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A portable air-quality station based on thick film gas sensors for real time detection of traces of atmospheric pollutants

A Fioravanti[1,2], A Bonanno[1], S Gherardi[3], M C Carotta[3] and A N Skouloudis[4]

[1] CNR-IMAMOTER Ferrara, Via Canal Bianco 28, FE, Italy
[2] Dipartimento di Chimica, Università di Parma, Parco Area delle Scienze 17A, PR, Italy
[3] Consorzio Futuro in Ricerca, Via Saragat 1, FE, Italy
[4] Institute for Environment and Sustainability, JRC, European Commission, VA, Italy

E-Mail: a.fioravanti@imamoter.cnr.it

Abstract. Different functional materials, single or mixed nano-crystalline semiconductor oxides, were synthesized via appropriated wet-chemistry routes. The powders were used to fabricate metal oxide (MOX) thick film gas sensors. Portable monitoring stations based on the aforementioned sensors were prepared, including electronics for acquisition, processing and wireless transmission of the data. Results of long term trials in field, carried out locating few units closely to as many conventional fixed-site monitoring stations, have been reported. The comparison was performed between the temporal evolution of the conductivity changes of the sensors with the pollutants' concentrations, as measured by the analytical instruments.

1. Introduction

Several EU directives [1,2] limit anthropogenic emissions of air pollutants. Despite such regulations, air pollution continues to damage human health and the environment with a significant proportion of the European urban population is still exposed to concentrations above limit values.

Atmospheric pollution monitoring is today performed by means of traditional analytical techniques in few fixed-site stations in urban areas. The equipment used is cumbersome and expensive, also requiring frequent maintenance and calibration. Thereby, low cost, portable and versatile equipment is an issue. The technology of thick film gas sensors is an optimal candidate to be implemented in such a device. However, the sensors have to measure traces of gases in the atmosphere with sensitivity and selectivity comparable to those of the analytical instruments. This achievement implies a careful coordination of all different processes involved, such as functional material preparation and its morphological and structural characterization, deposition of sensing layers, fabrication of optimal substrates, and electronics.

Aim of this work is to demonstrate that it is possible to determine with good precision and accuracy the pollutants' concentration in the atmosphere using specific sensors, if the aforementioned characteristics are optimized. To detect the various pollutants, thick film gas sensors, based on specific functional

materials, have been prepared and investigated with relation to the gases to detect, taking into account for each material the main interfering gases.

2. Experimental

2.1. Preparation and characterization of nano-ceramic materials

Wet chemical methods for powder synthesis have been investigated to prepare functional materials in form of nano-crystalline powders to obtain a high surface to volume ratio needed to amplify the gas response [3]. Simultaneous thermogravimetry and differential thermal analysis was carried out to study the conversion of precursors to oxides. Scanning or transmission electron microscopy and X-ray diffraction were used to analyze the morphology and the crystalline structure.

Passing to the specific materials, a $Ti_xSn_{1-x}O_2$ solid solution (hereinafter named TS) has been adopted to detect CO, due to the maximization of the response at a specific Ti molar ratio [4]. To detect BTX (benzene, toluene, xylene) the material is a solid solution of titanium, tantalum and vanadium (hereinafter named TTV), as described in [5]. For nitrogen oxides detection, the sensor has been prepared using iron lanthanum oxide [6]. To detect ozone, a sensor based on tungsten trioxide (hereinafter named W) has been used. The synthesis of this material and its microstructural characterization are described in [7].

2.2. Fabrication of thick film gas sensors

Through screen printing technique, the sensing film, the interdigitated contacts and the heater element are deposited on the same substrate. To print the sensing layers, a viscous paste must be prepared by adding to the functional material an organic vehicle and a small amount of a bonding agent to promote the film adhesion to the alumina substrate. After the printing, the thermal processes of drying (150-200 °C) and firing (650-850 °C) give to the film the desired electrical and micro-structural properties.

2.3. Laboratory electrical characterizations

The sensors were placed in a sealed test chamber, equipped with temperature and humidity sensors, maintained at a fixed ambient temperature of 25 °C. The flow-through technique was used to perform conductance measurements maintaining a flow rate of 0.5 l/min using synthetic air as carrier gas in dry or wet ($0 < RH < 60\%$) conditions. Dynamical responses of sensing films were obtained in presence of mixture of different gases by varying the operating temperature from 350 to 650 °C. The sensor response is defined as ratio between the conductance in presence of the target gas and the conductance in air.

2.4. In field electrical characterizations

Arrays of thick film gas sensors, assembled in small remotely controlled units, were used for on-site tests. They consist in small boxes to lodge the sensors, the electronic circuitry of each sensor and a main electronic control unit. The data are recorded in a data logger and transferred via GSM to an input data server. The sensor responses were studied in comparison with the pollutant concentrations as measured by the analytical instruments of fixed-site monitoring stations. In particular, IR and UV spectrophotometers for carbon monoxide and ozone, chemiluminescence analyzer for NO_x and gas chromatograph for BTX.

3. Results

3.1. Laboratory electrical behavior

For all sensors, conductance measurements as a function of operating temperature, in presence of a gas concentrations suitable for environmental monitoring, were performed to determine the best working temperature for each sensor. The measurements to determine the dependence of the conductance on the

gas concentration verified for all reducing gases the power law: $G_{gas} = G_{air} + \alpha C^{\beta}$, where G_{gas} is the conductance in presence of the test gas, G_{air} the conductance in presence of air, α is a constant depending on the measurement units, C is the gas concentration and β is a positive number. The result agrees with the theory of power laws for semiconductor gas sensors developed by Yamazoe and Shimanoe [8].

Electrical stability and repeatability are crucial features for sensors' performance to operate in long term trials. Some features of screen-printing technology, such as the high firing temperature or the opportunity to fabricate in one batch a lot of sensors, are crucial for making them the most reliable among the various kinds of MOX sensors. The experiment of the figure 1 highlights the good repeatability of a TTV sensor, alternately subjected to the two concentrations of 100 and 800 ppb of benzene for 24 hours.

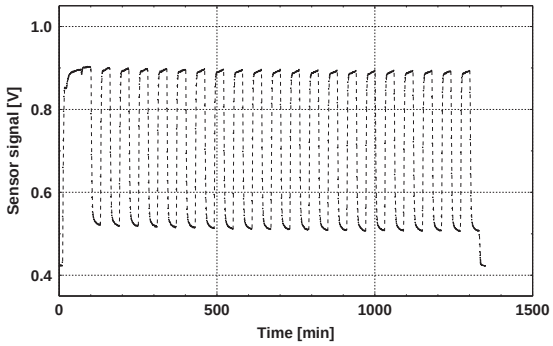

Figure 1. Alternate response of a TTV sensor to 100 and 800 ppb of benzene. The duration of a whole response is 1 h, the duty cycle is 50%.

It is well known that the water vapor partial pressure is the main interfering gas for MOX sensors. This is an important problem especially for carbon monoxide, when it is detected through a tin oxide sensor, as often the literature reports [9]. However, the problem can be approached in two ways: i) to develop functional materials with poor water vapor adsorbability, as in the case of TS sensors; ii) to compensate the signal due to overestimation caused by humidity as described in [10].

3.2. In field experiments

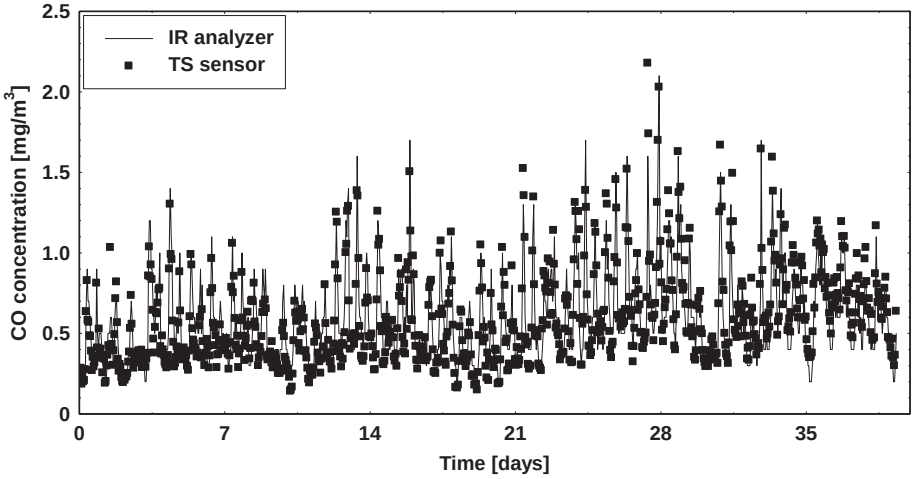

Figure 2. Forty days monitoring of carbon monoxide concentrations measured through a TS sensor and an IR analyzer.

In the figure 2, a comparison between the CO concentrations evaluated through a TS sensor and the measurements of an IR analyzer is reported. Due to the low influence of humidity on TS sensors, it wasn't necessary to compensate the sensor signal, although the low carbon monoxide concentration detected during the monitoring. An experiment devoted to test the reliability of sensors is reported in the figure 3. Two identical monitoring units were located beside a fixed-site monitoring station. Here, the behavior of the two W sensors toward ozone is reported during a monitoring two weeks long. It can be observed that the two sensors exhibited the same trend as well as the same behavior of the conventional analyzer.

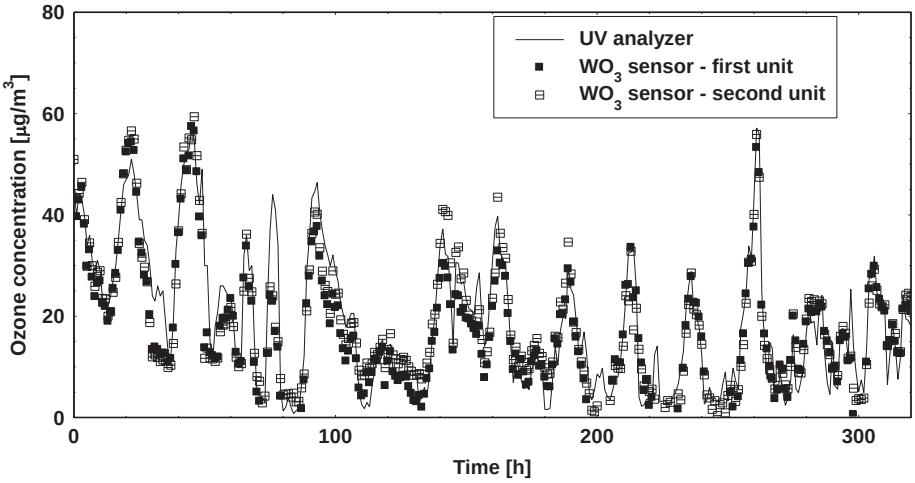

Figure 3. Comparison between the measurements of ozone carried out through two −nominally identical− W sensors and an UV analyzer.

4. Concluding remarks

Arrays of nanostructured thick film gas sensors based on different semiconducting oxides have been successfully used to detect atmospheric pollutants with the same trend observed by the conventional analytical techniques. The proposed instrumentation, due to its portability and low cost, can offer the possibility of enhancing the capacity to protect the population from air pollution and assess health risks.

5. References

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