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The Electronic Nose: Review on Sensor Arrays and Future Perspectives

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Over the last 40 years, the term "electronic nose" (EN) has defined a device equipped with an array of not selective gas sensors capable of providing a response as a function of a stimulus provided by volatile chemical compounds (VOCs). Numerous studies have started from this idea, which have led to significant improvements and advantages, especially useful for providing a device capable of monitoring situations and applications in real-time. Applications that have strongly pushed the evolution of the "electronic nose" technology away from the laboratories and closer to more complex and stimulating real situations (Comini and Sberveglieri, 2010). One of the very initial goals of the EN was to simulate the mammalian nose to obtain a fast response regarding the characteristics of the analyte, high sensitivity for odours and high discrimination between them. In the last few years, a lot of upgrades have been made to the EN technology, thanks to artificial intelligence, machine learning evolutions, stability of the sensing elements, cloud processing, predictive algorithms, etc. Thanks to this strong commitment of all, this technology is reopening great interest in the industrial and consumers application field, managing to arrive directly in the transformation chains. The types of gas sensors used are various and are based on the modification of a physical or chemical parameter caused by the gases themselves. Conductometer sensors are the most common, being able to transduce a chemical signal in an electrical resistance signal. Other types of sensors have been developed and can be part of a functional array: Optical sensor, polymer sensor, electrochemical gas sensor, Quartz microbalances or SAW (Paolesse et al., 2017). In this presentation we will review the different sensor arrays most commonly used and a brief history of their evolution. From the point of view of sensor preparation technology, the one based on MEMS is becoming more and more widespread. A brief mention will also be made of the sensors used in the EN standard (called S3+) made by Nano Sensor Systems S.r.l. spin-off of the University of Brescia. We will conclude by presenting the evolution of sensors in recent years to better understand how the multisensory, multidisciplinary and cloud computing approach has positively influenced the real potential of Electronic Noses.

1. Introduction

The concept of "electronic nose" was created for the first time in 1982 by Persaud and Dood (Persaud and Dood, 1982).They defined E-nose (EN) as an innovative tool equipped with an array of chemical a-specific sensors and appropriate pattern recognition system, capable of recognizing simple, or complex odors. The arrays, responsible for the final response, may be formed of different types of sensors. The most used are the semiconductor metal oxide sensors (MOS), which have been used with remarkable success in different fields such as food safety, quality control, environmental monitoring and human health. For instance, one of the possible applications of E-nose (Cipriano, 2018) has been the pathogen detection (Gobbi et al, 2010). Following this lead, the concept has undergone lots of upgrades. The major upgrades were in the structures and topology of gas sensors and in the analysis of sensor array data. In recent years, there has been an imposing evolution of data analysis techniques using artificial intelligence in a massive way as an example machine learning with very innovative algorithms also taken from other completely different sectors such as the financial sector. These are in terms of system monitoring allowing to extend it both in technical terms, with the use of more suitable,

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sustainable and ensuring new possibilities like the use of data-driven modeling to perform rapid early detection of defect in production chain, leading the monitoring in a decision support system (Sanaeifar et al, 2017). As it was explained from Boonah et al (2020), it has been successful and superior to conventional methods. Another important application of EN is the use in AMSs (Automatic Measurement Systems), to monitor the emissions of contaminants into the air (Cipriano, 2018). As a matter of fact, E-nose offers a method that is non-invasive, fast and requires little or no sample preparation, thus making it a user friendly tool. Improvements about machine learning technologies have also been performed. These have been a crucial part of all these research which led to the expansion of the production of EN in the world (Figure 1) and, as a consequence, to rapid extension related research topics with different applications (Karakaya, 2020).

Model	No. of sensors	Technology	Manufacturer	Country
NE S3+	**6**	**MOS Sensor**	**Nano Sensor System srl**	**Italy**
zNose	1	GC and solid state detector	Electronic Sensor Technology	USA
Electronic Nose	4	Conducting polymers	Electronic Nose Co. LTD	Thailand
FOODsniffer	1	MOS Sensor	ARS LAB US	USA
MK4	12	Solid state oxide sensor	E-Nose Pty Ltd	Australia
HERACLES Neo	2	Fast GC	Alpha MOS	France
307B Benchtop VOC Analyser	6 & 24	Organic semiconductor sensor	RoboScientific	UK
NeOse Advance	1	Inferometers and silicon photonics platform	Aryballe	France
MultiNose	1	GC and FID	Odotech	Canada
Variety of gas sensors and sensor modules		MOS, Catalytic, Electrochemical NDIR Sensors	FIGARO Engineering Inc.	Japan
Aeonose	3	MOS Sensor	The eNose Company	Netherlands

Figure 1 E-noses around the world from 2015 until 2021

2. Typologies of sensors in ENs

As previously mentioned, different types of chemical sensors have been selected for their sensitivity, stability and the ability to respond to complex gas spectra as usually are in the ENs (Figure 2). Another fundamental parameter for sensor analysis is the reproducibility. As a matter of fact, once the database is formed and in the case of a malfunctioning of one sensor, the substitution must be safe and sure. Otherwise, the dataset might be collected again.

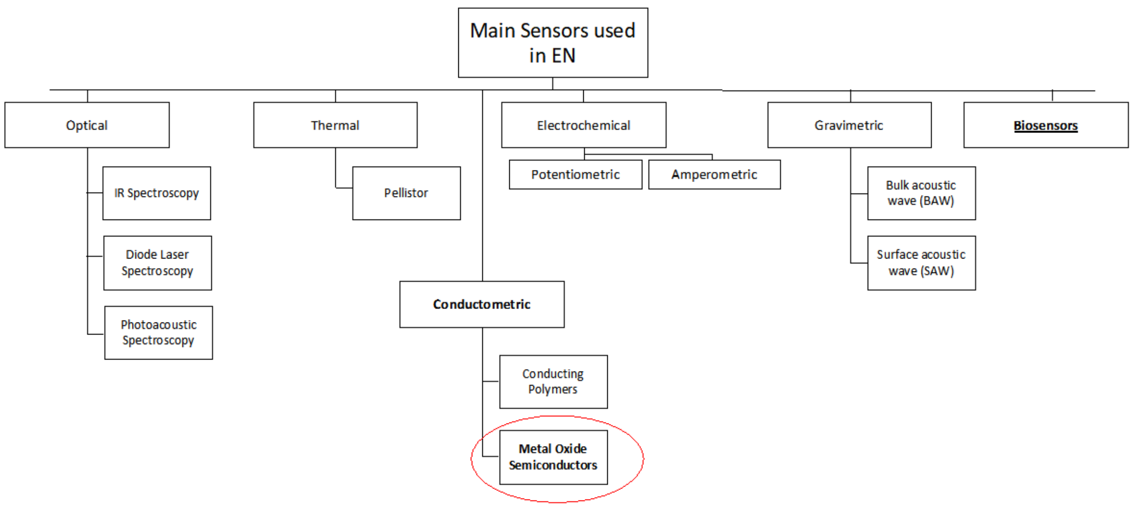


Figure 2 Main sensors used in Electronic Noses

Some of them, which can be part of sensor arrays, are consequently described:

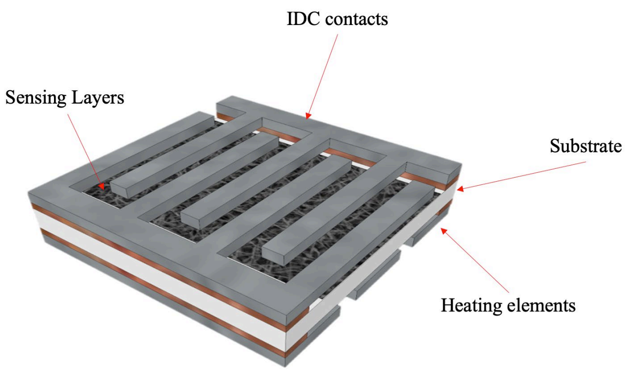
Optical sensors: Optical sensors are a type of chemical sensor in which electromagnetic radiation is transduced in an analytical signal. These sensors can be based on various optical principles (absorbance, reflectance, luminescence, fluorescence), covering different regions of the spectra (UV, visible, IR, NIR) (Wolfbeis, 1991).

One of the applications of optical sensor arrays in Electronic Noses is the selective detection of gases, such as the determination of oxygen or carbon dioxide.

SAW and Quartz microbalance sensors: These are mass sensors where the parameters can change regarding the analyte. As a matter of fact, it is possible to assist to frequencies and phases variations. These sensors are usually resonant structures made up of piezoelectric crystals or micro-cantilevers. Piezoelectric materials are used; as transducers and these range from quartz microbalances to surface acoustic wave devices.

Electrochemical sensors: Electrochemical sensors can be applied for the detection of gaseous analytes with the latter two most common. High temperatures can be accommodated using solid electrolytes and high temperature materials for sensor device construction. Overall, there are the following two main categories of electrochemical sensors (Karakaya et all, 2020):

Chemiresistive: Conductometric gas sensors, also named chemiresistors, transduce the presence in the atmosphere of a given chemical compound through a variation of their electrical resistance. They are based on semiconducting metal oxides, whose electrical properties are modulated by red-ox interactions with adsorbing gaseous molecules. It has been known for more than five decades that the electrical conductivity of metal oxide semiconductors (Figure 3) varies with the composition of the surrounding gaseous atmosphere. In order to have MOS sensors with great stability even for long periods of use, the crystallite size has been reduced in the last 20 years to achieve a significant increase in sensor performance.



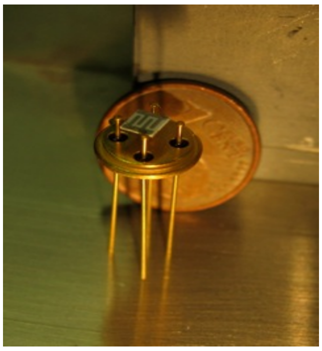


Figure 3 Typical structure of a conductometric MOX sensor.

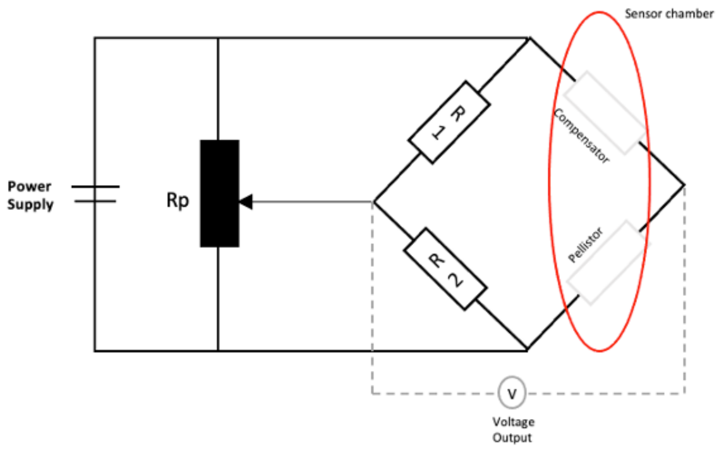


Figure 4 Wheaston bridge

The MOS sensor with reduced grain size show good sensitivity to many VOCs, short response time, a wide range of sensor coatings, low cost, good resistance to sensor poisoning, sensitivity to polar compounds. Although MOS sensors exhibit a wide-range response to a wide variety of different gases, their cross-sensitivity spectra can still be adjusted by their doping or the introduction of catalysts. One of the negative aspects in these sensors is the sensor drift which is caused by slow changes in the sensor baseline resistance as well as the response to the gas, thus mimicking the apparent changes in the target making it difficult to measure gas concentrations over time**.** A very extensive study on the causes and on how to intervene in the case of the most applied MOS semiconductor, that is SNO2, was reported recently **(**Sberveglieri G. 2022)**.** A possible hybrid approach combining k-NN and ANN can be used to evaluate the possibility of counteracting drift, using the dataset containing the measurements on the samples to be analyzed. The performances were compared with the k-NN algorithm. The two approaches do not differ from each other in terms of accuracy, although the best classification result was obtained with the hybrid method (Abbatangelo et all, 2020). The second class of conductometric sensor used in ENs are the ones based on porphyrin (Catini et al, 2015). These are small size sensors with a very high sensitivity, rapid response and recovery times, comfortable to integrate into measurement circuitry. Both classes present the following negative aspects: sensitivity to humidity, not low power consumption, sulphur and weak acid poisoning, limited precision and limited reproducibility. One of the easiest and most sensitive methods to control electrical resistance in conductometric sensors is the Wheaston bridge (Figure 4).

2.1 Innovation about electronic nose

Recently, a lot of upgrades have been performed regarding the electronic nose. Several aspects have been improved such as artificial intelligence, machine learning, stability of the sensing elements, cloud processing, predictive algorithms and internal flow.
The great interest in Electronic Noses has grown enormously in recent years, as shown by the increase in publications on the subject shown in Figure 5

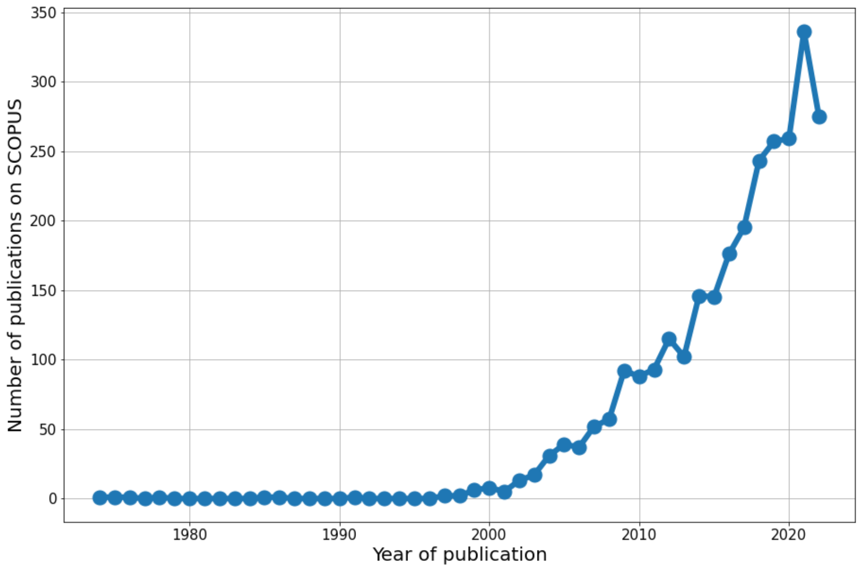


Figure 5 . Trend of publications on the Electronic Nose on SCOPUS as a function of the years

With regard to this, Nano Sensor Systems srl, spin off of University of Brescia, developed a new Electronic Nose (Figure 6). This innovative tool is equipped with an array of 6/9 MOX sensors, flow, temperature and humidity sensors. All data and graphs corresponding to the measurements are available in the NASYS webapp on Microsoft Azure. Each analysis will be structured in 3 different phases that will have specific times depending on the matrix being acquired:
1. "Before" or Phase 0: Sensor conditioning phase
2. "During" or Phase 1: Sampling phase

3. Phase of "After" or Phase 2: Phase of restoring the predefined baseline of the sensor

Figure 6 Nano Sensor Systems Electronic Nose

This EN has been successfully used in several applications such as microrganisms detection on food (Núñez-Carmona et all, 2020), characterization of EVOO (Abbatangelo et all, 2019) and coffee blends or jam recipes identification. As a matter of fact, an innovation study was performed regarding online detection of jam recipes in Menz&Gasser S.p.A., (Sede Legale Zona Industriale, 38050 Novaledo (TN), Italy) (Núñez-Carmona et all, 2019).

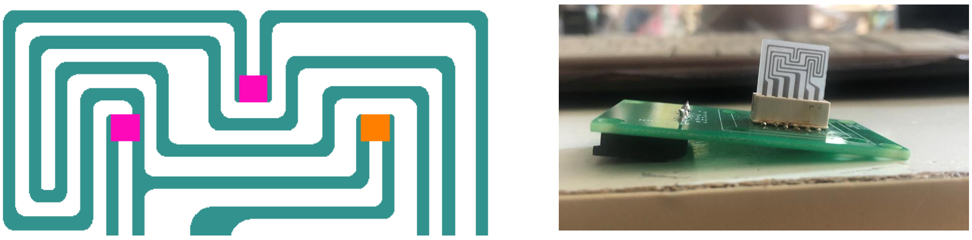


Figure 7 Triple MOX sensors

NASYS has designed and developed several sensor arrays and a mini array with three sensors which is reported in Figure 7 with different sensing layer on the same substrate, in order to achieve the right mechanical firmness and to reduce the power consumption of each sensor. The triple sensor developed by NASYS consists of an array of 3 different interchangeable sensing layers between the following:

1. SnO_2 at a working temperature of 300 ºC;
2. SnO_2+Au at a working temperature of 400 ºC;
3. SnO_2+Pd at a working temperature of 400 ºC;
4. SnO_2 at a working temperature of 350 ºC;
5. SnO_2 at a working temperature of 400 ºC.

The triple sensor, in order to be conditioned, is inserted in mini plug and play welded in a measured printed circuit board. This system allows an easy replacement of the sensor.

3. Conclusion

The ENs have had considerable progress in recent years therefore they are able to give important information in a short time and continuously, which cannot be done with other techniques. One of the great advances that have enabled the development of new generations of ENs have been the much more stable and reproducible gas sensors. This characteristic associated with the new possibilities of data processing and the development of very robust predictive algorithms has meant that the real applications of ENs have multiplied. The success of some ENs in the various applications is also due to the fact that experts in different areas such as Physics, Chemistry, Electronic Engineering and Artificial Intelligence as well as the expert of specific applications give a strong contribution to their development.

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