DOI 10.5162/EUROSENSORSXXXVI/PT5.285

The Right Nose for Electronic Noses

Max Köhne[1,2], Omar Tarek Penagos Carrascal[1], Gina Zeh[1], Tilman Sauerwald[1,2]
[1] Fraunhofer IVV, Giggenhauser Straße 35, 85354 Freising, Germany
[2] Saarland University, Department for Systems Engineering, 66123 Saarbrücken, Germany

Corresponding tilman.sauerwald@ivv.fraunhofer.de

Summary:

The article describes an instrument and a method for the characterization and validation of devices for instrumental odor measurement, especially miniaturized devices based inexpensive sensors. For this purpose, a test environment has been developed based on a combination of gas chromatography - mass spectrometry, odor measurement using olfactometry and sensor characterization. The system enables the connection of various gas sensors in a heated test chamber, which can be operated with an additional make-up gas flow. This allows testing conditions close to typical operating conditions, which is important for many sensor types e.g. metal oxide gas sensors. Our systems can measure rate constants for the kinetic processes on the sensor surface very efficiently allowing the modelling of virtual multi-sensors array using temperature-cycled operated (TCO). In this way, an optimized system approach can be quickly determined, set up and tested.

Keywords: instrumental odor measurement, electronic nose, gas chromatography, gas sensors

Introduction

Devices for instrumental odor measurement, so-called electronic noses, have been known for over 50 years [1] and they perform a variety of tasks in quality monitoring of raw materials and finished goods as well as in the measurement of odor emissions and environmental odors. Despite this success, the euphoria about these systems, especially in the 1990s, has not been fulfilled; small, inexpensive and fast systems still fall short in comparison to the human nose in terms of performance, especially when a large number of different odors are to be distinguished simultaneously. In addition, the training and calibration effort is very high. An efficient method of calibration could be a coupling of GC-MS/O and sensor array, which can integrate odor characterization and sensor characterization. Even though Hofmann et al. [2] described such a system as GC-SOMSA almost 25 years ago, it has not been used frequently. One reason is, that for many sensors the response to short gas pulses differs significantly from the response to static test gases. Another reason is that sensors are frequently operated in dynamic conditions, such as TCO to improve sensitivity and selectivity [3]. Therefore a sole measurement with a GC-SOMSA is not sufficient for a device characterization.

Recently we have demonstrated that a rate constant model is capable to predict the performance of sensors with TCO [4] and that short gas pulses can be used to determine the rate constants [5]. With this model it is possible to get a full characterization using a GC-SOMSA device and a small set of characterization measurements.

System concept

The test instrument (Figure 1) is based on a commercial GC (Thermo Scientific Trace 1610, Thermofisher) with mass spectrometer (Thermo Scientific ISQ 7610 Single Quadrupol Mass Spectrometer) equipped with an odor detector port (ODP). In parallel to the ODP a sensor port (SP) is connected in a split ratio of 1:1 between these ports.

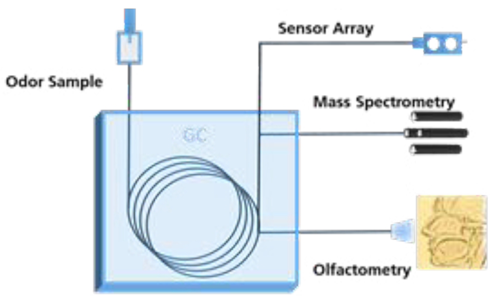

Figure 1: Schematic of the GC-SOMSA system modified after [1]

The transfer line to ODP and SP can be heated up to 200 °C to avoid condensation of semivolatiles. The sensor port is equipped with a heating cartridge, which allows a respective heating of the sensor port. However, the temperature will be restricted by the thermal stability of the sensor electronic, which is separated only by a thin insulating layer of Teflon. The maximum temperature needs, therefore, to be tested for each type of sensor device. For integrated devices it is typically restricted to 100 °C. The chamber can be flushed with a make-up gas flow e.g. of synthetic air in the range between 0-20 sccm.

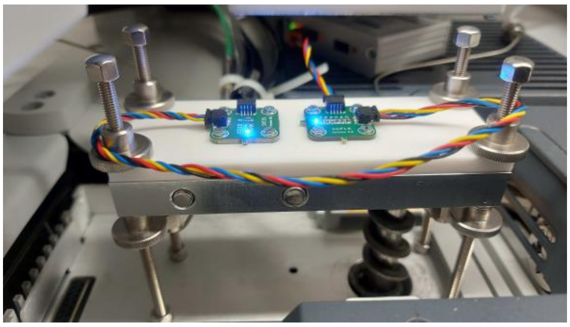

Figure 2: picture of the sensor port equipped with two sensor electronics

Sensor model

Metal oxide gas sensors can be described by a set of rate equations for the desorption and adsorption of gases at the surface. In typical operating conditions (low concentrations reducing gases in air) adsorbed oxygen is the most important species and the rate equation for the adsorption and desorption of oxygen can be used to model the sensor system. However, the rate for the desorption of oxygen is modulated by all reducing compounds, which is the case for most odorants. The desorption of oxygen is then modulated by the reaction with the reducing gas, which can typically exceed the spontaneous desorption by orders of magnitude as demonstrated in [4]. On the other hand the re-adsorption of oxygen is a relatively slow process which can be decoupled form the gas reaction. We have be demonstrated that at low operating temperature e.g. 50 °C no significant re-oxidation of the surface occurs over a period of several minutes. At higher temperature the processes still can be separated e.g. by forming the derivative of the sensor signal as long as the oxygen adsorption/desorption has a higher time constant as the reaction of oxygen with reducing gas.

Discussion

The development of electronic nose could profit from the recent advances in sensor integration as highly integrated gas sensor devices [6] enabling temperature-cycled operation at very low costs per item are available. However, system characterization and validation is often very costly and inhibit the use of those devices. To address this shortcoming, we have described of system and process for the characterization and validation of instrumental odor measurement devices and combined it with a recent model for gas sensors in temperature-cycled operation. This regenerates a very powerful tool for the development of new application specific solutions for odor measurement. The system is not only limited to this application, but can also be utilized for the development of small sensor-GC systems.

Literature

[1] J. W. Gardner, P. N. Bartlett, “A brief history of electronic noses“, Sensors and Actuators B, vol. 18-19, pp. 211-220, 1994.

[2] T. Hofmann, P. Schieberle, C. Krummel, A. Freiling, J. Bock, L. Heinert, D. Kohl, High resolution gas chromatography/selective odorant measurement by multisensory array (HRGC/SOMSA): a useful approach to standardize multisensory arrays for use in the detection of key food odorants, Sensors and Actuators B 41 (1997) 81-87

[3] A. Schütze and T. Sauerwald, “Dynamic Operation of Semiconductor Sensors,” in Semiconductor Gas Sensors, 2nd ed., R. Jaaniso and O. K. Tan, Eds. .

[4] C. Schultealbert, T. Baur, A. Schütze, S. Böttcher, and T. Sauerwald, “A novel approach towards calibrated measurement of trace gases using metal oxide semiconductor sensors,” Sensors Actuators B. Chem., vol. 239, pp. 390–396, 2017,

[5] T. Baur, A. Schütze, and T. Sauerwald, “Detection of short gas pulses for trace gas analysis,” Tech. Mess., vol. 84, no. s1, 2017, doi: 10.1515/teme-2017-0035.

[6] D. Rüffer, F. Hoehne, and J. Bühler, “New digital metal-oxide (MOx) sensor platform,” Sensors (Switzerland), vol. 18, no. 4, 2018