

# A Gas Chromatographic-like System for the Separation and Monitoring of Benzene, Toluene and Xylene Compounds at the ppb Level Using Solid State Metal Oxide Gas Sensors

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This paper reports recent advancements in the realization of a system based on solid-state metal-oxide gas sensors suitable for the detection of benzene, toluene and xylene (BTX) compounds in the ppb range for outdoor applications. The system follows a gas chromatographic-like approach in which a preconcentration trap and a separation column are used together with a SnO<sub>2</sub> thin film sensor fabricated on a micro-hotplate which had a very thin Si<sub>3</sub>N<sub>4</sub> membrane as a physical support for the entire sensor stack. Following this approach we were able to detect benzene, toluene and xylene separately at concentrations as low as 3 ppb in a gas mixture containing all three compounds. The feasibility of a very innovative, simple and cheap detection unit based on a metal semiconducting oxide layer as a detector in GC systems is presented here, and the degradation of the output signal experienced when the sensor is operated in a small chamber together with the preconcentration and the separation columns is discussed.

## 1. Introduction

Recently, attention towards volatile organic compounds such as benzene, toluene and xylene – BTX –, which are added to lead-free gasoline, has grown dramatically due to their

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toxicity and their carcinogenic effects. To evaluate the mid-range and long-term effects on human health, combined efforts based on a clinical survey of a large exposed population and on a continuous monitoring of these compounds are necessary. Continuous volatile organic compounds (VOC) monitoring helps also to correlate their concentrations in the open air with the main sources of pollutants, *e.g.* the vehicular traffic. In Table 1, a list of the compounds commonly taken as indicators of the outdoor air quality, and the concentration values corresponding to levels of attention and alarm which follow the European legislation, are reported. At the present time, such low concentrations are evaluated by monitoring stations equipped with standard analytical tools, with which BTX compounds are measured together with CO, O<sub>3</sub>, NO<sub>x</sub>, SO<sub>2</sub> and suspended particles (particularly PM 10). The analytical approaches followed are gas chromatography (GC) with PID or FID as detectors for the BTX, nondispersive infrared spectroscopy for the CO and chemoluminescence for NO<sub>2</sub>. These monitoring stations are large, have high power consumption, require high initial investment and have high maintenance costs.

On the other hand, recent advances in the development of solid-state conductometric gas sensors make this kind of device very attractive for environmental applications. The commercial sensors currently available on the market can detect VOC at minimum concentrations of few ppm. In a recent paper, we reported the performance of SnO<sub>2</sub>-based gas sensors deposited upon micromachined substrate heater elements having a very thin Si<sub>3</sub>N<sub>4</sub> membrane as a physical support for the entire sensor stack and capable of measuring BTX in the sub-ppm range.<sup>(1)</sup> Although the performance of these devices is very encouraging, a gap between the minimum detectable BTX concentration and the typical outdoor VOC concentration still exists. Besides the sensitivity problem, the conductometric gas sensors exhibit poor selectivity.

Within the European Esprit project SMOG (Smart air pollution MOonitorinG network), a consortium of research laboratories and industries is aiming to develop an innovative miniaturized monitoring station in which the analytical tools are replaced by solid state sensors based on thin film metal semiconducting oxides as detectors. The final goal of the project is the realization of a low-cost and low-maintenance gas monitoring system. In this consortium, the LAMEL Institute had the task of developing a system to selectively measure the BTX compounds in the outdoor environment. This paper reports the most recent advancements in the realization of such a system suitable for the detection of BTX in the ppb range.

Table 1  
Attention and alarm levels for gaseous species taken as indicators of the outdoor air quality.

Compound	Attention level	Alarm level
BTX ( $\mu\text{g}/\text{m}^3$ )	15	30
CO ( $\text{mg}/\text{m}^3$ )	15	30
O <sub>3</sub> ( $\mu\text{g}/\text{m}^3$ )	180	360
NO <sub>2</sub> ( $\mu\text{g}/\text{m}^3$ )	200	400

## 2. Materials and Methods

As is well known, the concentrations of BTX in the outdoor air to be monitored are very low (<10 ppb). State-of-the-art gas sensors based on metal semiconducting oxides are very attractive as detectors but their selectivity and sensitivity are still inadequate for the application we are discussing. To bridge the gap between minimum detectable concentration and typical outdoor concentration, allowing at the same time easy separation and detection of each BTX compound, a gas chromatographic-like approach has been followed.<sup>(2,3,4)</sup> A schematic view of the system layout is reported in Fig. 1. Basically, we miniaturized the main components of a GC system: the column used to preconcentrate the mixtures containing a few ppb of the BTX compounds by a factor of about 50 and the column used to separate each gaseous compound. In the latter case, instead of a very expensive capillary column, a very small spiral-shaped Pyrex column loaded with an ad-hoc prepared stationary phase has been used. The measurement cycle consists of two simultaneous phases. During the preconcentration, 40 sccm of a gas mixture containing BTX flows through a Pyrex trap (i.d.=1.5 mm, o.d.=3.5 mm) loaded with 0.04 g of Carbograph 4 (210 m<sup>2</sup>/g as specific surface area – 20/40 mesh) for 50 min.<sup>(5)</sup> The choice of the adsorbing material was made taking into account the retention capabilities to BTX (4 µg/g) and the release of unclassified compounds detected by the gas sensor during the desorption step. The Carbograph 4 material was found to guarantee sufficient retention for our application while minimizing the release of other compounds.

Before separation, the temperature of the preconcentration column is rapidly increased from RT to 290°C and maintained at 290°C for 3 min, and 15 sccm of synthetic air (SA)

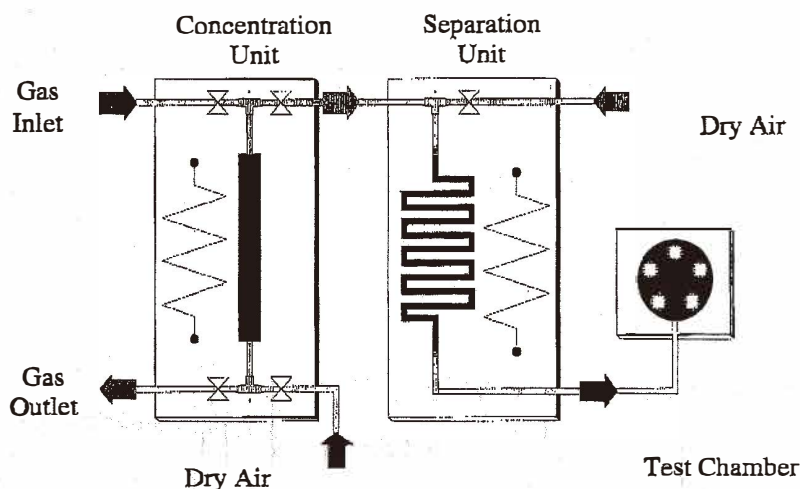


Fig. 1. Schematic drawing of the system containing the preconcentration unit, the separation unit and the sensor chamber.

flows in the direction opposite to that used during the preconcentration step. After 3 min the temperature of the preconcentration column is decreased to RT and a new preconcentration step is started. During the heating step, the BTX compounds were released by the preconcentration trap and injected into the gas separation device.

The main features necessary to the separation column were the BTX separation capability within an acceptable time (<45 min) at the lowest possible operating temperature to decrease the overall power consumption of the system. Since the gas sensors based on metal oxide semiconductors require the presence of oxygen to interact and reveal gas molecules, air is necessary as a gas carrier during the elution step. This requirement implies that polymeric materials commonly used for preconcentration which are sensitive to oxygen exposure, such as Tenax,<sup>(6)</sup> are unusable for this application.

To optimize the compound separation, 0.6–1.8 g of Carbograph 2 (12 m<sup>2</sup>/g as specific surface area)<sup>(5)</sup> loaded with different percentages of polar (Carbowax 20 M: 0.2–5%)<sup>(7)</sup> and unpolar (Apiezon)<sup>(8)</sup> as the active phase, and different operating temperatures (80–150°C) and carrier gas flows (10–20 sccm), have been used. In the final configuration, the chromatographic column for separation (l=250 mm, i.d.=2 mm, o.d.=4 mm) was filled with 1.3 g of Carbograph 2 coated with 0.2% Carbowax 20 M operated between 110 and 120°C. To keep the preconcentration factor high, the synthetic air (SA) flow through the column during the separation step was ≤20 sccm, with the sensors placed in a chamber having a small dead volume (–6 cm<sup>3</sup>). The entire system was operated under a slight vacuum (990 mbar).

To detect the presence of BTX in the separation column, Au-doped SnO<sub>2</sub> sensors were used. The sensing layer was deposited upon a Si micromachined structure which had a very thin (200 nm) Si<sub>3</sub>N<sub>4</sub> membrane as both a thermal insulating material and a physical support for the entire sensor stack.<sup>(1)</sup> Further details on the sample preparation and on the substrate heater element technology and device architecture are reported elsewhere.<sup>(1,5)</sup>

### 3. Results

#### 3.1 Au-doped SnO<sub>2</sub> sensor response to very small BTX concentrations

Before any attempt to evaluate the performance of the system in Fig. 1, the sensitivity to small concentrations of the BTX, CO and NO<sub>2</sub> compounds of Au-doped SnO<sub>2</sub> sensors was tested. The gas mixtures were prepared starting from certified gas cylinders containing high concentrations of the target gas in air by diluting the mixtures with chromatographic-grade SA by means of a computer-controlled gas distribution system equipped with mass flow controllers. For this test, each gas mixture has been separately injected and placed for a defined amount of time (20 min) into a std sensor chamber with about 600 cm<sup>3</sup> dead volume. The target gas injection was alternated with synthetic air only to completely purge the system and prepare it for the injection of the next gas mixture, the gas flow being fixed at 300 sccm. This test lasted for more than 1 week during which the gas sequence was repeated continuously. For the BTX and CO monitoring, the Au-doped SnO<sub>2</sub> sensor was operated in continuous mode at  $T=325^{\circ}\text{C}$ . To monitor NO<sub>2</sub> more efficiently, the sensor temperature was decreased from 325 to 250°C. Due to the low thermal mass of the substrate heater element, the sensing layer temperature quickly adjusts to the new value

and the film conductance accordingly. Because of the lower sensing layer temperature (250 rather than 325°C), the allowed amount of oxygen atoms adsorbed at the sensing layer surface as well as the amount of adsorbed water changed. The result of these two competing processes was increased film conductance, as shown in Fig. 2, where the baseline current rose from a fraction of  $\mu\text{A}$  to about  $5 \mu\text{A}$  (about 46 h from the beginning of the test). Looking at this figure, several issues deserve to be highlighted: first, the high sensitivity to low concentrations of BTX at a relatively low temperature ( $T=325^\circ\text{C}$ ); also, the low sensitivity of the detector to CO within the concentration ranges considered; finally, the good sensitivity and relatively short response time when the sensor operating at  $250^\circ\text{C}$  is exposed to low concentrations of  $\text{NO}_2$ .

In Fig. 3, the sensor response to sub-100 ppb BTX concentrations is reported. Ten ppb of either benzene or toluene+xylene can be easily detected by the Au-doped  $\text{SnO}_2$  sensor. To our knowledge, this is the first time that such low BTX concentrations have been measured with a semiconducting metal oxide sensing layer with such high sensitivity and with bypassing a preconcentration step. Based on these results, it appears likely that, using our sensors, sub-ppm BTX concentrations can be measured without any preconcentration step. However, metal oxide semiconducting sensors are poorly selective, and this unique approach to measuring such small BTX concentrations, where each compound is separately monitored, is the gas separation using the GC column as shown in Fig. 1. Taking into account that the sensor loses part of its sensitivity when operated in a very small dead volume, a gas preconcentration step is necessary to recover what the sensor loses in sensitivity.

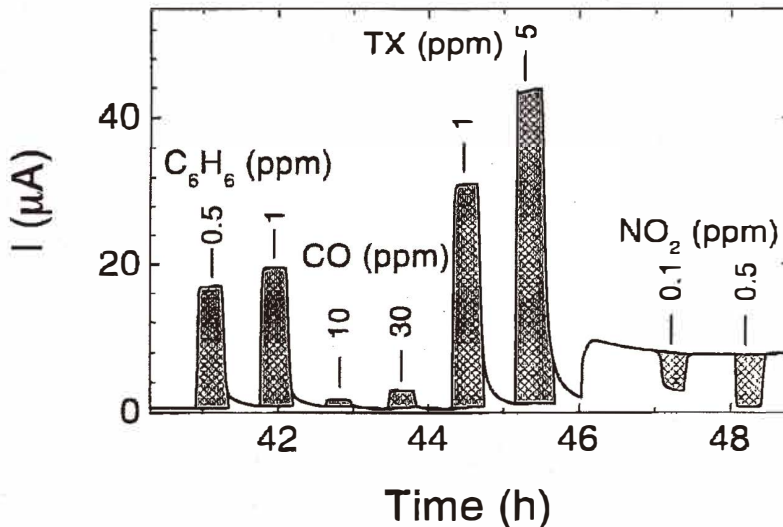


Fig. 2. Response of an Au-doped  $\text{SnO}_2$  sensing layer to BTX, CO and  $\text{NO}_2$ .

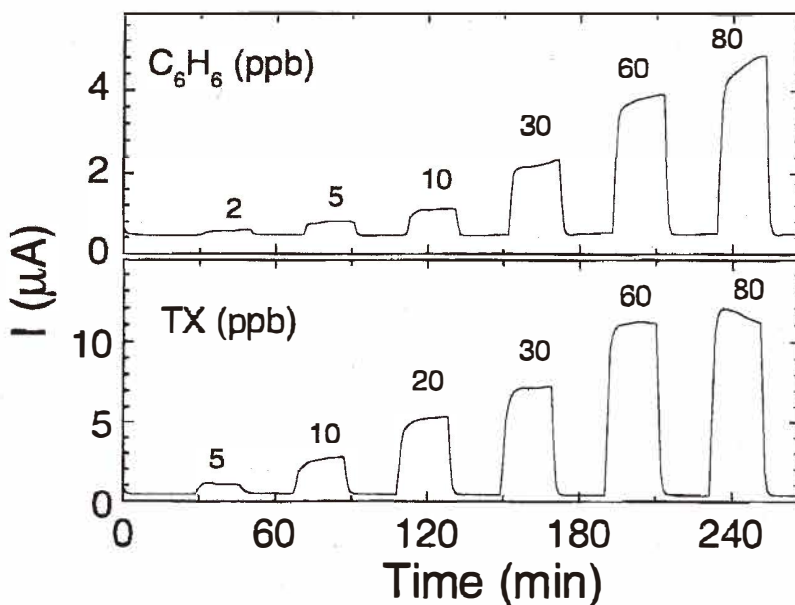


Fig. 3. Sensitivity of an Au-doped  $\text{SnO}_2$  sensor operated at  $325^\circ\text{C}$  towards BTX compounds at very low concentrations.

### 3.2 BTX separation and monitoring using a preconcentration, gas separation units and an Au-doped $\text{SnO}_2$ sensor as detector

In Fig. 4, the signal output of the sensor related to the separation and monitoring under different experimental conditions of BTX is reported. In this case, 5 ppm of BTX were directly injected into the separation column. No preconcentration was used. This characterization was necessary to determine the best operating conditions to obtain adequate separation between benzene and toluene and a complete separation of the three compounds within a defined time interval ( $<45$  min). In Table 2 a summary of the different conditions is reported. The time reported in the table refers to the peak-to-peak separation among the different compounds. We chose as optimum operating conditions  $110^\circ\text{C}$  and 15 sccm of SA flow during the separation of the BTX compounds. Using a smaller amount of the same phase, the BTX separation in Fig. 4 was obtained by operating the phase at  $90^\circ\text{C}$ . We believe that the operating temperature can be lowered well below this value by reducing the amount of separating phase loaded in the column and by slightly changing the preparation of the separating material. Work is in progress and the results will be reported elsewhere.

After the different elements reported in Fig. 1 were separately characterized, they were assembled together. To validate the entire approach, gas mixtures containing 3, 5, 25 and 50 ppb of BTX compounds have been used. To prepare the gas mixtures, we started from certified gas cylinders where the concentration of each compound was about two orders of

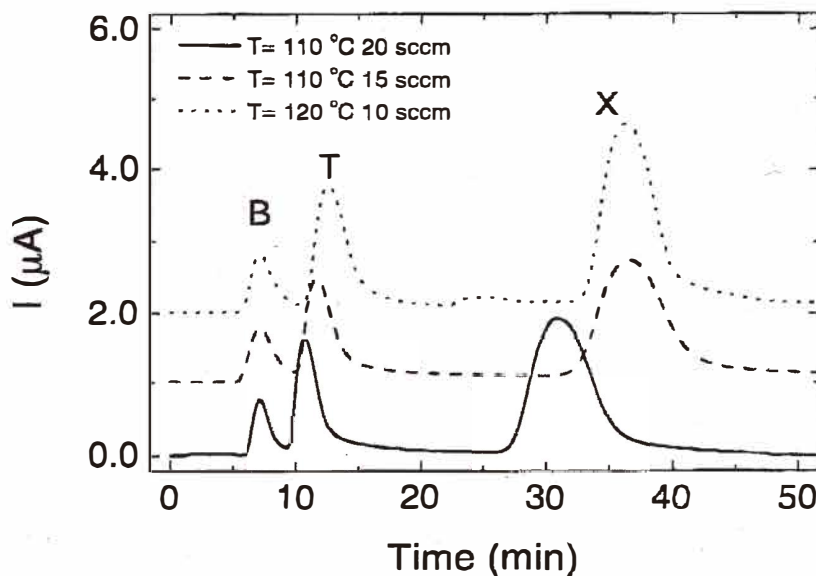


Fig. 4. Release time of each BTX compound using a 1.3 g of Carboxograph 2 coated with 0.2% Carbowax 20 M as a separation phase operated at two temperatures and under different gas flows. In this case a direct injection of 5 ppm of BTX (20 sccm for 1 min) was carried out to load the separation phase.

Table 2

Peak-to-peak separation time under the different experimental conditions.

Compound Flow & $T$	$C_6H_6$	Toluene $\Delta t$ (min)	Xylene $\Delta t$ (min)
20 sccm, $T=110^\circ C$	0	5.4	29.3
15 sccm, $T=110^\circ C$	0	4.6	29.2
10 sccm, $T=120^\circ C$	0	3.7	24.0

magnitude higher than the final concentration (5 ppb). This initial gas mixture was diluted in SA by a computer-controlled gas distribution system equipped with mass flow controllers where the degree of the uncertainty of the BTX concentration is estimated to be below 5%.

Figure 5 shows an example of the pattern from the separation phase after 3 and 5 ppb samples of BTX were preconcentrated, released, separated and monitored by the sensor. For each gas species, a distinct peak separate from the others by several minutes is observed, the total analysis time being about 35 min. As shown by the response recorded

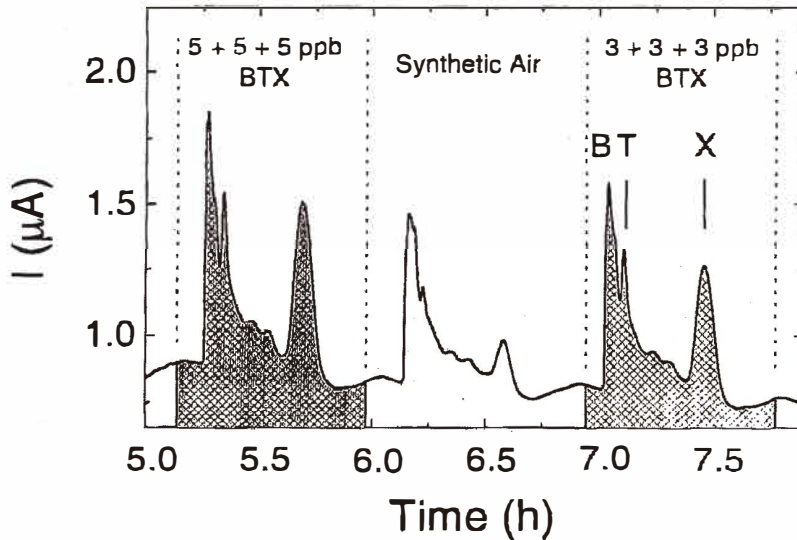


Fig. 5. Output pattern of sensor signal after preconcentration of 3 and 5 ppb of BTX and when only synthetic air is sampled.

for SA, an increase in the conductivity occurs during the elution phase. The particular output pattern, not observable using PID or FID, can be attributed to three superimposed phenomena: the release of unknown compounds from the Carbograph, an incomplete release of BTX by the preconcentration column during the elution phase and the preconcentration of BTX traces already present in the SA. In fact, as shown in Fig. 4, the sensor output recorded from the separation column appears flat and smooth except for the BTX peaks, while the behavior in Fig. 5 was observed when the preconcentration column was integrated in the system. With respect to the output pattern when only SA is sampled, the benzene peak superimposes on that of SA while distinguishable peaks are observed for toluene and xylene. Since the SA peaks overlap that of benzene, we should assume that the unknown compounds released by the Carbograph material in the trap, when it is heated at 290°C, are light compounds which pass through the gas separation column as quickly as benzene. Nevertheless, it is worthy to note that if a partial retention of BTX in the preconcentration column and/or SA contamination are present, the content of BTX detected is very low and it can be considered as a background for the measure.

Figure 6 compares the sensor output recorded when 3 ppb of BTX (---) or SA are sampled (----). The difference between the peak areas with and without pollutant gasses gives a clear picture of the BTX separation and measurement. In an attempt to correlate the different amounts of the BTX compounds with the sensor output, the net conductivity variation (—) was evaluated by subtracting point by point the data recorded in SA from those collected for the BTX mixture. The areas underlying each peak, as calculated from



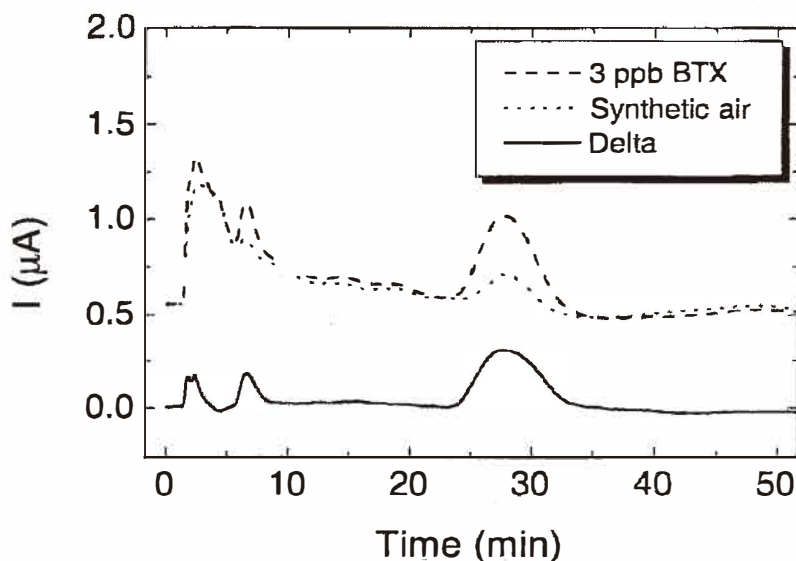


Fig. 6. BTX vs synthetic air peak-to-peak area subtraction to highlight the separation and measurement of preconcentrated 3 ppb of BTX.

this curve, were correlated with the pollutant concentration in the gas mixture. These results are reported in Fig. 7, in which the peak areas are plotted as a function of the benzene, toluene and xylene concentrations. Proportionality between the peak areas and the BTX concentration does exist. In particular, as shown in the inset, when the concentration of benzene in the preconcentrated mixture changes from 3 to 5 ppb, the peak area almost doubles. This change is large enough to allow easy detection of small variations in the concentration of the target compound. We can conclude that a quantitative analysis of benzene, toluene and xylene at low concentrations can be performed allowing the usage of this approach for the continuous monitoring of outdoor air quality in place of the standard analytical tools. Thus far, the peak area reproducibility and an error bar to apply to the data reported in the plot are in early stages. In fact, we do not have enough data to provide information with a consistent statistical meaning. At the present time, the results reported in this paper show the feasibility of using a metal semiconducting oxide layer as a detector in GC systems.

To obtain a reliable and stable sensor response to the different BTX concentrations, points which deserve to be further investigated are the sensor operating conditions of the chamber characterized by a very small dead volume, and the working conditions of the preconcentration and the separation columns. During the elution step and when just SA is sampled, the amplitude of the peak depends on the elution time and Carbograph temperature. A similar effect occurs for the materials of the gas separation phase: the higher the phase operating temperature, the higher the baseline current exhibited by the sensor. This

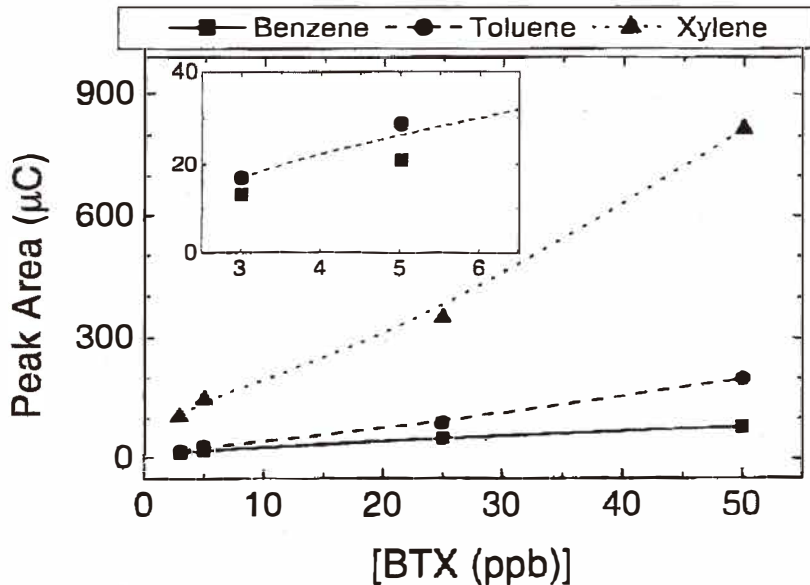


Fig. 7. Sensitivity to the BTX compounds as a function of the benzene, toluene and xylene concentrations in the initial gas mixture. In the inset: detail of the response at the lowest concentrations.

behavior can be explained by assuming that unknown compounds not revealed by conventional detectors are released by the preconcentrating and separating materials, affecting the data analyses and having unpredictable effects on the sensor performance stability over time. However, one of the most critical issues is the stability over time of the detector performance. In this case we observed that the sensor-operating mode plays a crucial role. So far, we have established the conditions to enable the operation of the system for up to six months with a four-sensor array where each sensor is operated sequentially. At the present time we do not have a physico-chemical understanding of faster sensor performance degradation when it is operated in a small volume environment or on the effect of the compounds released by the GC columns. To remedy this inconvenience and make the device lifetime longer, we are pursuing different strategies. The first one is decreasing of the operating temperature of the chromatographic stationary phase to have it work very close to room temperature, still maintaining a good separation of different light compounds. The second and even more appealing strategy is a further improvement in the sensor performance in which the BTX compounds are directly measured at the ppb level in a small sensor chamber without any preconcentration step. Very encouraging results have already been achieved and will be reported later.

#### 4. Conclusions

In this paper we have shown how a few ppb of BTX compounds can be monitored using a metal semiconducting oxide sensing layer combined with a preconcentration trap and a gas chromatographic separation column in a chromatographic-like system. Following this approach we were able to detect benzene, toluene and xylene separately at concentrations as low as 3 ppb. In this new miniaturized system, the capillary column has been replaced by a very cheap packed column operated at a temperature of around 100°C but with the possibility of lowering the operating temperature to 60–70°C. The detector has been replaced with a sensing layer based on an Au-doped thin SnO<sub>2</sub> sensing layer.

Following this approach, a quantitative analysis of benzene, toluene and xylene at very low concentrations, typically monitored in the outdoor air quality applications, can be performed. However, fast degradation of the sensor performances when operated in a chamber characterized by a very small dead volume necessary to keep the preconcentration factor high is observed. To make the analysis dependable and reproducible, new strategies which take into account the degradation of the sensor performance due to poisoning by compounds released from the preconcentration and separation materials must be considered.

The results reported in this paper show the feasibility of using a metal semiconducting oxide layer as a detector in GC systems. When the problems related to the degradation of the signal are successfully solved, very innovative, simple and cheap detection units based on the system architecture presented in this work or even simpler ones could be adapted to continuous as well as on-demand monitoring of the BTX compounds in place of standard analytical tools.

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