

Commercial Metal Oxide Gas Sensors For Breath Analysis Sensitive to Higher Alkane Vapours

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Abstract—Within an ongoing European project on breath analysis by IOMS, sensitivity of sensors to various VOCs is studied, as breath VOCs are considered as lung cancer biomarkers. Sensitivities of several commercial metal oxide sensors to various VOC have been studied. It was found that two sensors reacted to decane presence. This is an unusual property for metal oxide gas sensors. This paper shows obtained results and details the methodology employed to obtain them.

Keywords—Metal Oxide, Gas Sensor, VOC, Alkane, Electronic Nose, Breath.

I. INTRODUCTION

An Instrumental Odour Monitoring System (IOMS, also called electronic nose or e-nose) aims at qualifying mixes of gases. Its working principle relies on the non-specificity of its sensors: the system will give a general imprint of the whole mixture [1]. Specific proportions of several hundreds of compounds can be recognized, which makes it ideal for the identification and tracking of odours. It has been widely used in the field of environmental studies and the food industry, to name a few [2].

However, another field took interest in the IOMS: medicine. Breath sampling and analysis is being researched on since the 80's [3], and electronic nose quickly arose as an interesting solution to categorize breaths and recognize illnesses in a non-invasive way. The ongoing Pathacov project [4] aims at the creation of a tool for lung cancer screening by IOMS breath analysis. Within this European project, sensitivity of sensors to various VOCs is studied, as breath VOCs are considered as lung cancer biomarkers [5]. Among the candidate biomarkers in literature, several are higher alkanes, such as decane, undecane or dodecane [6]–[8].

In this article, we will discuss the results of a specific experiment involving commercial metal oxide semiconductor (MOS) sensors and n-decane vapour, which is usually not well detected by commercial MOS. Higher alkanes are usually too chemically stable to be oxidized by most heated metal oxides. It is to be noted however that experimental metal oxide sensors have been reported to react, although very slightly, to decane and other higher alkanes in the past. For example, a tungstene trioxide sensor can show a relative sensor response of 0.01, and the same sensor shows a relative sensor response of 0.16 and 0.22 for decanal and decanoic acid respectively [9], [10].

II. MATERIALS AND METHOD

The whole experiment revolved around measuring the sensitivity of an IOMS to various VOCs commonly found in lung cancer biomarker literature. One of these VOCs is n-decane [8], a straight chain alkane often thought to be too stable to react with metal oxide sensors at their usual

working temperature. However cross sensitivity and competition between compounds on the sensor surface can happen [2], and it was found pertinent to test all used compounds in a rigorous sensor testing procedure. The initial objective was to fully characterize commercial sensors to evaluate their fitness to detect cancer biomarkers in an environment similar to real breath sampling conditions.

The tested custom IOMS included seven metal oxide sensors that were radially and evenly placed inside a small volume (7.5mL internal volume) sensor chamber. The sensor chamber is made entirely of PTFE Teflon and also includes temperature and humidity sensors. The sensor chamber is controlled in temperature at 45°C by using a PID controller. The conductance of the MOS is measured and logged every second by a “Teensy 3.5” board and sent to a laptop for analysis. The setup is completed by a pump and a rotameter for flow control (200 mL/min), both are downflow to avoid any contamination. Tubing is made out of PFA and the whole device is kept at ambient temperature for this test. The sensors forming the IOMS were the TGS T2603 (Figaro Engineering®), GGS 3530T, 1430T, 2530T, 8530T (Umwelt Sensor Technik®), MP901 (Winsen®) and BME680 (Bosh®). These sensors were selected to have as little correlation between them as possible, in order that the sensor array gives as much information as possible. They were chosen based on the variety of gases they were built for, and on their previous use in healthcare IOMS literature.

Samples are synthesised by injecting between 0.1 µL and 1 µL of liquid VOC. 0.6µL of liquid decane (analytical grade n-decane (Merck®)) is injected inside an 8L Teflon bag filled with analytical air (Alphagaz™). The bag is then heated at 60°C in an oven for 30 minutes to ensure volatilisation of the injected droplets and homogenisation of the gases. The bag contains 9.5ppm of decane at this stage. The bag is then put into a pressure chamber at 1.7 atmospheres. The pressure forces the air out of the bag and into a dilution unit that controls the flow with mass flow controllers. Using several mass flow controllers, it is possible to dilute the decane and humidify the diluting air [11]. Using this principle, we bring the concentration down and create several samples with 0.1, 0.5, 1.0, 2.5 and 5.0ppm respectively. Humidity within the bag is brought to 40% relative humidity (at 20°C).

Part of the sample is adsorbed on a Tenax® TA filled cartridge and analysed using thermal desorption gas chromatography mass spectrometry (TD-GCMS). The samples are drawn on cartridges with a GilAir Plus Personal (Sensidyne®) sampling pump, that measures the volume of pumped sample. The GCMS setup is as follows: Trace GC oven and DSQII mass spectrometer (Thermo Fisher Scientific®) is coupled with a TD-100xr (Markes®) thermal

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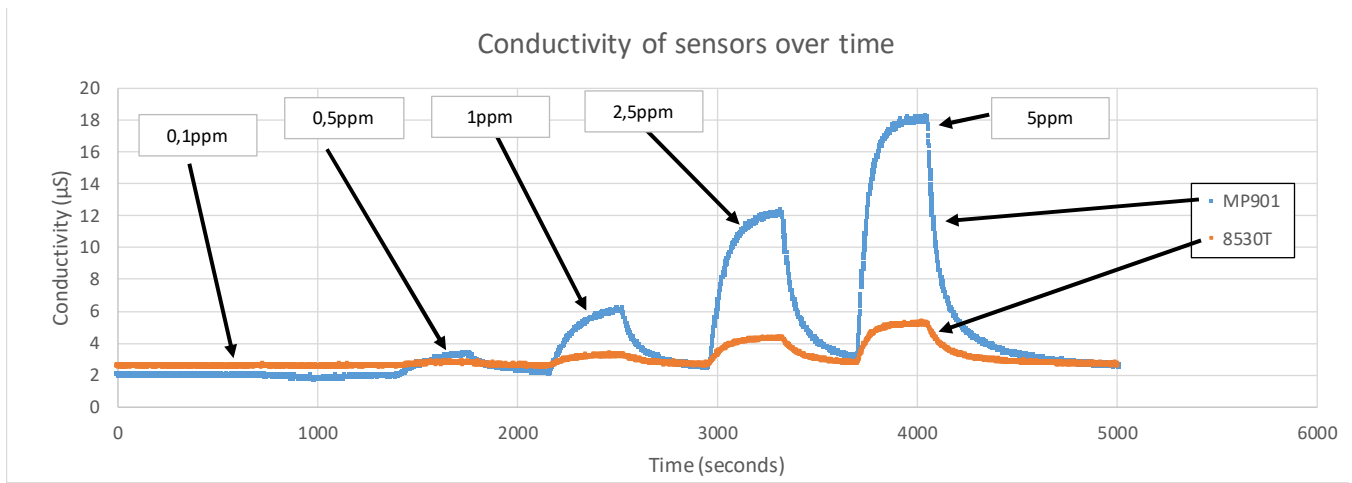


Fig. 1. Plot of the conductivity of sensors over time while submitted to increasing concentrations of n-decane in alternance with reference air.

desorber. To ensure good separation, a VOC-specialised capillary column is used (Rxi®-624Sil MS, 0.25mm ID 1.4µm 60m, Restek®). The samples are analysed using the following GC oven program: hold 50°C for 5min, 10°C/min to 180°C, 6°C/min to 205°C, hold 205°C for 5min. As the method of reference, GCMS was calibrated for decane. Regarding signal processing, the Area Under Curve (AUC) was acquired for decane peaks, using the automated AUC calculator within the Xcalibur™ software (Thermo Fisher®). This tool removes the baseline in the AUC calculation. Before sampling, cartridges were processed to obtain a blank sample, which was used in the background removal tool of Xcalibur. This reduces the influence of TDGCMS related contaminants. To make sure no contaminant could be found in the samples themselves, the absence of other unusual major peaks was confirmed for each chromatogram.

After adsorption, the rest of the gaseous sample is

connected to the IOMS. Using a three-point valve, the IOMS is submitted to either reference air or sample. Samples are measured for 4 minutes before switching to reference air for 5 minutes, and so on until all samples have been processed. Reference air is 40% RH (at 20°C) N6.0 grade air (Air Liquide®) drawn from a gas cylinder.

Raw data is processed to reduce its dimensionality. Using conductance value of each sensor, maximum peak height, area under curve and maximum peak slopes are computed for each sample. Obtained data is compared to concentrations measured by GCMS to confirm that the contents of the bags are as planned and the response of the sensors is linearly proportional to the amount of n-decane in the samples.

Limit of Detection (LOD) is calculated using logarithmic regression and signal-to-noise ratio. Calculation of the LOD was done using a method similar to what was previously used in literature [1], even if it should be noted that a more robust method could have been used[12]. The signal from a blank sample (40% RH pure air at 20°C) is considered as the background noise, and is normally distributed. A sensor is considered sensitive to a compound at a given concentration if its conductance rises by more than 3 times the standard deviation of the background noise. For 8530T and MP901, the signal needs to rise by, at least, 0.12 µS and 0.13 µS respectively. The LOD is estimated by finding the concentration for which the rise in conductivity (from the background noise) is null, using the logarithmic regression model computed from the samples (Fig. 2).

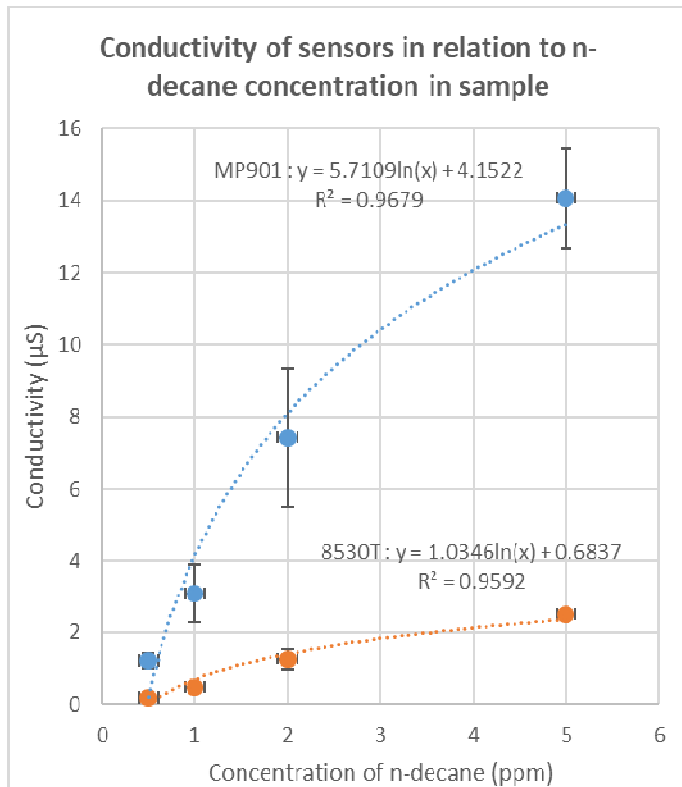


Fig. 2. Plot of the concentration of n-decane in relation to sensor response.

III. RESULTS AND DISCUSSION

As Fig. 1 shows, two sensors reacted significantly to the n-decane vapours. At 0.1 ppm, no reaction was observed for all sensors. From 0.5 ppm and above, sensor MP901 shows a response of 57.6% increase of its baseline value (0.74 relative sensor response, which is $(S-S_0)/S_0$, S_0 being baseline conductivity and S conductivity in decane sample). 8530T shows an almost imperceptible response to the analyte at this concentration, but begins to show a clear response at 1ppm (0.27 relative sensor response). All other sensors show a complete lack of response at all tested concentrations. LOD for n-decane is estimated for MP901 at around 0.25 ppm while LOD for 8530T is around 0.50 ppm. MP901 show the highest sensitivity of the two, with a response of about

3 μ S/ppb, against 0.5 μ S/ppb for 8530T. The plot of the n-decane concentration in relation to sensor response for corresponding samples (Fig. 2) shows what looks like the beginning of a saturation effect at higher concentrations, which is a common phenomenon across metal oxide gas sensors [2]. Response is linearly proportional to decane concentration under 2.5ppm for both sensors, saturation effect seems to occur between 2.5 and 5ppm. Saturation is likely to happen above 5ppm for both sensors.

The presence of other compounds due to a contamination during the dilution process or from liquid decane oxidation during storage could also be present in the sample and induce a sensor response. This would mean that the observed response would not be directly linked to decane itself. However, TDGCMS analysis for every sample shows no significant trace of contamination, and the n-decane peak is the only significant peak in the chromatogram. The mass spectrum shows no evidence of co-elution of decane with another compound that would have had the same retention time. In the case of a contamination by an oxidized compound such as an alcohol, aldehyde or ketone, a response from the other gas sensors would be expected. No such response was observed. Other compounds have been tested before and after this experiment, such as 1-propanol or heptanal, and a response from all sensors has been recorded. This shows that the other sensors and the electronics are working properly.

The exposure to n-decane has been repeated after several weeks, and both sensors have shown the same behaviour. To make sure no contamination from the dilution apparatus was at play, several blanks have been processed using the same procedure and no response was observed from any of the sensors. A fresh bottle of n-decane was used for another experiment and a similar response was observed from both sensors. The contamination of the samples by a compound with no affinity for the sorbent (i.e. invisible to GCMS analysis) is therefore unlikely.

Lastly, swapping the 8530T for an unused 8530T of the same age (stored under current) and exposing it to decane yielded similar signals, which seems to confirm the ability of 8530T to detect decane. At the time of publication, MP901 was not yet compared to the previous MP901 because of temporary technical troubles.

What makes MP901 and 8530T react to higher alkanes is unclear, as the detailed structure of their sensing surfaces (or any other insight) is not disclosed by the manufacturers. MP901 is sold as a generic sensor for VOCs and smoke detection. 8530T is sold as an ethanol sensor. An investigation of the composition of both of their sensing surface is needed to explain their behaviour.

IV. CONCLUSION

After the realised tests, the response of two sensors seem to correlate to the sample concentration in n-decane. It is likely that MP901 and 8530T sensors are sensitive to n-decane, and possibly other volatile higher alkanes as well.

Provided this result is repeatable in another laboratory, this finding is very interesting for alkane sensing with low

cost gas sensors. Some lung cancer biomarkers in literature are higher alkanes, according to GCMS studies on breath. Of course, a sensor capable of detecting decane could find other uses outside of healthcare.

Complete characterization of sensors is underway, which should give a more complete knowledge of which compounds can be detected by each sensor, as well as cross sensitivities to usual interfering compounds. These experiments will also give some insight on the interferences to be expected if these sensors are used for higher alkane sensing. Other tests include hysteresis analysis, sensitivities to biomarkers, response time, recovery time, drifting behaviour and lifetime, humidity and environmental temperature influence on sensors. These commercial sensors will be compared with prototypes sensors developed within the Pathacov project.

REFERENCES

- [1] J. Nicolas and A.-C. Romain, 'Establishing the limit of detection and the resolution limits of odororous sources in the environment for an array of metal oxide gas sensors', *Sensors and Actuators B: Chemical*, vol. 99, no. 2–3, pp. 384–392, May 2004, doi: 10.1016/j.snb.2003.11.036.
- [2] J. W. Gardner and P. N. Bartlett, *Electronic noses, principles and applications*. New York, NY, 1999.
- [3] M. Gordon, 'Volatile Organic Compounds in Exhaled Air from Patients with Lung Cancer', p. 5, 1985.
- [4] 'PATHACOV - Diagnostic de pathologies humaines par analyse de COV dans l'air expiré', PATHACOV, 2020. <https://pathacov-project.com/> (accessed Feb. 10, 2020).
- [5] J. Zhou, Z.-A. Huang, U. Kumar, and D. D. Y. Chen, 'Review of recent developments in determining volatile organic compounds in exhaled breath as biomarkers for lung cancer diagnosis', *Analytica Chimica Acta*, vol. 996, pp. 1–9, Dec. 2017, doi: 10.1016/j.aca.2017.09.021.
- [6] F. Monedeiro, M. Monedeiro-Milanowski, I.-A. Ratiu, B. Brożek, T. Ligor, and B. Buszewski, 'Needle Trap Device-GC-MS for Characterization of Lung Diseases Based on Breath VOC Profiles', *Molecules (Basel, Switzerland)*, vol. 26, no. 6, pp. 1789–, 2021, doi: 10.3390/molecules26061789.
- [7] A. Bajtarevic et al., 'Noninvasive detection of lung cancer by analysis of exhaled breath', *BMC Cancer*, vol. 9, no. 1, p. 348, Dec. 2009, doi: 10.1186/1471-2407-9-348.
- [8] G. Peng et al., 'Diagnosing lung cancer in exhaled breath using gold nanoparticles', *Nature Nanotechnology*, vol. 4, no. 10, pp. 669–673, Oct. 2009, doi: 10.1038/nnano.2009.235.
- [9] D. Kohl, L. Heinert, J. Bock, Th. Hofmann, and P. Schieberle, 'Systematic studies on responses of metal-oxide sensor surfaces to straight chain alkanes, alcohols, aldehydes, ketones, acids and esters using the SOMMSA approach', *Sensors and Actuators B: Chemical*, vol. 70, no. 1, pp. 43–50, Nov. 2000, doi: 10.1016/S0925-4005(00)00552-9.
- [10] A. Mukherjee and Y. Rosenwaks, 'Recent Advances in Silicon FET Devices for Gas and Volatile Organic Compound Sensing', *Chemosensors*, vol. 9, no. 9, p. 260, Sep. 2021, doi: 10.3390/chemosensors9090260.
- [11] P. Pérez Ballesta, A. Baldan, and J. Cancelinha, 'Atmosphere Generation System for the Preparation of Ambient Air Volatile Organic Compound Standard Mixtures', *Anal. Chem.*, vol. 71, no. 11, pp. 2241–2245, Jun. 1999, doi: 10.1021/ac981291i.
- [12] J. Burgués, J. M. Jiménez-Soto, and S. Marco, 'Estimation of the limit of detection in semiconductor gas sensors through linearized calibration models', *Analytica Chimica Acta*, vol. 1013, pp. 13–25, Jul. 2018, doi: 10.1016/j.aca.2018.01.062.