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Measurement of ozone in ambient air with microsensors : on-site campaign

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ABSTRACT

Ozone is actually one of the most important atmospheric pollutants in industrial countries. Measurement is well achieved by continuous monitors but a better information on ozone levels would be given by a denser monitoring network, made possible by using a lighter and cheaper technique like microsensors. Such sensors have been tested successfully in the laboratory. We have therefore undertaken a large on-site campaign, on air quality monitoring stations of the French Networks, to validate the use of microsensors on-site. First results of the campaign were improvements in conditioning and calibration procedures. Then, stabilised sensors showed most ozone values within an interval of $\pm 30\%$ of the concentrations given by the monitors.

INTRODUCTION

Ozone is a secondary pollutant produced by photochemical reactions between NO_x and VOCs. It is one of the major atmospheric pollutants in Europe, specially in summer, and during hot years like 2003, is suspected to be the cause of numerous deaths [1, 2]. Therefore, it is very important to precisely measure ozone when it occurs, so as to predict the evolution of the concentration, in order to reduce the sources of primary compounds. Measurement is generally done by continuous monitors installed in automatic stations distributed over the industrial countries where the primary pollutants are largely produced. But the monitoring stations are sometimes not situated at the locations where the ozone concentrations are the highest, in remote places like countryside or mountains, because of the needs (electrical power, data communication...). Also, continuous monitors are very sensitive and stable but expensive, so lighter and cheaper measurement techniques, which can be used in numbers, are very desirable. The possible use of microsensors sensitive and specific to ozone, besides the classical techniques of continuous monitors and the diffusion tubes, could be a very interesting alternative. After a promising evaluation of such sensors in the laboratory completed by on-site tests in Switzerland [3], we have decided to undertake a large on-site campaign in France, during 5 months of the summer 2002.

EXPERIMENTAL

Description of the campaign

Prototypes equipped with ozone microsensors, developed by MICS, have been installed on 13 continuous monitoring stations of the French Air Quality Networks, between early May and the end of September 2002. Stations were chosen to be representative of the various sites encountered in France, such as urban, industrial, rural, seaside, mountain sites, located from East to West and North to South of France. All the stations comprised at least a continuous ozone monitor for comparison.

Description of the apparatus and data acquisition

Prototypes were lightweight : they consisted in a solid plastic box, containing the electronics, with two holes at the bottom, for the ozone module and the temperature sensor. Electronics in the prototype emulated the sensor, which is heated at 400 °C, and allowed the calculation of ozone concentrations, corrected for ambient temperature, using the individual calibration factors determined individually for each sensor. Humidity variations were not corrected. The sensor module comprised the ozone microsensor, protected by an hydrophilic membrane, and a small memory which carried the calibration factors. Sensors modules were dismantled by the staff of the networks every 15 to 30 days, and sent to INERIS for recalibration. Prototypes had two connections wires of 10 meters : one for the electrical supply (220 V – 50 Hz), and the other one for acquisition of the sensor signal, in a 0-1 V range. This cable was connected to the data acquisition system of the monitoring station, like for the continuous monitors, allowing the staff to collect the data on the central system of each network. Ozone concentrations given by the microsensors and the monitors were averaged over periods of 15 minutes. Raw data from the microsensors were also stored in the prototype and collected

every time the sensor modules were dismantled. The staff of each Network sent all the data every 2 to 4 weeks to INERIS and MICS.

RESULTS AND DISCUSSION

New sensors are already sensitive to ozone, but as it is generally the case on most chemical sensors, the response is not constant over the first days of functioning. This corresponds to a rearrangement of the structure of the metal oxide. Over a period of 15 days, the difference between ozone concentrations, calculated from the sensor response and given by the monitor, increases dramatically : see fig. 1. It corresponds to a change during the time, of the sensor calibration curve with ozone concentration : see fig. 2. The third and fourth calibration curves become more similar and linear with ozone concentration, indicating a stabilisation of the sensor response. Such conditioned sensors give very good stability results at all atmospheric concentrations encountered (see figs. 3 and 4), within $\pm 30\%$ of the monitor response.

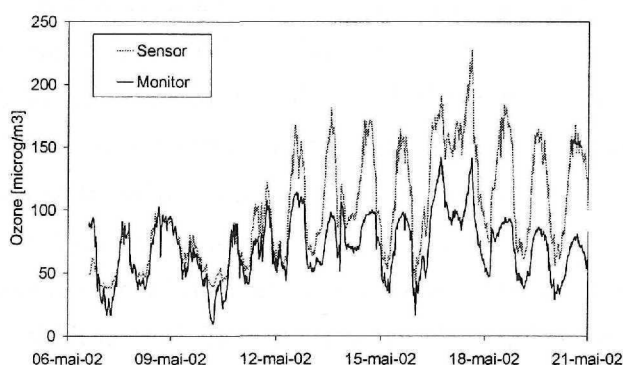


Fig. 1 : drift of the sensor response to ozone during the first 2 weeks

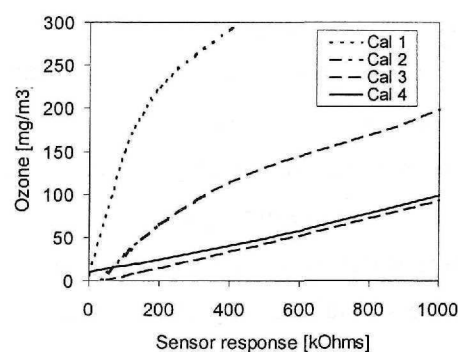


Fig. 2 : successive calibrations of a sensor (every 2 weeks)

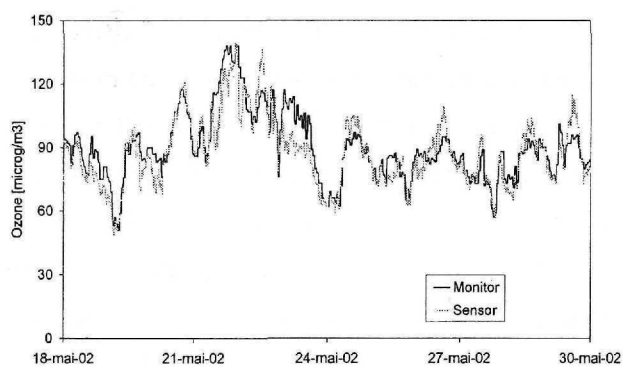


Fig 3 : comparison of the microsensor and monitor responses in Alsace (Donon station)

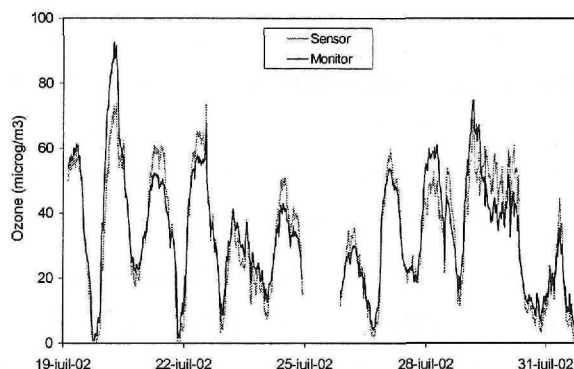


Fig. 4 : comparison of the microsensor and monitor responses in Verneuil (INERIS Lab.)

CONCLUSIONS

The previous study [3] showed that these ozone sensors are very little sensitive to NO_x, which could be the major interferences for ozone monitoring in ambient air. With a temperature compensation, good conditioning and calibration procedures, these ozone microsensors are an interesting technique to complement continuous monitors. They could be used in more locations than the monitors, with a good accuracy, which would allow a better mapping of ozone concentrations over a large area.

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