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# Use of a chromatographic column to improve the selectivity of the $SnO_2$ gas sensors: first approach towards a miniaturised device and selective with hydrogen fluoride vapours

J.-B. Sanchez[a,*], F. Berger[a], M. Fromm[a], M.-H. Nadal[b]

[a] *Laboratoire de Microanalyses Nucléaires, UMR CEA, UFR Sciences et Techniques, 16 route de Gray, 25030 Besançon Cedex, France*
[b] *Comissariat à l'Energie Atomique, CEA/VALDUC/DRMN, 21120 Is sur Tille, France*

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**Abstract**

Tin dioxide-based gas sensors were laid out at the exit of a chromatographic column for the selective detection of hydrogen fluoride in the atmosphere. After having selected a stationary phase adapted to this particular molecule, the sensor's signals were studied using various experimental parameters. In this paper a complete description of the experimental device and of the electrical responses is given. For the experiment, the gas sample was formed by a gas mixture of HF, $O_2$ and $N_2$. It was found that the optimal mode of detection corresponds to the sensitive element ($SnO_2$) having a temperature near to 500 °C with a carrier gas of oxidising nature (synthetic air). Moreover, it was found that with this experimental configuration, a minimum concentration of about 0.8 ppm was detectable.


*Keywords:* Semiconductor-based sensor; Gas chromatography; Selective sensor; Hydrogen fluoride

## 1. Introduction

It is essential today to be able to quickly analyse and control the surrounding atmosphere in order to prevent possible risks of pollution. With this in mind, many groups decided to work on the development of gas sensors for measuring toxic chemical compounds.

For these last 2 years, our laboratory has been interested in the development of an effective sensor adapted in particular to the detection of low-level concentration of hydrogen fluoride present in the atmosphere. This chemical compound can be used amongst other things in the field of micro-technology (micromachining of silicon), but it can also be an effective indicator for the accidental release of uranium hexafluoride ($UF_6$) in the atmosphere [1]. In the liquid or gas phase, its physico-chemical properties make it a very dangerous chemical compound, even at low concentration.

The use of tin dioxide-based thin film sensors seems to be an obvious compromise between the low cost, their small size, their high sensitivity (small change in gas composition causes change in resistance) and fast response to many pollutant gases. In spite of these considerations their selectivity still remains unsatisfactory for use in so far as a mobile system. Until now, different ways were exploited to improve the selectivity of tin dioxide-based gas sensors. We can quote as an example the works on sensor modulation temperature [2], adjustment of the grain size of $SnO_2$ [3], and more recently studies on mesoporous catalytic filters [4,5] or gas sensors covered with zeolitics films [6].

The first studies carried out showed that semiconductor gas sensors were sensitive to hydrogen fluoride

* Corresponding author. Tel.: +33 3 81 66 65 06; fax: +33 3 81 66 65 22.
*E-mail address:* jean-baptiste.sanchez@univ-fcomte.fr (J.-B. Sanchez).

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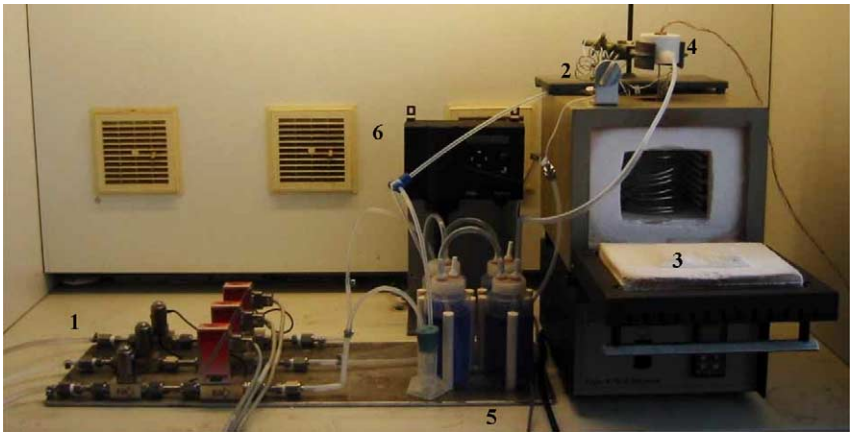


Fig. 1. Experimental device using $SnO_2$-based gas sensors as chromatographic detectors: (1) mass flow meters use for carrier gas and gas sample; (2) two position valve; (3) oven with the chromatographic column; (4) cell sensor; (5) basic trap; (6) warning system.

vapours in air [7,8]. These results are valuable only in a synthetic atmosphere without the presence of additional pollutant chemical compounds. For use in a real atmosphere, with various surrounding pollutants, these devices require a system of separation in order to improve their selectivity.

The general idea of this work, which forms part of preliminary studies by Barsan and Ionescu [9], is based on the use of a chromatographic column laid out upstream of the gas sensor. This device of separation must make it possible to separate the molecule hydrogen fluoride from the others molecules present in the analysed gas sample. Moreover, the semiconductor tin dioxide-based gas sensor must be able to re-transcribe the order of separation which takes place in the chromatographic column.

In this paper, we report our initial results using the chromatographic column as an original selective way for tin dioxide-based gas sensors. In the first part, we present the experimental device used. Next we show different electrical responses in order to understand the phenomena present at the interface of the $SnO_2$/gas sensor, show the influence of the nature of the carrier gas on the profile of the electrical responses, and fix parameters for future use of like chromatographic detectors.

## 2. Experimental section

The gas sensor used includes a semi-conducting metal-oxide layer and a silicon substrate with an integrated heater. These devices are commercially made by the Microsens Company in Neuchâtel (Switzerland).

Specially designed equipment was developed for the study of $SnO_2$ gas sensor's response after gas separation in the chromatographic column (Fig. 1). With this experimental set-up, $SnO_2$-based gas sensor receives the different gases from the sample loop in the background of the carrier gas ($N_2$ or synthetic air).

The use of a manual two position valve makes it possible to inject the volume of gas contained in the sample loop (300 μl) into the carrier gas. The operation of this type of valve is detailed in Fig. 2. With the valve in position A, the

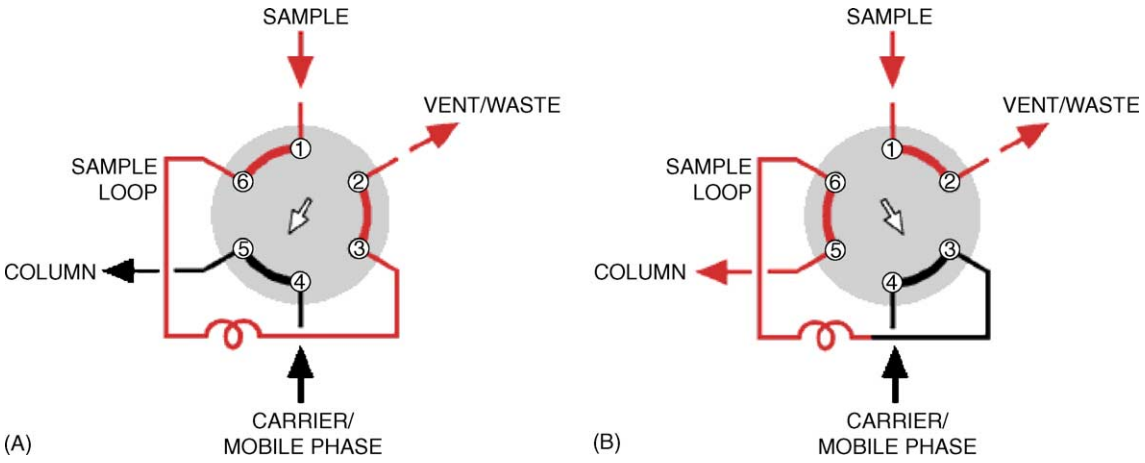


Fig. 2. Schematic representation of the operation of a two position valve.