NANOCARBONS : CHEMICAL FILTERS FOR THE SELECTIVE DETECTION OF NITROGEN DIOXIDE AND OZONE.

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Introduction

More than being an environmental problem, atmospheric pollution has become a real public health question. In Europe, in the United States or in several countries around the world, the law gives to everybody the right to inhale an air that does not affect his health and settles the right to be informed about the air quality he breathes [1]. Thus, air quality control networks such as AtMO in France or the Environmental Protection Agency (US EPA) in the United States have the responsibility to monitor pollutants continuously. To ensure this mission, two normalized method are used for the quantification of polluting species in atmosphere: passive samplers and gas analyzers. If the first is inadequate for a real time monitoring of pollutants concentrations and do not give access to the pollution peaks, the second is the most efficient, the most reliable and gives real time information despite of its restrictive use, its lack of mobility and its high cost.

Microsystems sensors seem a very interesting solution because of their compactness, their high degree of portability and weak cost price. However, to be competitive with the gas analyzers, these microsensors must show metrological characteristics close to the ideal sensor, i.e. sensitive, with weak threshold and high resolution, deliver reproducible measurements and especially be selective with targeted gas. Because of their high degree of toxicity and their increase in the atmosphere, our work was focused on nitrogen dioxide (NO_2) and ozone (O_3).

Experimental

To obtain selective microsensors selective towards NO_2 and O_3, our strategy consists in using a material highly sensitive to these oxidizing gases and inert towards the other species (reducing, COVs), namely copper phthalocyanine [2,3]. This material confers on the microsystem sensor a first degree of selectivity. If the development of a methodology of appropriate measure has allowed us to obtain a system sensitive and selective with ozone [4], the strategy developed to arrive at the selectivity towards NO_2 is the placement of chemical filters being able to eliminate integrality from O_3 without amending the concentration of NO_2. The nanocarbon materials seem relevant one.

Our team currently develops a chemical filter containing nanocarbons, impermeable to ozone and inert towards nitrogen dioxide. The capacity of filtration of certain types of nanocarbons (of nanodiscs, of single and multi wall nanotubes, nanofibers) towards two gases was given in a range of concentrations ranging between 20 and 200 ppb. Being well-known for its filter capacity towards O_3, the indigo is used like reference material. A first selection according to the output of filtration in O_3 and NO_2 was carried out between the various compounds, in particular of the indigo/nanocarbon composites. With equal outputs of filtration, the final selection of the chemical filter will rest then on the comparison of their durabilities.

Results and Discussion

The reactivity of O_3 with indigo is well-known [5] and has been exploited for the development of filtering cartridges [6,7] or optical ozone sensors [8-10].

Firstly, the filtering yield of indigo powder towards the two target gases has been quantified. Taking into consideration uncertainties, the filtering yield towards O_3 remains close to 100% while NO_2 remains lower than 5±5% in the 20-200 ppb concentration range. So, indigo can be considered as a strongly selective ozone chemical filter.

In the reaction between O_3 and indigo molecules the O_3 molecules have a strong affinity with carbon double bonds. The noted gas absorption capacity of carbonaceous materials (such as activated carbons) seems to be very interesting too. Thus, we drew our attention on nanocarbon structures.

The interests of these nanostrutured carbons lie in their high specific surface areas, besides of their well-defined and uniform adsorption sites. Different kinds of structure have been tested to find the most efficient materials, such as activated carbons, graphite, single and multi wall nanotubes (SWCNTs and MWCNTs respectively), carbon nanofibres (CNFs) and a mixture of carbon nanodiscs and nanocones (CNDs). All are commercial products. To emphasize the importance of the structure of these nanomaterials, and to identify the interaction mechanisms, some of them underwent some physical or chemical treatments.

These samples were exposed to NO_2 and O_3 gases at concentration rates corresponding to those present in real atmospheres (from 20 to 200 ppb). Taking into account uncertainties, CNDs exhibit the most interesting filtering yield: 100% towards O_3 against 4±3% towards NO_2.

Experimental results obtained for the different nanostructured carbons are shown in fig. 1. This highlights the efficiency of this new kind of chemical filter. We search a good ozone filter exhibits 100% of filtering toward O_3 and a low filtering power to NO_2. Compared with indigo, CNDs show more interesting characteristics.

To attest of the efficiency of this chemical filter, CNDs were integrated in the fluid circuit upstream the sensitive element. Methodology employed to carry out this series of test is identical to that described above during the tests of tender of the microsystem under O_3. Experimental results obtained for a concentration range between 20 to 200 ppb (fig. 2) shows that the responses of the sensor towards O_3 are very low in comparison with the responses towards NO_2 which evolve as a function of the pollutant concentration.

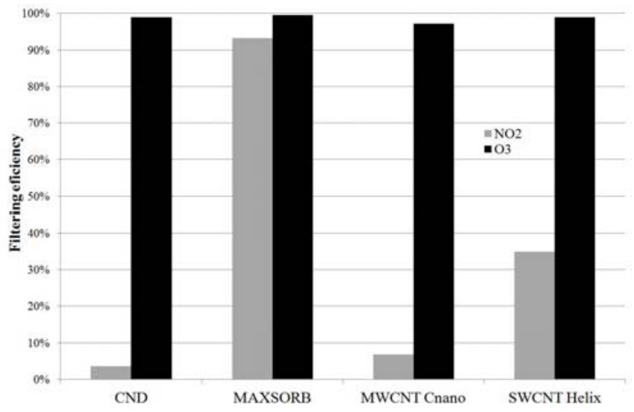

Fig. 1 Filtering efficiency of the different nanocarbon materials towards O_3 (■) and NO_2 (■) in the 20 to 200 ppb range.

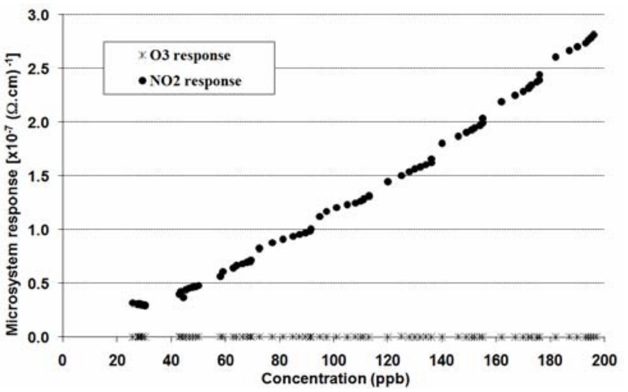

Fig. 2 Sensor microsystem responses versus gas concentration for O_3 (∗) and NO_2 (●) in the range 20-200 ppb.

Conclusions

The present work is devoted to the use of nanocarbons materials as an efficient chemical of ozone. The nanocarbons, all commercial, were initially used without any modification of their structure. In order to better understand and to better interpret the concerned mechanisms, certain materials have sudden chemical and/or mechanical processing thus amending their properties of surface (modification of the chemicals of surface by fluorination), their specific surface and their graphitization (thermal treatment and ball-milling).

Test realized in laboratory show an interesting behavior of the carbon nanodiscs. In comparison with the indigo, their filtering yield is equal to100% towards O_3 compared with 4±3% towards NO_2 (indigo: 100% towards O_3 compared with 5±5% towards NO_2).Under purified air, it seems that CNDs partly desorb O_3 molecules suggesting a possible regeneration of this chemical filter.

The association of this intrinsic selectivity, a methodology exploiting to the maximum the capacities of the sensitive material and the use of a chemical filter make our device very competitive in comparison to commercial analyzers. Measurements campaigns in real outdoor conditions corroborate results obtained in laboratory. Another way is investigated: the non covalent grafting of indigo on various nanocarbons (tubes and fibres), to cumulate filtering yield efficiency of indigo and benefits of nanocarbons.

References

[1] Law n°96-1236 of 30 Decembre 1996 on air and the rational use of energy, Official Journal L220-1, 1 January 1997.

[2] Maleysson C, Passard M, Blanc J-P, Battut V, Germain J-P, Pauly A, Demarne V, Grisel A, Tiret C, Planade R. Elaboration and tests of microelectronically designed gas sensors with phthalocyanine sensitive layers. Sensors and Actuators B 1995;26-27:144-149.

[3] Brunet J, Germain J-P, Pauly A, Blanc J-P. Comparisons between NO2 and O3 sensing properties of phthalocyanines and n-InP thin films in controlled and noncontrolled atmospheres. Sensors Journal 2004, IEEE;4:735-742.

[4] Brunet J, Germain J-P, Pauly A, Lauron B, Varenne C. A methodology of measurements for phthalocyanine gas sensors dedicated to the detection of ozone and nitrogen dioxide. Results in urban air pollution context, Sensors for Environmental Control, ISBN: 981-238-338-7, edited by World Scientific Publishing 2003:188-192.

[5] Alexy M, Voss G, Heinze J. Optochemical sensor for determining ozone based on novel soluble indigo dyes immobilised in a highly permeable polymeric film. Analytical and Bioanalytical Chemistry 2005;382:1628-1641.

[6] Penrose WR, Pan L, Stetter JR, Ollison WM. Sensitive measurement of ozone using amperometric gas sensors. Analytica Chimica Acta 1995;313:209-219.

[7] Viricelle J-P, Pauly A, Mazet L, Brunet J, Bouvet M, Varenne C, Pijolat C. Selectivity improvement of semi-conducting gas sensors by selective filter for atmospheric pollutants detection. Materials Science and Engineering C 2006;26:186-195.

[8] Felix EP, De Souza KAD, Dias C.M, Cardoso AA. Measurements of ambient ozone using indigo blue-coated filters. Journal of AOAC International 2006;89:480-485.

[9] Maruo YY. Measurement of ambient ozone using newly developed porous glass sensor. Sensors and Actuators B 2007;126:485-491.

[10] Li J, Li Q, Dyke J.V, Dasgupta PK. Atmospheric ozone measurements with an inexpensive and fully automated porous tube collector-colorimeter. Talanta 2008;74:958-964.