$S_{I\,sensor} = \frac{S_{V\,measured}}{\left(A_{LNA}(f)\right)^2} \quad (6)$$

where $S_{I\,sensor}$ is the intrinsic current spectral density of sensor, and $S_{V\,measured}$ is the measured noise voltage spectral density. $A_{LNA}(f)$ is the measured frequency response of the gain of the SR570 low noise current amplifier. Fig. 2 gives an example of current spectral density of the sensor under 10ppm of CO (curve1). All measured spectra clearly show Lorentzian components according to adsorption-desorption noise theory. Indeed, the noise generated due to the adsorption of a gas on an adsorption site with a given adsorption energy has a Lorentzian spectrum. For the three studied gases, we observe that two Lorentzians dominate the low frequency spectrum. Over 1 kHz we observe white noise mainly composed of the thermal noise due to sensitive layer resistance and the thermal noise of the amplifier due to the

feedback resistor. Details of spectral decomposition are also plotted in Fig.2. Measured noise spectra is higher by one or more orders of magnitude compared to amplifier noise level (curve 6). The extracted noise parameters of spectral decomposition of all measured spectra are reported in Tab. 2. For all studied gas concentrations, the thermal noise is below 10^{-26} A^2/Hz indicating a resistance of the sensitive layer varying around 1MΩ. The evolution of thermal noise is consistent with the evolution of the resistance of the sensitive layer in the presence of each of the three studied gases.

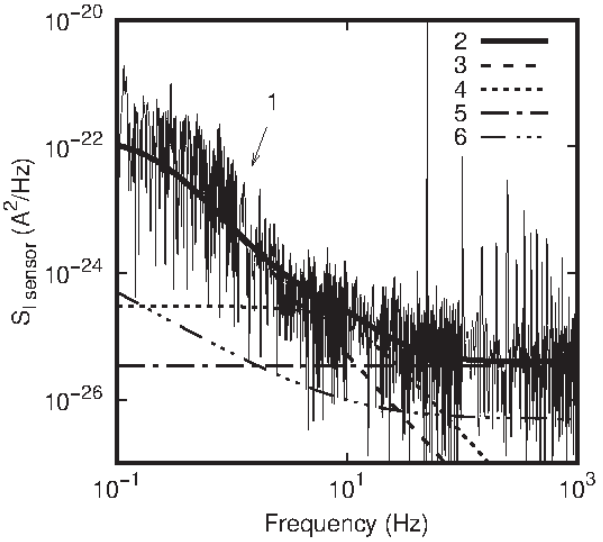

Fig. 2. Spectral decomposition of a noise response under CO (10 ppm): measurements (curve 1), total noise (curve 2), adsorption-desorption noise modeled by two lorentzians (curve 3 and 4), white noise proportional to the resistance of the sensor (curve 5); extracted noise model of low-noise current preamplifier (curve 6).

TABLE II. VALUES OF THE LORENTZIANS CUT-OFF FREQUENCY F_{C1} AND LOW FREQUENCY MAGNITUDE S_i FOR THE VARIOUS GASES CONCENTRATION USED IN THE MEASUREMENT PROCESS.

Gas / Concentration	S_1 (A^2/Hz)	f_{C1} (Hz)	S_2 (A^2/Hz)	f_{C2} (Hz)	S_{Th} (A^2/Hz)
O_3 / C1	7 10^{-21}	0,1	1 10^{-25}	5	3 10^{-26}
O_3 / C2	8 10^{-21}	0,1	1 10^{-25}	5	2,5 10^{-26}
O_3 / C3	1 10^{-20}	0,1	4 10^{-25}	5	2 10^{-26}
O_3 / C4	1,2 10^{-20}	0,1	5 10^{-25}	5	1,5 10^{-26}
NO_2 / C1	3 10^{-23}	0,2	7 10^{-25}	5	5 10^{-26}
NO_2 / C2	2 10^{-23}	0,2	9 10^{-25}	5	4,5 10^{-26}
NO_2 / C3	1,5 10^{-23}	0,2	7 10^{-25}	5	4 10^{-26}
NO_2 / C4	1 10^{-23}	0,2	7 10^{-25}	5	3,5 10^{-26}
CO / C1	1,2 10^{-22}	0,2	7 10^{-25}	10	2,5 10^{-26}
CO / C2	1,3 10^{-22}	0,2	3 10^{-25}	10	2,8 10^{-26}
CO / C3	1,5 10^{-22}	0,2	3 10^{-25}	10	3 10^{-26}
CO / C4	2 10^{-22}	0,2	3 10^{-25}	10	3,2 10^{-26}

The first derivative of noise current spectral density of the measured gas sensor noise is calculated using (2) and extracted parameters of TABLE II. In Fig.3 we present the plots of the first derivative of the PSD of the gas sensor noise response under four concentrations of nitrogen dioxide. We obtain similar curves for ozone and carbon monoxide. For the three gases, we clearly observe that the first derivative of the measured gas sensor noise spectrum presents a negative minimum according to the developed theory in [8]. These negative minimums are reported in TABLE III and have specific value ranges for each gas.

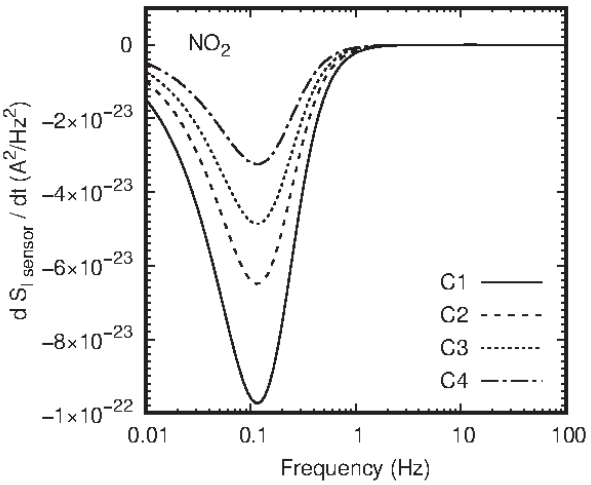

Fig. 3. Plots of the first derivtive of noise current spectral density of the four concentrations of nitrogen dioxide.

TABLE III. MINIMUM OF THE FIRST DERAVATIVE OF THE PSD OF THE GAS SENSOR NOISE (A^2/Hz^2)

Gas	Concentration			
	C1	C2	C3	C4
O_3	-4 10^{-20}	-5,2 10^{-20}	-6,2 10^{-20}	-7,8 10^{-20}
NO_2	-9,8 10^{-23}	-6,5 10^{-23}	-5 10^{-23}	-3,2 10^{-23}
CO	-3,9 10^{-22}	-4,2 10^{-22}	-4,9 10^{-22}	-6,5 10^{-22}

In Fig. 4, we plot the product $f \cdot \left(S_{\delta I_{sensor}}(f) - S_{Th}(f)\right)$ in the case of ozone, nitrogen dioxide and carbon monoxide using the extracted parameters in TABLE II. Over 100 Hz, we observe a 1/f slope as predicted by (3) for all concentrations of studied gases. On the other hand, at low frequencies, the behavior is different for each gas. For NO_2, the curves of the product of noise current spectral density by the frequency show two maximums of approximately equal values while the maximum at lower frequency is higher for CO_2. The curves for ozone have a particular behavior because of the higher sensitivity of tungsten trioxide to this gas. This high sensitivity to ozone is characterized by a higher low frequency noise level compared to other gases. The values in TABLE II show that the first Lorentzian for ozone is predominant due to a desorption-adsorption process on a preferred adsorption site.

So, the quantity $f \cdot \left(S_{\delta I_{sensor}}(f) - S_{Th}(f)\right)$, has a maximum which is characteristic of the nature of the detected gas. Detecting this maximum is a sensitive method to identify a gas. This result confirms that the choice of this parameter seems interesting for the identification of the detected gas compared to other parameters such as the average slope of the

product $f \cdot S_{\delta I_{sensor}}(f)$ [10] or the characteristic frequency of the maximum of this same product [11].

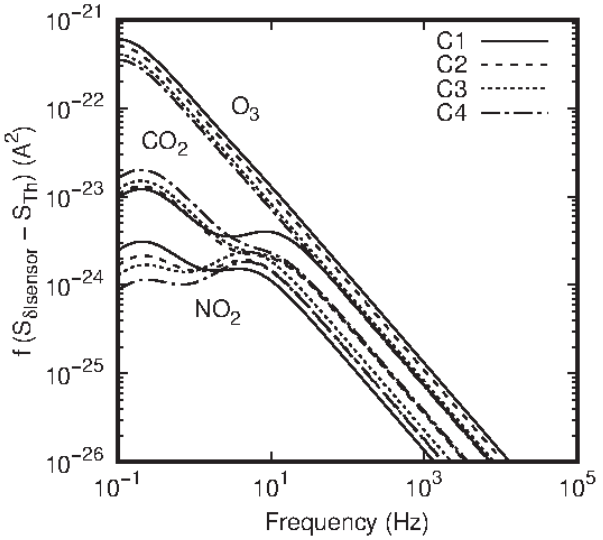

Fig. 4. Plots of the quantity $f \cdot \left(S_{\delta I_{sensor}}(f) - S_{Th}(f)\right)$ for four concentrations of ozone (O_3), nitrogen dioxide (NO_2) and carbon monoxide (CO) detected by metal-oxide gas microsensor with tungsten trioxide (WO_3) sensing layer.

The ability to discriminate several gases using our different noise spectroscopy-based gas identifying methods has been evaluated by the principal component analysis (PCA). PCA is a commonly used unsupervised and robust pattern recognition approach for analysis of multivariable data. It is a statistical procedure that enables to convert a set of observations of possibly correlated variables into a new set of values called principal components. In PCA, the score plots show the relations between these analyzed variables (different concentrations of the three gases in our studies). PCA has been performed using the extracted spectral parameters of the spectral decomposition method (TABLE II), the first derivative method's (TABLE III) and the method of the product of the frequency by the noise current spectral density (maximum of the product). The scores plot of the first two principal components is given in Fig. 5 and shows that a clear discrimination is possible between the three studied gases.

V. Conclusion

In this paper, we have presented the recent developed gases identification methods based on noise spectroscopy. These methods are based on precise spectral decomposition of measured noise responses of micro sensor under gases. For each method, we observe possibilities to discriminate the nature of detected gas. In particular, the minimum of the first derivative of noise current spectral density is different for each studied gases. Similarly, we have observed that the maximum of the product of noise current spectral density by the frequency is characteristic of the nature of the detected gas. Finally, the PCA multivariable analysis method has been applied to all extracted spectral data. So, we have shown that it is possible to identify the nature of detected gas using noise spectroscopy-based methods.

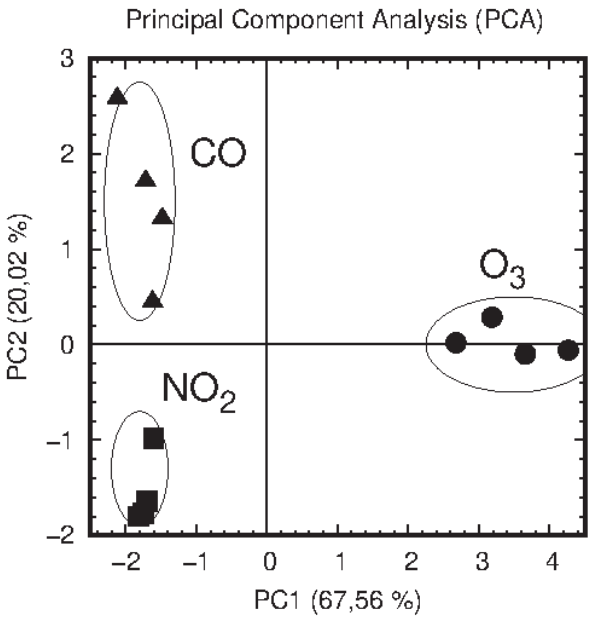

Fig. 5. PCA scores plot of the quantity $f \cdot \left(S_{\delta I_{sensor}}(f) - S_{Th}(f)\right)$ for four concentrations of ozone (O_3), nitrogen dioxide (NO_2) and carbon monoxide (CO) detected by metal-oxide gas microsensor with tungsten trioxide (WO_3) sensing layer.

References

[1] J. Gutiérrez, M.C.Horrillo, “Advances in artificial olfaction: sensors and applications,” *Talanta 124*, pp. 95–105, 2014

[2] L. Capelli , S. Sironi, R. Del Rosso, “Electronic Noses for Environmental Monitoring Applications”, Sensors 2014, 14, 19979-20007; doi:10.3390/s141119979

[3] J. Yan et al., « Electronic Nose Feature Extraction Methods: A Review », Sensors, vol. 15, nº 11, p. 27804-27831, nov. 2015.

[4] J. M. Smulko et al., « New approaches for improving selectivity and sensitivity of resistive gas sensors: a review », Sensor Review, vol. 35, nº 4, p. 340-347, sept. 2015.

[5] L. B. Kish, R. Vajtai, and C.-G. Granqvist, “Extracting information from noise spectra of chemical sensors: Single sensor electronic noses and tongues”, *Sens. Actuators B*, Vol. 71, pp. 55–59, 2000.

[6] J. Solis, L. Kish, R. Vajtai, C. Granqvist, J. Olsson, J. Schnürer, and V. Lantto, “Identifying natural and artificial odours through noise analysis with a sampling-and-hold electronic nose,” *Sensors and Actuators B: Chemical*, Vol. 77, no. 1, pp. 312–315, 2001.

[7] S. Gomri, T. Contaret, J. Seguin, K. Aguir, M. Masmoudi, “Noise Modeling in MOX Gas Sensors”, *Fluctuation and Noise Letters, Vol*. 16, No. 2 (2017) 1750013.

[8] S. Gomri, T. Contaret, J. L. Seguin. "A New Gases Identifying Method with MOX Gas Sensors using Noise Spectroscopy", *IEEE Sensors Journal, Vol.18, No.16, (2018) DOI: 10.1109/JSEN.2018.2850817.*

[9] S. Gomri, J.L. Seguin, T. Contaret, T. Fiorido, K. Aguir, “A Noise Spectroscopy based Selective Gas Sensing with MOX Gas Sensors”, *Fluc. and Noise Lett.,* Vol.17, No.2, (2018).

[10] B. Ayhan, C. Kwan, J. Zhou, L.B. Kish, K.D. Benstein, P.H. Rogers, S. Semancik, *Fluctuation enhanced sensing (FES) with a nanostructured, semiconducting metal oxide film for gas detection and classification*, Sensors and Actuators B 188 (2013) 651-660.

[11] S. Rumyantsev, G. Liu, R. A. Potyrailo, A. Balandin, and Michael S. Shur, *Selective Sensing of Individual Gases Using Graphene Devices*, IEEE Sensors J. vol 13, NO. 8 (2013) 2818-2822.