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Tin dioxide gas sensor as a tool for atmospheric pollution monitoring: Problems and possibilities for improvements

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The monitoring of atmospheric pollution needs network of gas sensors in order to increase the number of measuring points. For this goal, tin dioxide sensors have been evaluated. Their potentials and limitations (selectivity and stability), are presented via on-site experiments of urban pollution control. The study shows that some global information indicating mainly the traffic pollution can be obtained. The general problem of long-term stability and selectivity of SnO_2 sensors is discussed. Some specific solutions are proposed, for example, a chemical treatment in the case of instability due to SO_2. The problem of the dual response to oxidising and reducing gases is discussed, especially in regard to CO/NO_2 detection. To solve this problem, the use of active filters is proposed. For example, a thin film of rhodium deposited above the sensing material allows to filter NO_2. The use of a platinum filter has also been applied to improve the selectivity for the reducing gases. The results point out the difficulty to control this type of device in thin film technology. On the contrary, with thick films obtained by screen-printing, the possibility to separate HC from VOC (CH_4 from CO and C_2H_5OH) is demonstrated. Some preliminary results concerning the use of a MnO_2 filter are also presented in order to control the ozone reaction. The possibilities offered by signal processing are finally discussed using a multi-variable approach with 90 days aged sensors. AC measurements are exploited to improve the selectivity for the oxidizing gases NO_2 and O_3. The results obtained with a model built with atmospheric air as carrier gas appear promising. © *2003 Kluwer Academic Publishers*

1. Introduction

Following the new EU directive [1], air quality prediction appears as an urgent need that explains the great emphasis for atmospheric transport and dispersion models [2]. These models must take into account many parameters such as meteorological conditions and relief [3]. For some particular applications, for example urban air quality modeling, more local conditions must be also considered, especially the frame of the town, its infrastructure and the traffic. Effectively, in order to have a better understanding of pollution creation and of the movement of the pollutants, it becomes necessary to study the spatial distribution of the pollution and consequently to increase the number of measurement nodes [4]. Due to this complexity, it is important to have data to develop the models but also to check their quality. In reality, the measurements for urban air pollution are performed by the networks, thanks to stations equipped with selective analysers for many pollutants. Although these stations are very reliable, it is unrealistic to see an increase in the number of measurement nodes because of the high cost of acquisition and maintenance of such stations and equipment. An alternative solution would be to use low-cost chemical micro-sensor arrays and distribute them across the network and to validate the models [5–7].

Contrary to specific analysers using physical properties (for example UV and IR spectroscopy), the micro-sensors are based on physico-chemical principles. Usually, their sensitivity is sufficient for most of the applications, but their selectivity is often only partial and this constitutes the main limitation for applications requiring a selective detection of one constituent. However, by considering the low-cost and the miniaturization of a micro-sensor compared to an analyser and the possibility to use sensor networks to multiply the information, chemical micro-sensors can sometimes constitute a cheaper alternative or a complementary technique for gas detection depending on the application requirements.

In the case of urban pollution, the pollutant gases are mainly CO, NO_x (NO and NO_2) and HC (mixtures of burned and unburned hydrocarbons). The challenge for the development of gas sensors is becoming increasingly important with the requirements of the car manufacturers to use such devices directly in the cars. Many applications are currently being considered. On one hand, there is a need for monitoring the air quality in the passenger compartment with a control of the ventilation by filtration of the incoming air in case of pollution [8–10]. On the other hand, it becomes necessary to measure the gas concentrations directly in the exhausts for combustion control [11]. This latter aspect is strategically more important for the car manufacturers because sensors are needed for the control of the engine, as well as the control and diagnosis of the different devices used for post-treatment (OBD II rules) [12].

In both cases, urban pollution and automobile applications, the main gases to be detected are the ones previously mentioned (CO, NO_x, and HC), but also some other gases like SO_2, CO_2, O_3. The sensors must be low-cost, should have high sensitivity, and be stable and selective. The two last requirements are generally more difficult to satisfy at the moment and they constitute the main limitations for the use of gas sensors. There is a current effort to develop and to use chemical micro-sensors for the atmospheric pollution control. The research and development are primarily focused on CO sensors [13, 14], NO_x sensors with a special attention to the dual response between oxidizing and reducing gases, HC and VOC sensors and more recently the CO_2 sensors. The problem of SO_2 detection seems now less important compared to 1980's situation, taking into account the reduction of sulphur content in fuel [15]. For the CO_2 detection, which is becoming more and more important in relation to the global warming, the studies are mainly focused on the potentiometric sensors based on ionic materials like β-alumina [16] NASICON [17], and more recently LIPON [18].

Among the various types of micro-sensors (catalytic, electrochemical or potentiometric, semiconductor, etc.), the semiconductor sensors based on tin dioxide are the only sensors (except the oxygen sensors based on YSZ for automotive applications), which have been commercially well developed. Nevertheless, their use is limited because of their dual response: decreasing response (electrical conductance of the material) with oxidizing gases and increasing response with reducing gases [19]. This is particularly the case for automotive applications where high concentrations of CO and NO_2 can be simultaneously present. To solve this problem, several types of sensing materials are currently being studied. For example, it has been recently proposed to use perovskite films [6] for the separation of NO_2 and CO contributions for environmental monitoring, or InP resistive structures [20] for the monitoring of oxidizing gases such as NO_2 and O_3 in environmental pollution, or FET structures with Au and Pt films for O_3 detection [21]. For pollution control, the problem of the detection of ozone becomes a key point. For oxidizing gases, and especially for ozone, WO_3 is a material which presents interesting sensing properties with regards to interfering reducing gases, for example, for O_3 detection [22] or for NO_x detection [23]. WO_3 is also proposed for the combined detection of reducing gases NH_3 and NO [24].

For air quality monitoring, there are several studies dealing with the improvement and use of tin dioxide gas sensors. For example, the doping by Pd [25] or by Au and Pt [26] can be used to differentiate CO and NO_x. Of course, the multi-sensor devices also offer some interesting possibilities for these differentiations. The combination of SnO_2 sensors for CO and In_2O_3 sensors for NO_2 has been proposed [27] for the air quality monitoring in cars (flap regulation) and more recently an array using SnO_2, TiO_2 and In_2O_3 sensing materials has been developed for atmospheric pollutant monitoring [28]. Even if tin oxide sensors suffer from poor performance compared to analytical techniques like gas chromatography or IR and UV spectrometry, these types of sensors will be certainly used in the future for various applications in connection with pollution control, especially in order to develop networks of low-cost sensors with an increased number of measuring nodes. Tin oxide sensors are the only one currently being marketed (e.g., Japanese products by Figaro or Nemoto, European products by MiCS, Capteur or UST, etc.). This fact will certainly contribute to the real development of applications with such sensors. In this sense, it is important to test and evaluate the potentials of tin oxide sensors for atmospheric pollution control, as well as their limitations.

The aim of this paper is to show the potentials of tin oxide micro-sensors for air pollution measurements and several possibilities to improve their performances. The results of on-site experiments concerning traffic pollution monitoring in urban roads, tunnels, city centre are presented. The problem of long-term stability is discussed. The use of filters to improve the selectivity is presented with various examples in relation to the pollution control, especially for the dual detection of oxidizing and reducing gases. Finally, new possibilities offered by the signal treatment is discussed, in particular the AC measurements and the exploitation of the argument of the conductance versus the AC frequency.

2. On-site experiments for urban pollution control

2.1. Tin dioxide sensors preparation and laboratory tests

Tin oxide sensors are *n*-type semiconductor materials with an electronic conductivity which depends on the nature of the surrounding atmosphere and temperature. The resistance variation is the result of the chemisorption of the gas on the material surface. With an *n*-type semiconductor, such as SnO_2, for which the main charge carriers are electrons, the adsorption of a reducing gas donates electrons, and thus increases the electrical conductivity. On the contrary, an oxidant gas, such as NO_2, will lead to a decrease of the conductivity. The charge transfer between the gas and the material requires the gas ionisation and thus a good catalytic activity of the sensing material. The selectivity depends on the sensor temperature and on all the chemical processes on the surface of the sensing material. Consequently, the performance of this type of sensors depends on the microstructure of the sensing materials and on the technology used for heating the substrate.

The micro-sensors used in the first part of this study for on-site experiments are constituted of a tin oxide bar

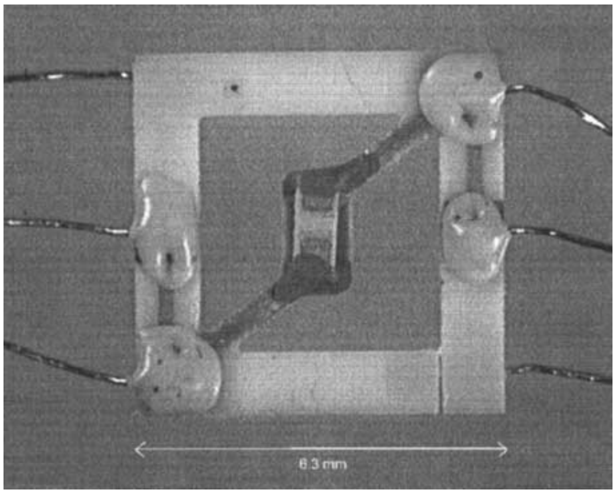


Figure 1 Photograph of the sintered sensor on an alumina substrate.

($1 \times 0.5 \times 0.2$ mm^3) obtained by sintering of tin oxide powder compact. Two gold electrodes are deposited by screen-printing on this bar in order to ensure good electrical contacts. The resulting sensing element is attached with gold paste on a heating substrate made of alumina. The heater is a screen-printed platinum resistor deposited on the back side of the alumina substrate and the whole sensing element is inserted in a casing (Fig. 1). The sensor is monitored by an electronic card which performs the thermal regulation in the range 20–500°C and which can deliver a signal proportional to the conductance of the sensor. These sintered sensors and the electronic unit have been developed in collaboration with a French company [29, 30].

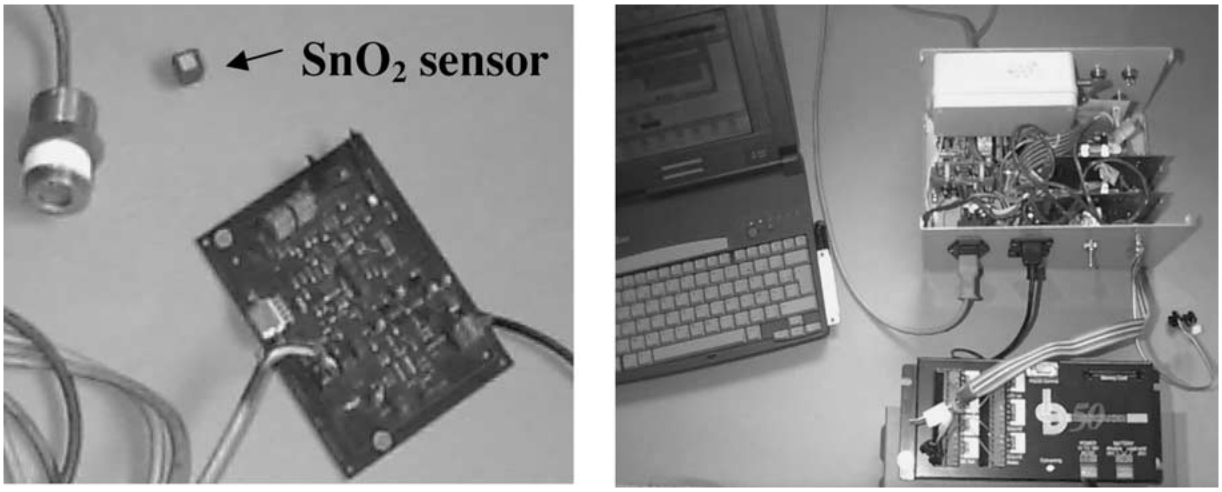
Laboratory test benches allow the characterization under various gases (carbon monoxide, methane, ethanol and also nitrogen oxides) of the different types of sensors after their fabrication. A portable device ($300 \times 250 \times 200$ mm^3) has been developed for on-site experiments. It includes two gas sensors with their own electronic circuits, a pump for the gas circulation and a data recorder (Fig. 2). The system, which can work either with a 220 V AC or 12 V DC supply, is self-contained and can be easily set on various sites for measurements. The data recorder has a capacity of 12000 points, sufficient for example to record 4 signals during 1 month with a 1/4 h frequency. The data are then transferred to a computer to be analysed in the laboratory.

Typical responses of the sintered sensors on a laboratory test bench to ethanol (50 ppm in air), carbon monoxide (300 ppm in air) and methane (1000 ppm in air) are shown in Fig. 3, which represents the variation of the conductance versus the sensor temperature. The gas flow is set at 5 l/h and cycles consisting of an isotherm at 500°C for 30 min and a decrease of the temperature to 20°C in 5 min are performed for each gas. The conductivity measurement is performed during the temperature decrease via an electrical circuit. These tests are performed to control the sensor behaviour. It is noted that the sensor is not selective as it gives responses to all gases. However, the sensitivity for each gas depends on the temperature. It is maximum at 500°C for methane (representative of hydrocarbons) and at around 320°C for carbon monoxide. Consequently, it is possible to modify the selectivity by adjustment of the operation temperature.

2.2. First set of on-site experiments (city of Lyon, 1988)

SnO_2 sensors have been used for experiments in city environment with the first set of experiments in Lyon about fifteen years ago. The sensor was placed directly along a street in the downtown and also in a road tunnel. The signal was recorded and compared with the response of an IR analyser used for CO measurement. Over a period of one day, two peaks of pollution were generally observed corresponding to the maximum traffic of cars in the morning and in the evening rush hours. The typical curves recorded during this first set of experiments have previously been reported [31].

The correlation between the gas sensor and the IR analyser is very good (Fig. 4) and shows potential of such sensors for monitoring of the urban pollution.



(a) (b)

Figure 2 (a) Photograph of a sensor with its casing, a ADF head and electronic unit and (b) Photograph of the portable device including 2 sensors, a data recorder and a PC to transfer data.

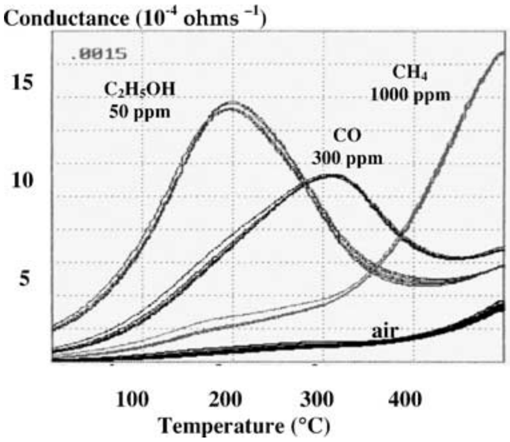


Figure 3 Response (conductance Ω^{-1}) versus temperature of a sintered sensor on a laboratory test bench in air, ethanol (50 ppm in air), carbon monoxide (300 ppm in air), and methane (1000 ppm in air).

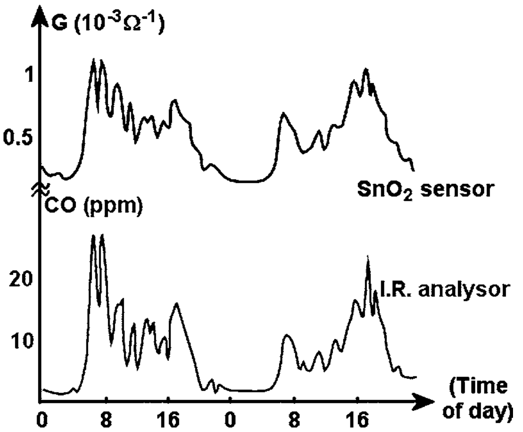


Figure 4 Correlation between the response of a sintered SnO$_2$ sensor and CO concentrations measured by an IR analyser during the Lyon experiments (1988).

On the basis of such correlation, a possible conclusion could be that the sensor is selective to CO. In fact, it has been proved that all the gases are produced by the cars with the same ratio. When the CO concentration increases, the concentrations of the other gases increase also in the same ratio. As a consequence, even if the sensors are not completely selective for CO, their response constitutes a good measurement for the intensity of the urban pollution due to the traffic. Similar experiments have also been performed in a road tunnel with the same type of devices. The only difference is the range of CO concentrations which are higher in the tunnel: from 20 to 200 ppm in the tunnel against 1 to 20 ppm on the street. Concerning the interfering gases, it can be noticed that no difference is observed between the two sites: the two sets of measurements are in good agreement with a cross-over near 20 ppm (Fig. 5).

2.3. Drifts of SnO$_2$ sensors and solution to stabilize the sensors

On top of poor selectivity, poor stability of tin dioxide sensors is a major limitation for their use in industrial applications. The drift observed can be the consequence of various phenomena such as the morphological evolution of the sensing material (grain growth) or chemical irreversible reactions of some gases. During the first set of experiments in the city of Lyon, such instabilities of the sensors were observed. They were believed not to be connected to the morphological evolution because the sensors were aged before their use for several weeks in the laboratory test bench. The drift was observed in both applications (street and tunnel) and the evolution was always an increase of the conductance of the sensors in the range of 20 to 50% over a period of one month. An example is reported in Fig. 6 for a tunnel experiment: after 20 days the signal of the sensor is multiplied by a factor of 4.

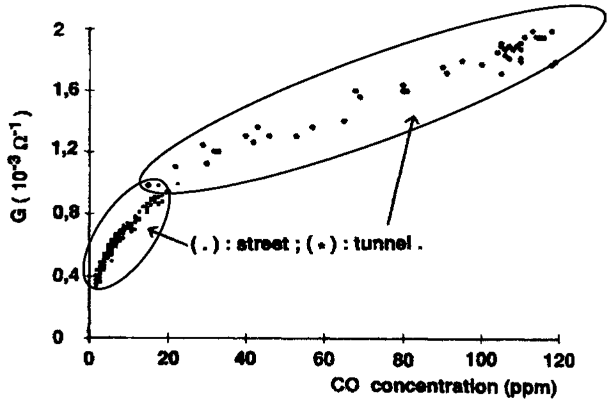


Figure 5 Response of a sintered SnO$_2$ sensor versus CO concentration for road (0–20 ppm) and tunnel (20–200 ppm) during Lyon experiments (1988).

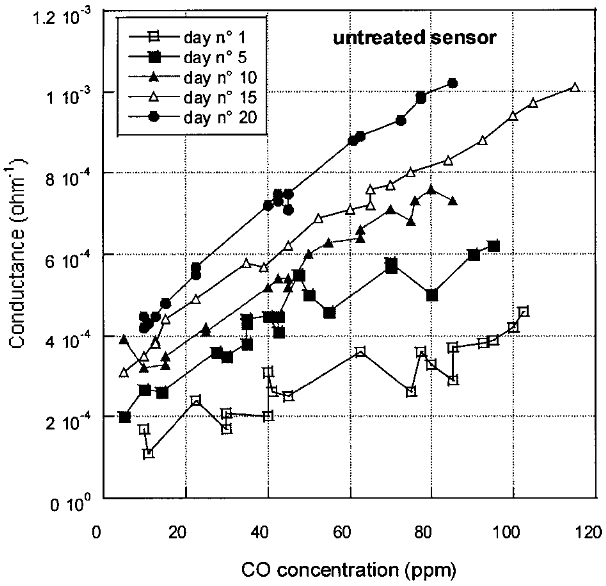


Figure 6 Instability of the signal (increase) of a pure sintered SnO$_2$ sensor during experiments in a tunnel (for 1 month in Lyon, 1988).

After ageing in streets or tunnel, the sensing materials were analysed with different chemical analysis. The major results have been obtained with TPD (Thermal Programmed Desorption): some sulphate species are present on the surface of the tin dioxide only for the aged sensors. These species are certainly the consequence of the irreversible reaction of SO$_2$ [32, 33] which is always present is the atmospheric pollution, even if the concentrations are very low (generally less than 1 ppm).

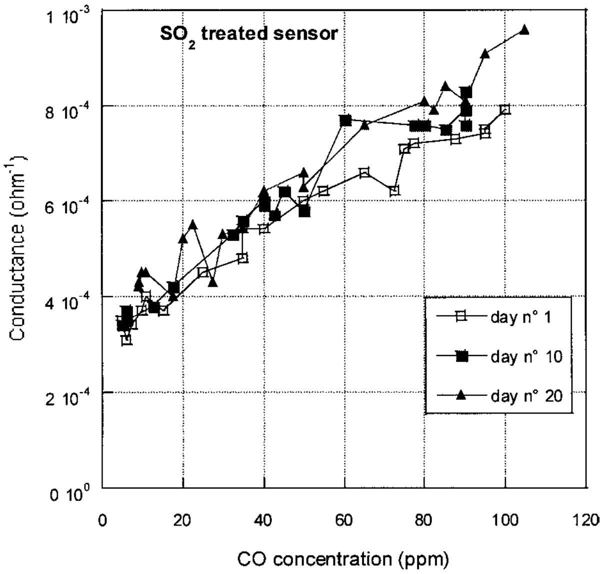


Figure 7 Stability of the signal of a SO_2 pre-treated SnO_2 sensor during experiment in a tunnel (for 1 month in Lyon, 1988).

To confirm this irreversible effect, complementary tests were carried out in the laboratory bench with SnO_2. Even at a high operation temperature (500°C), the continuous pollution of the air by 0.5 ppm SO_2 produces an irreversible increase of the sensor signal (50% after 5 days under a flow of 50 cc/mn).

In order to avoid such instability, the sensors were pre-treated in SO_2 before their use. Such a gaseous treatment had been used in the past to improve the stability (and also the selectivity) of sintered tin dioxide sensors, especially with respect to the effect of humidity. For the tunnel experiments, a typical result obtained with a pre-treated sensor is reported in Fig. 7. Such sensors are very stable compared to the untreated sensors. It was verified that the effect of the pre-treatment is stable and no drift was observed for a 6-month period with these sensors.

2.4. Second set of on-site experiments (city of Saint-Etienne, France in 1998)

A new set of on-site experiments were conducted in the center of another city (Saint-Etienne) in collaboration with AMPASEL association (*Association de Mesure de la Pollution Atmosphérique sur l'agglomération de Saint-Etienne et le département de la Loire*), which is in the network of pollution control node in France. The portable device described previously was put inside a station of the network and connected at the outlet of the analysers (CO, NO, NO_2, SO_2). Thus, the pollutant concentrations determined by the analysers could be compared with the sensor signal. Two measurement campaigns were conducted from May 20th through June 10th and from August 11th through 31th in 1998. Two sensors were set under the same conditions at 320°C and their signals were recorded every 10 min. These signals were issued from the electronic card (analog output in millivolts) and were not calibrated, but the comparison of their relative variation was possible. A good reproducibility between the two sensors was observed during both the measurement periods. This is illustrated in Fig. 8, which shows their signals of two different days of the first campaign (May 28th and June 5th).

Sensor signals and values of the mean hourly concentrations of CO, NO, NO_2 measured by AMPASEL can be seen in Figs 9 and 10 over the two campaign periods of three days (26–28 May, 16–18 August). The experimental curves representative of the sensor signal were computerized with a period of ten minutes and were not smoothed. This explains the noisy aspect of the sensor signal compared to the curves representative of the gas concentrations which are a mean concentrations over one hour.

It can be observed that the variations of the concentrations of the three gases (CO, NO, NO_2) are qualitatively very similar. As mentioned for previous experiments close to an urban street, when the pollution is mainly the result of the traffic, all the gases are produced with similar ratio. This is the case for the pollutants measured in this station situated in the city centre, close to an important street. Moreover, a close correlation between the pollutant concentrations and sensor responses can be established from Figs 9 and 10. This good agreement is obtained over the whole measurement period of the two campaigns. The response time of the sensor is in the same range of that of the analysers (checked in laboratory test bench). It is also possible to detect without any problem short pollution peak such as the ones observed on August 17th (Fig. 10).

Contrary to the results obtained during the past first set of tests in Lyon, no particular problems of stability were noted over the duration of these campaigns (23 and 21 days) although the sensors were not pre-treated. The correlation between the CO concentration and the sensor signal can be seen in Fig. 11, which represents

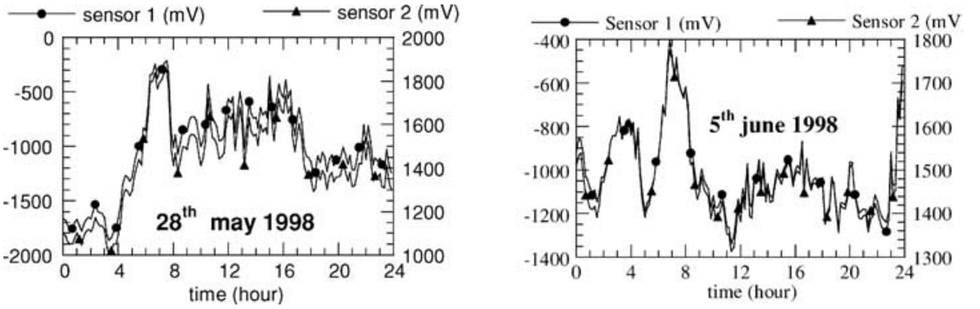


Figure 8 Reproducibility of the signals (acquisition period of 10 min) of two sensors over 24 h for 2 days of the campaign of measurement in the centre of Saint-Etienne.

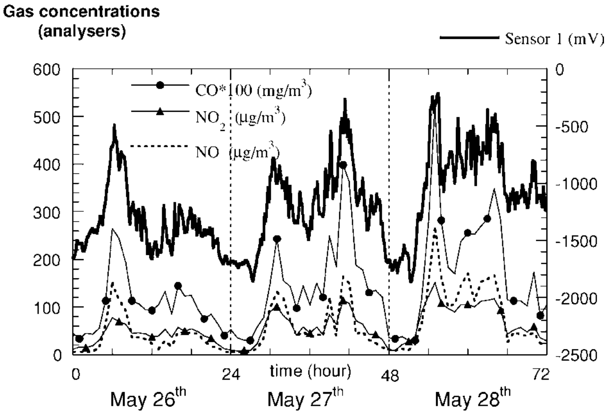


Figure 9 Comparison of gas concentrations (CO, NO and NO_2) determined by gas analysers of AMPASEL station and of the sensor signal for the period from 26 to 28 May, 1998.

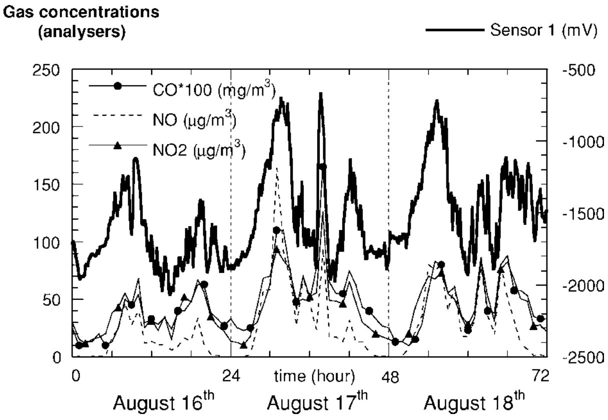


Figure 10 Comparison of gas concentrations (CO, NO and NO_2) determined by gas analysers of AMPASEL station and of the sensor signal for the period from 16 to 18 August, 1998.

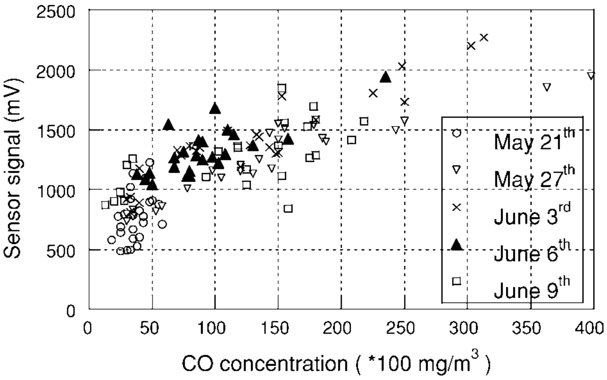


Figure 11 Correlation between CO concentration (IR gas analyser) and the sensor signal (mV) for 5 days of the measuring campaign in Saint-Etienne centre (1998).

this correspondence for different days during the 1998 campaign. No major drift in signal is observed. The sensors were very similar for the two sets of experiments, especially for the sensing material, which was a small bar of sintered material prepared from the same commercial tin oxide powder. The difference in stability is certainly related to the SO_2 contamination of the urban atmosphere, which was higher in Lyon in 1988 than in St-Etienne in 1998. This fact can be explained by the differences of atmospheric pollutions for the two cities (many plants and big industrial companies near Lyon), but also certainly by the consequence of the reduction of sulphur contents in the fuel consistent with the regulations and legislations in the EC.

3. Selectivity improvement using gas filters and membranes

3.1. Dual response with CO and NO_x and rhodium filter solution

The difficulty to detect nitrous oxides with SnO_2 sensors is well known [34, 35]. The problem is related to the dual response of such metallic oxides to reducing or oxidizing gases [36, 37]: on one hand reducing gases (CO, HC, NO, etc.) increase the conductance of SnO_2 (*n*-type) and on the other hand oxidizing gases (NO_2 or O_3) decrease the conductance. Consequently in the presence of both types of gases the response signal of the sensor can be close to zero. Many authors have recently described this behaviour [34]. This is especially the case in automotive applications for the detection of CO or HC in the presence of NO_x and also for the detection of NO in the presence of NO_2 (or NO_2 in the presence of NO).

We have observed such dual response in past experiments for air quality control in automotive application with the goal to filter the incoming air in the passenger compartment when the pollution is too high (AQS application: Air Quality Systems). As a consequence of the results exposed in the previous section concerning the on-site experiments in cities, the response of SnO_2 sensors could be considered as a good indication of the CO concentration and consequently could be used with success for the AQS. Nevertheless, that it is not the case in the AQS experiments. When the car is directly placed behind a diesel car, the signal of the sensor is close to zero resulting from the presence of NO_2, even if the concentration is very low. This behaviour is due to the very large influence of NO_2 on tin oxide regardless of the sensor type (sintered, thin or thick films). An example is reported in Fig. 12 in the case of SnO_2 thin film sensors. These sensors are prepared by the deposition of a CVD film [38] on an alumina substrate equipped with a platinum heater on the other side. The response

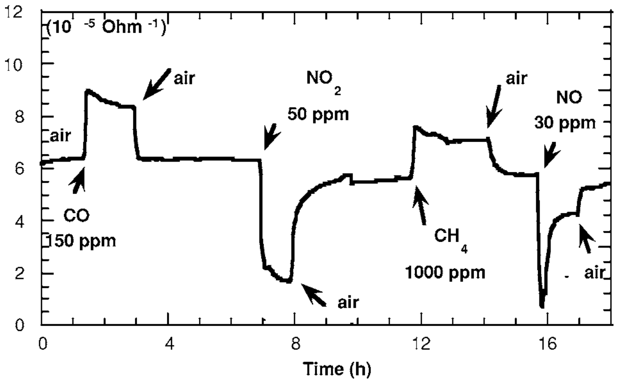


Figure 12 Dual response of a thin film SnO_2 sensor to oxidising (NO_2) and reducing gases (CO and CH_4). Special behaviour of NO resulting from a few ppm NO_2 in the NO injection.

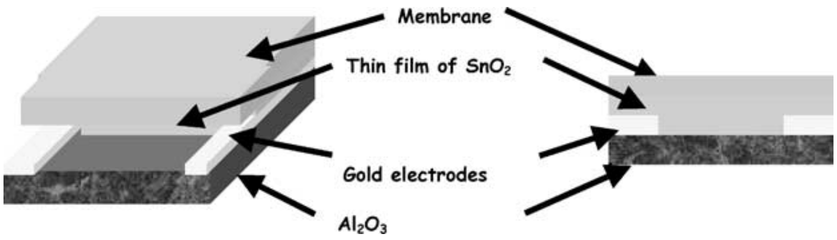


Figure 13 Principle of the use of thin film filter to improve the selectivity of sensors.

of such sensors is positive (increase of conductance) under CO (150 ppm) or CH_4 (1000 ppm) and negative under NO_2 (100 ppm). It is noted that under NO (30 ppm) the response is also negative, contrarily to the expected positive response. The reason is the presence of a few ppm of NO_2 in the flux of NO which are very difficult to avoid because of the very quick transformation of NO to NO_2 in air at ambient temperature (NO_2 is not stable above 450°C).

In order to improve the selectivity of tin dioxide gas sensors, we have started a research program several years ago, which consists of using filters above the sensing material [39]. With thin film gas sensors it is possible to filter the gases near the surface by the use of porous films deposited directly onto the sensing material (Fig. 13). These filtering layer can be either metallic films with catalytic activity or porous ceramics (Al_2O_3, SiO_2, Si_3N_4, etc.) with permeation ability. Some interesting results have been obtained with platinum or palladium films deposited above tin oxide films to improve the selectivity for the detection of CO or CH_4 and especially to reduce the sensitivity to C_2H_5OH. Previously, we have published studies for H_2 detection with SiO_2 filter [40] or the methane detection with a Pd filter [41], and more recently those with catalytic filter on Ga_2O_3 sensors [42] or thick film of Pd on SnO_2 sensors [43].

A similar approach can also be used to solve the problem of the dual response to the NO_x gases. The objective is to avoid or to reduce largely the negative response to NO_2 in order to be able to use the SnO_2 sensors in automotive applications to control the pollution, for example by measuring the CO and NO concentrations. The choice of the metal for the filter has been based on the catalytic metals generally added in catalytic converters to transform the gases and reduce the pollution after the exhausts. A part of these results has been previously reported [39]. These experiments have been realized with tin oxide thin film sensors covered with very thin films of various metals. The experiments have been realised in laboratory tests bench equipped with IR and UV analyzers for the measurement of CO, NO and NO_2 concentrations. The metals are platinum, palladium, copper, molybdenum and rhodium. In fact some of them are in the oxide form according to the working temperature (Pd and Cu) or to the oxidation reaction (Mo). The best results were obtained with rhodium (Table I): the negative sensitivity to NO_2 is largely reduced and above all the sensitivity to NO remains positive although the gaseous phase contains some low ppm NO_2. To confirm this, further experiments were carried out with two sensors one with filter and the other without and the results are shown in Fig. 14. We can easily observe that the curve corresponding to the pure SnO_2 film shows the dual response to CO (positive) and NO_2 (negative). On the contrary, for SnO_2 film covered with rhodium film, the negative response under NO_2 is virtually cancelled while the positive response to CO remains constant.

TABLE I Sensitivities ($(G_{gas} - G_{air})/G_{air}$) of pure and covered with 10 nm rhodium SnO_2 sensors thin films to CO, NO and NO_2 at 450°C

Sensor/gas	CO 300 ppm	NO 150 ppm	NO_2 100 ppm
Pure SnO_2	+0.40	−0.68	−0.92
+Rh	+1.22	+0.1	−0.43

Such filters must certainly be optimized in order to be used in real industrial applications. There are several main difficulties to control their use. Firstly, such solutions can be proposed only with thin and thick sensing materials and consequently the problem is to control a multi-film structure, with all problems related to chemical diffusions. The other problem is the thermal stability of these complex structures and especially the control of the long-term catalytic activity of the material used as the filter. Similar to our studies, several other studies are currently in development for other types of applications, for example with success for domestic sensors [41]. Moreover, the future sensing devices will be certainly multi-sensor systems and the development of sensors with selectivity modifications using gas filters is completely in agreement with such objectives. Furthermore, we study membranes based on ceramic materials, which can be used only as a protective layer. For example, we have demonstrated with a potentiometric sensor that it can be used directly in automotive

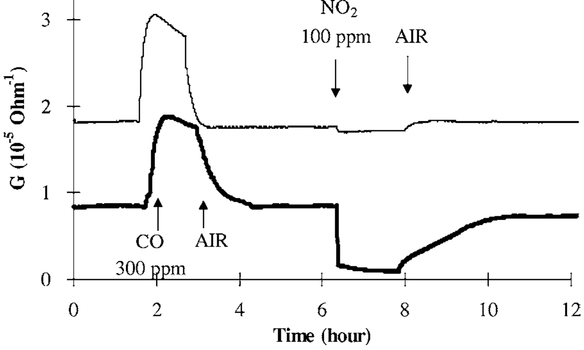


Figure 14 Comparison of the responses for a pure and a Rhodium (10 nm) covered SnO_2 thin films to CO (300 ppm) and NO_2 (100 ppm).

exhausts [44] with a thick porous alumina layer. The future objectives are to incorporate catalytic elements in thick film filters to obtain active membranes. We will develop in the next section some aspects of the difficulties and potentials of such filter solutions to improve the selectivity of sensors.

3.2. Some aspects of the selectivity improvement of SnO_2 sensors by superficial Pt films

Some correlation between the responses of SnO_2 gas sensors and the concentrations of CO, NO and NO_2 have been exposed in Sections 2.2 and 2.4 for on-site experiments. The problem of the dual response between CO and NO_2 has also been previously discussed. Nevertheless, and even if the contribution of oxidising gases could be removed, it is a well established fact that there are several reducing gases which contribute to the positive response of SnO_2 sensors placed in urban atmosphere. Of course, the CO contribution appears as the main contribution and this is clearly demonstrated with our on-site experiments reported above. But, it can be expected that several HC compounds, aliphatic CxHy, aromatic as BTX (benzene, toluene and xylene) or VOC, are also present in these urban sites and contribute to the electrical response of the sensors. In order to have a more selective response to these gases than to CO, we have applied filters for CO.

For this study, we have chosen to improve the selective detection of methane (representative of aliphatic HC) versus CO and C_2H_5OH representative of many VOC interfering gases. The catalytic activities of several metallic filters have been tested and platinum appears as the best catalytic metal for this gas separation. It is necessary to perform this study only with thin or thick films and not with sintered materials, both for the sensing material and for the filters. The first experiments were conducted with CVD film of SnO_2 and sputtered thin films of Pt (thickness between 1 and 50 nm). All experimental conditions were described in a previous paper [45]. The films were deposited onto several types of substrates: alumina for physical characterisations, porous ceramic substrates for catalytic activity and finally sensors substrates for validations. The catalytic activity of a very thin Pt film is reported in Fig. 15. The conversion rates for CO, C_2H_5OH and CH_4 are obtained with vertical catalytic reactor with gaseous transfer through the sample (thin film on porous ceramic substrate).

The measurements of the catalytic activity of Pt show that above 500°C, this metal is very efficient for the total oxidation of CO and C_2H_5OH, but CH_4 does not react. Consequently, this behaviour can be used for the selective detection of CH_4. The catalytic activity was correlated to the sensing properties of the $SnO_2 + Pt$ structure. Firstly, the membrane strongly decreases the sensor response to alcohol, which is in agreement with the catalytic tests. In the CO case, at high temperature (500°C), although Pt is very efficient in regards of CO oxidation, it does not strongly decrease the sensor response. A mechanism has been proposed, based on oxygen exchange between Pt particles and SnO_2 film during CO oxidation. On the other hand, at temperatures lower than 150°C, the Pt membrane induces a strong increase of the conductance under CO. We have shown that this electrical behaviour only results from Pt particles and not from SnO_2 thin film. Finally, the CH_4 response is slightly decreased, which is not in good agreement with the catalytic properties of Pt.

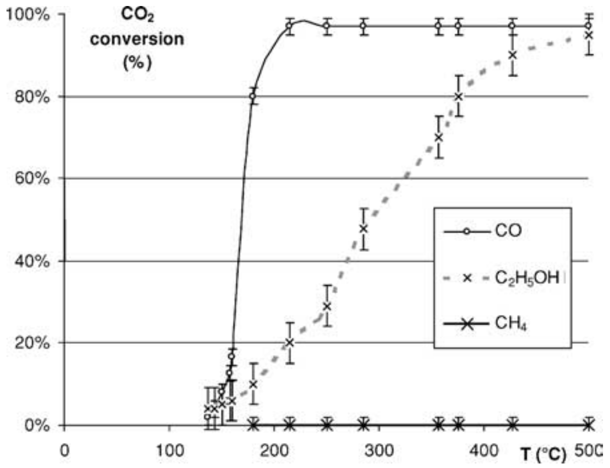


Figure 15 Catalytic activity versus temperature for a 1 nm platinum film under diluted gases in air (CO 300 ppm, C_2H_5OH 100 ppm and CH_4 1000 ppm).

For a small platinum layer thickness (10 nm) the conductance of SnO_2 film decreases with increasing platinum thickness. This effect is attributed to additional oxygen species on SnO_2, resulting from an enhanced oxygen dissociation by Pt. Above the thickness of 10 nm, the conductance of the film increases with the thickness. It could be interesting to increase the Pt thickness in order to increase the catalytic conversion. But, the electrical measurements have shown that the platinum membrane thickness has to be limited to avoid a short-circuit of the SnO_2. In conclusion, it appears that all phenomena occurring on these thin structures are very difficult to control and consequently to exploit for gas sensors. Finally, it was decided to use insulating layer between the sensing material and the platinum film. The objective was to separate the electrical effects occurring on the two layers with a ceramic film (Al_2O_3 or SiO_2). This also allows to increase the thickness of the platinum film without electrical short-circuit. Nevertheless, the realisation of complex structures (SnO_2-isulator-Pt) with thin film technology is very difficult to achieve, and the results were not reproducible. The final adopted solution was to use the thick film technology to produce both the sensing element and the insulating layer. Some details on the tin oxide thick film and on the sensor structure can be found in a previous publication [46]. Typical microstructures of SnO_2 and SiO_2 thick films can be seen in Fig. 16.

While metallic inks are commercially available, the inks for tin oxide and porous SiO_2 coating were prepared in the laboratory. Thick film inks were prepared by adding an inorganic binder (with low softening point) and a solvent to the inorganic powder (SnO_2: Prolabo France, SiO_2: Aerosil Degussa). The inorganic binder is usually used to achieve a reliable adhesion between the substrate and the thick film. All

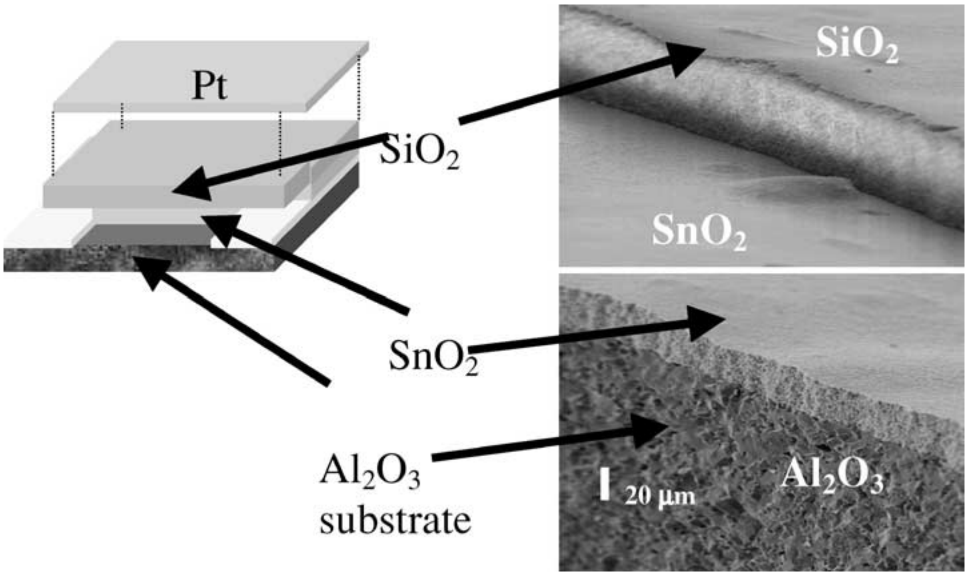


Figure 16 Thick film device with a SiO$_2$ insulating layer between thin platinum filter and thick film of SnO$_2$ (20 mm thick SnO$_2$, 40 mm thick SiO$_2$).

inks were screen-printed with an AUREL MOD C 890 screen-printer.

Rectangular (2 × 4-mm^2) SnO$_2$ thick films were then screen-printed on alumina substrates with gold electrodes. The films were dried at 100°C followed by heat treatment at 700°C for 16 h. The average thickness was about 20 μm. For SnO$_2$ ink, no inorganic binder was added to organic binder. Square SiO$_2$ thick films (5 × 5 mm^2) were screen-printed on the SnO$_2$ thick film, and the films were dried at 100°C. Sintering of the film was carried out by heating at a temperature 700°C for 1 h. Several SiO$_2$ film thicknesses were deposited (20 μm to 80 μm). A thin film of platinum was deposited on the top of the sensing layer (thick SnO$_2$ film or thick SnO$_2$ film with the insulating coating) by sputtering with argon ions from a metallic platinum target (thickness between 1 and 50 nm). No annealing was performed before electrical tests.

Thick film sensor prototypes with their own platinum heating element were also prepared by screen printing. The thick films of SnO$_2$ were deposited on the top of alumina substrates (38 × 5 mm) with the same geometries as above (2 × 4 mm). A view of such a sensor is reported in Fig. 17, the Pt heater is also at the top but on the back side of the substrate. The sensors were equipped with four gold electrodes in order to test the quality of the electrical contacts.

As in the previous study, the catalytic activity of the different films were evaluated versus the thickness of the films (thick SnO$_2$, thick SiO$_2$ and thin Pt). Electrical performances of the new structures thick SnO$_2$ film + thick insulator coating (SiO$_2$) + Pt were tested. It was verified that the thickness of the SiO$_2$ has no influence on the electrical conductance. But the important result is that, contrary to thin film structures, a good correlation between catalytic tests and the effects on the sensor response is now obtained with a platinum film deposited above the SiO$_2$ layer (Fig. 18).

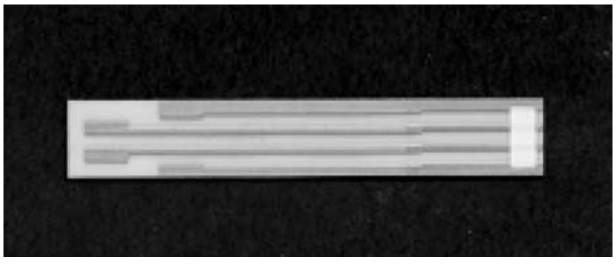


Figure 17 Thick film sensors on an alumina substrate.

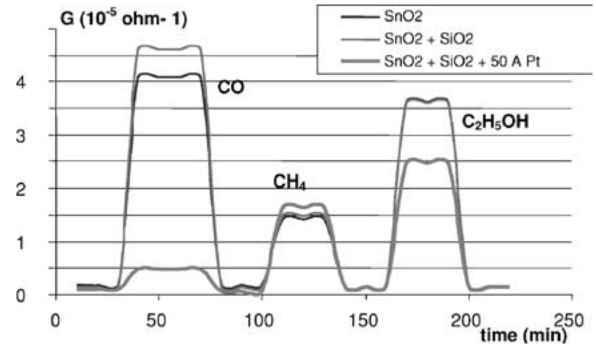


Figure 18 Electrical responses to CO (300 ppm), CH$_4$ (1000 ppm) and C$_2$H$_5$OH (50 ppm) of the three sensors: SnO$_2$, SnO$_2$ + SiO$_2$ and SnO$_2$ + SiO$_2$ + Pt (20 μm thick SnO$_2$, 40 μm thick SiO$_2$ and 5 nm Pt).

For CO, we observed very low response when the platinum film was deposited onto the silica film now in good agreement with the catalytic activity. The response for CH$_4$ is also not affected, as predicted. On the other hand, the correlation for C$_2$H$_5$OH is not completely in agreement with the catalytic activity. All the experiments were carried out near 500°C and at this temperature, C$_2$H$_5$OH must be fully decomposed. This could be related to the influence of the water produced by the decomposition reaction.

Moreover, and contrary to thin film devices, new experiments performed without the thick SiO$_2$ films showed that good correlation was also obtained in the thick SnO$_2$ film + Pt structure, when a contact between Pt and SnO$_2$ is materialised. In thick film structures, no insulator coating seems to be necessary. A new model is currently under development [47] taking into account the influence of the thickness of the SnO_2 film with an action of the species produced by the Pt film located at the electrodes.

To conclude on the use of a platinum filter to improve the selectivity of tin oxide sensors with respect to reducing gases, we can assume that such solutions will be certainly an alternative way to control the performances of gas sensors. These solutions could constitute in the future generic solutions for various types of gas sensors. In the field of atmospheric pollution monitoring, some problems for the detection of HC, BTX or VOC could be solved using selective membranes and filters directly placed on the sensing material.

3.3. Potentiality of MnO_2 filter for ozone detection and interfering problems

For atmospheric pollution monitoring, and still regarding the problem of dual response between reducing and oxidising gases, it would be interesting to filter out ozone. This could be an advantage to detect reducing gases without problem, but it could also constitute a solution to obtain indirect information on the concentration of ozone by comparison of the signals of two sensors, with and without an ozone filter. In several analytical techniques, a common solution proposed to filter ozone with a good efficiency is to use a filter made of manganese oxide MnO_2 [48]. We have recently started a research program to test such a solution and to develop thick film sensors with a MnO_2 filter.

The influence of CO and O_3 were evaluated on a thick film SnO_2 sensor similar to that used in the previous section. The sensor was placed in a cell on a laboratory testing bench equipped with a generator of ozone constituted with an UV lamp (Sonimix 3001 from *L.N. Industries SA*). The working temperature of the sensor was fixed at 450°C. A set of mass-flow controllers allowed generation of very low concentrations of ozone, which were controlled with an ozone analyser (1003 AH from *Evironnement SA*). The response of the sensors to CO concentrations in the range 2.5 to 60 ppm are reported in Fig. 19a. The response of the same sensor under similar conditions to O_3 concentrations in the range 25 to 250 ppb are reported on Fig. 19b. We observed the positive response to CO (increase of electrical conductance) and negative response to O_3. The relative variations of response are more important to ozone, taking into account the very low concentrations injected in the ppb range in comparison of those for CO in the ppm range. We also observed an apparently bad reversibility of the sensor after ozone injection with practically no recovery. This can be mainly attributed to the experimental set-up with adsorption of ozone in the gas and it is very difficult to avoid this problem for very low concentration of ozone in the range of ppb.

TABLE II Efficiency of MnO_2 filter to stop ozone: comparison of powder and thick film at 20°C and 400°C (measurements performed with an ozone analyser)

	Without MnO_2 filter	With MnO_2 filter	Variation (%)
Powder at 20°C	97 ppb	14 ppb	85%
Thick film at 20°C	181 ppb	153 ppb	15%
Powder at 400°C	96 ppb	28 ppb	70%
Thick film at 400°C	25 ppb	20 ppb	22%

Moreover, we tested the influence of ozone injection on top of CO injection. The response reported in Fig. 20 demonstrates the influence of ozone. For example, an injection of 0.5 ppm (∼484 ppb) of ozone decreases the response to 11 ppm of CO by a factor 2. These results point out the necessity to filter ozone in order to have a selective response to CO with tin oxide sensors for atmospheric control.

The efficiency of MnO_2 was tested with a furnace placed before the ozone analyser. We compared the efficiency of MnO_2 powder (1 g) deposited on a porous ceramic substrate and thick film of MnO_2 deposited on the same porous substrate. The results are reported in Table II for two temperatures, ambient and 400°C. Above 450°C, it was verified by XRD that MnO_2 begin to change to oxidized forms (e.g., Mn_2O_3). With the powder, the rate of ozone conversion is high, between 70 and 85%. With the porous thick films of MnO_2, the rates range from 15 to 30%. Although the rates in the thick films are lower than those obtained in the powder, these preliminary experiments seem to demonstrate the possibility to filter ozone with thick films. The difference of activity can be related to the degree of porosity of the thick films in comparison to the bed of powder. During these experiments, it was difficult to fix

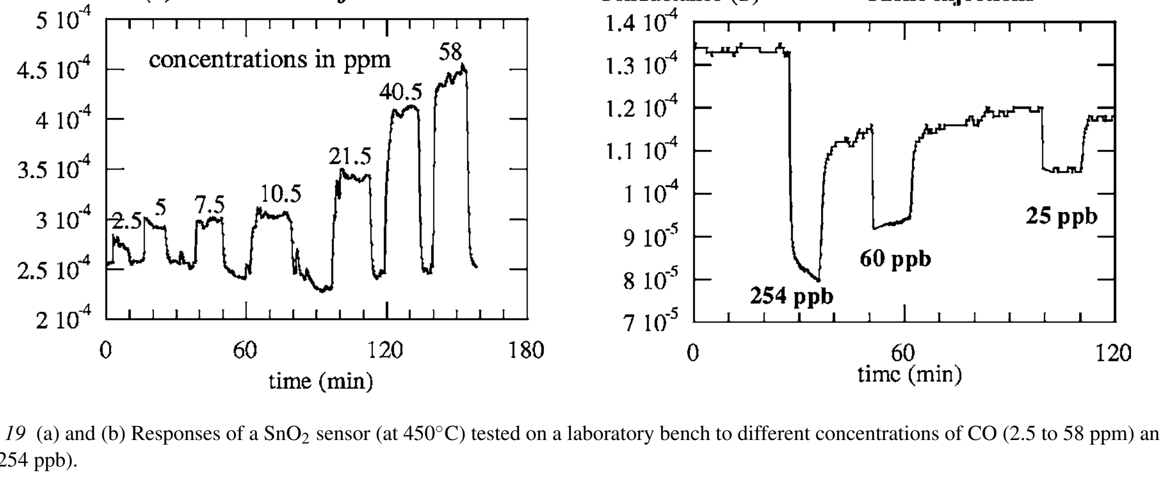


Figure 19 (a) and (b) Responses of a SnO_2 sensor (at 450°C) tested on a laboratory bench to different concentrations of CO (2.5 to 58 ppm) and O_3 (25 to 254 ppb).

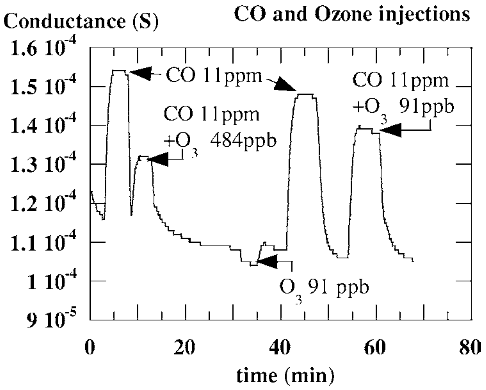


Figure 20 Response of a SnO_2 sensor (at 450°C) tested on a laboratory bench to simultaneous injections of CO and O_3.

the concentration of ozone because the time of stabilisation was very long and not very reproducible. This is certainly in relation with the adsorption of ozone in several parts of the testing bench. These experimental difficulties explain the variations of ozone concentrations during the different experiments. Consequently, the results cannot be used at the moment as quantitative results, but only as an indication for a possible solution.

Nevertheless, one interesting point is the fact that no real difference of activity is observed between room temperature and the working temperature of 400°C. Long term experiments were also performed without any significant degradation of MnO_2. As a consequence, the deposition of the thick film directly above the SnO_2 film can be possible and the system operational to filter ozone above SnO_2.

4. Possibility offered by signal processing: multivariate approach

4.1. Procedure of treatment and results under standard gases

There are two ways to use multi-component analysis in order to measure gas concentration with semiconductor gas sensors: The first is the multi-sensor approach where different kinds of sensors are used simultaneously. For atmospheric monitoring, there are several recent publications in this area [28, 49]. The second approach is the multivariate approach where several independent variables are measured on one sensor [50, 51]. The results presented below constitute an example of this second approach. The aim here is to find new parameters in order to have more selectivity and which have useful properties after a long time of operation (typically, more than 90 days). The different variables are the AC conductance (modulus and argument) for different frequencies (0 to 50 kHz) and different temperatures (150 to 530°C). Contrary to DC measurements, AC measurements appear interesting to be used to separate some gases. Such an idea has been already tested, in particular with oxidant gases [52].

For the measurements, a particular temperature cycle is applied: it constitutes an isothermal dwell at 530°C for 30 min followed by a linear temperature decrease down to 100°C in 5 min. Acquisition is performed during the decreasing ramp with a period corresponding to a variation of 10°C. In order to have a good stability, only sensors with more than 90 days of operation are presented here. We first tried to study our sensors with gas standards. This classic "instrumentation" approach allows us to compare different sensors and to know what the most interesting parameters are. We used these gas standards:

- Carbon monoxide CO: 0 to 20 ppm,
- Ozone O_3: 0 to 300 ppb
- Nitrogen dioxide NO_2: 0 to 500 ppb.

A humidification system allowed to have various values of relative humidity between 20 and 80%. We used thick film sensors realized as described previously in Section 3.2 by screen printing from non-conventional inks without inorganic binder. The substrates were alumina substrates (38 × 5 mm), with a Pt heater on the back side. The presented results are generally related to screen-printed SnO_2 sensors. Nevertheless, some results obtained with screen-printed WO_3 sensors are also reported in Fig. 21.

For carbon monoxide, the sensitivity G/G_0 which was initially greater than 5 for 20 ppm, greatly decreased after 60 days, and consequently became unusable for 90 days sensors. Under ozone or nitrogen dioxide, we observed a decrease of the modulus of the conductance at any frequency at low temperature (250°C). The

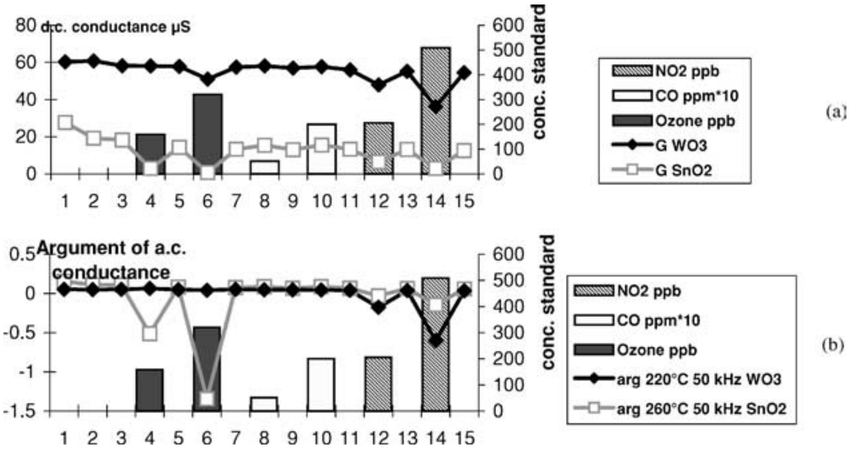


Figure 21 Measurements with thick SnO_2 and thick WO_3 sensors for different standard gases: (a) d.c. conductance and (b) argument of a.c. conductance.

argument, initially null at high temperature or without oxidizing gas, decreased to $(-\pi/2)$ above a "transition temperature" which depends on frequency, concentration and nature of the gas (O_3 or NO_2). So, it seems to be difficult to measure O_3 and NO_2 independently. But we observed too that while thick SnO_2 sensors are more sensitive to O_3, thick WO_3 sensors are more sensitive to NO_2. As a consequence, a multi-sensor approach can probably allow us to measure separately the two gases.

4.2. Results with real pollution measurement

Results presented now were obtained with a thick SnO_2 sensor (that was more than 90 days old) during 3 days where the real concentrations were obtained from conventional analyzers (Fig. 22). The conductance modulus shows a high increase (up to 3 times) when there are periods of pollution (Fig. 22a): this is incompatible with the measured CO (always less than 5 ppm).

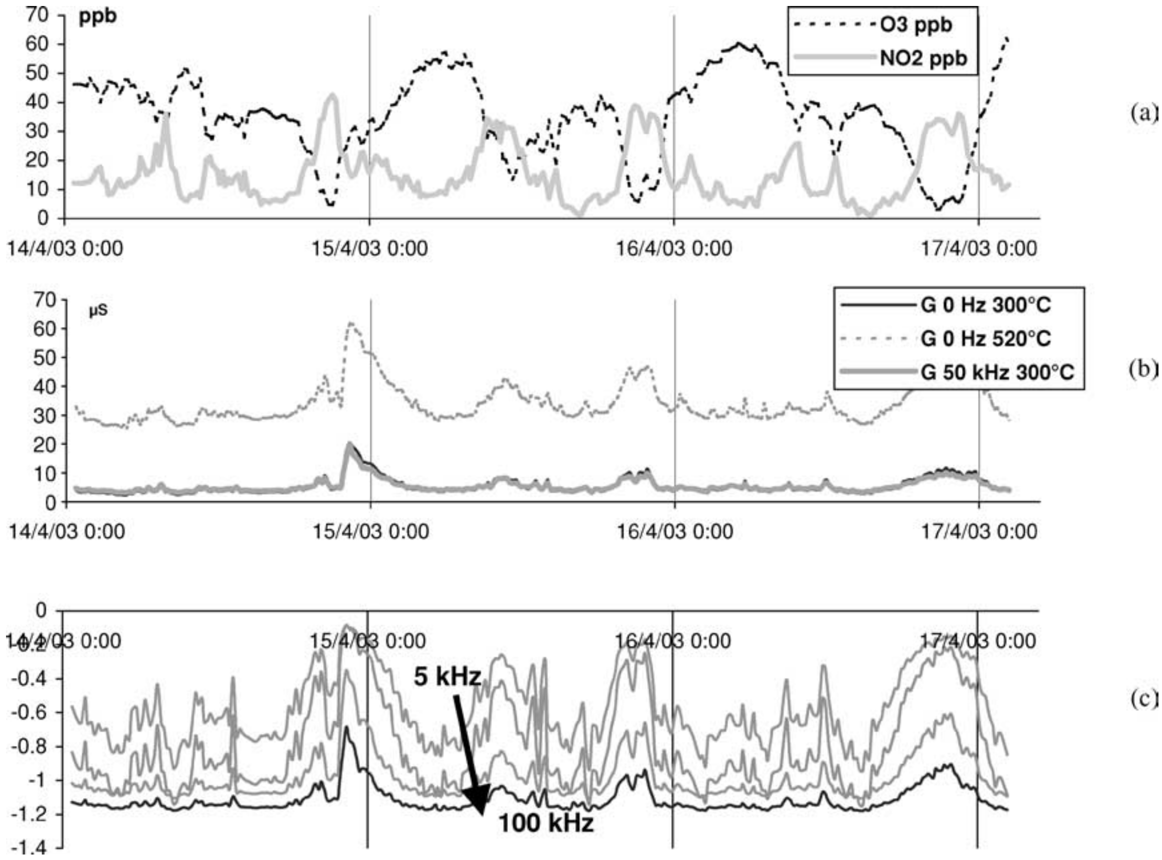


Figure 22 Three days of atmospheric pollution measurement: (a) conventional analysers; (b) a.c. and d.c. conductance, and (c) a.c. conductance argument for several frequencies.

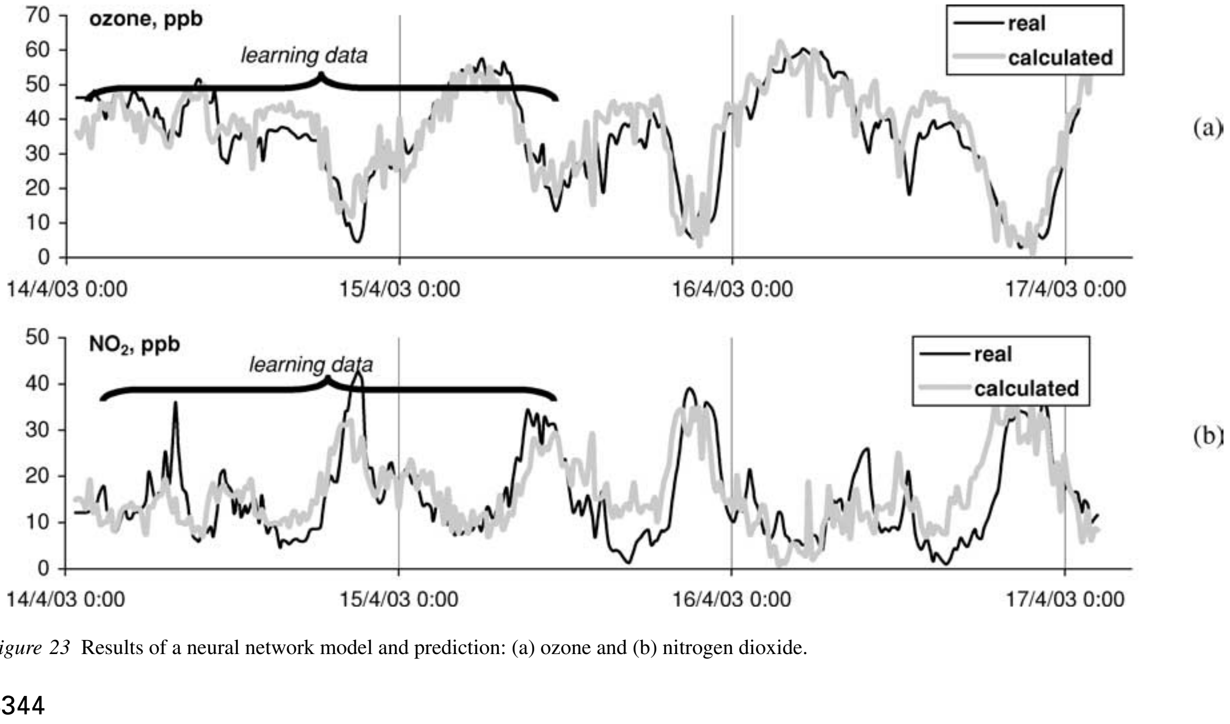


Figure 23 Results of a neural network model and prediction: (a) ozone and (b) nitrogen dioxide.

Furthermore, these sensors have a poor sensitivity to CO. This is also incompatible with NO_2 or O_3 pollution because these oxidizing gases decrease the conductance. The presence of reducing gases, such as hydrocarbons, can be responsible of these results, but we have no data about these species.

It can be observed in Fig. 22b, high variation of the conductance argument depending on frequency and temperature, probably due to oxidizing gases like O_3 or NO_2. In order to exploit these interesting results, we built a component model with a back-propagation neural network algorithm. We used data from the same 3 days experience.

Results reported in Fig. 23 show a correct correlation between data obtained with analyzers and data calculated from sensors for O_3 and NO_2 pollutions. Nevertheless, the greatest care must be taken in our conclusion and we have to remind that with O_3 and NO_2 standards these two species cannot be measured independently. Apparently, our results may be due to the fact that NO_2 and O_3 pollution are anti-correlated: the primary pollutants associated with NO_2 destroy the ozone.

This method of calibration with real pollution has allowed us to have realistic but corrected results with a multivariate analysis applied with only one sensor. Our current studies concern a multi-sensor approach (in particular with WO_3 sensors), in order to be able to measure coarsely but separately NO_2, O_3 and something that can be called "hydrocarbons".

5. Conclusion

The development of models for air quality monitoring and prediction requires data of the atmospheric emissions. Measurements of gaseous pollutants by chemical micro-sensors can be considered as a complementary tool to the stations equipped with analytical apparatus because they can increase the number of measurement points. Among the available micro-sensors, tin dioxide semiconductor sensors were tested for such applications. It is easy to record during on-site experiments a signal from SnO_2 sensors which appears in good correlation with gas concentrations measured by analytical techniques, for example for CO. In fact, as for many other applications, there are several problems which prohibit or complicate the use of these sensors for atmospheric pollution control; problems with the long term stability and above all with the poor selectivity.

The problem of instability is rather difficult to overcome since there is no control over the nature of gases present in the atmosphere and consequently the sensor may encounter irreversible reactions on the surface. For example, we have clearly demonstrated that the presence of a very low concentration of SO_2 can be at the origin of the sensor's drift. The important point in this case has been to use this effect to stabilise the sensor before its use. This type of treatment can certainly be adopted case by case with other gases if we have a clear view of the mechanisms of interaction with these gases.

For the selectivity, a current approach consists of using gas filters deposited directly above the sensing elements. Such solutions can be carried out only with thin and thick film materials. In the case of pollution control, the dual problem of simultaneous detection of oxidising and reducing gases is a very hard problem, especially with tin dioxide sensors. Many recent publications and current studies are devoted to the dual problem of detection of CO and NO_2, partly in relation to the air quality control for automotive applications. With thin films of SnO_2, we have demonstrate that the use of a rhodium filter can stop NO_2 and a selective detection of CO is possible. Of course, the development of industrial sensors using such solution will be certainly possible only after major R&D, perhaps with other more interesting catalytic materials after long term tests.

As platinum is a metal with well identified catalytic properties, we have studied the possibilities offered for selectivity improvement in order to be able to detect reducing gases in atmospheric pollution. We have pointed out the possibility, for example, to stop alcohol and CO without action on methane. Nevertheless, the phenomena occurring are difficult to control, especially in relation to the direct contact between platinum and tin oxide. In order to increase the efficiency of the Pt filter, i.e. the thickness of the platinum films without electrical short-circuit, the use of an insulating layer between the sensing material and the metallic filter is necessary. This type of solution were tested with success using screen-printed thick film materials. In general, for all multi-layers systems, the thick film technology appears more interesting than with thin films according to the problems of chemical diffusions. In the future, the solution of selective filters will be certainly a basic point for the development of multi-sensors devices. Nevertheless, taking into account that these future devices will be partly produced by micro-electronic technology on silicon substrates, it will be necessary to be able to deposit thick films with these technologies. The filter approach is also currently tested in our laboratory to control the action of ozone. The chosen material is MnO_2. The conversion rate of this oxide as powder has been tested with success, both at 20 and 400°C. Thick films of MnO_2 were deposited on porous substrates and they seem to present a conversion rate sufficient to consider their use for selective sensors.

For selective detection, much efforts are now focussed on multi-sensors devices and associated signal analysis. In our case, we chose to investigate the multivariate analysis with only one sensor. The exploited parameters can be the DC conductance versus the temperature of the sensors. It appears also very interesting to exploit the argument of the conductance in AC measurements. This type of exploitation was realised only on aged sensors after 90 days running. Interesting results were obtained for oxidising gases (NO_2 and O_3) depending on the temperature and on the frequency of measurement. It appears that the argument conductance can be used with success with a component model built with a back-propagation neural network algorithm.

References

1. J. SAUL GARCIA DOS SANTOS-ALVES and R. FERNANDEZ PATIER, *Sensors and Actuators* B **59** (1999) 69.
2. L. J. HUNTER, G. T. JOHNSON and I. D. WATSON, *Atmos. Environ.* **26B** (4) (1992) 425.

3. R. BERKOWICZ, F. PALMGREN, O. HERTEL and E. VIGNATI, *Sci. Total Environ.* **189/190** (1996) 259.
4. W. B. JONHSON, F. L. LUDWIG, W. F. DABBERDT and R. J. ALLEN, *J. Air Poll. Contr. Assoc.* **23** (1973) 490.
5. M. C. CAROTTA, G. MARTINELLI, L. CREMA, C. MALAGU, M. MERLI, G. GHIOTTI and E. TRAVERSA, *Sensors and Actuators* B **76** (2001) 336.
6. G. MARTINELLI, M. C. CAROTTA, M. FERRONI, Y. SADAOKA and E. TRAVERSA, *ibid.* **55** (1999) 99.
7. H. MEIXNER, J. GERBLINGER and M. FLEISCHER, *Sensors and Actuators B: Chemical* **15**(1–3) (1993) 45.
8. A. ZEPPENFELD, K. INGRISH, M. BAUER, I. DENK and B. ZIEGENBEIN, in Proceeding of Sensor 97 (Nuremberg 97 May) (1997) Vol. B1, p. 113.
9. G. WIEGLEB and J. HIETBAUM, *Sensors and Actuators* B **17** (1994) 93.
10. K. OTO, A. SHINOBE, M. MANABE, H. KAKUUCHI, Y. YOSHIDA and T. NAKAHARA, *ibid.* **77** (2001) 525.
11. H. MEIXNER, J. GERBLINGER, U. LAMPE and M. FLEISCHER, *ibid.* **23** (1995) 119.
12. C. PIJOLAT, C. PUPIER, C. TESTUD, R. LALAUZE, L. MONTANARO, A. NEGRO and C. MALVICINO, *J. Electroceram.* **2**(3) (1998) 181.
13. H. TORVELA, A. HARKOMA-MATTILA and S. LEPPAVUORI, *Sensors and Actuators* B **1** (1990) 83.
14. G. B. BARBI, J. P. SANTOS, S. SERRINI, P. N. GIBSON, M. C. HORRILLO and L. MANES, *ibid.* **25** (1995) 559.
15. R. LALAUZE, J. C. LE THIESSE, C. PIJOLAT and M. SOUSTELLE, *Solid State Ion.* **12** (1984) 453.
16. J. LIU and W. WEPPNER, *Solid State Commun.* **76** (1990) 311.
17. S. YAO, S. HOSOHARA, Y. SHIMIZU, N. MIURA, H. FUTATA and N. YAMAZOE, *Chem. Lett.* (1991) 2069.
18. C. H. LEE, S. A. AKBAR and C. O. PARK, *Sensors and Actuators* B **80** (2001) 234.
19. M. A. MARTIN, J. P. SANTOS, H. VASQUEZ and J. A. AGAPITO, in Proceeding of Eurosensors XII (Southampton 98 Sept. 1998) p. 1036.
20. L. TALAZAC, J. BRUNET, V. BATTUT, J. P. BLANC, A. PAULY, J. P. GERMAIN, S. PELLIER and C. SOULIER, *Sensors and Actuators B: Chemical* **76**(1–3) (2001) 258.
21. M. ZIMMER, M. BURGMAIR, K. SCHARNAGI, A. KARTHIGEYAN, T. DOLL and I. EISELE, *Sensors and Actuators* B **80** (2001) 174.
22. K. AGUIR, C. LEMIRE and D. B. B. LOLLMAN, *ibid.* **84** (2002) 1.
23. T. S. KIM, Y. B. KIM, K. S. YOO, G. S. SUNG and H. J. JUNG, *ibid.* **62** (2000) 102.
24. X. WANG, N. MIURA and N. YAMAZOE, *ibid.* **66** (2000) 74.
25. R. RELLA, P. SICILIANO, S. CAPONE, M. EPIFANI, L. VASANELLI and A. LICCIULLI *ibid.* **58** (1999) 283.
26. S. NICOLETTI, L. DORI, G. C. CARDINALI and A. PARISINI, *ibid.* **60** (1999) 90.
27. G. WIEGLEB and J. HEITBAUM, *ibid.* **17** (1994) 93.
28. M. C. CAROTTA, G. MARTINELLI, L. CREMA, M. GALLANA, M. MERLI, G. GHIOTTI and E. TRAVERSA, *ibid.* **68** (2000) 1.
29. C. PIJOLAT, *Ceramurgia* **5** (1995) 257.
30. R. LALAUZE, C. PIJOLAT and J. P. COUPUT, “Procédé, capteur et dispositif de détection de traces de gaz dans un milieu gazeux,” Patents: FR 8119536 (1981), EC 4485667 (1984), US 824018722 (1984), JP 1753030 (1993).
31. C. PIJOLAT, C. PUPIER, M. SAUVAN and G. TOURNIER, *Sensors and Actuators* B **59** (1999) 195.
32. R. ROMPPAINEN, H. TORVELA, J. VAANANEN and S. LEPPAVUORI, *ibid.* **8** (1985) 271.
33. A. KESHAVARAJA, B. S. JAYASHRI, A. V. RAMASWAMY and K. VIJAYAMOHANAN, *ibid.* B **23** (1995) 75.
34. H. E. ENDRES, W. GOTTLER, R. HARTINGER, S. DROST, W. HELLMICH, G. MULLER, C. BOSCH-BRAUNMUHL, A. KRENKOW, C. PEREGO and G. SBERVEGLIERI, *ibid.* **35/36** (1996) 353.
35. J. SANTOS, P. SERRINI, B. O’BEIRN and L. MANES, *ibid.* **43** (1997) 154.
36. I. SAYAGO, J. GUTIERREZ, L. ARES, J. I. ROBLA, M. C. HORRILLO, J. GETINO and J. A. AGAPITO, *ibid.* **24/25** (1995) 512.
37. G. WILLIAMS and G. S. V. COLES, *ibid.* **24/25** (1995) 469.
38. L. BRUNO, C. PIJOLAT and R. LALAUZE, *ibid.* **18/19** (1994) 195.
39. M. SAUVAN and C. PIJOLAT, *ibid.* **58** (1999) 295.
40. C. D. FENG, Y. SHIMIZU and M. EGASHIRA, *J. Electrochem. Soc.* **144**(1) (1994) 220.
41. H. DEBEDA, L. DULAU, P. DONDON, F. MENIL, C. LUCAT and P. MASSOK, *Sensors and Actuators* B **44** (1997) 248.
42. M. FLEISCHER, S. KORNELY, T. WEH, J. FRANK and H. MEIXNER, *ibid.* **69** (2000) 205.
43. G. G. MANDAYO, E. CASTANO, F. J. GRACIA, A. CIRERA, A. CORNET and J. R. MORANTE, *ibid.* **87** (2002) 88.
44. E. BILLI, J. P. VIRICELLE, L. MONTANARO and C. PIJOLAT, *IEEE Sensors Journal* **2**(4) (2002) 342.
45. P. MONTMEAT, C. PIJOLAT, G. TOURNIER and J. P. VIRICELLE, *Sensors and Actuators* B **84** (2002) 148.
46. B. RIVIERE, J. P. VIRICELLE and C. PIJOLAT, “Development of Tin Oxide Material by Screen-Printing Technology for Gas Sensor Application,” *Sensors and Actuators* B **93**(1–3) (2003) 531.
47. P. MONTMEAT, J. C. MARCHAND, R. LALAUZE, J. P. VIRICELLE, G. TOURNIER and C. PIJOLAT, “Physico-Chemical Contribution of Gold Metallic Particles to the Action of Oxygen on Tin Dioxide Sensors,” *Sensors and Actuators* B **95**(1–3) (2003) 83.
48. I. TERADA and S. ARAI, “Ozone Filter and Process for Reducing the Same,” US patent No 5.698.165 (Dec. 1997).
49. R. MENZEL and J. GOSCHNICK, *Sensors and Actuators B: Chemical* **68**(1–3) (2000) 115.
50. M. N. ABBAS, G. A. MOUSTAFA and W. GOPEL, *Anal. Chim. Acta* **431** (2001) 181.
51. P. BREUIL, N. PERDREAU and C. PIJOLAT, *Analusis* **28**(7) (2000) 633.
52. U. WEIMAR and W. GOPEL, *Sensors and Actuators* B **26/27** (1995) 13.

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