

# Chemoresistive Sensors: A New Approach to Understand the Detection Mechanism of Biogenic Gases

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## Summary:

This work aims to provide a novel approach to better understand the detection mechanism of chemoresistive gas sensors for complex volatile compounds, such as biogenic gases. The chemical species formed during analyte-sensor interaction on the sensing layer surface were investigated through *operando* diffuse reflectance infrared Fourier transform spectroscopy. Chemisorption analyses further improved the understanding of the sensing mechanism and material selectivity by characterizing the acid-base nature of the active sites of the functional layer.

**Keywords:** chemoresistive gas sensors, *operando* analyses, sensing mechanism, complex VOCs detection, chemisorption analyses

## Background, Motivation and Objective

Chemoresistive sensors, such as metal oxide (MOX) semiconductor-based gas sensors, belong to the class of electrical sensors and the interaction of the gas with the receptor unit is based on reversible redox processes over its surface. The interest in chemoresistive sensors has grown over the years because robustness, sensitivity, cost-effectiveness and small size make them attractive for a wide range of applications, including emerging technology for the Internet of Things.

Over the past decades, *operando* approaches, surface studies, and theoretical simulations have shed light on the surface processes that drive the gas sensing responses [1] for small molecules, such as NO<sub>2</sub>, CO, H<sub>2</sub>, O<sub>3</sub>, and more deeply investigated the intermediate reactions of sample VOCs, such as ethanol, acetone and acetaldehyde. Nevertheless, these sensors can also detect more complex VOCs, such as biogenic gases (with a mostly natural origin) like terpenes. These gases have functional groups with different characteristics, making it challenging to comprehend their interaction with the sensing surface.

The motivation for the present work is to employ a novel approach to understanding the detection mechanism of complex gaseous mol-

ecules, that combines the investigation of surface chemical species formed during the analyte-sensor interaction through *operando* diffuse reflectance infrared Fourier transform spectroscopy (DRIFT) with the characterization of MOX active sites via chemisorption analyses. The latter can be used to understand the selectivity of a specific MOX compared to other materials.

Limonene has been used as a case study, as it is a biogenic gas belonging to the class of terpenes. It is widely exploited in the food and beverage industry, as a flavoring and preservative element, or in beauty and personal care products, in household products, and as the active principle in ecological pesticides. It is a VOC, with a time-weighted average threshold limit value (TLV-TWA) of about 30 ppm. As a result, sensors for in-situ and real-time monitoring of limonene leakage in industrial settings are required. The optimal material for limonene sensing was selected among seven nanostructured MOXs based on WO<sub>3</sub>, ZnO and SnO<sub>2</sub>, synthesized through different strategies for their functionalization, which were used to produce thick film sensors.

## Description of the New Method

FTIR spectroscopy investigates the fundamental molecule vibrations by exploiting the mid-infrared (mid-IR) radiation. In DRIFT configura-

tion, it is one of the most advanced and effective methods to analyze rough surfaced solid samples. Therefore, this technique has been used to characterize the chemical species formed over the surface of the sensing films in presence of limonene, while acquiring the sensors electrical response, namely, in *operando*. Fig. 1 shows the gas test chamber collocated inside the sample compartment of a Vertex 70 IR spectrometer (Bruker) with a liquid-nitrogen-cooled MCT detector used to record the time resolved DRIFT spectra.

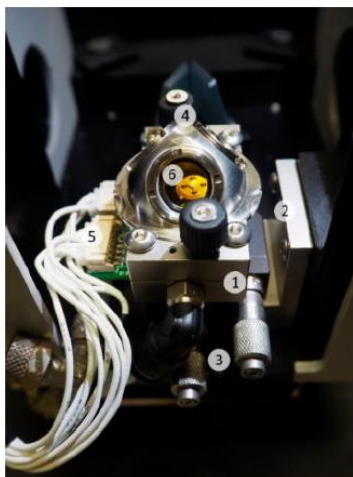


Fig. 1. Photo of the *operando* gas test chamber representing the main cell body (1), the cell support (2), the vacuum-compatible precision XY micro-stage (Standa) (3), the IR dome (4), the connection for electrical measurements via JST connectors (5) and a chemoresistive sensor (6). Reprinted from [2].

The sensor-gas interactions derived from *operando* DRIFT spectroscopy, and responsible for the device sensitivity, were induced by the reactivity of MOX active sites. Then, for the best performing material, were carried out experiments of temperature programmed reduction (TPR) with 5 % H<sub>2</sub>/Ar gas mixture (40 ml/min) and of temperature programmed desorption (TPD) with pure ammonia and CO<sub>2</sub>, in lab made apparatus with a Gow-Mac thermal conductivity detector (TCD). These analyses deepened the comprehension of the role of the acid-base nature of the active sites in the detection of limonene.

## Results

Between the seven nanostructured films based on different MOXs, the WO<sub>3</sub>-based one turned out to be the most suitable for the development of chemoresistive limonene sensors operating at low temperatures, demonstrating good sensitivity, cross-selectivity, and humidity-independent behavior for concentrations higher than 20 RH% [3]. The DRIFT absorbance spectrum (Fig. 2b) acquired during exposure of 2 ppm of limonene Fig. 2 (a) showed many peaks

attributed to different molecule bonds over the surface of WO<sub>3</sub>. *Operando* DRIFT analyses in the presence of humidity and probe molecules were also performed for completeness. Chemisorption analyses confirmed the mainly acidic nature of WO<sub>3</sub> active sites, contributing to the sensing mechanism proposal that will be described in the presentation.

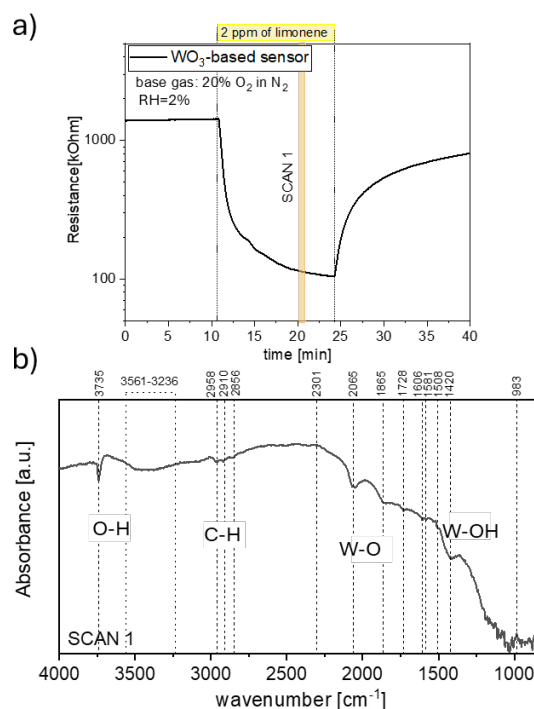


Fig. 2. (a) Resistance of WO<sub>3</sub>-based sensor self-heated at 200°C, before and after exposure to 2 ppm of limonene. The yellow bar evidenced the period during which the AB spectra shown in (b) was acquired.

## References

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