URSI-B EMTS 2025, Bologna, 23–27 June

The progress of the development of the electronic nose based on microwave gas sensors

Stanisław Karcz(1), Anna Paleczek (1), Dominik Grochala(1), Mateusz Kocoń(1), Łukasz Błajszczak(2), Kamil Staszek(3) and Artur Rydosz*(1)
(1) The Biomarkers Analysis LAB, AGH University of Krakow, Al. Mickiewicza 30, 30-059 Krakow,
(2) The Department of Surface Engineering and Materials Characterization, AGH University of Krakow
(3) The Microwave Research Group, AGH University of Krakow

Abstract

Electronic noses (e-noses) are pervasive devices for enhanced gas-sensing applications in many industrial applications, including environmental protection, indoor quality air control, and, recently, medical/clinical diagnosis. However, implementing e-noses based on microwave gas sensors is still pending. This paper presents the development of a microwave-based e-nose with six sensors, where various metal oxides have been used as gas-sensitive layers. Thanks to machine learning algorithms, the *2n+2* gases can be selectively detected. However, the theoretical analysis suggests that more gases can be distinguished when thermal and frequency modulation are conducted and when the thickness of the gas-sensitive layer is optimized.

1. Introduction

The development of gas sensors enables the utilization of such devices in daily life, including air quality and air pollution monitoring, air quality indoor comfort measurements, several industrial (e.g., in petroleum processing) applications, and recently medical applications (e.g., exhaled breath analysis - EBA). Using gas sensors in EBA was possible thanks to developing cheap, easy-to-use, and efficient gas-sensitive layers supported by machine learning algorithms. The research achievements in this field pave the way for the development of electronic noses that can compete with conventional analytical apparatus such as selected-ion flow-tube mass spectrometry (SIFT-MS), gas chromatography-mass spectrometry (GC-MS) [1]. Several electronic noses have been developed and released on the market, for example, the Cyranose® 320, the aeoNose™, and the SpiroNose [2]. However, all approaches mostly use gas sensors operating in the direct current (DC) mode, including metal oxide (MOX) based gas sensors. Electrochemical, optical, and photoacoustic gas sensors have also been investigated, although they still await commercial e-nose implementation.

Microwave-based gas sensors (MGS) are quite a novel concept in gas-sensing applications, although they have been researched for over two decades [3]. The MGS concept is based on two approaches: resonant frequency shift and wideband measurements [4]. Both methods provide pros and cons, so the decision about what measurement should be used is highly related to the target gas measurement and environmental limitations. Financial aspects should also be taken into account. It has to be underlined that there is still a lack of commercially available e-noses based on microwave-based gas sensors. One of the significant advantages of the MGSs is the ability to operate at room temperature instead of higher temperatures, such as 300-500°C, known for MOX-based gas sensors. Moreover, the changes in the microwave measurement parameters pave the way for enhanced sensitivity and selectivity, allowing the development of e-noses capable of detecting gases in the mixture of compounds, as in the exhaled human breath where more than 3500 volatile organic compounds (VOC) have been detected so far. Each breath consists of approximately 500 VOCs [5]. One limitation of developing such an e-nose device is the requirement for a gas-sensing chamber where all sensors in the matrix can be placed. It is mandatory to evaluate the gas-sensing response at the same condition, mainly when low target gas concentrations are evaluated – such as part per million (ppm) or lower.

This paper presents the progress made by the Biomarkers Analysis LAB and the Microwave Research Group research groups at AGH University of Krakow in developing an e-nose based on microwave gas sensors.

2. The concept of the electronic nose for microwave-based gas sensors

The central part of the electronic nose is the gas-sensing chamber, where all sensors are placed and tested under the same conditions, including relative humidity changes (RH%) and temperature (T). Although the microwave-based gas sensors showed promising results in operating at room temperature (RT), the increased operating temperature (OT), in many cases, enables thermal modulation of the gas-sensing layer (e.g., the gas-sensing layer based on metal oxides). Thus, the sensitivity and/or selectivity can be modulated. For example, a sensor based on copper oxide showed various selectivity when operated at lower and higher temperatures [6]. Therefore, the microwave-based e-nose is equipped with external heaters that can be used in parallel or separately if only one sensor needs to be heated. If such a case is required, the gas sensor chamber should probably be divided into two zones: one where the sensors are working at RT and another where increased OT is used to avoid influencing one sensor to another. Figure 1 shows the developed gas-sensing chamber where microwave-based gas sensors (n=6) are installed with additional heaters (Fig. 1C). The heater is based on a plate heater that achieves OT 250°C.

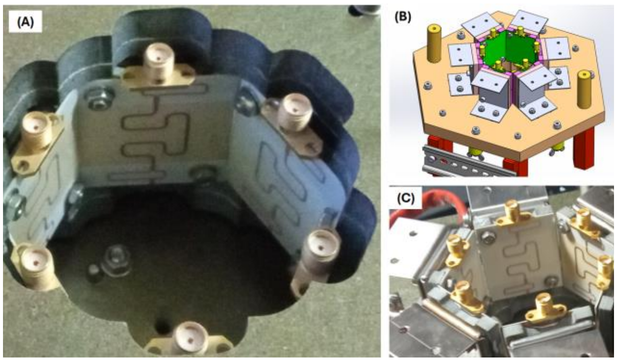

Figure 1. (A) The photo of the sensors installed in the chamber; (B) the mocap of the sensor installation with heaters; (C) the photo of the sensors installed with the heaters before other elements of the e-nose construction.

The microwave circuits are meander-shaped lines (Fig. 1A) with a 0.05” transmission line width fabricated on RO4003™ microwave laminate. 50 Ohm matching was achieved to the eight-port reflectometer (8PR) equipped with four quadrature couplers (4QC), two in-phase power dividers (2-IPPD), and a transmission line to equalize the electrical length of suitable singles lines, as presented previously. The calibration protocol was described in detail in [7]. All sensors (here: 6) are connected to a CCR-38S360 (Teledyne Relays) mechanical switch to enable microwave measurements with a single unit. The major limitation of the mechanical switch is the total number of switches that can be done during the lifecycle of such a device. Therefore, we have developed a measurement protocol that reduces the number of switches without losing essential information about the gas-sensing characteristics.

3. Results and Discussion

The e-nose setup (Figure 2) was developed as a proof of concept. The prototype was mostly fabricated with 3D-printed parts; however, the design can be adapted depending on industrial demand. The setup is vertically oriented. The gas-sensing chamber has 6 sensors, separate heaters, and a heating control unit. The gas inlet/outlet ports are placed in the middle of the gas-sensing chamber; thus, the gas stream is equally distributed to each sensor. The mechanical switch is connected via waveguides. Two fans are installed to reduce the heat transfer via waveguides to the switch module. The microwave circuit measurement unit is also connected to the mechanical switch via a central waveguide. The prototype is software controlled by a Python-based application.
The major limitation of the mechanical switch is the number of switches that can be made. In gas-sensing applications, parameters such as resistivity, conductivity, voltage/current, or microwave parameters such as phase changes and S-parameters [8] are used to calculate the gas concentrations. The measurements are in specific time slots, as illustrated in Figure 3. Each sensor is tested in the continue mode once per cycle, starting with S1 and ending with S6. In contrast, during other cycles, the signal features (here, phase signal) are measured shortly before and after the introduction of gases into the gas-sensing chamber. Further, the gas sensor response (S) is calculated, for example, as $S=\varphi_{gas}-\varphi_{air}$, where φ_{gas} and φ_{air} represent the phase values under exposure to target gas and synthetic air (or ambient air), respectively.

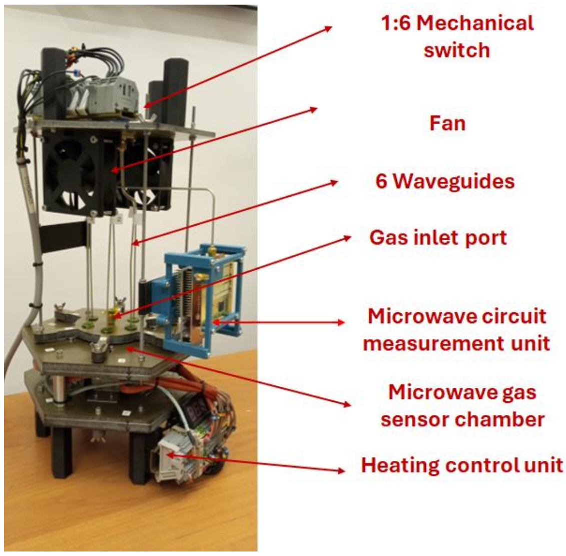

Figure 2. The developed e-nose setup for R&D of MGSs. The setup enables testing up to six sensors under exposure to target gases in the same environmental conditions: relative humidity and temperature, as well as at various operating temperatures due to the utilization of separate heaters for each sensor in the setup.

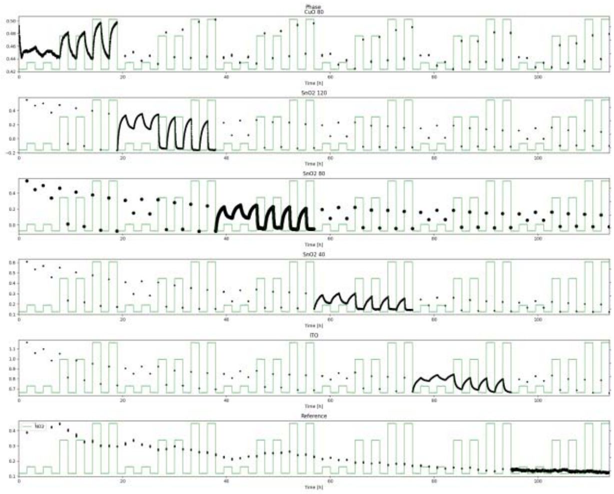

Figure 3. The gas-sensing characteristics of the six sensors installed in the setup, where sensors S1-S5 are covered by a gas-sensitive layer (various metal oxides were used), and S6 is a reference sensor without a gas-sensitive layer.

Generally, the gas-sensing layer is chosen depending on the target gas detection. For example, graphene oxide (GO)-based sensors have been evaluated for enhanced acetone detection at room temperature using microwave gas sensors [9]. The developed sensor’s reflection coefficient was measured at 2.4 GHz in the 0-200 ppm range of acetone and other common VOCs such as ethanol, methanol, and isopropanol. In another approach, CuO-based MGS were evaluated under exposure to acetone in the 0.5-5 ppm range [10]. The reflection coefficient was measured with a novel wideband multiport reflectometer. Thanks to the advanced measurement protocol where measurement uncertainty can be precisely adjusted, the detection limit was estimated at 0.05 ppm. At the same time, 0.5 ppm was measured due to the system's gas-dosing limitations. In addition, the developed CuO-based sensors showed a stable response after 105 days of continuous testing [10]. Recently, WO_3-based MGS was tested in automotive applications, where NO_2 concentrations in the city and countryside in Poland were evaluated [11]. The research results have shown that ~410 nm of WO_3 is the optimal thickness of the NO_2-sensitive layer in a rash environment (high RH%). Interestingly, the WO_3-based sensors showed responses (defined as phase changes/GHz) to NO_2, C_2H_5OH, and C_8H_{10}, while C_3H_8 and C_3H_6O did not affect the sensor's properties. NO_2 was also a research subject for MoO_3-based microwave sensors [12]. However, a single frequency of 5.8 GHz was used instead of a wide-range frequency operation. Such an approach enables the reduction of microwave components and reduces the cost and complexity of the measurement setup. The reference sensors were used to compensate for the ambient condition. However, the selectivity was not outstanding, and cross-sensitive issues must be considered. Moreover, the MOX-based MGSs were evaluated above the 10 GHz range. In paper [13], CuO, SnO_2, WO_3, and TiO_2 sensors have been tested in the 100-1200 GHz range. However, the sub-THz measurements require more sophisticated measurement methods and devices. It can be an interesting approach for space applications. On the other hand, SnO_2-based [14] gas-sensing films were also tested in the Hz-kHz range.

In summary, the e-nose based on microwave gas sensors must include parameters such as (**i**) several gas sensors that can be installed. At some point, this number results from the number of gases that must be detected according to the *2n+2* hypothesis; (**ii**) the type of the gas-sensing layers. However, this issue is limited by the deposition techniques that can be used, and (**iii**) operating temperatures. It has been proven that for MOX-based sensors, the sensitivity and selectivity can be modulated by thermal modulation (e.g., detection of one gas at lower temperatures – room temperature, and another gas at higher temperatures); (**iv**) the thickness and form of the gas-sensitive layer (e.g., nanorods, nanofilms, nanowires). However, this parameter is limited by the microwave circuit design and fabrication method: Cu-based laminate microfabrication vs. silicon technology; (**v**) the operating mode: resonant vs. wideband frequency measurements and frequency range (kHz-THz). The decision on this should be supported by budget planning for the e-nose fabrication if more than one prototype is coming.

Besides the abovementioned issues, ML algorithms (MLA) can enhance sensitivity and selectivity. MLA and neural networks can improve sensitivity using data preprocessing techniques, such as noise reduction, long-term sensor drift elimination [15], and advanced feature extraction methods. Advanced models, such as neural networks [16] or support vector machines (SVM) [17], can be trained to detect even minimal variations in the signal amplitude or phase, leading to higher accuracy in identifying low-concentration gases.

Classification algorithms such as k-nearest neighbors (k-NN), random forests, or deep learning models can be used to increase selectivity, which enables the detection of differences in multidimensional data collected from multiple gas sensors. Additionally, dimensionality reduction techniques such as principal component analysis (PCA) [18] can be used to visualize data in a reduced feature space and provide visualizations that will enable better feature analysis. Feature importance analysis, e.g. using the SHAP [19] method, allows for visualization of the impact of each feature on the model decision. This enables optimization of layer parameters such as layer composition, thickness, and operating temperature.

As mentioned earlier, MLA, particularly those using adaptive models and drift compensation techniques [20], can also improve the stability of sensor responses over time by eliminating drift caused by environmental factors, sensing material aging, or operating conditions changes. In the case of the microwave gas sensors, the number of MGSs implicates the number of gases that can be detected. Therefore, we suggested that *2n+2* gases can be detected if *n* MGSs are used. The analysis is based on the table shown in Figure 4. The table was made based on previous measurements [11,13-14]. Thus, we considered two cases where *n* was equal to 1 and 2. In the case of *n* =1, *2n+2* is then 4. We will only modify the measurement frequency if we analyze sensors numbered S6 (WO_3, RT, THz) and S10 (WO_3, RT, GHz), RT, and GHz). Therefore,

- S10 shows a positive response to C_8H_{10} a slightly negative response to C_2H_5OH, and a moderately negative response, which could indicate C_3H_8, NO_2, or acetone. If S6 reacts with a low positive reaction, we can identify acetone.
- Assuming S10 does not respond to methanol or responds positively (we lack data for this), if S6 shows a low positive response and S10's reaction is different from low or moderately positive, it is likely methanol.

In the case of *n=2*, *2n+2*=6. The measurements are the same as those of S6 and S10. Additional sensors S1 (SnO_2, 175°C, kHz) and S5 (SnO_2, RT, THz). We modify the measurement temperature and frequency. Thus:

- A high response from S1 indicates H_2S.
- No response from S1 combined with a moderate response from S10 suggests propane or NO_2.

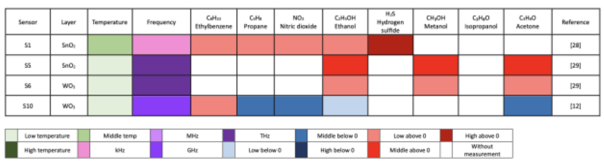

Figure 4. Sensors' response summary.

4. Conclusions

E-noses enable enhanced gas-sensing detection, and by combining them with machine learning algorithms, sensitivity, and selectivity can be improved. In the case of microwave gas sensors based on metal oxides, where wideband and resonant measurement methods are used, various oxides, including p-type and n-type, and different operating temperatures, the number of gases that can be detected by using *n* sensors is as well as *2n+2*. The theoretical analysis suggests that more gases can be distinguished when thermal and frequency modulation are conducted and when the thickness of the gas-sensitive layer is optimized.

5. Acknowledgements

The National Science Centre Poland has supported under the NCN OPUS 2021/41/B/DT7/00276 grant.

References

[1] P. Saxena and P. Shukla, "A Review on Gas Sensor Technology and Its Applications" in Computational and Experimental Methods in Mechanical Engineering, V. V. Rao, A. Kumaraswamy, S. Kalra, and A. Saxena, Eds. Singapore: Springer, 2022, vol. 239, pp. 345-358.

[2] A. Rabehi, et al., "Advancements and Prospects of Electronic Nose in Various Applications: A Comprehensive Review" Applied Sciences, vol. 14, no. 11, p. 4506, 2024. doi: 10.3390/app14114506.

[3] J. Rossignol, et al., "Microwave-based gas sensor with phthalocyanine film at room temperature" Sensors and Actuators B: Chemical, vol. 189, pp. 213-216, 2013. doi: 10.1016/j.snb.2013.03.092.

[4] N. Ida, "Microwave Measurement Techniques" in Microwave NDT, Springer, 1992, vol. 10, pp. 110-130. doi: 10.1007/978-94-011-2739-4_5.

[5] W. Miekisch, et al., "Diagnostic potential of breath analysis—focus on volatile organic compounds" Clinica Chimica Acta, 347, 1, pp. 25-39, 2004. doi: 10.1016/j.cccn.2004.04.023.

[6] A. Rydosz, A. Szkudlarek, "Gas-Sensing Performance of M-Doped CuO-Based Thin Films Working at Different Temperatures upon Exposure to Propane" Sensors, vol. 15, no. 8, pp. 20069-20085, 2015. doi: 10.3390/s150820069.

[7] K. Staszek, et al., "A least-squares approach to the calibration of multiport reflectometers," in IEEE MTT-S, doi: 10.1109/IMaRC.2013.6777712.

[8] K. Staszek, et al., "Six-port microwave system for volatile organic compounds detection," SNB, vol. 245, pp. 882-894, 2017.

[9] K. Staszek, et al., "Microwave system with sensor utilizing GO-based gas-sensitive layer and its application to acetone detection," SNB, vol. 297, p. 126699, 2019. doi: 10.1016/j.snb.2019.126699.

[10] J. Sorocki, et al., "Wideband microwave multiport-based system for low gas concentration sensing and its application for acetone detection," SNB, vol. 323, p. 128710, 2020. doi: 10.1016/j.snb.2020.128710.

[11] A. Paleczek et al., "An NO_2 sensor based on WO_3 thin films for automotive applications in the microwave frequency range," SNB, vol. 376, p. 132964, 2023. doi: 10.1016/j.snb.2022.132964.

[12] D. Grochala, et al. "Nitrogen Dioxide Detection by the Utilization of MoO_3-based Gas Sensing Layer and Eight-port Reflectometer in the Microwave Frequency Range," 2022 IEEE Sensors USA, 2022, pp. 1-4, doi: 10.1109/SENSORS52175.2022.9967099.

[13] A. Rydosz, et al. 'Selected Metal Oxides Thin Films for Gas-Sensing Application in The Microwave Frequency Range', *EUROCON 2023 - 20th International Conference on Smart Technologies, Proceedings*, pp. 558–561, 2023, doi: 10.1109/EUROCON56442.2023.10198975.

[14] B. Szafraniak et al., "SnO_2-based sensor for H_2S detection in exhaled human breath", 35th URSI GASS 2023, 10.23919/URSIGASS57860.2023.10265599.

[15] S. Lu *et al.*, 'An Improved Algorithm of Drift Compensation for Olfactory Sensors', *Applied Sciences 2022, Vol. 12, Page 9529*, vol. 12, no. 19, p. 9529, Sep. 2022, doi: 10.3390/APP12199529.

[16] P. Bulucu, et al., 'Multi-Sensor E-Nose Based on Online Transfer Learning Trend Predictive Neural Network', *IEEE Access*, vol. 12, pp. 71442–71452, 2024, doi: 10.1109/ACCESS.2024.3401569

[17] V. A. Binson, et al., 'Prediction of Pulmonary Diseases with Electronic Nose Using SVM and XGBoost', *IEEE Sens J*, vol. 21, no. 18, pp. 20886–20895, Sep. 2021, doi: 10.1109/JSEN.2021.3100390.

[18] H. Abdi and L. J. Williams, 'Principal component analysis', *Wiley Interdiscip Rev Comput Stat*, vol. 2, no. 4, pp. 433–459, Jul. 2010, doi: 10.1002/WICS.101.

[19] 'Welcome to the SHAP documentation — SHAP latest documentation'. Accessed: January 7, 2025. [Online]. Available: https://shap.readthedocs.io/en/latest/index.html

[20] N. Dennler, et al., 'Drift in a popular metal oxide sensor dataset reveals limitations for gas classification benchmarks', *SNB* vol. 361, p. 131668, Jun. 2022, doi: 10.1016/J.SNB.2022.131668.